



# Development of a dynamic model for direct copper electrowinning operations

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Dissertation presented for the degree of Doctor of Philosophy in the Faculty of Engineering at Stellenbosch University

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> > December 2023

## DECLARATION

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Date: December 2023

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### ABSTRACT

Innovation is essential for fostering sustainable and environmentally conscious growth in copper production, particularly for operations employing resource-intensive direct copper electrowinning. A dynamic model can be coupled with advanced control strategies in an innovative approach to addressing the control and optimisation challenges associated with copper electrowinning. Previous studies have primarily focused on steady-state models, and limited research has been conducted on dynamic models for copper electrowinning. Consequently, this project aimed to develop a dynamic model for copper electrowinning, with a specific focus on the direct electrowinning process.

The main original contribution of this project is the validated semi-empirical dynamic copper electrowinning model. The model can be calibrated for a specific tankhouse, including direct electrowinning operations. An offline parameter-fitting approach was developed for fitting initial model parameters, and for use when limited data are available. The project also introduced an accompanying online parameter-fitting approach that uses moving horizon estimation to continuously adjust the model parameters based on evolving input data. The approach ensures the parameters remain up to date as process conditions change. The least-squares error objective function was selected for use in the online approach, with two types of system models investigated: fundamental and surrogate. The surrogate models were investigated mainly as a future-orientated strategy for online parameter-fitting using computationally intensive datasets.

The model incorporated a conceptual resistance network, mass conservation equations, and reactionrate and mass-transfer kinetics. Key performance indicators (copper yield, current efficiency, and specific energy consumption) were used to quantify electrowinning performance. The model included input variables such as current, and the concentrations of copper, iron, nickel, cobalt, and sulfuric acid. The effect of nickel and cobalt were accounted for through existing empirical density and conductivity correlations, and a newly regressed limiting-current density correlation.

Validation using dynamic industrial tankhouse data showed the credibility of the model for representing real-life systems. The average normalised residual mean square errors over the five 14-day validation cycles investigated (with the online approach activated) were 10.0%, 29.3%, 79.2%, and 3.9%, for the current efficiency, copper plating rate, specific energy consumption, and potential, respectively. The quantifier values for the specific energy consumption were consistently above the threshold for acceptable model fit. Caution was, therefore, advised in interpreting the model-predicted specific energy consumption values. Overall, the model's performance, particularly with inclusion of the online parameter-fitting approach, however, exhibited satisfactory agreement with the industrial data.

The developed model has the potential to make a meaningful contribution to the field. The model's versatility and accuracy make it a valuable tool for use in operator training, process monitoring, and early-fault detection. It also opens avenues for exploration of advanced control strategies. By leveraging these potential benefits, operations can enhance productivity, reduce costs, and minimise environmental impact. It is recommended that future work should focus on developing online data validation strategies to further enhance model fidelity, as well as exploring advanced surrogate model structures.

#### **OPSOMMING**

Innovasie is noodsaaklik om volhoubare en omgewingsbewuste groei in koperproduksie te kweek, veral vir bedrywe wat hulpbron-intensiewe direkte koperelektroherwinning gebruik. 'n Dinamiese model kan gepaar word met gevorderde beheerstrategieë in 'n innoverende oplossing tot die beheer en optimaliseringsuitdagings geassosieer met koperelektroherwinning. Vorige studies het hoofsaaklik op bestendige toestand modelle gefokus, en beperkte navorsing is uitgevoer op dinamiese modelle vir koperelektroherwinning. Vervolgens het hierdie projek beoog om 'n dinamiese model vir koperelektroherwinning te ontwikkel, met 'n spesifieke fokus op die direkte elektroherwinningproses.

Die hoof oorspronklike bydrae van hierdie projek is die gevalideerde semi-empiriese dinamiese koperelektroherwinningsmodel. Die model kan gekalibreer word vir 'n spesifieke tenkhuis, insluitend direkte elektroherwinningsbedrywe. 'n Aflyn parameter-passing benadering is ontwikkel vir die passing van aanvanklike modelparameters, en vir gebruik wanneer beperkte data beskikbaar is. Die projek het ook 'n gepaardgaande aanlyn parameter-passing benadering bekendgestel wat bewegende horisonberaming gebruik om aanhoudend die modelparameters aan te pas gebaseer op dinamiese insetdata. Die benadering verseker dat die parameters op datum bly soos proseskondisies verander. Die minste kwadraatfout doelfunksie is gekies vir gebruik in die aanlynbenadering, met twee tipes sisteemmodelle: fundamenteel en surrogaat. Die surrogaatmodelle is hoofsaaklik ondersoek as 'n toekomsgeoriënteerdestrategie vir aanlyn parameter-passing met rekeningkundige intensiewe datastelle.

Die model het 'n konseptuele weerstandnetwerk, massabehoudvergelykings, en reaksietempo en massaoordrag kinetika geïnkorporeer. Sleuteldoeltreffendheidindikators (koperopbrengs, stroomdoeltreffendheid, en spesifieke energiegebruik) is gebruik om die doeltreffendheid van die proses te kwantifiseer. Die model het insetveranderlikes soos stroom, en die konsentrasies van koper, yster, nikkel, kobalt, en swaelsuur, ingesluit. Die effek van nikkel en kobalt is in rekening gebring deur bestaande empiriese digtheid en konduktiwiteitskorrelasies, sowel as 'n oorspronklike beperktestroomdigtheidskorrelasie.

Die geldigheid van die model is bevestig deur validasie wat, onder andere, dinamiese industriële tenkhuisdata gebruik het. Die gemiddelde genormaliseerde residu gemiddelde vierkantsfoute oor die valideringsiklusse (met die aanlynbenadering geaktiveer) was 10.0%, 29.3%, 79.2%, en 3.9%, vir die stroomdoeltreffendheid, koperplateringtempo, spesifieke energiegebruik, en potensiaal, onderskeidelik. Die waardes vir die spesifieke energiegebruik was konstant bo die drumpel vir aanvaarbare modelpassing. Oor die algemeen het die model, veral met insluiting van die aanlyn parameter-passing benadering, egter bevredigende ooreenstemming met die industriële data getoon.

Die ontwikkelde model het die potensiaal om 'n betekenisvolle bydra tot die veld te maak. Die model se veelsydigheid en akkuraatheid maak dit 'n waardevolle hulpmiddel vir gebruik in operateurafrigting, prosesmonitering en vroeë foutopsporing. Die model kan verder ook gebruik word vir die ondersoek van gevorderde beheerstrategieë. Deur middel van vir hierdie potensiële modeltoepassings kan produktiwiteit verhoog word, kostes verminder word, en omgewingsimpak geminimeer word. Dit word voorgestel dat toekomstige werk moet fokus op die ontwikkeling van aanlyndatavalideringstrategieë om die modelgetrouheid te verbeter, sowel as op die ondersoek van gevorderde surrogaatmodelstrukture.

## ACKNOWLEDGEMENTS

I would like to thank the following people, for their assistance and contribution to this project:

- Dr Margreth Tadie and Prof Christie Dorfling, for this opportunity and your exceptional guidance and support throughout this project.
- The South African Minerals to Metals Research Institute (SAMMRI) for funding the project and providing valuable insights from an industry perspective.
- The industry partner for their indispensable support during this project.
- Prof Kathy Sole and Prof Guven Akdogan for their invaluable insights.
- Mr Anton Cordier, Mr Stuart Milne, Mr Alvin Petersen, Mr Oliver Jooste, Mr Heinrich Bock, and Mrs Mieke de Jager for the assistance and support during completion of this project.
- Mrs Hanlie Botha for the assistance with analyses.
- My support-network: Francois Heunis, Sasha Kasperski, Wessel Horak, Cara Haller, and my parents.

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## LIST OF TERMS

Term	Description
AAS	Atomic absorption spectrophotometry
Comex	New York mercantile exchange
DAE	Differential-algebraic equation
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IoT	Internet of things
KPI	Key performance indicator
LHS	Latin hypercube sampling
LME	London metal exchange
LOOCV	Leave-one-out-cross validation
MAPE	Mean absolute percentage errors
MHE	Moving horizon estimation
MPC	Model predictive control
NOLH	Nearly orthogonal latin hypercube
nRMSE	Normalised residual mean square error
ODE	Ordinary differential equation
OFAT	One-factor-at-a-time
PLS	Pregnant leach solution
PRESS	Prediction sum of squares
PVC	Polyvinyl chloride
RDE	Rotating disc electrode
RMSE	Residual mean square error
SEC	Specific energy consumption
SEM	Standard error of the mean
TDS	Total dissolved solids

# CHAPTER 1 INTRODUCTION

#### 1.1 BACKGROUND

The demand for copper is expected to reach 36.6 Mt annually by 2031 (Crooks et al., 2023). Highpurity copper is thermally and electrically conductive, has high ductility and is corrosion-resistant, making it ideal for use in the electronics, telecommunications, energy, construction, and automotive industries (Kulczycka et al., 2016). The use thereof in the growing electric vehicle and renewable energy industries, as well as novel applications in hospital infrastructure, will continue to drive the demand (Lee and Shin, 2018; Michels et al., 2015; Van Doremalen et al., 2020).

The production of high-purity copper from copper-containing ores involves either a hydrometallurgical or pyrometallurgical method. The hydrometallurgical method currently produces approximately 20% of the total copper processed globally. This method is expected to see an increase in popularity due to its perceived reduced environmental impact and ability to extract copper from low-grade ores and scrap (Schlesinger et al., 2011a). The final process in the hydrometallurgical method for copper extraction is electrowinning.

Electrowinning is an energy-intensive process with approximately 2 MWh used per t copper produced (Wiechmann et al., 2010). All the energy is, however, not used in the deposition of copper. Up to 30% of the energy is wasted due to electrolyte resistance and subsidiary reactions (which are associated with impurities), short circuits, and stray currents (Schlesinger et al., 2011b). This wastage is specifically relevant to direct copper electrowinning operations where efficiencies are commonly low, largely due to the absence of preceding processing steps.

Direct copper electrowinning, where copper is recovered directly from a leach solution without the use of solvent extraction, typically entails high concentrations of impurities such as iron and nickel. This impure electrolyte produces copper of a lower purity, at a lower current efficiency, and higher specific energy consumption (SEC). Whilst current efficiencies for post-solvent extraction electrowinning operations can be as high as 95%, those for direct electrowinning operations can be as low as 65% (Beukes and Badenhorst, 2009). Capital expenditure to improve efficiency (such as the inclusion of upstream purification) is often either not justifiable, or not viable. Consequently, innovation is important to ensure operations employing direct electrowinning, mainly situated in developing African countries (Schlesinger et al., 2011b), produce copper at an acceptable quality and efficiency, whilst aligning with global sustainability goals.

The reactive-based control strategies, usually employed in electrowinning processes, often lead to suboptimal tankhouse performance (Komulainen et al., 2009). In recent years, advanced control strategies, such as model predictive control (MPC), have gained traction for application in the mineral processing and extractive metallurgical industries (Crooks et al., 2023; Hodouin, 2011). This includes electrowinning tankhouses, where the implementation of advanced process control is also increasingly being considered (Schlesinger et al., 2022). The lack of adequate process models has, however, contributed to the stunted implementation of MPC in industrial copper electrowinning tankhouses (Bergh and Yianatos, 2001; Komulainen et al., 2009). A suitable dynamic model is not only required for the development of MPC strategies, but it can also be used to compare MPC to conventional controllers, quantifying the advantage of using the more complex strategy before the investment of resources (Appl et al., 2020; Hodouin, 2011).

Steady-state semi-empirical models for the copper electrowinning process have previously been developed using fundamental relationships and experimental data (Aminian et al., 2000; Free et al., 2006; Tucker, 2019). These models present the foundation for the prediction of electrowinning process performance at an industrial scale. Limited research has, however, been conducted on the development of dynamic models for the prediction of copper electrowinning performance (Filianin et al., 2017; Lie and Hauge, 2008; Wiebe, 2015; Wu et al., 2021, 2020).

Dynamic modelling has the potential to improve processes throughout the whole value chain (Sánchez and Hartlieb, 2020). The focus should, however, be on processes where the potential value is the greatest (Klein and Walsh, 2017). Consequently, the resource-intensive, low-efficiency nature of direct copper electrowinning confirms it as an ideal candidate. Nevertheless, despite direct electrowinning still being investigated as a feasible technology for select new applications (Åkre and Rosseland, 2019; Fathima et al., 2022; Gorgievski et al., 2009; Holmin et al., 2019; Marsden et al., 2007), the majority of traditional tankhouses currently in operation purify their advance electrolyte using a solvent extraction step before electrowinning (Sole et al., 2019). It is, therefore, important to note that developing a dynamic model specifically for direct electrowinning operations does not exclude it from use for post-solvent extraction plants.

#### **1.2 PROBLEM STATEMENT**

A dynamic model of the direct copper electrowinning process presents an opportunity to address the control and optimisation challenges associated with the resource-intensive, low-efficiency electrowinning process. The model can be used to develop advanced control strategies, such as MPC, which will enable real-time optimisation and the generation of adaptive control actions. There is scope in the current body of literature for the development of a dynamic semi-empirical model that accurately predicts the process performance of a full-scale direct copper electrowinning tankhouse. The semi-empirical nature of the model allows for the incorporation of the theoretical basis required to make the

model easily adaptable for use in different full-scale copper electrowinning tankhouses, whilst requiring less development than a purely theoretical model. The model accommodates the complex chemistry associated with the direct electrowinning electrolyte to predict the key performance indicators (KPIs) (current efficiency, copper yield, and SEC) with high fidelity. Moreover, the model uses only input variables that are readily available in industrial tankhouses, or that have the potential to be readily measured using available technologies. The developed model is validated using a combination of bench-scale and industrial electrowinning data to ensure that it is sufficiently accurate for its intended purpose.

#### **1.3 AIM AND OBJECTIVES**

A semi-empirical steady-state model for the prediction of copper electrowinning performance has previously been developed as an initial step towards the development of a dynamic model for application in process control (Tucker, 2019). This project aims to apply the understanding developed in previous studies on copper electrowinning to develop a dynamic semi-empirical model for copper electrowinning operations, with a specific focus on the direct electrowinning process.

Four objectives followed to achieve this aim:

- i. Evaluation of existing, or development of new, property correlations to describe the complex physicochemical relationships in direct copper electrowinning electrolytes.
- Development of a high-fidelity conceptual semi-empirical dynamic model for direct copper electrowinning operations, that can also be applied to post-solvent extraction electrowinning, and computerising the model using appropriate software.
- Development of an online parameter-fitting approach as a means of continuously updating the model parameters based on an evolving dataset.
- iv. Validation of the dynamic model and parameter-fitting approach using qualitative consistency checks and quantitative model accuracy indicators, as measured against dynamic experimental and industrial tankhouse data.

#### **1.4 SCIENTIFIC CONTRIBUTIONS**

The following summarises the original scientific contributions presented in this dissertation.

Research efforts have shown the value of dynamic models for the leaching and solvent extraction processes in process monitoring and control applications (Knoblauch, 2015; Komulainen, 2007; Miskin, 2016; Strydom, 2017). Very few dynamic models, however, exist for copper electrowinning (Filianin et al., 2017; Lie and Hauge, 2008; Wiebe, 2015; Wu et al., 2021, 2020). Moreover, the validity of the models that do exist is restricted to specific industrial copper

production plants, or their predictive performance is inadequate. The semi-empirical nature of the predictive high-fidelity dynamic model, developed and validated in this project, means that it can be fit to a specific copper electrowinning tankhouse, ensuring versatility. Consequently, the developed model is expected to make a meaningful contribution to industry.

ii. The physicochemical properties of copper electrowinning electrolytes hold considerable economic importance. Accurate models of the physicochemical electrolyte properties are required for use in the electrowinning model developed in this project but could also be used in other industrial applications, such as aiding the development of process optimisation strategies.

A considerable amount of literature has been published on modelling the effect of composition and temperature on the physicochemical properties of copper electrolytes. The component concentrations investigated by Kalliomäki et al. (2021) (the current state-of-the-art) do not, however, encompass the full range of operating conditions applicable to typical direct copper electrowinning operations (Robinson et al., 2013; Sole et al., 2019). This observation is notable because the empirical model form tends to lack robustness of prediction and is limited to interpolation based on the data used for model development (Eksteen and Reuter, 2003; Tsamandouras et al., 2013).

Moreover, although a correlation for predicting the limiting-current density for electrorefining applications has previously been developed and validated by Kalliomäki et al. (2019), no such model is known to exist for predicting the limiting-current density of direct electrowinning operations. The inclusion of components such as arsenic, and omission of iron and cobalt are expected to limit the applicability of the existing model for electrowinning operations. Accordingly, this project extends the literature by validating the existing physicochemical property correlations for the full range of applicable conditions and regressing a correlation for predicting the limiting-current density of direct copper electrowinning operations.

iii. The availability of a suitable parameter-fitting approach is required to fit the developed model to a specific tankhouse, thereby leveraging the flexibility of the semi-empirical modelling approach. Additionally, online parameter-fitting is often required to obtain a model that is sufficiently accurate for advanced predictive control applications (Hedengren and Eaton, 2017). Tucker et al. (2021) has previously highlighted the value of steady-state parameter-fitting for calibrating the corresponding steady-state electrowinning model to bench-scale electrowinning data. Nonetheless, no dynamic online parameter-fitting approach specifically applied to electrowinning processes could be found in literature. Consequently, an original parameter-fitting approach, based on existing methods, was developed that can continuously refit for the model parameters using a dynamic input dataset.

# CHAPTER 2 LITERATURE REVIEW

#### 2.1 INTRODUCTION

In this chapter, the fundamental principles that form the theoretical basis of the developed electrowinning model are discussed (Section 2.2). Following this, the copper electrowinning process is considered in an industrial context to ensure that the model is usable on an industrial scale (Section 2.3). The majority of available literature regarding industrial copper electrowinning is specifically applicable to post-solvent extraction electrowinning operations. As such, the discussion undertaken in this chapter includes information pertaining to post-solvent extraction electrowinning operations but highlights where direct electrowinning operations may differ. Lastly, existing models are assessed (Section 2.4) in order to demonstrate the original contribution made by this project (Section 2.5).

#### 2.2 FUNDAMENTAL ELECTROWINNING PRINCIPLES

#### 2.2.1 General Electrochemical Principles

Electrowinning involves immersing metal cathodes and inert anodes in an electrolyte, applying an electrical current between the electrodes, and plating pure copper from the electrolyte onto the cathodes (Schlesinger et al., 2011b). Electrowinning is an example of a commercial process that utilises electrolytic cells, a type of electrochemical cell in which an external voltage (greater than the opencircuit potential of the cell) is to be present for electrochemical reactions to occur. Electrolytic cells consist of two electrodes separated by an electrolyte, with electrochemical reactions occurring at the interface of the electrode and electrolyte. Therefore, the overall electrochemical reaction is broken up into two half-cell reactions, with reduction occurring at one electrode and oxidation at the other. Equation 2.1 gives the general form of an electrochemical reaction (Beukes and Badenhorst, 2009).

$$0^{n^+} + ne^- \leftrightarrow R \qquad [2.1]$$

where 0 is the oxidised species, R is the reduced species, and n is the stoichiometric coefficient.

Each half-cell reaction is associated with a specific standard potential, defined as the potential of the reduction relative to the normal hydrogen electrode, which is assigned a potential of 0.00 V (Ciobanu et al., 2007). The overall standard cell potential is calculated as the difference between the standard potentials of the half-cell reactions occurring at the anode and cathode (Equation 2.2) (Newman and Thomas-Alyea, 2004). The overall standard cell potential is a measure of the energy available to externally drive charge between the electrodes, under standard conditions (Bard and Faulkner, 2001). The standard conditions are defined as all dissolved substances having an activity of

1, and all gaseous substances partaking in the reaction having an effective pressure of 1 atm (Carmo, 2019). A spontaneous reaction is characterised by a positive overall standard cell potential and corresponding negative change in Gibbs free energy (Ciobanu et al., 2007).

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 \qquad [2.2]$$

where  $E^0$  is the standard reduction potential (V).

The Nernst equation is used to correct for the reduction potential under non-standard conditions (Equation 2.3) (Beukes and Badenhorst, 2009). It gives the reduction potential as a function of the standard reduction potential, the activity of the species at the electrode surface, temperature, and number of electrons exchanged in the electrochemical reaction. The Nernst equation presupposes fast, reversible reactions, which imply that the concentration of species at the electrode surface is maintained close to their equilibrium values (Bard and Faulkner, 2001).

$$E = E^0 + \frac{RT}{nF} \ln\left(\frac{a_0 n^+}{a_R}\right)$$
 [2.3]

where *E* is the reduction potential (V),  $E^0$  is the standard reduction potential (V), *F* is Faraday's constant (96 485 C per equivalent mol), *R* is the gas constant (8.314 J/(mol K)), *T* is the temperature (K), *n* is the stoichiometric coefficient (dimensionless), and *a* is the activity (dimensionless).

The activity is a measure of the effective concentration of a species in a solution under non-ideal conditions. The activity of a species is calculated using Equation 2.4 (Werner et al., 2018). The activity coefficient accounts for the deviation from ideal behaviour; it is, therefore, unity for ideal solutions (Samson et al., 1999). An ideal solution will have interactions equal to those of the pure components (Kugel, 1998).

$$a_i = \gamma_i \left(\frac{C_i}{C^0}\right)$$
 [2.4]

where  $a_i$  is the activity of the species (dimensionless),  $\gamma_i$  is the activity coefficient of the species (dimensionless),  $C_i$  is the molar concentration (mol/L), and  $C^0$  is the reference concentration (1 mol/L).

The activity coefficients of species in non-ideal electrolytic solutions can be determined using various models. The conventional Debye-Hückel model can predict the activity coefficient of a solution with an ionic strength of 10 mmol/L or less (Aqion, 2016). The ionic strength is a measure of the total ion concentration in the solution, with ions that have more charge having stronger electrostatic interactions with other ions. The Davies equation is a modified version of the Debye-Hückel model with an additional term accounting for more phenomena. The Davies equation can predict the activity coefficient of a solution with an ionic strength of up to 500 mmol/L (Aqion, 2016). The Pitzer model is, however, one of the only proposed models that appears to accurately predict the thermodynamic

behaviour of concentrated electrolytic solutions (Samson et al., 1999). The Pitzer model can predict the activity of a solution with an ionic strength higher than 1 mol/L. Samson et al. (1999) proposed a modified version of the Davies equation with a range of validity similar to the Pitzer model, but that is mathematically simpler. The Samson et al. (1999) model was, therefore, selected for use in this project (Equations 2.5, 2.6, and 2.7). The dielectric constant, required to calculate the model parameters, was determined using an empirical relationship developed by Werner et al. (2018) (Equation 2.8). The empirical relationship is valid for a dielectric constant between 140 and 170.

$$\ln(\gamma_i) = -\frac{A \, z_i^2 \sqrt{IS}}{1 + B \, r_i \sqrt{IS}} + \frac{(0.2 - (4.17 \times 10^{-15}) \, IS) A \, z_i^2 \, IS}{\sqrt{1000}}$$
[2.5]

$$IS = 0.5 \Sigma z_i^2 C_i \qquad [2.6]$$

$$A = \frac{\sqrt{2} F^2 e_0}{8 \pi \left(\epsilon_0 \epsilon_r R T\right)^{\frac{3}{2}}} \quad \text{and} \quad B = \sqrt{\frac{2 F^2}{\epsilon_0 \epsilon_r R T}} \qquad [2.7]$$

$$\epsilon_r = 127.9614 + 0.01378 \, IS + 5.6111 \times 10^{10} \, r_i + 2.5422 |z_i| \qquad [2.8]$$

where A is the A parameter in the Debye-Hückel model (dimensionless), B is the B parameter in the extended Debye-Hückel model (dimensionless),  $z_i$  is the charge of the species (dimensionless), IS is the ionic strength (mol/m<sup>3</sup>),  $r_i$  is the species radius (m),  $C_i$  is the molar concentration (mol/m<sup>3</sup>),  $\epsilon_0$  is the permittivity of the vacuum (8.85 × 10<sup>-12</sup> F/m),  $\epsilon_r$  is the dielectric constant (dimensionless), and T is the temperature (K).

#### 2.2.2 Electrowinning Reactions

A simplified representation of the electrolytic cell used in copper electrowinning is given in Figure 2.1. The preceding leaching and optional solvent extraction steps produce a  $CuSO_4$ — $H_2SO_4$ — $H_2O$  electrolyte, with sulfuric acid as the main component (Schlesinger et al., 2011a). When the external potential is present, current flows through the electrolyte between the electrodes, initiating the electrochemical reactions required to produce the plated copper. The electrons in the cathode and cupric ions in the electrolyte react at the cathode–solution interface, forming solid copper. Simultaneously, the oxidation of water occurs at the anode forming hydrogen ions and oxygen gas. Sulfate-based solutions generate sulfuric acid (Wollschlaeger, 2018). The oxygen gas bubbles rise to the surface of the electrolyte, burst, and release droplets of sulfuric acid, which results in acid mist.



Figure 2.1: Schematic representation of a simplified electrolytic cell showing the reduction of  $Cu^{2+}$  to solid copper at the cathode, and the oxidation of water to form oxygen bubbles at the anode (adapted from Bard and Faulkner, 2001).

The half-cell reactions for copper reduction and water oxidation, with their respective standard reduction potentials, are given in Equations 2.9 and 2.10 (Schlesinger et al., 2011a). The overall standard cell potential is calculated to be -0.89 V (Equation 2.2). The negative overall standard cell potential, and corresponding positive change in Gibbs free energy, implies that the reaction for the electrowinning of copper is non-spontaneous.

$$Cu_{(aq)}^{2+} + 2e^- \rightarrow Cu_{(s)} \qquad E_{cathode}^0 = +0.34 V \qquad [2.9]$$

$$2H_{(aq)}^{+} + \frac{1}{2}O_{2(g)} + 2e^{-} \rightarrow H_2O_{(l)} \qquad E_{anode}^{0} = +1.23 V \qquad [2.10]$$

The overall cell reaction, obtained by combining Equations 2.9 and 2.10, and considering the sulfate ions originating from the copper sulfate in the electrolyte, is given in Equation 2.11. The products formed are solid plated copper, oxygen gas, and dissociated sulfuric acid (sulfate ions and hydrogen ions).

$$Cu_{(aq)}^{2+} + SO_4^{2-} + H_2O \rightarrow Cu_{(s)} + \frac{1}{2}O_2 + 2H^+ + SO_4^{2-} \qquad E_{cell}^0 = -0.89 V \quad [2.11]$$

The electrolyte used in the electrowinning process, however, contains impurities originating from the ore. Iron is a major impurity in copper-containing ores. Iron undergoes cyclic reduction and oxidation at the cathode and anode, respectively (Equation 2.12) (Schlesinger et al., 2011a). Notably, the reduction of ferric ( $Fe^{3+}$ ) to ferrous ( $Fe^{2+}$ ) ions occurs more readily than copper reduction, due to the higher reduction potential of 0.77 V (compared with the 0.34 V of the copper reduction). The presence of iron, therefore, has a significant impact on the key performance indicators (KPIs) of the process and should be considered in any model attempting to simulate copper electrowinning operations.

$$Fe^{3+}_{(aq)} + e^- \leftrightarrow Fe^{2+}_{(aq)} \qquad E^0 = +0.77 V \qquad [2.12]$$
## 2.2.3 Kinetic Mechanisms

The two kinetic mechanisms involved in copper electrowinning are the mass-transfer and electrochemical reaction mechanisms. The overall mechanism comprises the following steps: the mass transfer of the ion of interest to the electrode surface, the electrochemical charge-transfer reaction, and the deposition of a solid (or the mass transfer of a product away from the electrode into the bulk electrolyte). The slowest step will determine the overall rate.

# 2.2.3.1 Mass-Transfer Mechanism

The mass transfer of a species from the bulk electrolyte to the electrode surface occurs via convection, diffusion, and migration, as shown for cupric ions undergoing reduction in Figure 2.2. The first step in the mass-transfer mechanism is the convection of cupric ions from the bulk electrolyte to the electrode surface region. Convection is divided into natural convection, which occurs through a concentration or temperature gradient, and forced convection, which occurs through mechanical stirring. Diffusion predominantly occurs once the ions are in the electrode surface region, with the concentration gradient being the driving force. The cupric ions diffuse from the bulk electrolyte to the surface of the electrode where the electrochemical reaction occurs (Newman and Thomas-Alyea, 2004). The final mass-transfer mechanism, migration, occurs in addition to diffusion and takes place in the bulk electrolyte away from the electrode, where the concentration gradients are generally small (Bard and Faulkner, 2001; Newman and Thomas-Alyea, 2004). Migration refers to the movement of ions in response to the gradient in electrical potential, which results from the external current applied to the electrowinning cell.



Figure 2.2: Schematic representation of the mass transfer of cupric ions undergoing reduction from the bulk electrolyte to electrode surface occurring via convection, diffusion, and migration (adapted from Bard and Faulkner, 2001 and Werner et al., 2018)

After the ions are transported to the electrode surface via the mass-transfer mechanisms, the electrochemical reaction takes place. In the case of a solid product forming, such as when the cupric ion is reduced to form solid copper, deposition of the atom on the electrode surface occurs. For a product that remains in solution, such as the ferric or ferrous iron ion, the product diffuses back into the bulk electrolyte.

The rate of mass transfer of the ions from the bulk electrolyte to the electrode surface is described by the Nernst–Planck equation for one-dimensional mass transfer along the *x*-axis (Equation 2.13) (Bard and Faulkner, 2001). In industrial applications, a circulation tank is used to minimise the concentration gradient over the *y*- and *z*- axes (the axes parallel to the electrode surface), motivating their exclusion from the Nernst–Planck equation (Beukes and Badenhorst, 2009). The three terms on the right-hand side of the equation describe the contributions of diffusion, migration, and convection to the ionic flux, or overall transport of ions from the bulk electrolyte to the electrode surface.

$$J_i(x) = -D_i \left(\frac{\partial C_i(x)}{\partial x}\right) - \frac{n_i F}{R T} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i(x) v(x) \qquad [2.13]$$

where  $J_i(x)$  is the flux (mol/(s.cm<sup>2</sup>)),  $D_i$  is the diffusion coefficient (cm<sup>2</sup>/s),  $C_i(x)$  is the molar concentration (mol/cm<sup>3</sup>),  $n_i$  is the stoichiometric coefficient (dimensionless), F is Faraday's constant (96 485 C per equivalent mol), R is the universal gas constant (8.314 J/(mol K)), T is the temperature (K),  $\phi(x)$  is the potential (V), and v(x) is the velocity (cm/s).

The Nernst–Planck equation can be simplified for application in industrial electrowinning by excluding the effects of migration and convection. The effect of migration can be minimised by providing a large quantity of inert electrolyte that does not interfere with the electrochemical reactions at the electrode (Beukes and Badenhorst, 2009). Najim (2016) supports this by stating that the inert sulfuric acid, present in the electrolyte, has a high solution conductivity and a large number of ions that serve as the major current carrier, eliminating the effect of migration on the flux of cupric ions to the electrode surface. The effect of convection is eliminated by assuming that the solution velocity at the electrode surface is negligible. This elimination is based on the assumption that mixing is ineffective at the electrode surface (Bard and Faulkner, 2001; Beukes and Badenhorst, 2009). Taking the contributions of migration and convection to be negligible greatly reduces the complexity of the Nernst–Planck equation, leaving diffusion as the only contributor to the ionic flux. The rate of mass transfer is, therefore, proportional to the concentration gradient at the electrode surface, as per the first term in Equation 2.13, yielding Equation 2.14 (Bard and Faulkner, 2001).

$$v_{mt} = D_i \left(\frac{dC_i}{dx}\right)_{x=0}$$
 [2.14]

where  $v_{mt}$  is the rate of mass transfer to a surface (mol/(s.cm<sup>2</sup>)) and x is the distance from the electrode surface (cm).

Moreover, a linear concentration gradient can be assumed within the Nernst diffusion layer (Bard and Faulkner, 2001) (Figure 2.3). The concentration profiles (solid lines) and diffusion layer approximations (dashed lines) are plotted on the figure for two different electrode potentials. The first electrode potential (Figure 2.3, line 1) is where the species concentration at the surface ( $C_{i,surface}$ ) is approximately half of the bulk species concentration ( $C_{i,bulk}$ ). The second potential (Figure 2.3, line 2) is where the surface concentration is zero, and the current density is equal to the limiting-current density. The profiles reach steady-state outside the Nernst diffusion layer because mixing maintains the concentration of the species in the bulk electrolyte.



Figure 2.3: Concentration profiles (solid lines) and diffusion layer approximation (dashed lines) at two different electrode potentials. The electrode surface corresponds to x = 0, whilst  $\delta_i$  represents the boundary layer thickness (redrawn from Bard and Faulkner, 2001).

The equation resulting from the linear approximation describes the ionic flux as a function of the diffusion coefficient, boundary layer thickness at the electrode surface, and the change in concentration between the bulk electrolyte and the electrolyte at the electrode surface (Equation 2.15) (Bard and Faulkner, 2001). The boundary layer thickness is a function of the fluid flow and the cell geometry (Free et al., 2006). The boundary layer thickness can be combined with the diffusion coefficient to produce a proportionality constant called the mass-transfer coefficient (Equation 2.16) (Bard and Faulkner, 2001). The mass-transfer coefficient for diffusion can be considered as an effective mass-transfer coefficient, which includes all applicable mass-transfer effects when used in an electrochemical model (Tucker, 2019). It can be shown that the rate of the reaction and, therefore, the rate of mass transfer when it is the limiting step, is a function of the current density (Equation 2.17) (Bard

and Faulkner, 2001). Equation 2.17 is, in turn, a form of Faraday's law. Combining Equations 2.16 and 2.17 yields Equation 2.18.

$$v_{mt} = \frac{D_i}{\delta_i} \left( C_{i,\text{bulk}} - C_{i,\text{surface}} \right)$$
 [2.15]

$$v_{mt} = m_i \left( C_{i,\text{bulk}} - C_{i,\text{surface}} \right)$$
[2.16]

$$v_{rxn} = v_{mt} = \frac{i}{nF}$$
[2.17]

$$i = n F m_i \left( C_{i,\text{bulk}} - C_{i,\text{surface}} \right)$$
[2.18]

where  $\delta_i$  is the boundary layer thickness at the electrode surface (cm),  $m_i$  is the mass-transfer coefficient (cm/s),  $v_{rxn}$  is the net rate of the electrode reaction (mol/(s.cm<sup>2</sup>)), and *i* is the current density (A/cm<sup>2</sup>).

# 2.2.3.2 Electrochemical Reaction Mechanism

An electrochemical reaction occurs after the mass transfer of the ions from the bulk electrolyte to the electrode surface. Coupled reactions such as adsorption, desorption, nucleation, and crystallisation occur in addition to the electrochemical reaction. According to Bard and Faulkner (2001), the applicable coupled reactions can be included in the heterogeneous electron-transfer reaction-rate mechanism. The electrochemical reaction for the reduction of copper entails the heterogeneous transfer of electrons from the electrode to the cupric ion, located at the surface of the electrode. Additionally, the reduction of copper involves adsorption, nucleation, and crystallisation to form a solid copper product that deposits on the electrode surface. The deposited copper product changes the electrode surface and, as a result, affects the rate of electron transport (Burheim, 2017; Doloi and Bhattacharyya, 2020).

The driving force for a non-spontaneous electrochemical reaction is overpotential, with the rate of the reaction controlled by the magnitude of the potential difference between the two electrodes (Bard and Faulkner, 2001). Overpotential refers to the magnitude of the change from a system's equilibrium potential resulting from the resistance to an introduced electrical current (Doloi and Bhattacharyya, 2020). The total overpotential consists of the activation, concentration, and resistance overpotentials (Burheim, 2017). The activation overpotential refers to the energy required to drive the electron transfer (Bard and Faulkner, 2001). The concentration overpotential is the energy required to drive the transport of ions to and from the electrode surface, and the resistance overpotential refers to the potential drop across the thin oxide layer that forms on the electrode surface over time (Doloi and Bhattacharyya, 2020). The overpotential for a system is calculated using Equation 2.19 (Bard and Faulkner, 2001).

$$\eta = U - E \qquad [2.19]$$

where  $\eta$  is the overpotential (V), U is the potential (V), and E is the reduction potential (V).

The Butler–Volmer equation (Equation 2.20), offers an indirect method to determine the rate of an electrochemical reaction, assuming that the reaction is not mass-transfer limited. The current density, determined via Equation 2.20, can be used to calculate the reaction rate (i.e., the mass of species reacted over time), using Faraday's law (Equation 2.21). The Butler–Volmer equation is a good approximation of the current density required for the specific reaction, given a certain overpotential at the electrode, when the current density is less than approximately 10% of the smaller limiting-current density at the anode and cathode (Bard and Faulkner, 2001).

$$i = i_0 \left[ \exp\left(\frac{-\alpha \, n \, F}{R \, T} \, \eta\right) - \exp\left(\frac{(1-\alpha) \, n \, F}{R \, T} \, \eta\right) \right]$$
[2.20]

where *i* is the current density (A/m<sup>2</sup>),  $i_0$  is the exchange current density (A/m<sup>2</sup>), and  $\alpha$  is the charge-transfer coefficient (dimensionless).

$$v = -\frac{s_i M_i I}{n F}$$
[2.21]

where v is the rate of the electrochemical reaction (g/s),  $s_i$  is the stoichiometric coefficient (negative if formed),  $M_i$  is the molecular mass (g/mol), and I is the current (A).

The right-hand side of the Butler–Volmer equation can be divided into two terms. The first term describes the rate of the cathodic component of the reaction and the second term the rate of the anodic component. For a reduction reaction the calculated current density is positive, as the first term dominates over the second term at the associated negative overpotential. Conversely, for an oxidation reaction, and the associated positive overpotential, the calculated current density is negative (Bard and Faulkner, 2001). The Butler–Volmer equation for an arbitrary system, showing the current density as a function of overpotential, is represented in Figure 2.4. It is noted that at a sufficiently negative or positive overpotential, the respective anodic or cathodic term of the Butler–Volmer equation is negligibly small (Tucker, 2019).



Figure 2.4: Schematic representation of a current density-overpotential curve, showing the cathodic, andic, and net components of the Butler-Volmer equation (adapted from Bard and Faulkner, 2001 and Tucker, 2019).

The Butler–Volmer equation contains two parameters that are dependent on the individual electrowinning cell: the exchange current density ( $i_0$ ) and charge-transfer coefficient ( $\alpha$ ). The exchange

current density is dependent on the concentrations of reactants and products, temperature, the electrolyte–electrode interface, and impurities on the electrode surface. According to Newman and Thomas-Alyea (2004), the exchange current densities for real-life systems can vary from less than  $1 \times 10^{-8}$  A/m<sup>2</sup> to more than 100 000 A/m<sup>2</sup>. The effect of the exchange current density on the reaction-rate kinetics, described by the Butler–Volmer equation, is shown graphically in Figure 2.5. Lower values of the exchange current density correspond to a more horizontal curve, alluding that a higher overpotential is required to deliver a current density, and vice versa for higher values of exchange current density. As the mass-transfer effects are not included, the overpotential associated with any reaction consists only of the activation overpotential. Lower exchange current densities result in slower reaction kinetics, therefore, requiring a larger activation overpotential for any particular current (Bard and Faulkner, 2001).



Figure 2.5: Schematic representation of the effect of a change in the exchange current density ( $i_0$ ) on the Butler–Volmer equation (adapted from Bard and Faulkner, 2001 and Tucker, 2019).

The charge-transfer coefficient is the fraction of the electrostatic potential energy affecting the reduction rate in an electrode reaction, with the remaining fraction affecting the corresponding oxidation rate (Guidelli et al., 2014). Figure 2.6 presents the effect of the charge-transfer coefficient on the reaction-rate kinetics, as described by the Butler–Volmer equation. A larger charge-transfer coefficient results in faster kinetics for cathodic reactions (top left quadrant), with a less negative overpotential translating into a larger current density and, therefore, plating rate. A larger charge-transfer coefficient, however, results in the opposite effect for the anodic reactions (bottom right quadrant), with a more positive overpotential required to translate into a more negative current density (Tucker, 2019). For copper reduction, the charge-transfer coefficient must have a value between 0 and 2 to ensure the forward and reverse components of the Butler–Volmer equation have the correct sign in the exponent of each term. Typical values of the charge-transfer coefficient for copper reduction lie between 0.2 and 2 (Newman and Thomas-Alyea, 2004).



Figure 2.6: Schematic representation of the effect of a change in the charge-transfer coefficient ( $\alpha$ ) on the Butler–Volmer equation (adapted from Bard and Faulkner, 2001 and Tucker, 2019).

## 2.2.3.3 Combined Mass-Transfer and Reaction Mechanism

The ionic flux density, which is proportional to the current density (as described in Section 2.2.3.1), reaches a limit when the surface concentration of the corresponding species approaches zero. This mass-transfer limit to the current is known as the limiting-current density (Free et al., 2013). In other words, when the limiting-current density is applied, the electrochemical reaction is occurring at the maximum possible rate for the current mass-transfer conditions (Ettel, 1981). Therefore, any potential increase after the limiting-current density is reached will not increase the rate of the electrochemical reaction (Das and Gopala, 1996). The limiting-current density is influenced by the hydrodynamics of the system, such as the Nernst diffusion layer thickness, the concentration of ions, and the temperature (Cifuentes and Simpson, 2005; Gopala and Das, 1992).

The effect of the limiting-current density is graphically shown in Figure 2.7 for an arbitrary cathodic reduction reaction. When the Butler–Volmer equation is used to relate the current density to the overpotential the relationship is exponential, as shown by the solid line. A more realistic representation of the relationship is, however, given when combining the reaction-rate and mass-transfer kinetics, as shown by the black dashed line. Combining the reaction-rate and mass-transfer kinetics results in the reaction rate levelling off as it approaches the limiting-current density, represented by the grey dashed horizontal line.



Figure 2.7: Schematic representation of current density-overpotential curves comparing the mixed effects of masstransfer and reaction kinetics, and only reaction kinetics (Butler-Volmer equation) (redrawn from Tucker, 2019).

The Butler–Volmer equation can be modified to include the mass-transfer kinetics, as shown in Equation 2.22. The standard Butler–Volmer equation presupposes that the ion concentration at the electrode surface does not differ significantly from that in the bulk solution. The modified Butler–Volmer equation, however, includes a mass-transfer factor. The mass-transfer factor is the concentration of the respective ion at the electrode surface per the concentration in the bulk electrolyte.

$$i = i_0 \left[ C_{\rm R} \, \exp\left(\frac{-\alpha \, n \, F}{R \, T} \, \eta\right) - C_0 \, \exp\left(\frac{(1-\alpha) \, n \, F}{R \, T} \, \eta\right) \right] \qquad [2.22]$$

where  $C_{\rm R} = \frac{C_{\rm R,surface}}{C_{\rm R,bulk}}$  (1 when the species is plated) and  $C_{\rm O} = \frac{C_{\rm O,surface}}{C_{\rm O,bulk}}$ , for  $O^{n^+} + ne^- \leftrightarrow {\rm R}$ 

During copper electrowinning, the ferric ions, present as an impurity in the ore, are reduced more readily than the cupric ions when current is applied. As discussed in Section 2.2.2, this is because ferric reduction has a higher reduction potential. The limiting-current density is, therefore, first reached for the reduction of iron and only thereafter will any additional applied current be allocated for the reduction of the cupric ions (Gopala and Das, 1992). The current that is applied to the electrowinning cell should, therefore, translate to a current density high enough such that the desired copper reduction rate is attained, but not exceed the limiting-current density for copper reduction.

Industrial electrowinning plants generally operate at below 50% of the limiting-current density for copper reduction, otherwise the current becomes unevenly distributed and the deposited copper has a rough surface with nodular formations (Aqueveque et al., 2015; Gopala and Das, 1992). Once the limiting-current density is exceeded, the process becomes electrically inefficient and copper powder is formed, instead of adherent copper plating (Gopala and Das, 1992).

The concentration of the respective ion at the electrode surface, required in the modified Butler–Volmer equation, is not easily determined. Consequently, in this project, the standard Butler–Volmer equation was selected for modelling industrial electrowinning. As previously mentioned, it is a good approximation of the current density if the current density is less than approximately 10% of the smaller limiting-current density at the anode and cathode (Bard and Faulkner, 2001). The limiting-current density is, therefore, used to comment on the use of the standard Butler–Volmer equation during model validation (Chapter 9).

# 2.3 INDUSTRIAL COPPER ELECTROWINNING

# 2.3.1 Process Description

The hydrometallurgical method for extraction of copper consists of leaching, solvent extraction (for the majority of operations), and electrowinning (Komulainen, 2007). Figure 2.8 illustrates the flow of the general method that includes a solvent extraction step, whilst Figure 2.9 shows the method excluding solvent extraction (i.e., direct electrowinning).



Figure 2.8: Block flow diagram for hydrometallurgical extraction of copper via leaching, solvent extraction, and electrowinning (redrawn from Tucker, 2019).



Figure 2.9: Block flow diagram for hydrometallurgical extraction of copper via leaching and direct electrowinning (adapted from Burchell et al., 2017).

The choice of leaching method is based on the mineralogy of the ore, the copper grade, and the particle size (Schlesinger et al., 2011c). Heap leaching is used for the majority of copper extracted hydrometallurgically and is employed by most North and South American operations (Schlesinger et al., 2011c; Sole and Tinkler, 2016). In the African Copperbelt, agitated tank leaching is, however, widely used due to the high copper grade and presence of readily acid-leachable minerals (Schlesinger et al., 2011c; Sole and Tinkler, 2016).

Agitated leaching is comparatively more expensive but can attain very high copper recoveries (close to 100%) over a shorter residence time (hours, rather than months or years) (Schlesinger et al., 2011a; Sole and Tinkler, 2016). The high recovery combined with the higher ore grade processed by African operations (3% to 5% acid-soluble copper) result in a pregnant leach solution (PLS) with a high copper concentration (Sole and Tinkler, 2016). Where heap leaching typically results in a copper concentration of between 1 g/L and 6 g/L in the PLS, the concentration can be as high as 40 g/L for operations employing agitated leaching (Schlesinger et al., 2011a, 2011b). The PLS produced via heap leaching is too dilute in copper, and too impure, for electrowinning and the copper must be transferred to a concentrated copper electrolyte via solvent extraction (Schlesinger et al., 2011a).

The solvent extraction process consists of extraction and stripping processes (Figure 2.8). During the extraction process, the PLS is contacted with an organic extractant that reacts selectively with copper over the other metal cations present. The raffinate, which is barren in copper and high in acid, is recycled to be used as a lixiviant in the leaching process. Subsequently, during the stripping process, the loaded organic phase is contacted with the spent electrolyte, stripping the copper from the organic phase, and forming the advance electrolyte having a high cupric ion concentration.

Although the PLS obtained from agitated leaching operations is often sufficiently high in copper to be used directly in electrowinning, solvent extraction is typically employed by these operations to reduce the concentrations of impurities present in the electrolyte. A few operations do, however, treat PLS directly by electrowinning for copper recovery. These operations are mainly situated in African and Asian countries. Direct copper electrowinning from ore leach solutions produces copper of a lower quality and with reduced efficiency due to the impure electrolyte (Schlesinger et al., 2011b). It is also necessary to electrowin copper from the electrolyte to much lower concentrations because the spent electrolyte cannot be recycled to the solvent extraction step (Schlesinger et al., 2011b). This is usually done via a two-step electrowinning process where the first circuit reduces the copper from approximately 40 g/L to 20 g/L (slightly lower than for post-solvent extraction electrowinning) (Schlesinger et al., 2011b). The second circuit, termed liberator cells, reduce the copper to as low as 5 g/L producing very poor copper cathodes in the process. The copper produced in the liberator cells is usually sent to anode furnaces for melting and electrorefining (Schlesinger et al., 2011b). The produced spent electrolyte is very high in acid and is returned to the leaching step (Schlesinger et al., 2011b).

Direct electrowinning is also implemented in several base-metal refineries, which use concentrate or matte leach solutions that contain much higher levels of copper than when leaching from ore (up to 70 g/L) (Schlesinger et al., 2022). This includes operations, specifically in South Africa, where copper is produced as a by-product of other metals refining (Sole et al., 2019). These operations are able to produce London Metal Exchange (LME) grade copper (Schlesinger et al., 2022).

Approximately 120 000 t of copper were produced via direct electrowinning in 2010 (ICSG, 2010). This value is, however, expected to decrease as the implementation of solvent extraction increases in African operations, despite numerous challenges (Sole and Tinkler, 2016). Accordingly, it is essential that the model developed in this project, specifically for direct electrowinning operations, must also be applicable to post-solvent extraction electrowinning to ensure it is future proof.

## 2.3.2 Tankhouse Design

Electrowinning tankhouses consist of circuits of interconnected electrowinning cells. A typical electrowinning cell consists of alternating cathodes and anodes with a typical anode–cathode spacing of 50 mm (Figure 2.10). Generally, the electrolyte flows continuously through a manifold at the bottom, and overflows at one of the sides, ensuring a constant volume of electrolyte. The cells contain between 60 and 80 cathodes, with one more anode than cathode per cell (Beukes and Badenhorst, 2009; Schlesinger et al., 2011c).



Figure 2.10: Schematic representation of a typical electrowinning cell (adapted from Tucker, 2019).

Electrowinning cells are connected using intercell busbars to form a complete electrical circuit, with a tankhouse consisting of an average of four circuits, and each circuit containing approximately 120 cells (Aqueveque et al., 2015). Three types of intercellular connections are currently available for use in industrial electrowinning tankhouses: the Walker configuration, the Optibar configuration, and the triple segmented (backup bypass system) configuration (Wiechmann et al., 2012).

The Walker configuration uses busbars to connect anodes of one cell and the cathodes of the adjacent cell to create a series circuit (Aqueveque et al., 2015; Walker, 1901). The Optibar configuration uses

busbars to connect a single cathode of one cell to a single anode from the adjacent cell. The Optibar configuration has been successfully implemented on industrial scale for at least one electrowinning tankhouse (Wiechmann et al., 2012). No industrial application of the triple segmented configuration has been reported in literature, but one electrowinning tankhouse is evaluating industrial prototypes (Wiechmann et al., 2019).

By far the most common configuration of intercellular connections is the Walker configuration (Wiechmann et al., 2012). A simplified representation showing how the Walker configuration is used to connect six cells to form a circuit is given in Figure 2.11. For a specific cell, the busbar that holds the anodes connects them electrically, whilst the corresponding cathodes receive the current through the electrolyte and deliver it to the busbar that holds both the corresponding cathodes and the anodes of the adjacent cell. The circuit is powered by a rectifier that converts the current from alternating to direct current (Wiechmann et al., 2002). The current density carried by the busbars is designed to be approximately  $1.2 \text{ A/m}^2$  (Beukes and Badenhorst, 2009).



Figure 2.11: Schematic representation showing six cells connected to form a circuit, using the Walker configuration (redrawn from Tucker, 2019).

# 2.3.3 Key Performance Indicators

KPIs for the electrowinning process include the quality of the produced cathodes, the yield of copper, and the energy consumed during the process. A model that simulates the copper electrowinning process would require the KPIs as the main output variables.

# 2.3.3.1 Quality

The first indication of quality is the purity or grade of the produced copper. The purity of the copper cathode is specified by various international metal exchanges. The LME and New York Mercantile Exchange (Comex) specify a copper purity of 99.9%, with only 0.0065% impurities allowed for

Grade A copper (LME, 2020). The purity of the copper is determined by analysing the chemical compounds in the cathodes. Samples of the cathode are analysed to determine the chemical composition, typically using techniques such as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

The second indication of quality is the morphology of the deposited copper. The orientation of the copper grain growth and surface morphology of the produced copper is important for downstream physical handling, as well as market acceptance (Moskalyk et al., 1999). The physical quality of the deposited copper is determined at the end of the process using a machine that works with two high-resolution cameras and a high-power light (Aqueveque et al., 2015). This automated method is widely used, but some plants still rely on trained workers to identify irregularities (Rantala and Virtanen, 2006).

# 2.3.3.2 Yield

The yield of copper refers to the mass of copper produced through the electrowinning process. A typical industrial electrowinning process produces cathodes that are plated with 50 kg to 55 kg of copper on each side of the stainless-steel blank (Schlesinger et al., 2011c).

# 2.3.3.3 Energy Consumption

Electrowinning is an energy-intensive process, requiring a cell voltage of approximately 2.0 V (Schlesinger et al., 2011c). In recent years the focus has shifted to the environmental impact of large industries, including the carbon footprint generated by electrowinning tankhouses. It is, therefore, imperative for the process to be operated with a conscious effort to increase energy efficiency and decrease energy consumption. Two methods of quantifying the energy consumption of the process, current efficiency and specific energy consumption (SEC), are discussed below.

Current efficiency is defined as the proportion of the total current that produces solid copper. A practical approach for determining the current efficiency is suggested by Beukes and Badenhorst (2009), where the amount of copper produced is divided by the theoretical amount calculated from a form of Faraday's law (Equation 2.24), as shown in Equation 2.23.

$$\beta = \frac{m_{\text{Cu,measured}}}{m_{\text{Cu,theoretical}}}$$
[2.23]

where  $\beta$  is the current efficiency (fraction) and *m* is the mass (kg).

$$m_{i,\text{theoretical}} = -\frac{s_i M_i I t}{n F} \qquad [2.24]$$

where  $m_{i,\text{theoretical}}$  is the mass of the species produced (g),  $s_i$  is the stoichiometric coefficient (negative if formed),  $M_i$  is the molecular mass (g/mol), I is the current (A), and t is the time (s).

The remainder of the current not used to produce solid copper is wasted by side-reactions occurring at the cathode, short circuits, stray currents, corrosion of deposited copper, and deposited copper falling off the cathodes (Moats, 2012; Schlesinger et al., 2011c). Moats (2012) elaborated, stating that the sources of inefficiency are often related. The reduction of ferric iron and/or dissolved oxygen can lead to either side-reactions occurring or corrosion of the deposited copper. From an operational standpoint the result is, however, similar: a decrease in current efficiency. Consequently, Moats (2012) motivated discussing the effect of these components in terms of reduction reactions, whilst recognising that corrosion could also be occurring.

It is commonly accepted that the main factors that decrease the current efficiency is the presence of iron in the electrolyte, and inadequate housekeeping. Inadequate housekeeping can lead to an increase in short circuits and stray currents. For the specific tankhouse studied, Moongo and Michael (2021) reported that short circuits had the most significant effect on the current efficiency. Bringing short circuits under control resulted in a 5.4% increase in current efficiency. A root cause analysis showed that, among other factors, low copper concentration in the spent electrolyte (caused by poor process control), and poor cathode smoothing agent control were responsible for the short circuits at the specific tankhouse investigated (Moongo and Michael, 2021).

The SEC is a measure of the electricity, supplied as a source of power, used during electrowinning, and can be calculated using Equation 2.25. The SEC in an electrowinning cell is approximately 2000 kWh/t, with only about 30% constituting the theoretical power requirement for copper reduction (Schlesinger et al., 2011b). The contributions to the total power consumption in a typical electrowinning cell are shown in Figure 2.12. Isolating the *x*-axis shows the contributions of components to the total cell voltage. The total voltage consists of the thermodynamic potential requirement of 0.89 V ( $E^0$ ), the cathodic overpotential of between 0.05 V and 1 V ( $\eta_c$ ) the anodic overpotential of approximately 0.5 V ( $\eta_o$ ), the potential drop over the electrolyte of between 0.25 V and 0.3 V ( $IR_s$ ), and a potential drop due to hardware resistance of approximately 0.3 V ( $IR_h$ ) (Schlesinger et al., 2011b). Isolating the *y*-axis shows the contributions to the total current. When combining the two axes, the contribution of a component to the total power consumption can be viewed as an area on Figure 2.12.

$$SEC = \frac{I U_{\rm T} t}{m_{\rm Cu,measured}}$$
[2.25]

where SEC is the specific energy consumption (kWh/t), I is the current (A),  $U_T$  is the total voltage (V), t is the time (h), and  $m_{Cu,measured}$  is the mass of copper produced (kg).



Figure 2.12: Current and voltage contributions to power consumption in a typical copper electrowinning cell (redrawn from Schlesinger et al., 2011b).

# 2.3.4 Variables Affecting Performance

It is important to identify the process variables that influence the KPIs. The effect of changes in these variables must be accounted for by the electrowinning model to ensure accurate predictions of the KPIs.

# 2.3.4.1 Electrical Input

The electrical input, or power supplied, is determined by the required current density. The current density is an important process variable as it influences the yield and quality of the deposited copper. The rate of copper production increases with increasing current density (Schlesinger et al., 2011c). Operating at current densities above the limiting-current density could, however, result in uneven plating and nodular growths, leading to short circuits and decreased copper quality.

Current densities for post-solvent extraction tankhouses typically vary between 200 A/m<sup>2</sup> and 375 A/m<sup>2</sup> but can be as high as 460 A/m<sup>2</sup>, depending on the impurities present in the electrolyte (Bard and Faulkner, 2001; Beukes and Badenhorst, 2009; Schlesinger et al., 2011b). The impure electrolyte used in direct copper electrowinning means that these operations are forced to operate at much lower current densities (140 A/m<sup>2</sup> to 220 A/m<sup>2</sup>), than their post-solvent extraction counterparts (Robinson et al., 2013; Sole et al., 2019).

### 2.3.4.2 Electrolyte Composition

The advance electrolytes used by direct copper electrowinning operations typically contain 40 g/L to 70 g/L Cu (Robinson et al., 2013; Sole et al., 2019). An increase in the copper concentration will improve the quality of the deposited copper and marginally increase the current efficiency but could lead to copper sulfate crystallisation and a slight increase in electrolyte resistance (Aminian et al., 2000;

Dini and Snyder, 2011; Schlesinger et al., 2011b). A significant decrease in the copper concentration could lead to a decrease in plating rate due to insufficient diffusion for delivering cupric ions to the electrode boundary layer (Tucker, 2019).

The acid concentration used by direct copper electrowinning operations (41 g/L to 90 g/L  $H_2SO_4$ ) is much lower than the electrolyte acidities used by post-solvent extraction operations (up to 180 g/L  $H_2SO_4$ ) (Robinson et al., 2013; Sole et al., 2019). This lower acid concentration is necessary because the spent electrolyte is typically returned to the leaching circuit (Sole et al., 2019). Although the lower acid concentration will have a negative effect on the electrolyte conductivity, as elucidated in Chapter 3, the corrosion of lead-alloy anodes has been shown to decrease with decreasing acid concentrations (Andersen et al., 1974).

Various impurities, originating from the copper-containing ore, are also present in the electrolyte used for copper electrowinning. The major impurities present in direct copper electrowinning electrolytes are discussed below. Impurities typically associated with industrial copper electrorefining electrolytes, but not prevalent in electrowinning electrolytes (such as arsenic, antimony, and bismuth) (Moats et al., 2012), are excluded from the discussion.

## Iron

As previously discussed, iron has a significant effect on the KPIs for copper electrowinning (Section 2.2.2). This substantial impact results from iron reduction being more thermodynamically favourable than copper deposition and not kinetically hindered (Moats, 2018). The presence of ferrous iron in concentrations greater than 1 g/L has, however, been shown to inhibit the formation of the  $MnO_2^-$  based slime discussed later in this section (Ipinza et al., 2003; Zhang and Cheng, 2007). Ipinza et al. (2003) explained that this is because ferrous iron is oxidised preferentially to the manganese ions, preventing the formation of  $MnO_2$ . Andersen et al. (1974) also stated that iron, similar to nickel and cobalt, has a moderate effect on inhibiting the corrosion of lead-alloy anodes. They, however, emphasised that this is only the case if iron is present in relatively high concentrations (8 to 10 g/L), and that any benefit of adding iron for this purpose is negated by the detrimental effect thereof on the KPIs.

#### Nickel

Direct copper electrowinning electrolytes typically contain a high background of nickel (20 g/L to 65 g/L), establishing nickel as an important impurity to consider when modelling the process (Robinson et al., 2013; Sole et al., 2019). Despite this, most of the published literature regarding the effect of nickel is focused on the copper electrorefining process, likely because the presence of nickel is known to influence the mass-transfer conditions. Copper electrorefining utilises similar process conditions to

electrowinning in terms of temperature, electrolyte composition, additives, and applied current density. A key difference is, however, the mass-transfer-limited nature of copper reduction for industrial copper electrorefining, compared with the reaction-rate-limited nature of copper reduction for electrowinning (Jarjoura and Kipouros, 2006; Kalliomäki et al., 2019). In this section the limited literature pertaining to the effect of nickel on the KPIs of electrowinning is supplemented by literature specific to electrorefining. The effect of nickel is discussed cognisant of the reaction-rate-limited nature of copper reduction swill not be discussed in depth.

The first consideration is the co-electrodeposition of nickel during copper electrowinning. Vegliò et al. (2003) and Kalliomäki et al. (2019) confirmed that the selective deposition of copper and nickel is possible for electrowinning and electrorefining, respectively. Since the standard reduction potential of Ni<sup>2+</sup> is 587 mV lower than that of Cu<sup>2+</sup>, nickel is not reduced during copper extraction (Aromaa, 2007). Sahlman et al. (2021) investigated nickel contamination of the cathode during copper electrorefining and also explained that nickel co-electrodeposition is, thermodynamically, extremely unlikely as it would require the copper concentration in the electrolyte to be almost zero. Although Sahlman et al. (2021) observed traces of nickel for two copper cathodes plated during laboratory-scale experiments, it was suggested that this was probably due to precipitated nickel sulfate. Sahlman et al. (2021) further investigated particle entrapment and the possibility of electrolyte inclusion. It was determined that particle entrapment was the most significant source of cathode contamination by nickel during electrorefining. The impact of particle entrapment on the KPIs will likely be limited to the quality of deposited copper.

Another factor that could impact the quality of the deposited copper is the change in physicochemical properties effected by the presence of nickel, as described by Subbaiah and Das (1994). Changes in the physicochemical properties were shown to affect the surface methodology and crystal orientation of the copper significantly. Aside from the effect of changes in the physicochemical properties on the quality, the effect on the remaining KPIs is also of importance for developing a high-fidelity model. The adverse effect of nickel on the physicochemical properties of electrolytes, and the accompanying decrease in the mass-transfer conditions and limiting-current density of the copper electrodeposition process, has been the subject of several studies (Jarjoura et al., 2003; Kalliomäki et al., 2021, 2017, 2016; Price and Davenport, 1981, 1980; Subbaiah and Das, 1989). Consequently, it is well established that conductivity decreases with increasing nickel concentration, whilst density and viscosity increase.

The presence of nickel (together with iron and cobalt) has, further, been shown to inhibit the corrosion of lead anodes (Andersen et al., 1974). Ipinza et al. (2003) studied electrowinning slimes from industrial electrowinning tankhouses and found the main constituent to be lead sulfate originating from anode corrosion. Consequently, nickel could reduce the formation of slime by reducing the corrosion of lead

anodes. Although the formation of slime influences the mass-transfer conditions during electrorefining, the main effect during copper electrowinning is expected to be the contamination of copper cathodes when the slime becomes suspended (Ipinza et al., 2003), and the increase in power consumption due to the anode slime resistance voltage drop.

### Cobalt

It has been well established that the presence of cobalt in copper electrowinning electrolytes reduces lead anode corrosion and lowers the overpotential for water oxidation. The mechanism of action for the cobalt ions, however, remains open to debate (as explained in the comprehensive review done by Nikoloski and Nicol (2008)). Although studies by Nguyen et al. (2008) and Nguyen and Atrens (2008) seem to have contributed additional clarification, studies supporting their findings are required.

As inexpensive lead-alloy anodes remain the most widely used electrode for many industrial applications, the corrosion of lead anodes continues to be a pertinent issue (Abbey and Moats, 2017; Robinson et al., 2013; Sole et al., 2019). Clancy et al. (2013) explained that the lead in the anode reacts with the sulfate in the electrolyte to form PbSO<sub>4</sub>. Oxygen evolution occurs after the PbSO<sub>4</sub> reacts with water to form a protective passive layer of PbO<sub>2</sub> (Abbey and Moats, 2017). Authors have previously attributed the decrease in lead corrosion in the presence of cobalt to the formation of cobalt oxides in the pores of the protective PbO<sub>2</sub> film (Andersen et al., 1974; Rey et al., 1938), or the absorption of cobalt from the electrolyte onto the anode surface (Bagshaw, 1997).

Koch (1959a, 1959b) and Rey et al. (1938) have also previously inferred that the reduced potential of the lead anode, in the presence of cobalt ions, results in less lead oxidation. Work conducted by Nguyen et al. (2008), however, contradicts this suggestion as the amount of lead oxidised was found to be independent of anodic current density. Instead, Nguyen et al. (2008) and Nguyen and Atrens (2008) stated that the cobalt ions changed the structure, morphology, and chemical composition of the protective film from a loose porous film to a thin dense film. They suggest that this less porous layer is responsible for hindering the oxidation of PbSO<sub>4</sub> to PbO<sub>2</sub>, decreasing the rate of oxidation for the lead anode.

The overpotential needed for the oxidation of water is high on lead anodes partly due to the potential needed to form and sustain the passive PbO<sub>2</sub> layer mentioned above (Abbey and Moats, 2017). Nguyen et al. (2008) suggested that the decrease in potential observed in the presence of cobalt ions may indicate that the oxygen evolution is more rapid on the thin dense PbO<sub>2</sub> film, as opposed to the loose porous film formed in the absence of cobalt. On the other hand, an additional pathway for oxygen evolution could also explain the decrease in anodic potential in the presence of cobalt (Koch, 1959b). This pathway involves the oxidation of  $Co^{2+}$  ions, followed by the oxidation of water by the  $Co^{3+}$  ions,

decreasing the anodic potential (Gendron et al., 1975). Moreover, Abbey and Moats (2017) have shown that cobalt and iron individually, but also jointly reduces anode potential. It is, therefore, possible that cobalt, iron, and manganese interact at or near the anode surface, resulting in decreased anodic potential (Abbey and Moats, 2017).

#### Manganese

Manganese is present in most African electrolytes due to the prevalence of agitation leaching. Typical concentrations of manganese in these electrolytes range from 330 mg/L to 670 mg/L (Robinson et al., 2013; Sole et al., 2019). Manganese has been shown to increase the density and viscosity of copper electrolytes, whilst decreasing the conductivity (Subbaiah and Das, 1994). Nonetheless, only a handful of studies discuss the effect of manganese on copper electrowinning outside of the impact on the physicochemical properties of the electrolyte.

It is known that the oxidation of manganese occurs during copper electrowinning, specifically during plant start-up due to the high overpotential required for oxygen evolution on new anodes (Yu and O'Keefe, 2002). The oxidation of manganese can also occur during normal operation if the double layer formed on the anode (discussed below) dissolves or if the iron concentration decreases to below 0.8 g/L (or preferably 1 g/L to 1.5 g/L) (Bwando et al., 2023). Bwando et al. (2023) explained that this minimum threshold of iron (specifically ferrous iron) is required to stabilise the electrolyte oxidation-reduction potential and prevent the oxidation of manganese, or to consume oxidised species if already formed.

Wang et al. (2021) summarised a two-fold effect of manganese on copper electrowinning: the formation of a double layer on the anode (referred to above), and changes to the oxygen evolution reaction. The double layer is formed when Mn<sup>2+</sup> is oxidised on the surface of the anode to form solid manganese dioxide and other high-oxidation state manganese substances (Ipinza et al., 2003). Ipinza et al. (2003) reported that this double layer is composed of a thick outer layer of non-adhering and flaking scales, and a thin protective inner layer that adheres to the electrode. The protective inner layer could potentially affect the corrosion of the lead anode. However, due to the loose and porous nature of the outer layer and the weak adhesion of the substrate the layer gradually falls off, along with the protective inner layer, and forms part of the anode slime (Elrefacy et al., 2020; Wang et al., 2021). The slime affects not only the quality of the deposited copper, but also the current efficiency and power consumption (Cheng et al., 2000; Elrefacy et al., 2020; Subbaiah and Das, 1994; Zhang and Cheng, 2007). Aside from minimising the concentration of manganese to below 40 mg/L, Mirza et al. (2016) suggested diligent housekeeping (removing and cleaning the anodes at regular intervals) as the most suitable solution for mitigating the effect of anode slimes aggravated by the presence of manganese.

The second effect of manganese on copper electrowinning, as discussed by Wang et al. (2021), is the effect on the oxygen evolution reaction. The presence of manganese in the electrolyte reduces the charge fraction for oxygen evolution (Tjandrawan, 2010). The extent of the effect of manganese on the oxygen evolution reaction is dependent on the composition of the lead-alloy anode used during electrowinning (Tjandrawan, 2010). For example, when oxidising Pb-Ca-Sn anodes at 2.0 V for 24 hours in the presence of 1 g/L manganese ions, 70% of the charge was used for oxidation of manganese ions. This value was reduced to approximately 10% when using Pb-Ag anodes, as silver exhibits a catalytic effect on the oxygen evolution reaction.

For African electrolytes, which contain high concentrations of cobalt, the extent of the discussed effects will likely be limited. This is because cobalt is thought to limit oxidation of manganese by promoting the evolution of oxygen (Elrefaey et al., 2020; Tjandrawan, 2010). Furthermore, iron is expected to be present in adequate concentrations in the majority of direct electrowinning operations to mitigate the oxidation of manganese, if present, during operation.

## 2.3.4.3 Electrolyte Additives

Various electrolyte additives are used to increase the performance of the electrowinning process, including chloride and smoothing agents. Chloride ions aid in the growth of dense, fine-grained, low-impurity copper deposits (Schlesinger et al., 2011c). The chloride levels should, however, be kept below 30 mg/L to avoid pitting corrosion of the stainless-steel cathodes (Beukes and Badenhorst, 2009).

Smoothing agents are added to aid in the plating of dense and smooth copper and minimise the entrapment of electrolyte impurities (Schlesinger et al., 2011c). Smoothing agents can be classified as brighteners, levelers, or suppressors (Vereecken et al., 2005). Brighteners tend to refine the grain structure by catalysing the copper reaction, thereby producing bright cathode surfaces (Moats et al., 2016). Levelers help produce a smooth surface by inhibiting the growth of protrusions, and inhibitors act as current suppressors, affecting both the copper dissolution and deposition (Moats et al., 2016). Similar to electrorefining operations, direct copper electrowinning operations typically use thiourea and Avitone as additives (Robinson et al., 2013; Sole et al., 2019). Typical thiourea concentrations for electrowinning applications range from 0.5 mg/L to 3 mg/L (Hiskey and Cheng, 1998).

At 100% to 320% excess thiourea, Ngandu (2016) observed a decrease in current efficiency for increases in thiourea concentration, when investigating the suitability of thiourea as a selenium/tellurium precipitating agent. At thiourea concentrations of 10 mg/L, more closely resembling actual industrial conditions, Ngandu (2016), however, reported a very small decrease in current efficiency (from 96.06% to 96.01%). Ngandu (2016) further stated that the addition of organic additives (such as thiourea) is known to increase the cathodic overpotential as a result of the additive being adsorbed onto the electrode surface.

#### 2.3.4.4 Electrolyte Temperature

The temperature of the electrolyte influences the current efficiency, power consumption, and quality of the deposited copper. The effect of temperature on the current efficiency seems to be dependent on the concentration of copper in the electrolyte. Alfantazi and Valic (2003) reported a decrease in current efficiency for an increase in temperature (from 40 °C to 60 °C) at high copper concentrations (65 g/L), when no iron is present. At low copper concentrations (25 g/L) they reported an increase in current efficiency for an increase in temperature. Similarly, Ehsani et al. (2016) reported an approximately 2% increase in current efficiency for an increase in temperature from 20 °C to 50 °C, for an electrolyte containing 30 g/L Cu and no iron. Although no explanation is provided for the decrease in current efficiency at higher copper concentrations, Ehsani et al. (2016) suggested that the increase in current efficiency at lower copper concentrations results from the acceleration of the electrochemical reaction and reduction in viscosity. The reduced viscosity enhances the diffusion of ions and increases the current efficiency. Increasing the temperature of an electrolyte with a high ferric concentration, however, increases the diffusion rate of this ion as well, thereby decreasing the current efficiency. In experimental work conducted by Das and Gopala (1996) on an electrolyte solution containing 37 g/L Cu and 2 g/L Fe<sup>3+</sup>, the current efficiency decreased from 88.6% to 84.4% with a temperature increase from 30 °C to 60 °C.

An increase in temperature has been shown to result in a decrease in power consumption. Panda and Das (2001) observed a decrease in power consumption (1400 kW/t to 1220 kW/t) when the temperature was increased from 30 °C to 60 °C. Moreover, Ehsani et al. (2016) reported an approximately 10% reduction in energy consumption when increasing the temperature from 20 °C to 50 °C. The decrease in power consumption when the temperature is increased is suggested to be the result of an increase in conductivity (Panda and Das, 2001). Beukes and Badenhorst (2009) reported the optimal temperature for conductivity, and therefore power consumption, as between 45 °C and 50 °C. Direct copper electrowinning operations operate at the higher end of this range (up to 60 °C) as the risk of organic degradation, applicable to post-solvent extraction operations, is not present (Robinson et al., 2013; Sole et al., 2019).

Literature reports contradicting findings for the effect of temperature on the quality of the deposited copper. Cooper and Mishra (1987) reported an improvement in quality for a temperature increase from 20 °C to 50 °C. Panda and Das (2001) also observed an increase in quality for a temperature increase of 30 °C to 60 °C. Ehsani et al. (2016), however, reported an increase in surface roughness for an increase in temperature from 20 °C to 50 °C. Ehsani et al. (2016) suggested that this is the result of insufficient time for crystal structures to form, due to the increase in the rate of the electrochemical reaction.

#### 2.3.4.5 Electrolyte Flow Rate

The electrolyte flow rate is specified to provide an interfacial cathode velocity of between 0.05 and  $0.1 \text{ m}^3/\text{h}/(\text{m}^2 \text{ of available cathode surface area})$ , with 0.08 being the standard value (Beukes and Badenhorst, 2009). The interfacial cathode velocity affects the boundary layer at the cathode surface and, therefore, the mass-transfer rates of ions (Beukes and Badenhorst, 2009).

#### 2.3.4.6 Electrolyte Resistance

The electrolyte resistance is the electrical resistance of the ions present in the electrolyte and contributes to a loss in voltage over the electrowinning cell. It is a function of the electrolyte specific resistivity, which is in turn dependent on the electrolyte conductivity (influenced by the composition and temperature), and the interelectrode distance (Wiechmann et al., 2011) (Equation 2.26). The electrolyte resistance can account for up to 24% of the SEC, making it an important consideration for energy consumption reduction (Kalliomäki et al., 2016; Price and Davenport, 1981, 1980; Wiechmann et al., 2010).

$$R_s = \frac{d}{\kappa A} \qquad [2.26]$$

where  $R_s$  is the electrolyte resistance ( $\Omega$ ), d is the interelectrode distance (m),  $\kappa$  is the conductivity (S/m), and A is the cross-sectional area of the electrode used in plating (m<sup>2</sup>).

#### 2.3.4.7 Hardware Resistance

Hardware resistance results from the resistance to current in the metal equipment pieces in the electrowinning circuit including electrodes, hanger bars, busbars, the rectifier, and contacts between pieces. It is dependent on the type of material, as well as the size and age of the equipment and will, therefore, be different for each plant (Tucker, 2019). It remains constant during the electrowinning process as it is a function of the cell design.

## 2.3.4.8 Electrodes

The majority of copper electrowinning tankhouses use permanent cathode technology (Hiskey, 1999; Schlesinger et al., 2011c). This technology entails employing reusable stainless-steel blank cathodes, identical to the cathodes used in electrorefining. Some older or smaller plants may still be using copper starter sheets, but many are switching over to stainless-steel cathodes where the benefits can justify the capital investment (Robinson et al., 2013; Sole et al., 2019).

Rolled Pb-Ca-Sn alloy anodes are the most popular choice for copper electrowinning tankhouses (Robinson et al., 2013; Sole et al., 2019). Direct electrowinning tankhouses, however, prefer the use of cast Pb-Sb anodes (Abbey and Moats, 2017; Robinson et al., 2013; Sole et al., 2019). At the higher temperatures direct electrowinning tankhouses operate at, the Pb-Ca-Sn alloy can recrystallise. This recrystallisation leads to reduced strength and higher corrosion, compared with the Pb-Sb alloy (Felder and Prengaman, 2006).

## 2.3.4.9 Housekeeping

Schlesinger et al. (2011b) underlined the importance of good housekeeping practices in maximising both the purity of the produced copper cathode and the energy efficiency of the tankhouse, as supported by other literature sources (Joy et al., 2010; Kumar et al., 2010; Pfalzgraff, 1999). Good housekeeping practices include the timely detection and mitigation of electrical shorts, straightening of cathode blanks, and electrode alignment and spacing (Sole et al., 2019).

Although the presence of iron in the electrolyte is known to contribute to a decrease in current efficiency, the relationship between iron concentration and current efficiency was not as significant as expected for the tankhouses surveyed by Sole et al. (2019) and Robinson et al. (2013). Consequently, Sole et al. (2019) advised that factors such as electrical housekeeping, anode age and maintenance, cleaning anode slime, and the age of the tankhouse are key when optimising the energy usage of electrowinning tankhouses.

Automation of tankhouses can significantly improve tankhouse housekeeping practices, assisting with maintaining good electrode arrangements, uniformity of current distribution, and rapid short detection (Schlesinger et al., 2011b). A high-fidelity dynamic model can, for example, predict optimal tankhouse performance, given the specific operational and design variables. Following, the predicted performance can be compared with the actual tankhouse performance to enable preventative housekeeping.

## 2.3.5 Measurements of Variables

To ensure that the model can be used in industrial electrowinning tankhouses, it is imperative that the required input and output variables be readily measured or have the potential to be readily measured. The availability and accuracy of measurements for each process variable is, therefore, assessed in this section. Sole et al. (2019) emphasised that an increasing use of automation and intelligent monitoring systems are likely to dominate advances in electrowinning. As is the case for the oil and gas industry, factors such as wireless transmitters, a reduction in the cost of measurement technology, and increased regulations that require monitoring, are expected to increase the number of available measurements (Hedengren and Eaton, 2017). Consequently, although some of the advanced measurement strategies

discussed below are not currently commonplace, it is likely that industry will move towards standardising implementation thereof in the future.

# 2.3.5.1 Rectifier Current

Two types of sensors are typically used to measure the direct rectifier current that flows to the cells across the busbars in industrial electrowinning plants: Hall-effect sensors and fibre-optic current sensors (Aqueveque et al., 2015; Ziegler et al., 2009). Hall-effect sensors are magnetic field sensors. When current passes through a magnetic core's aperture, a magnetic flux is induced in the core, with a voltage generated proportional to the magnetic flux. This voltage induction is known as the Hall effect. The induced voltage is amplified and measured. Since the voltage is proportional to the current, the current can be quantified.

Fibre-optic current sensors make use of Faraday's effect in an optical-fibre loop around the currentcarrying busbar (Bohnert et al., 2007a). A commercially available 500 kA fibre-optic current sensor has been shown to have accuracy and repeatability well within 0.1%, for applied currents ranging between 3 kA and 300 kA (Bohnert et al., 2007a). The sensor uses a negligible amount of power and space when compared with Hall sensors, which can have a large power loss and can weigh up to 2000 kg (Bohnert et al., 2007a). Fibre-optic current sensors are typically employed for current magnitudes above 1 kA. For smaller current magnitudes, Hall sensors would be less expensive (Bohnert et al., 2007b).

#### 2.3.5.2 Cathodic Current

The typical methods of current distribution monitoring used in industrial electrowinning tankhouses include infrared imaging, cell voltage monitoring, and handheld Gauss or individual cathode-current measurement devices (Fraser et al., 2013). Infrared imaging uses the temperature difference that occurs because of the difference in heat generated between poor electrode contacts or short circuits, and normal cathodes. The infrared cameras can be handheld or crane mounted. Cell voltage monitoring devices can detect current distribution problems as they are typically accompanied by changes in cell voltage. Handheld Gauss or individual electrode current measurement devices are composed of a stick-mounted Hall-effect sensor and entail tankhouse workers continuously roaming the tankhouse to take measurements (Aqueveque et al., 2015; Fraser et al., 2013).

Individual cathodic current measurement, based on lineal radiometric Hall-effect sensors and ferromagnetic flux concentrators, is possible, but currently only non-commercial experimental prototypes are available (Aqueveque et al., 2015, 2010; Wiechmann et al., 2007). The Hatch HELM Tracker is a notable exception and has been retrofitted and tested at industrial electrowinning plants. The tracker enables continuous measurement of the current flowing through every electrode in a tankhouse. It works by measuring the magnetic field generated by the current passing through the

cathode header bar (Grant et al., 2017). The tracker currently also measures the cell voltage, with future developments including built-in sensors for electrolyte temperature, concentration, and flow (Fraser et al., 2013).

### 2.3.5.3 Cell Voltage

Commercially implemented cell voltage monitoring devices, such as the MIPAC Cell View (You et al., 2009) and Outotec Cell Sense (Kim and You, 2007), provide wireless monitoring of individual cell voltages for electrowinning cells that have equipotential intercell bar connections. The voltage is measured in parallel connections over all the anode–cathode pairs in the cell (Aqueveque et al., 2015). For electrowinning cells with current-source intercell bar connections it is theoretically possible to measure the voltage over each anode–cathode pair, but no commercially implemented monitoring devices are available (Aqueveque et al., 2015). The Outotec Cell Sense system has been used to successfully identify short circuits in the early phase of development in an industrial electrowinning tankhouse (Rantala, 2013). Rantala (2013), however, further reported that although cell voltage measurements for early-fault detection. This challenge stems from the cell voltage being dependent on the operating conditions of the cell, as well as being a function of various other process measurements (such as the electrolyte composition and temperature). It is, therefore, crucial that the operating conditions are evaluated together with the online cell voltage measurements for use in fault detection (Rantala, 2013).

### 2.3.5.4 Electrolyte Concentration

Online instruments for measuring the copper, iron, and sulfuric acid concentrations in electrolytes are commercially available. This includes the Courier HX system from Outotec (2021), which uses high-performance x-ray fluorescence technology, supplemented by titrators, to perform elemental analyses and analyse ionic contents, such as sulfuric acid. Sparse sampling of electrolyte for laboratory analysis seems, however, to be the current industry-standard due to the slow process dynamics (Rantala, 2013). Typically, atomic absorption spectrophotometry (AAS), or in smaller tankhouses titrations, are used to analyse for the electrolyte composition.

# 2.3.6 Control of the Copper Electrowinning Process

The exact configuration of every industrial electrowinning tankhouse is dependent on the specific plant. Nevertheless, a process flow diagram for a typical copper electrowinning process is shown in Figure 2.13. The advance electrolyte, Stream 1, is combined with the resistively heated spent electrolyte, Stream 2, originating from the electrowinning cells (EW-101). The recirculating electrolyte, Stream 3, is pumped through a heat exchanger (E-101) where it is heated to the desired temperature via contact with hot water or steam, or alternatively, resistively heated using the spent electrolyte stream, Stream 4. The heated recirculating electrolyte is split equally between the electrowinning cells (EW-101) before combining and exiting as the spent electrolyte, Stream 4. The diagram shows two electrowinning cells (EW-101), but industrial tankhouses can consist of upwards of 500 cells (Robinson et al., 2013). The solid copper cathodes, Stream 5, are harvested from the electrowinning cells (EW-101). The spent electrolyte, Stream 4, is split into three streams: the recycle to be combined with the advance electrolyte (Stream 2), the recycle to the leaching step (Stream 6), and a bleed stream (Stream 7) that regulates the level of impurities in the cells.



Figure 2.13: Process flow diagram of electrowinning for the hydrometallurgical extraction of copper (redrawn from Tucker, 2019).

The overall control objective of an industrial plant for the hydrometallurgical extraction of copper is the production of high-quality copper, whilst maximising the net revenue of the plant. It should be noted that the control objective for South African base-metal refineries, where copper is produced as a minor by-product may, however, differ. Regardless, the control of the plant relies on operators continuously manipulating the setpoints for the basic controllers, meaning that the control loops are decentralised with manual setpoints for flow rates, levels, pumps, and valves (Komulainen, 2007).

The process includes long delays and complex interactions between the variables; therefore, optimal performance of the plant is seldom achieved (Komulainen, 2007). These plants, however, continuously capture large amounts of process data that can be used in advanced control systems, such as model predictive control (MPC). Applications of MPC are ubiquitous in industries such as refining and petrochemicals (Darby and Nikolaou, 2012), and are becoming more common in other industries such as mining, mineral processing, and extractive metallurgy (Crooks et al., 2023; Hodouin, 2011; Qin and Badgwell, 2003).

Control systems can be classified as either reactive or predictive, based on how sensor measurements are used, and control actions are generated. Reactive-based control strategies, currently implemented in electrowinning process control, use historical and current system states, as recorded by sensors, to generate control actions (Gaffoor, 2020). The controller, therefore, has no foresight of future process dynamics and is vulnerable to continuously changing process behaviour and anomalies. Currently, the electrowinning process is usually operated as a current-controlled process, where it is carried out at a fraction of the limiting-current density (Los et al., 2014).

The control loop for the rectifier (IIC-101, Figure 2.13) is designed to maintain the direct current consistent with a setpoint, which is manually adjusted by the operator (Bergh and Yianatos, 2001). The objective of the control loop is to protect the rectifier from overheating and prevent the decrease of cathode purity that occurs when the limiting-current density is breached (Bergh and Yianatos, 2001). For base-metal refineries, where the spent electrolyte is typically recycled to the leach circuit, or sent for further downstream processing, the composition and flow rate of the spent electrolyte will also influence the control philosophy.

A second control loop (TIC-101, Figure 2.13) is included for maintaining the electrolyte temperature at a constant setpoint by controlling the flow of hot water or steam to the heat exchanger (E-101, Figure 2.13) (Bergh et al., 2001). Sensors for temperature, level, flow, pressure, and conductivity are used, with all motors, stirrers, pumps, and valves being controlled. Typically, the monitoring of cell voltage and temperature, which is measured using an infrared camera installed on the handling crane, allows for short circuits to be traced.

In contrast, predictive-based control systems, such as MPC, perform dynamic, real-time optimisation of a process to generate actions that are adaptive to disturbances and consider the dynamic behaviour of the process (Gaffoor, 2020). The copper electrowinning process, specifically direct electrowinning, is characterised by time delays, multivariable behaviour, and nonlinearities (Lie and Hauge, 2008). This, combined with the continuous generation of large amounts of process data, makes direct copper electrowinning an ideal candidate for MPC and other predictive-based control systems. Advanced process control is already increasingly being considered for use in tankhouses, having the potential to improve current efficiency, productivity, and safety (Romero et al., 2007; Schlesinger et al., 2022).

An MPC controller requires additional components that are not required in conventional reactive controllers (Figure 2.14). A model that accurately describes the steady-state and dynamic behaviour of a process, over the whole operating range, including non-linear behaviour, is an essential feature of MPC (Bergh and Yianatos, 2001; Moser et al., 2020). The difficulty of predicting major disturbances and the corresponding effects on the final product, as well as the lack of process models applicable to industrial plants, have previously prevented the implementation of MPC for electrowinning tankhouses

(Bergh and Yianatos, 2001; Komulainen et al., 2009; Komulainen, 2007). A promising solution is the application of a dynamic model that is integrated with a means of updating according to an evolving dataset (Appl et al., 2020; Moser et al., 2020; Rosen et al., 2015; Sinner et al., 2020; Tao et al., 2019). This additional feature, which allows for continuous calibration of the model using tankhouse data, is ideal for use in MPC where accurate representation of process behaviour is essential.



Figure 2.14: Block flow diagram of a typical MPC controller (redrawn from Gaffoor, 2020).

Dynamic process models have already been developed and validated for leaching (Dorfling, 2012; Knoblauch, 2015; Miskin, 2016) and solvent extraction (Komulainen, 2007). The dynamic leaching process model provided a framework within which improved control strategies (Knoblauch, 2015) and fault diagnosis strategies (Miskin, 2016; Strydom, 2017) were investigated. Similarly, the dynamic solvent extraction model was used to investigate the performance of MPC as an advanced control system for the industrial copper solvent extraction process (Komulainen, 2007).

Komulainen (2007) suggested that the dynamic solvent extraction model should be combined with a dynamic electrowinning model to enable real-time optimisation. Moreover, real-time plant-wide optimisation, which requires the implementation of advanced control systems (such as MPC), is proposed by Bergh and Yianatos (2001) to be the optimal control approach for a leaching/solvent extraction/electrowinning plant. It entails adjusting the operating conditions as a function of the raw ore properties and feed rate, metal market prices, and reagent costs. MPC is expected to be a convenient control algorithm for the combined system due to the good interaction and time-delay handling properties. Additionally, accurate model predictions can provide early-fault detection, and a means of quantifying the advantage of using more complex control strategies (Appl et al., 2020).

# 2.4 MODELS

# 2.4.1 Empirical Property Correlations

As mentioned in the introduction of this dissertation (Section 1.4), the physicochemical properties of copper electrowinning electrolytes hold considerable economic importance. Developing accurate models of the physicochemical electrolyte properties has a twofold economic benefit for electrowinning tankhouses. Firstly, the correlations can form an integral part of the development of a high-fidelity dynamic process model (as done in this project). The potential benefit of such a model has been previously discussed and is well-documented for similar processes (Eksteen and Reuter, 2003; Knoblauch, 2015; Komulainen, 2007; Miskin, 2016; Strydom, 2017). Secondly, as these properties can be strongly influenced through the adjustment of the composition and temperature of the copper electrolyte (Kalliomäki et al., 2019), the models can aid cost optimisation and enable productivity improvements.

The four main physicochemical properties of concern for copper electrolytes are conductivity, density, viscosity, and the diffusion coefficient for the cupric ion. Electrolyte conductivity directly impacts the energy consumption of the copper electrowinning process (Price and Davenport, 1980). According to Kalliomäki et al. (2021) the electrolyte conductivity (via the electrolyte resistance) can account for 12% to 24% of the total energy consumption in electrowinning. Density and viscosity also affect the energy consumption by influencing the mass and heat-transfer conditions (Price and Davenport, 1981; Subbaiah and Das, 1989). In a similar vein, Bauer and Moats (2020) highlighted the significance of changes in the mass-transfer conditions on the quality of the deposited copper.

Changes in the physicochemical properties (specifically viscosity and the diffusion coefficient) will also impact the limiting-current density (Kalliomäki et al., 2016; Subbaiah and Das, 1994). The limiting-current density is an important consideration for electrowinning operations due to the detrimental effect on the quality of copper produced if the limiting-current density is breached. Moreover, the form of the Butler–Volmer equation used in this project to develop the electrowinning model is only a good approximation of the current density required for a specific reaction when the current density is less than approximately 10% of the smaller limiting-current density at the anode and cathode (Bard and Faulkner, 2001). Consequently, although the limiting-current density is not strictly a physicochemical property, it is included in discussions pertaining to these properties.

A considerable amount of literature has been published on modelling the effect of composition and temperature on the physicochemical properties of copper electrolytes. The discussion in this section is not meant to be an exhaustive analysis of all developed models. Instead, the focus will be on the recent work of Kalliomäki et al. (2021, 2017, 2016) and Lehtiniemi et al. (2018) as their models have been

proven to be superior to the classical models, within the investigated ranges. Furthermore, only Kalliomäki et al. (2017), Lehtiniemi et al. (2018), and Kalliomäki et al. (2021) have published data that include industrial validation of their models.

Kalliomäki et al. (2017) developed models for the viscosity and density of copper electrorefining electrolytes. Both the viscosity and density models proved more accurate than the classical models of Price and Davenport (1981) for predicting the properties of industrial electrolytes. Lehtiniemi et al. (2018) proposed improved models for copper electrorefining conductivity, based on models previously published by Kalliomäki et al. (2016). The models were validated using values measured from an industrial electrolyte. The best performing conductivity model was determined to be better at predicting the conductivity of the industrial electrolyte than the model developed by Price and Davenport (1981). A systematic error of approximately 8.5% was, however, still observed for predicting the conductivity (Lehtiniemi et al., 2018).

Kalliomäki et al. (2021) investigated the causes of the inaccuracies in the models proposed by Kalliomäki et al. (2017) and Lehtiniemi et al. (2018) in order to build more rigorous models for industry applications. Subsequently, refined regression models for predicting conductivities, viscosities, and densities of industrial copper electrolytes were proposed, based on measurements from both synthetic and industrial electrolytes. Separate models were developed for the properties of copper electrowinning and copper electrolytes, with the discussion limited to the electrowinning models for the purpose of the current project. Generally, the developed models predicted the conductivities and viscosities of the industrial electrowinning electrolytes, obtained from Glencore Nikkelverk, with higher accuracy than previously proposed models (Kalliomäki et al., 2021).

The temperature and component concentration ranges investigated by Kalliomäki et al. (2021) (and previous studies) are given in Table 2.1, along with the typical industrial conditions for direct copper electrowinning operations. Only the conductivity model developed by Kalliomäki et al. (2021) for low sulfuric acid concentrations (< 142 g/L) was considered in Table 2.1. It is clear that the component concentrations investigated by Kalliomäki et al. (2021) do not encompass the full range of operating conditions applicable to typical direct copper electrowinning operations (Robinson et al., 2013; Sole et al., 2019). This finding is notable because the empirical model form tends to lack robustness of prediction and is limited to interpolation based on the data used for model development (Eksteen and Reuter, 2003; Tsamandouras et al., 2013). Consequently, the existing physicochemical property correlations developed by Kalliomäki et al. (2021) require evaluation for the wide range of component concentrations associated with direct copper electrowinning.

Also shown in Table 2.1 are the conditions investigated by Kalliomäki et al. (2019) for the development of a correlation to predict the limiting-current density for electrorefining operations. The inclusion of

components such as arsenic and omission of iron and cobalt are expected to limit the applicability of the existing model for electrowinning operations. As far as it is known, no comparable correlation has been developed specifically for electrowinning operations. This statement excludes correlations for the diffusivity coefficient that can be used to calculate the limiting-current density using an approximation of the boundary layer thickness, as done by Bauer and Moats (2020).

Table 2.1: Su	ummary o	of existing	physicochemica	al property	/ models	with	conditions	used	during	model	develop	oment,
along with ty	pical ind	ustrial cond	litions for direct	copper ele	ectrowini	ning.						

Model	т (°С)	<i>x</i> Cu (g/L)	<i>x</i> H₂SO₄ (g/L)	xFe (g/L)	xNi (g/L)	xCo (g/L)	<i>x</i> Other (g/L)
Direct EW conditions (Robinson et al., 2013; Sole et al., 2019)	50 – 70	30 – 90	20 – 120	0.5 – 6	20 – 65	0 – 3	
Price and Davenport (1980) Density, conductivity, viscosity (ER and EW)	20 – 70	10 – 60	10 – 220				
Price and Davenport (1981) Density, conductivity	20 – 60	5 – 55	10 – 225	0 – 20	0 – 20		As 0 – 10
Subbaiah and Das (1989) Density, conductivity, viscosity	30	38.5 – 41.6	143.2 – 163.5	0.78 – 15.8	0.84 – 19.6	0.9 – 17.3	Mn 0.9 – 19.9
Jarjoura et al. (2003) Density and viscosity (ER)	20 – 60	40	160		0 – 40		
Kalliomäki et al. (2016) Conductivity (ER)	50 – 70	40 – 60	160 – 220		0 – 20		As 0 – 30
Kalliomäki et al. (2017) Density and viscosity (ER)	50 – 70	40 – 60	160 – 220		0-20		As 0 – 64
Lehtiniemi et al. (2018) Conductivity (ER)	50 – 70	40 – 60	160 – 220		0 – 20		As 0 – 64
Kalliomäki et al. (2019) Limiting- current density (ER)	50 – 70	40 – 60	160 – 220		0 – 20		As 0 – 45
Kalliomäki et al. (2021) Density and viscosity (EW)	50 – 70	40 – 60	80 – 223	0 - 10	0 – 20	0 – 5	As 0 – 30
Kalliomäki et al. (2021) Conductivity (EW)	50 – 70	40 – 90	50 – 142	0-10	0 – 30	0 – 5	As 0 – 30

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## 2.4.2 Steady-State Models of the Electrowinning Process

Aminian et al. (2000) developed a steady-state phenomenological model for copper electrowinning, which was combined with a model for solvent extraction. The electrowinning model was developed using mass conservation equations and fundamental electrochemical equations. The equations were constrained using the resistance network modelling approach. The model allowed for the prediction of the spent electrolyte composition and current in the circuit, for a given cell voltage, advance electrolyte composition, and flow rate. Parameters for the solvent extraction model were fitted using experimental data, with parameters for the electrowinning model fitted from literature data and using the results of two sampling campaigns carried out at a solvent extraction/electrowinning pilot-plant.

The combined solvent extraction/electrowinning simulator was validated against steady-state data from the pilot-plant. The observed results were in good agreement with the simulated data, except for the iron concentration in the advance and spent electrolytes (Aminian et al., 2000). The validated simulator was used to identify the effect of the copper concentration in the leached solution and cell voltage on the current efficiency and spent electrolyte copper concentration. Applications of the solvent extraction/electrowinning simulator include improving the understanding of the process and studying the effect of process variables on the current efficiency and recovery of copper. Aminian et al. (2000) stated the intention of expanding the solvent extraction/electrowinning simulator to include a model for ore leaching. Applications of the completed model are reported to include process simulation, optimisation, design, and ultimately investigating different control strategies (Aminian et al., 2000).

Free et al. (2006) simultaneously solved thermodynamic, mass transfer, and electrochemical kinetic equations to form a steady-state model for predicting experimental-scale electrowinning performance. The goal of the model was to predict the effect of electrolyte composition, voltage, current density, contact resistance, temperature, electrode spacing, and fluid flow on the current efficiency, power consumption, electrodeposit morphology, and electrodeposit distribution. The effect of gas evolution on the effective resistance to ion mass transfer was included by approximating the solution conductivity, which is inversely related to resistivity, using the Maxwell equation. The model, however, used idealised model parameters from literature for the Butler–Volmer equation and did not incorporate parameter fitting, limiting the application thereof. Furthermore, literature values were used for the activity coefficients. The model was validated by comparing the predicted results with experimental data obtained from a laboratory-scale electrowinning experiment, consisting of a lead anode and copper cathode (Free et al., 2006). The predicted steady-state values for current efficiency and power consumption were compared with obtained experimental data. A scale-up approach to model more than one electrode pair was not reported as part of the model.

A unique characteristic of the model is the ability to provide information pertaining to the prediction of localised growths, which could potentially lead to short circuits. According to Free et al. (2006), the main reason for localised growth is greater access to the flow of electrolyte. Areas with high electrolyte flow rates are stated to receive a greater flux of depositing ions and, therefore, tend to grow more rapidly (Free et al., 2006). This effect was included in the model by combining the Navier–Stokes equation and the equation for the ion mass-transfer current density.

Khouraibchia and Moats (2010) performed a statistical analysis to understand the effect of several variables on copper electrowinning performance. The effects of copper concentration, ferric iron concentration, and current density were investigated on current efficiency and SEC. Steady-state empirical models were developed to describe the current efficiency and SEC, shown in Equations 2.27 and 2.28, respectively. The model-predicted values were compared with experimental results generated in a two-electrode laboratory-scale electrowinning setup, as well as values from seven industrial plants reported in literature. The current efficiency model was able to predict the experimental results with a maximum error of 0.55% and the industrial values with a maximum error of 2.9%. The SEC model, however, predicted the experimental results with errors of between 0.33 kWh/t and 8.55 kWh/t. Additional to the large range of errors for predicting the experimental results, the model also predicted lower values than those observed industrially. Khouraibchia and Moats (2010) stated that the lower predicted industrial values were the result of the non-standard anode material and experimental-scale of the setup used to develop the model. The general trends were, however, argued to correlate with industrial trends (Khouraibchia and Moats, 2010).

$$\beta = 88.19 - 4.91 x_{\text{Fe}^{3+}} + 0.52 x_{\text{Cu}^{2+}} + 1.81 \times 10^{-3} i - 6.83 \times 10^{-3} (x_{\text{Cu}^{2+}})^2 + 0.028 (x_{\text{Fe}^{3+}}) (x_{\text{Cu}^{2+}}) + 4.015 \times 10^{-3} (x_{\text{Fe}^{3+}}) i \qquad [2.27]$$

SEC = 
$$1453.6 + 64.21 x_{Fe^{3+}} - 11.46 x_{Cu^{2+}} + 0.144 (x_{Cu^{2+}})^2 - 0.692 (x_{Fe^{3+}}) (x_{Cu^{2+}})$$
 [2.28]

where  $\beta$  is current efficiency (%), x is the concentration (g/L), and i is current density (A/m<sup>2</sup>).

Tucker (2019) developed a semi-empirical steady-state model for the prediction of current efficiency, SEC, and copper yield for a copper electrowinning process, using the model developed by Aminian et al. (2000) as a basis. Tucker (2019) improved upon the model by calculating the species activity coefficients, instead of assuming ideal behaviour. Furthermore, iron was included as a major impurity in the electrolyte and its cyclic reduction and oxidation were modelled together with the reduction of copper and oxidation of water. A parameter-fitting approach, based on experimental data generated in a bench-scale electrowinning setup, was used to obtain the parameters used in the mass-transfer and Butler–Volmer equations. The model included a current loss parameter, which accounted for additional side reactions (other than the cyclic reduction and oxidation of iron, which was already included), short circuits, insufficient equipment contact, and stray currents. The model was validated

using steady-state experimental and industrial data. The model showed good agreement between the model-predicted and experimental values. The model-predicted industrial values were scattered but the model was able to predict the performance of various industrial tankhouses to some extent, using the parameters determined from the experimental data. Tucker (2019) considered the model as a first step towards a predictive dynamic model of the electrowinning process.

Table 2.2 outlines a summary of the steady-state models discussed above, as well as the limitations associated with each of the models. The steady-state model developed by Tucker (2019) is determined to be best suited for use as the basis of a dynamic model. This is due both to the semi-empirical nature, which makes it applicable to a wide range of tankhouses, and the incorporation of non-idealised variables. Furthermore, apart from the empirical model developed by Khouraibchia and Moats (2010), the model developed by Tucker (2019) is the only model to include the effect of iron as an impurity in the electrolyte. Iron is a major impurity in copper electrowinning and incorporating it is essential to model the behaviour of a real-life tankhouse. Components of the model developed by Free et al. (2006) could potentially be incorporated in the dynamic model at a later stage, if required. This includes the ability to predict localised growths by incorporating the Navier–Stokes equation.

Model	Classification	Validation	Limitations			
Aminian et al. (2000)	Steady-state semi- empirical model based on literature data	Steady-state validation based on pilot-scale data	Activity of species at electrode estimated assuming Raoult's law is valid. Does not account for effects of additives or impurities such as iron. Water losses due to evaporation and effects of oxygen evolution are neglected.			
Free et al. (2006)	Steady-state semi- empirical model based on idealised literature data	Steady-state validation based on experimental data	Used idealised parameters from literature. Used literature values for activity coefficients. Does not account for effects of additives or impurities such as iron.			
Khouraibchia and Moats (2010)	Steady-state empirical model based on experimental data	Steady-state validation based on experimental data and industrial data	Underpredicts industrial energy consumption. Only accounts for effects of copper, ferric iron, and current density.			
Tucker (2019)	Steady-state semi- empirical model based on experimental data	Steady-state validation based on experimental data and industrial data	Does not account for effect of additives but includes iron as an impurity. Water losses due to evaporation and effects of oxygen evolution are neglected.			

Table 2.2: Summary of existing steady-state electrowinning models and associated limitations.

# 2.4.3 Dynamic Models of the Electrowinning Process

Lie and Hauge (2008) developed a dynamic model of a specific industrial copper production process, including slurification, leaching, purification, and electrowinning sections, with the goal of using the model for improved process control. The model consisted of steady-state overall mass conservation equations, dynamic species mass conservation equations for each section, reaction kinetics for the leaching section, and electrochemical reactions for the electrowinning section. The model provides an alternative approach to solving for the current efficiency. Using available measurements, and the steady-state model, the current efficiency was determined using regression, instead of using mass-transfer and reaction kinetics, as done by Aminian et al. (2000). Steady-state species mass conservation equations and overall mass conservation equations were combined with the operating parameters to find the steady-state concentrations for the electrowinning process, and the mass flow rate of copper produced was combined with the known applied current to find the current efficiency. The calculated current efficiency term includes current leakages and accounts for electrowinning tanks not in production.

Dynamic species mass conservation equations were used to develop a dynamic model of the electrowinning section of this specific plant. Additional measurements from the process were used to validate the steady-state model. The dynamic responses of the model to step increases and decreases in input variables were in good agreement with the authors' expectations, but the model was not validated using dynamic data. Anushka et al. (2016) developed an optimal control strategy for the improved control of chemical compositions within the electrowinning process at the abovementioned industrial copper production plant, using the model developed by Lie and Hauge (2008). The work done showed the potential for improvement of control, if a dynamic model became available that accurately describes the specific process.

Wiebe (2015) developed a dynamic semi-empirical model for a specific industrial copper electrowinning tankhouse using mass- and energy-conservation equations, as well as Faraday's law. The semi-empirical model was divided into a model for the copper concentration and a model for the temperature. The focus of the overall model was to predict the dynamic variation in copper concentration of the electrolyte and the cell temperature, with changes in inlet conditions, for process monitoring and control purposes. The model for the copper concentration was limited to predicting the advance electrolyte copper concentration, using the applied current and the spent electrolyte copper concentration. Although this shows the potential of the model to aid in monitoring a process variable that is not continuously measured online (such as the advance electrolyte copper concentration), it does not include the ability to predict KPIs. A year's worth of measurable data were collected from available instruments in the electrowinning tankhouse, for use in parameter fitting and validation of the model. A sampling rate of 18 minutes was selected as a trade-off between noise and loss of information.
The current efficiency, volume, and residence time were assumed to remain constant over time and combined with the molecular mass of copper, Faraday's constant, and the number of electrons involved in the copper deposition reaction to form a single parameter. This single parameter and the residence time were solved by using a parameter-fitting approach utilising half of the collected industrial data. Using a parameter-fitting approach to estimate the current efficiency, assuming a constant current efficiency, has some similarities to the approach used by Lie and Hauge (2008). The other half of the collected data with measured data showed that the model was a reasonable fit. The work done by Wiebe (2015) showed that industrial electrowinning data can be used to successfully train and validate a dynamic model.

Filianin et al. (2017) developed an empirical model (using partial least-squares regression) to predict the current efficiency for copper electrowinning operations. The copper, iron, and sulfuric acid concentrations in the advance electrolyte, flow rate, current applied, electrolyte temperature, and mass of copper extracted in the previous process step (solvent extraction) were selected as model inputs. The input variables were selected based on previous literature and a process correlation matrix. The developed model was calibrated using daily average historical industrial data covering 214 consecutive days. The dataset included measured sensor data, as well as current efficiency values calculated based on the mass copper produced in the electrowinning circuit. Cross-validation, (a resampling method discussed further in Chapter 7), was employed during calibration of the model. An arbitrary selection of 10 out of the 214 samples were left out during model calibration and used to evaluate the performance of the model on independent predictions.

Filianin et al. (2017) concluded that the daily averaged values used for model calibration were not useable for predicting the effect of multiple parameters on current efficiency. This finding was based on the significant variance of predicted current efficiency values and bad overall model performance (Filianin et al., 2017). In other words, Filianin et al. (2017) argued that daily averaging brings random variation to the multivariate model. The model validation done by Filianin et al. (2017), therefore, highlights the challenges faced when developing an empirical model for a process where only low-frequency, low-quality data are available. Nevertheless, Filianin et al. (2017) identified two potential applications of the model: analysis of adjustable variables in combination with metal concentrations to maximise the current efficiency, and the development of an inefficiency-free calibration that can be used to detect abnormal process behaviour.

Wu et al. (2021, 2020) developed empirical neural network-based models for predicting the SEC and current efficiency of a copper electrowinning operation. A genetic algorithm based back propagation neural network model was proposed for predicting the current efficiency and potential as intermediate variables, before finally calculating the predicted SEC (Wu et al., 2020). In a separate article Wu et al. (2021) discusses using a particle swarm optimisation back propagation neural network model

specifically for predicting the current efficiency. Both models have the advance electrolyte copper and sulfuric acid concentrations, as well as the current density, as inputs. The models were trained using industrial data obtained from a copper electrowinning tankhouse. The data consisted of 6060 samples. Validation of the models was done by extracting 500 arbitrary samples from the training set in order to assess the prediction accuracy when using previously unseen testing data. Based on the validation results, Wu et al. (2021, 2020) asserted that the models can be used to accurately predict the SEC and current efficiency of the industrial copper electrowinning tankhouse used as a case-study. No mention was made regarding the effect of potential impurities in the electrolyte on the model accuracy. It is not clear what impurity concentrations, if any, were present in the advance electrolyte stream of the tankhouse used as a case-study.

Table 2.3 outlines a summary of the dynamic models discussed above, as well as the limitations associated with each model. Although the model developed by Wu et al. (2021, 2020) was able to predict the KPIs of the plant on which it was trained, it does not seem to account for the effect of key electrolyte impurities (such as iron). Consequently, as the composition of the electrolyte used for model validation is not clear, it is not possible to comment on the use and accuracy of the model for tankhouses where impurities affect the KPIs.

The unsatisfactory performance of the model developed by Filianin et al. (2017) also highlighted a key limitation associated with empirical models – a large quantity of good quality process data are required to develop a high-fidelity model (Di Caprio et al., 2023; Karniadakis et al., 2021). Roffel and Betlem (2006) suggested that the number of data points must be at least 50 to 100 times the number of model parameters, and for machine learning models (such as deep neural networks) the minimum number of data points can be as high as 1000 (Roffel and Betlem, 2006). The quality and range of the available data are also important as empirical models lack robustness of prediction and are limited to interpolation based on historical data (Eksteen and Reuter, 2003; Tsamandouras et al., 2013). This means that the data must be a good representation of the process considered as these models cannot predict dynamics that are not reflected in the training data (Roffel and Betlem, 2006; Xu et al., 2017). This presents a potential challenge in an industrial setting where the process is subject to control, and measurements may be difficult to obtain (Di Caprio et al., 2023).

Eksteen and Reuter (2003) further argued that empirical models may provide short-term accuracy, but they could have problems with long-term stability. This vulnerability, combined with the fact that this model structure may not reflect the fundamental properties of the system (Eksteen and Reuter, 2003), mean that empirical models may be useful for identifying tankhouse-specific conditions for optimal performance, but they are generally not suitable for control applications.

The model developed by Lie and Hauge (2008), on the other hand, is a purely fundamental model. The main advantage of a fundamental model over an empirical model is that it provides a rationale to extrapolate (Tsamandouras et al., 2013). However, whilst fundamental models are more robust, their complex nature means that they are time-consuming to develop and lack accuracy when applied for process control. Eksteen and Reuter (2003) elaborated on the issue of model fidelity by explaining that these models normally do not have solution times within the timeframe of process control. Moreover, they argued that many of the underlying phenomena are not understood well enough to allow for the development of credible fundamental models. Although this statement was originally made in the context of modelling bath-type furnaces, it is argued that it also rings true for some phenomena that occur during electrowinning. For example, the presence of cobalt has been documented to have various effects on the electrowinning process, including lowering the oxygen overpotential, but no clear mechanism has been established (Nikoloski and Nicol, 2008). Notwithstanding, fundamental models may contribute significantly to process understanding once more certainty regarding the underlying phenomena is obtained (Eksteen and Reuter, 2003; Roffel and Betlem, 2006).

Semi-empirical modelling, referred to as hybrid modelling in some publications, combine fundamental models with empirical models to support enhanced model qualities (Kurz et al., 2022; Schopfer et al., 2005). Semi-empirical modelling, therefore, focusses on developing an optimal model design with respect to robustness, rigorousness, accuracy, interpretability, versatility, and extrapolability (Galeazzi et al., 2023; Schuppert, 1999; Thompson and Kramer, 1994). Kurz et al. (2022) argued that semi-empirical modelling has the potential to improve the Pareto trade-off between model accuracy and simulation cost significantly, adding that this brings scientific computing in engineering to the next level. Roffel and Betlem (2006) further stated that semi-empirical models have a dynamic behaviour that corresponds well to the original process, a crucial characteristic for developing a model for optimisation and control.

Semi-empirical modelling is also useful for cases where there is not sufficient information available regarding the underlying phenomena of a process, such as the bath-type furnace case discussed by Eksteen and Reuter (2003). Eksteen and Reuter (2003) demonstrated that a semi-empirical modelling approach is both feasible and has an accuracy acceptable for process control for the furnace process, the modelling of which has similar challenges to other metallurgical processes (such as electrowinning). Moreover, Eksteen and Reuter (2003) added that the semi-empirical approach means that fundamental process relationships, such as mass balances, can be satisfied through data reconciliation. The approach also allows for adaptive prediction, the first step towards predictive control, through continued parameter estimation as new data become available (Eksteen and Reuter, 2003).

Despite the advantages associated with semi-empirical modelling, there are also limitations that require mitigation. These limitations include structural and practical identifiability issues, and correlation

between model parameters. The structural identifiability of a model ensures that for a given set of input and output training variables (i.e., experiment), the model parameter set has one unique solution, independent of the experimental design (Eudy et al., 2015). Even if the model itself is structurally identifiable, it may suffer from practical non-identifiabilities (Hengl et al., 2007). This may be due to using training data of an inadequate size and quality, or due to lack of sensitivity of the model-predicted output to differences in the parameters (Tsamandouras et al., 2013).

Tsamandouras et al. (2013) suggested adapting the experimental design as one possible solution for both structural and practical identifiability issues. For structural identifiability issues the experimental design can be perturbed in order to provide additional information. Similarly, for practical identifiability issues an optimal experimental design can be used to improve the collection of data. This confirms the importance of using properly controlled experimental data for model training and validation, even if industrial data are available. Tsamandouras et al. (2013) further recommended performing a sensitivity analysis to ensure that the model output is sensitive to the model parameters (this is done in Chapter 7). The final limitation discussed by Tsamandouras et al. (2013) is where high correlation between parameters may result in biased, imprecise, and sometimes unrealistic parameter estimates. Tsamandouras et al. (2013) recommended using a literature value for one parameter if two parameters are highly correlated.

The abovementioned limitations emphasise that semi-empirical models are not exempt from the datarelated problems that are common for empirical models, as the approach is also partially dependent on industrial data. Consequently, Eksteen and Reuter (2003) underlined the importance of high integrity data. Industrial data are, however, seldom of high quality, motivating the use of data validation strategies (Eksteen and Reuter, 2003). Nevertheless, the existing model developed by Wiebe (2015) provides encouraging results for the use of dynamic industrial electrowinning data to train and validate semi-empirical models. The model, however, relies on the assumption that the current efficiency remains constant throughout the electrowinning process. The inclusion of this assumption severely restricts the use of the existing model as a predictive tool. Furthermore, the effect of important input conditions, such as the advance electrolyte iron concentration, on output variables is excluded.

Model	Classification	Validation	Limitations
Lie and Hauge (2008)	Dynamic theoretical model	Steady-state validation based on industrial data	Regression used to estimate current efficiency from known applied current using steady-state model, take constant steady-state current efficiency of 77.8%. Unclear whether impurities are included in current efficiency term. Does not account for effects of mass-transfer or reaction kinetics. Assumed constant electrolyte density.
Wiebe (2015)	Dynamic semi- empirical model based on industrial data	Limited dynamic validation based on industrial data	Assumed constant current efficiency. Does not account for effects of additives or impurities such as iron.
Filianin et al. (2017)	Dynamic empirical model based on industrial data.	Cross-validation done during calibration, based on industrial data.	Purely empirical model does not account for fundamental behaviour. Model was not able to accurately predict current efficiency based on available low-frequency industrial data. Does not predict energy consumption.
Wu et al. (2021, 2020)	Dynamic empirical model based on industrial data.	Cross-validation done during training, based on industrial data.	Purely empirical model does not account for fundamental behaviour. Does not account for effects of additives or impurities such as iron. Requires large set of training data. Computationally expensive to train.

Table 2.3: Summary of existing dynamic electrowinning models and associated limitations.

# 2.5 LITERATURE OUTCOMES

The literature review conducted in this chapter highlighted the crucial fundamental electrowinning principles that formed the basis of the semi-empirical electrowinning model, developed in this project. An emphasis was placed on the industrial context; ensuring that the model was developed cognisant of the available data, challenges, and opportunities. In this vein, the review motivated the investigation of advanced control strategies, which require the availability of a high-fidelity dynamic process model, for direct copper electrowinning. In conclusion of the literature review, the main shortcomings in the published literature, relevant to the development of a suitable dynamic model for direct copper electrowinning, are, therefore, highlighted.

Reviewing available literature underlined that various steady-state models have previously been developed for the copper electrowinning process (Aminian et al., 2000; Free et al., 2006; Tucker, 2019). Limited research has, however, been conducted on the development of dynamic models for the prediction of copper electrowinning performance (Filianin et al., 2017; Lie and Hauge, 2008; Wiebe, 2015; Wu et al., 2021, 2020). Furthermore, the validity of the dynamic models that do exist is restricted

to specific industrial copper production plants or their predictive performance is not sufficient for application in process control. Additionally, the existing models do not account for the variable electrolyte composition and wide range of impurities required to accurately simulate the direct electrowinning process.

The semi-empirical modelling approach, selected for use in this project, presents an opportunity to calibrate the developed model for a specific tankhouse, and dynamically refit the model parameters to ensure updated predictions. Tucker et al. (2021) has previously successfully implemented an offline parameter-fitting approach to calibrate a steady-state semi-empirical model for use in predicting the performance of a specific copper electrowinning process. Such an offline parameter-fitting approach has value for fitting initial parameter estimates and for use if limited data are available. An online parameter-fitting approach is, however, required to improve model-fidelity. This implementation, where industrial data are acquired and used to update a model, is similar to digital twinning (Galeazzi et al., 2023; Kurz et al., 2022; Wright and Davidson, 2020). Digital twins represent a future-orientated approach to process modelling.

Data are required for developing, training, validating, and implementing the model. Measurements of all main process variables (current applied, potential, electrolyte composition, mass copper plated, and electrolyte flow rate) are commonplace in industrial electrowinning operations (Aqueveque et al., 2015). Rhinehart (2021), however, adds that tankhouses have historically been built with the minimum investment in instrumentation required to effect adequate safety and control. Consequently, the availability of industrial data might be limited in older and smaller tankhouses. A successful dynamic model of the direct copper electrowinning process should be sufficiently robust to use data of a quality and frequency commonly found in industry.

Although strategies for model validation are discussed extensively in literature (Forrester and Senge, 1980; Knoblauch, 2015; Sargent, 2013), existing models for electrowinning have only been subjected to limited validation. This includes comparing steady-state model-predicted values with pilot-plant values (Aminian et al., 2000), experimental values (Free et al., 2006; Tucker, 2019), and industrial values (Tucker, 2019). Both Lie and Hauge (2008) and Wiebe (2015) also compared model-predicted dynamic values with the corresponding real-life industrial values. Rigorous validation, including evaluation of the internal model-structure and assumptions, verification of the computerised model, and operational validation is, however, required to ensure the developed model is sufficiently accurate for the intended purpose thereof (Moser et al., 2020; Sinner et al., 2020; Tao et al., 2019; Wright and Davidson, 2020).

The literature review further outlined several correlations for predicting the physicochemical properties of copper electrolytes. Empirical property correlations are necessary to develop a model that accurately

accommodates the complex fundamental chemistry associated with the variable electrolyte composition of direct copper electrowinning operations. The correlations developed by Kalliomäki et al. (2021) were identified as the current state-of-the-art, due to both the improved accuracy compared with previous correlations, and the validation conducted using industrial electrowinning data. Nonetheless, Kalliomäki et al. (2021) did not validate the correlations for the full concentration ranges of copper, nickel, and sulfuric acid applicable to the direct copper electrowinning tankhouses surveyed by Sole et al. (2019). Moreover, although a correlation exists for predicting limiting-current density for electrorefining applications, no comparable correlation could be found specifically for electrowinning operations.

In summary, a high-fidelity, flexible, dynamic model for copper electrowinning operations is not currently available, motivating the model development undertaken in this project. The model must be representative of a current-controlled electrowinning process, as this is the current mode of operation for the majority of industrial tankhouses. Furthermore, the model must be sufficiently flexible to be used on different full-scale electrowinning tankhouses for predicting the KPIs, using only available input variables. Incorporating an online parameter-fitting approach would enable updating the model based on an evolving dataset, resulting in high fidelity predictions. Lastly, the dynamic behaviour of the model must be validated to ensure that it is sufficiently accurate and comprehensive for its intended purpose.

# CHAPTER 3 PROPERTY CORRELATIONS

## 3.1 INTRODUCTION

In this chapter, the empirical physiochemical property correlations that form part of the developed electrowinning model are considered. Firstly, background is provided regarding the regression model building process used to develop and validate these correlations (Section 3.2). Following, the experimental methodology used to generate density, conductivity, and limiting-current density data for copper electrowinning electrolytes is discussed (Section 3.3). The generated experimental data are used to evaluate the existing physicochemical correlations developed by Kalliomäki et al. (2021) over the full range of operating conditions applicable to direct copper electrowinning, for density (Section 3.4) and conductivity (Section 3.5). Finally, the experimental limiting-current density data are used to develop a new correlation for predicting the limiting-current density of copper electrowinning operations (Section 3.6).

# 3.2 BACKGROUND

The iterative regression model building process discussed by Montgomery et al. (2012) comprises of three main steps: model selection and fitting, model adequacy checking, and model validation (Figure 3.1). The first step, model selection and fitting, in turn, consists of model specification, model selection, and model fitting. Model specification refers to the process of determining what independent variables should be included in the regression equation (Montgomery et al., 2012). Montgomery et al. (2012) emphasised that the specification of a regression model should be based mainly on fundamental theoretical considerations, rather than empirical or methodological ones. Model selection and fitting for the included coefficients. This first step also included analysing the fitted model coefficients to ensure that they are stable and that their signs and magnitudes are reasonable, based on available literature (Montgomery et al., 2012).

The second step, model adequacy checking, focusses on investigating the fit of the regression model to available training data and testing for lack of fit, mainly through residual analysis. Model adequacy checking also serves to diagnose violations of the basic regression assumptions (Montgomery et al., 2012). The final step, model validation, on the other hand, is concerned with assessing the model performance on previously unseen validation data.

For the existing density and conductivity correlations developed by Kalliomäki et al. (2021) the focus in this chapter will be on the final step of the process shown in Figure 3.1; validation of the models

using previously unseen data. The first and second step of the process have been adequately addressed by Kalliomäki et al. (2021), and the objective in this project is limited to evaluating the performance of the correlations for the wide range of component concentrations associated with direct copper electrowinning. For the newly developed limiting-current density correlation, the entire process is discussed in order to ensure the correlation is sufficiently robust for its intended application.



Figure 3.1: Process for regression model fitting of physicochemical properties of electrolytes (adapted from Montgomery et al., 2012).

## 3.3 EXPERIMENTAL METHODOLOGY

## 3.3.1 Experimental Design

The selected experimental design allowed for the validation of the property correlations developed by Kalliomäki et al. (2021) and the development of a limiting-current density model for the electrolyte compositions typically employed in direct copper electrowinning. The manipulated variables and ranges were informed by typical industrial electrolyte compositions for direct copper electrowinning (Robinson et al., 2013; Sole et al., 2019). Arsenic and manganese were not included in the experimental design. Although Kalliomäki et al. (2021) included arsenic in their property correlations, it is not expected to be a common impurity in direct electrowinning electrolytes and was, consequently, excluded. Similarly, manganese was excluded because the major species in copper electrowinning electrolytes have previously been found to be the most relevant for the prediction of physicochemical properties (Chibwe and Tadie, 2021).

Direct copper electrowinning operations typically use Avitone and thiourea as electrolyte additives (Robinson et al., 2013). The validation work conducted by Kalliomäki et al. (2021) for the density and conductivity correlations included electrolytes from the Glencore Nikkelverk tankhouse which, according to Robinson et al. (2013), uses Avitone and glue as smoothing agents. On the other hand, the correlation developed by Kalliomäki et al. (2019) for predicting the limiting-current density of copper electrorefining applications, excluded the effect of electrolyte additives.

Test work conducted by Bauer and Moats (2020) found that although the addition of chloride (up to 20 mg/L) increased the diffusivity slightly (thereby potentially impacting the limiting-current density), most other additives tested did not have a pronounced effect. Consequently, thiourea was included in

the synthetic electrolyte at a fixed concentration of 35.2 mg/L for the density and conductivity tests, but not for the limiting-current density tests. This concentration was based on a typical thiourea dosing rate of 150 g/t cathode, together with typical tankhouse specifications (Sole et al., 2019).

A  $2^{k-2}$  fractional factorial design was selected with k = 6, meaning six manipulated variables at two levels each, as shown in Table 3.1. This design allowed for model adequacy testing (as described by Montgomery et al. (2012)), whilst producing an acceptable number of experiments. Moreover, the factorial design ensured that interactions between variables, if present, could be interpreted correctly. The design also yields results that are valid over the whole range of experimental conditions, as each variable can be estimated at several levels of the other variables (Montgomery, 2012). The latter is an important consideration because empirical correlations cannot be extrapolated. Three independent replicate experiments were conducted at the centre points of the design to comment on the reliability of the experimental data. This experimental design led to a total of 19 experiments for the density and conductivity tests, as per Appendix A (Table A.1). For the limiting-current density tests the design was repeated at three different fixed rotating rates, resulting in 57 experiments.

Manipulated Variable	-1	1
Copper concentration (g/L)	30	90
Iron concentration (g/L)	0.5	6
Nickel concentration (g/L)	20	65
Cobalt concentration (g/L)	0	3
Sulfuric acid concentration (g/L)	20	120
Temperature (°C)	50	70

Table 3.1: Manipulated variables for physiochemical properties experiments as coded variables.

#### 3.3.2 Materials

A synthetic electrolyte containing sulfuric acid, copper, iron, nickel, and cobalt was prepared using analytical grade copper sulfate pentahydrate, ferric sulfate monohydrate, nickel sulfate hexahydrate, and cobalt sulfate heptahydrate. Thiourea was also included in the electrolyte used to determine the density and conductivity. The electrolyte was prepared according to the concentrations specified in the experimental design (Appendix A, Table A.2).

## 3.3.3 Equipment

#### 3.3.3.1 Density and Conductivity

A heating bath (Julabo, CORIO C heating immersion circulator), capable of accommodating several 250 mL glass bottles was used to heat the synthetic electrolyte to the desired temperature (Figure 3.2).

The conductivity measurements were carried out using an Orion Star A325 conductivity meter, calibrated with a standard electrolyte having a high conductivity and heated to temperatures in the range of the experiments. The density measurements were carried out using a 50 mL standard pycnometer. The simplicity, acid-resistance, and sufficient accuracy of the pycnometer established it as the method of choice above alternatives such as electronic meters or hydrometers, as supported by Chibwe (2020).



Figure 3.2: Schematic representation of the heating bath setup for measuring the electrolyte density and conductivity.

#### 3.3.3.2 Limiting-Current Density

A rotating disk electrode (RDE) system (Gamry, RDE710) was used to conduct the linear sweep voltammetry tests required to determine the limiting-current density of an electrolyte with known composition. The system consisted of a 175 mL jacketed reactor vessel, a rotating disk motor unit, a potentiostat (Gamry, Interface 1000 Model 04085), a Ag/AgCl reference electrode (in 3 M KCl, 0.21 V vs normal hydrogen electrode), a graphite counter electrode, and a stainless-steel working electrode (Figure 3.3). The reference electrode had a main body length of 110 mm and diameter of 9 mm, with a diameter of 4 mm at the glass junction. The working electrode had a surface area of 19.64 mm<sup>2</sup>. The system was connected to a computer in order to input parameters and generate voltammograms via the appropriate software (Gamry, PHE200TM physical electrochemistry software).



- 1. Hot water circulation feed
- 2. Counter electrode
- 3. Working electrode
- Jacketed reactor vessel
   Reference electrode
- 5. Reference electrode
- 6. Hot water circulation purge
- 7. Gamry Interface 1000 Potentiostat 8. Rotating disk motor unit

Figure 3.3: Schematic representation of the RDE setup.

#### 3.3.4 Methods

## 3.3.4.1 Density and Conductivity

The experiments for measuring the density and conductivity of an electrolyte with known composition were conducted by first preparing the synthetic electrolyte solution. Following, the prepared synthetic electrolyte was poured into a 250 mL bottle and positioned in the heating bath. The heating bath was switched on and the electrolyte in the bottle was allowed to reach the required temperature, stirring every 15 minutes. The bottle was kept sealed with a bottle stopper to minimise evaporation. Upon the heating bath indicating that the desired temperature was reached, the temperature of the electrolyte was confirmed using the conductivity meter, and the conductivity measurement taken. The density measurement was, thereafter, taken by extracting a 50 mL volume of the electrolyte with a syringe and depositing it in the weighed and calibrated pycnometer. The final mass of the pycnometer was noted, and the density measurement. The pycnometer measurements gave specific gravities that were converted to densities from published water density measurements (NIST, 2023). A detailed procedure for conducting the density and conductivity measurements is supplied in Appendix A (Section A.2.1).

#### 3.3.4.2 Limiting-Current Density

The linear sweep voltammetry tests were conducted by first preparing the synthetic electrolyte solution and heating it to the desired temperature using a magnetic hot plate. Simultaneously, the heating bath connected to the jacketed reactor vessel was allowed to reach the desired temperature. Subsequently, 150 mL of the heated synthetic electrolyte was poured into the jacketed reactor vessel, and circulation of the jacket water started. The counter electrode and reference electrode were, thereafter, inserted via the ports on the jacketed reactor vessel. The working electrode was positioned so that the working electrode tip was immersed approximately 1.0 cm into the synthetic electrolyte solution. Excessive immersion may corrode the shaft or tip if the solution seeps into the joint between the shaft and tip (Cohen, 2018).

At this point it was ensured that the counter electrode and reference electrode were equidistant from the working electrode. This is necessary to reduce the effect of the electrolyte resistance (Chibwe, 2020). The motor unit was switched on and rotation was carried out for at least 5 minutes before commencing the linear sweep voltammetry test to ensure steady-state hydrodynamic conditions at the electrode (Chibwe, 2020). Rotation rates of 1.6 rad/s, 3.1 rad/s, and 10.5 rad/s were used. The lower limit of the range was selected based on an estimate by Sarswat (2010) for the average angular velocity equivalent for the parallel plate electrode case (similar to the industrial process setup), whilst the upper limit was taken to be the same as that used by Kalliomäki et al. (2019).

Finally, the linear sweep voltammetry tests were conducted by sweeping the potential cathodically from 0.03 V to -0.75 V vs the reference electrode, at a scan rate of 10 mV/s and scan step of 5 mV. The sweeping range was selected based on the standard copper reduction potential (Chibwe, 2020). Furthermore, the range would ensure that the reduction of copper ions was diffusion limited and that hydrogen was not discharged (Chibwe 2020). The generated voltammograms were used to determine the limiting-current density, as detailed by Chibwe (2020).

#### 3.3.4.3 Analytical Methods

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), performed at the Department of Chemical Engineering at Stellenbosch University, was used to determine the concentrations of copper, iron, nickel, and cobalt in the prepared synthetic electrolyte samples. The quantification range of ICP-OES for copper, iron, nickel, and cobalt is 0.05 mg/L to 100 mg/L, and the total dissolved solids (TDS) are required to be below 2 mass per cent. Samples were, therefore, diluted by a factor of 1010 using two-fold series dilution.

### 3.4 DENSITY MODEL

#### 3.4.1 Model Selection and Fitting

The general form of the density models discussed in this section is presented in Equation 3.1. Table 3.2 presents the model coefficients for the model developed by Kalliomäki et al. (2021) ("Model KM") as well as those for the classical model developed by Price and Davenport (1981) ("Model PD,") and a reference model. The reference model was regressed based on the experimental data generated in Section 3.3. Use of the reference model is restricted to comparing the regressed coefficients with those obtained by Kalliomäki et al. (2021) to assess the stability, signs, and magnitude.

$$\rho = a_1 + a_2 x \text{Cu} + a_3 x \text{H}_2 \text{SO}_4 + a_4 x \text{Ni} + a_5 x \text{Fe} + a_6 x \text{Co} + a_7 x \text{As} + a_8 T$$
[3.1]

where  $\rho$  is the density (g/L), *a* is the model coefficient, *x* is the concentration (g/L), and *T* is the temperature (°C).

Term	Reference Model	Model PD	Model KM
Constant	$1.005 \times 10^{3}$	1.022 × 10 <sup>3</sup>	1.018 × 10 <sup>3</sup>
<i>x</i> Cu	2.008	2.24	2.247
<i>x</i> H₂SO₄	4.546 × 10 <sup>−1</sup>	5.5 × 10 <sup>-1</sup>	5.111 × 10 <sup>-1</sup>
<i>x</i> Ni	2.451	2.24	2.338
<i>x</i> Fe	5.822	2.37	1.717
xCo	-4.321 × 10 <sup>-1</sup>	_	1.758
xAs	_	1.04	9.446 × 10 <sup>-1</sup>
Т	-1.233 × 10 <sup>-1</sup>	-5.8 × 10⁻¹	-5.754 × 10 <sup>-1</sup>

Table 3.2. Terms and their coefficients for the density reference model, Model PD, and Model KM.

The signs and magnitudes of the majority of coefficients for the three models presented in Table 3.2 correspond well with each other, and what is expected from literature. Previous studies have established that increasing temperatures decrease the electrolyte density, whilst increasing concentrations of copper, nickel, and sulfuric acid result in an increase (Chibwe and Tadie, 2021; Jarjoura et al., 2003; Kalliomäki et al., 2021, 2017, 2016; Price and Davenport, 1981, 1980; Subbaiah and Das, 1989). Other common metallic electrolyte components such as iron, manganese (Price and Davenport, 1981; Subbaiah and Das, 1989), and cobalt (Subbaiah and Das, 1989), have also been reported to increase the electrolyte density. Price and Davenport (1981) suggested that similar to copper and nickel, this is due to the addition of large, high molecular mass metal cations and  $SO_4^{2-}$  anions to the solution.

The negative coefficient obtained for cobalt concentration in the reference model is, therefore, unexpected. Based on the typical reasons for unexpected model coefficient signs, as discussed by Mullet (1976), it is suggested that the unexpected sign results from the small range of cobalt concentrations investigated (0 g/L to 3 g/L). As mentioned during discussion of the experimental design (Section 3.3.1), the investigated range is based on typical industrial conditions for direct copper electrowinning operations (Robinson et al., 2013; Sole et al., 2019). This range is, however, slightly smaller than the 0 g/L to 5 g/L Co investigated by Kalliomäki et al. (2021).

Regarding the magnitudes of the coefficients in Table 3.2, both Price and Davenport (1981) and Subbaiah and Das (1989) confirmed that temperature only has a small effect on the density, supporting the corresponding coefficients. The coefficient for nickel concentration obtained by Kalliomäki et al. (2021) is the largest, followed closely by the coefficient for copper concentration. This strong dependency on nickel concentration aligns well with the results obtained by Jarjoura et al. (2003). The electrolyte density increased by approximately 0.002 g/L for every 1 g/L Ni (within a range of 0 g/L to 40 g/L Ni) (Jarjoura et al., 2003). Accordingly, the model coefficients for the model developed by Kalliomäki et al. (2021) overall show reasonable stability, signs, and magnitudes.

#### 3.4.2 Model Validation

#### 3.4.2.1 Model Predictive Performance

The predictive performance of the density Model KM is assessed using the experimental data generated in this project, spanning the whole range of conditions typically found in direct copper electrowinning. This experimental data are termed the "confirmation tests". The validation results for Model KM are presented in Figure 3.4, for the conditions detailed in Table 3.1. Additionally, the performance of the classical Model PD and the reference model, regressed based on the confirmation tests, is also included. In Figure 3.4 (a) a parity plot of the modelled versus measured density is given. Figure 3.4 (b) gives the residual values showing the prediction error (predicted – measured) compared with the measured values and the zero-residual line.



Figure 3.4: (a) Measured vs model-predicted densities and (b) measured vs residuals of model-predicted densities, of copper electrowinning electrolytes for Model PD, Model KM, and a reference model regressed using the values measured in this project. Error bars denote the standard error of the mean (SEM), calculated using three independent experiments.

Table 3.3 reports the correlation coefficients for the least-squares fit of the respective models, where available, alongside the coefficients for the model fit to the confirmation test data. The least-squares fit data are the data used to originally regress the respective models, whilst the confirmation test data refer to the experimental data generated in this project. The  $R^2$  value for Model KM determined for the confirmation test data (0.973) shows only a slight decrease from the original least-squares fit  $R^2$  (0.989).

For the reported normalised residual mean square error (nRMSE) values, a perfect match between the model-predicted value and actual value would lead to a nRMSE of zero. Accordingly, less accurate model predictions would lead to higher nRMSEs. The equations used to calculate the residual mean square error (RMSE) and the normalised version thereof (nRMSE) are discussed in detail in Chapter 7 (Equation 7.1 and Equation 7.3, respectively). As confirmed by the R<sup>2</sup> and nRMSE values supplied in

Table 3.3, Model KM can be successfully extrapolated to predict the densities of typical direct electrowinning electrolytes.

Description	Model PD*		Model KM†			Reference model			
Description	R <sup>2</sup>	nRMSE (%)	Ν	R <sup>2</sup>	nRMSE (%)	Ν	R <sup>2</sup>	nRMSE (%)	Ν
Least-squares fit	_	_	_	0.989	_	117	0.995	_	17
Confirmation tests	0.980	0.899	17	0.973	1.05	17	—	0.464	_

Table 3.3: Correlation coefficients for density Model PD, Model KM, and the reference model, based on their respective least-squares fit and the confirmation tests.

\*Price and Davenport (1981) +Kalliomäki et al. (2021)

Although the number of data points for the confirmation tests (17, excluding replicates) is just below the minimum of 20 suggested by Montgomery et al. (2012) to give a reliable assessment of the model's performance, the validation done in this project is meant to complement the original validation done by Kalliomäki et al. (2021) (using 117 data points). Overall, both qualitative analysis of the graphs and quantitative analysis of the correlation coefficients show the model has an acceptable goodness of fit for use in predicting the density of direct copper electrowinning electrolytes.

## 3.5 CONDUCTIVITY MODEL

#### 3.5.1 Model Selection and Fitting

The general form of the conductivity models discussed in this section is presented in Equation 3.2. Table 3.4 presents the model coefficients for the model developed by Kalliomäki et al. (2021) ("Model KM,") alongside those for the classical model developed by Price and Davenport (1981) ("Model PD,") and a reference model. Only the conductivity model developed by Kalliomäki et al. (2021) for low sulfuric acid concentrations (< 142 g/L) was considered in this project. The reference model was again regressed based on the experimental data generated in Section 3.3 ("confirmation tests.")

 $\kappa^* = a_1 + a_2 x Cu + a_3 x H_2 SO_4 + a_4 x Ni + a_5 x Fe + a_6 x Co + a_7 x As + a_8 T + a_n \text{ (combined effect term)}$ [3.2]

where  $\kappa$  is conductivity (S/m) (<sup>\*</sup>1/ $\kappa$  for Model PD), *a* is the model coefficient, *x* is the concentration (g/L), and *T* is the temperature (°C).

Term	Reference Model	Model PD	Model KM
Constant	-3.903	3.20 × 10 <sup>-2</sup>	1.9442
<i>x</i> Cu	4.601 × 10 <sup>-2</sup>	7.30 × 10⁻⁵	$1.328 \times 10^{-1}$
<i>x</i> H₂SO₄	3.953 × 10⁻¹	-5.60 × 10⁻⁵	3.386 × 10⁻¹
<i>x</i> Ni	4.991 × 10 <sup>-2</sup>	9.60 × 10⁻⁵	-6.85 × 10 <sup>-2</sup>
<i>x</i> Fe	1.590	4.50 × 10⁻⁵	4.15 × 10 <sup>-2</sup>
xCo	-4.275 × 10 <sup>-2</sup>	_	-1.533 × 10 <sup>-1</sup>
xAs	-	1.30 × 10⁻⁵	—
Т	1.155 × 10⁻¹	$-1.46 \times 10^{-4}$	-2.88 × 10 <sup>-2</sup>
<i>x</i> Cu · <i>x</i> H₂SO₄	-1.561 × 10 <sup>-3</sup>	_	-2.8 × 10 <sup>-3</sup>
<i>x</i> H₂SO₄ · <i>x</i> Ni	−1.785 × 10 <sup>-3</sup>	_	$-1.3 \times 10^{-3}$
<i>x</i> H₂SO₄ · <i>x</i> Fe	-1.134 × 10 <sup>-2</sup>	_	-2.6 × 10 <sup>-3</sup>
xH2SO4 · T	1.522 × 10 <sup>-4</sup>	_	$2.0 \times 10^{-3}$
<i>x</i> Ni · <i>x</i> Fe	-7.638 × 10 <sup>-3</sup>	_	$4.5 \times 10^{-3}$

Table 3.4. Terms and their coefficients for the conductivity reference model, Model PD, and Model KM.

Table 3.4 shows that although interaction terms did affect the conductivity in Model KM, the single terms had the greatest magnitudes. Kalliomäki et al. (2016) explained that when interaction terms are present, the sign of an individual term coefficient, or interaction term coefficient should, however, not be interpreted individually, but as a combined effect of all variables that have an effect in the model equation. To this extent, the surface plots shown in Figure 3.5 were used to discuss the effect of the interaction variables on the conductivity. The surface plots are only shown for the model of interest, Model KM. Although the signs and magnitudes of the model coefficients could not be assessed directly, the behaviour of the model is shown to be reasonable.



Figure 3.5: Surface plots showing the effect of (a) Cu and  $H_2SO_4$  concentration, (b) Fe and  $H_2SO_4$  concentration, (c) Fe and Ni concentration, and (d) temperature and  $H_2SO_4$  concentration on the conductivity, using Model KM. If not varied variables were kept constant at the centre point of the range specified in Table 3.1 (60 g/L Cu, 3.3 g/L Fe, 42.5 g/L Ni, 1.5 g/L Co, 70 g/L xH\_2SO\_4, 60 °C).

The dependency of conductivity on the main electrolyte components and temperature has been well established. Metal components decrease the conductivity whilst increased concentrations of sulfuric acid increase the conductivity (Price and Davenport, 1981; Subbaiah and Das, 1989). The conductivity is decreased by the presence of the large metal cations whilst highly mobile, small H<sup>+</sup> cations, supplied by the sulfuric acid, increase the conductivity (Price and Davenport, 1981). Increases in temperature increases the mobility of the ions, thereby increasing the conductivity (Price and Davenport, 1981).

Figure 3.5 (a) shows the effect of sulfuric acid and copper concentrations on the conductivity, per Model KM. The figure indicates that conductivity increased with increased sulfuric acid concentration, as expected. Furthermore, the figure shows that conductivity increased slightly with increased copper concentrations at lower sulfuric acid concentrations, but that the conductivity increased with decreased copper concentration at high sulfuric acid concentrations. Price and Davenport (1981) reported similar behaviour, stating that below 20 g/L H<sub>2</sub>SO<sub>4</sub> an increasing copper concentration (at constant H<sub>2</sub>SO<sub>4</sub>)

increased conductivity, but that above 40 g/L  $H_2SO_4$  the opposite occurred. According to Price and Davenport (1981), the exact sulfuric acid concentration at which the effect of copper reverses is temperature dependent, but it is always noticeable.

Figure 3.5 (b) shows the effect of sulfuric acid and iron concentrations on the conductivity, according to Model KM. As expected, the figure again indicates that the conductivity increased with increased sulfuric acid concentration. The figure also shows that the conductivity increased slightly with increased iron concentrations. Although not expected per the available literature, the increase in conductivity resulting from the increased iron concentration is very slight.

Figure 3.5 (c) shows the effect of nickel and iron concentrations on the conductivity, according to Model KM. The figure indicates that the conductivity increased with decreased nickel concentrations, as expected. Furthermore, the figure shows that at high nickel concentrations the conductivity increased with decreasing iron concentrations, as expected. At low nickel concentrations, the conductivity, however, slightly decreased with decreasing iron concentrations. As previously, the effect of the iron concentration on the conductivity was, however, very slight.

Figure 3.5 (d) shows the effect of sulfuric acid concentration and temperature on the conductivity, per Model KM. Again, the figure indicates that the conductivity increased with increased sulfuric acid concentration. The figure also shows that at the lower sulfuric acid concentrations the temperature had little to no effect on the conductivity. At the higher sulfuric acid concentrations, the conductivity increased with increasing copper concentrations, as expected.

#### 3.5.2 Model Validation

#### 3.5.2.1 Model Predictive Performance

Both Model PD and Model KM were shown to be less accurate than the reference model at the lower conductivities forming part of the confirmation tests, with Model PD showing substantial inaccuracy (Figure 3.6). The lower conductivity measurements were taken from the electrolytes having low sulfuric acid concentrations (20 g/L) and high nickel concentrations (65 g/L). Upon investigation it was determined that Model PD exhibited the same prediction inaccuracies at lower conductivities when the original data used by Price and Davenport (1981) were used. Lehtiniemi et al. (2018) seem to support the observed challenge with Model PD, reporting that the model did not fit the conductivity values for the electrowinning range used during model development by Price and Davenport (1981).

The data used to develop Model KM only included sulfuric acid concentrations as low as 50 g/L and nickel concentrations as high as 30 g/L. Nevertheless, it was determined that Model KM can be successfully extrapolated to predict the conductivities of typical direct electrowinning electrolytes. This was confirmed by the  $R^2$  and nRMSE values supplied in Table 3.5. In this table, the  $R^2$  and nRMSE

values are again reported for the original least-squares fit of the respective models, alongside the fit of the models to the confirmation test data generated in this project. Additionally, correlation coefficients are also reported for the model fit to industrial validation data. Kalliomäki et al. (2021) used the industrial electrowinning data, obtained from Glencore Nikkelverk, to comment on the predictive performance of the model developed in their work (Model KM), as well as that of the previously developed Model PD.

Similar to the density Model KM, the validation done in this project is intended to complement the rigorous validation completed by Kalliomäki et al. (2021). Both qualitative analysis of the graphs and quantitative analysis of the correlation coefficients show the model has an acceptable goodness of fit for use in predicting the conductivity of direct copper electrowinning electrolytes.



Figure 3.6: (a) Measured vs model-predicted conductivities and (b) measured vs residuals of model-predicted conductivities, of copper electrowinning electrolytes for Model PD, Model KM, and a reference model regressed using the values measured in this project. Error bars denote the SEM, calculated using three independent experiments.

Description	Model PD*			Model KM†			Reference model		
Description	R <sup>2</sup>	nRMSE (%)	Ν	R <sup>2</sup>	nRMSE (%)	Ν	R <sup>2</sup>	nRMSE (%)	Ν
Least-squares fit	—	_	_	0.998	_	119	0.997	2.44	17
Industrial <sup>+</sup>	0.908	_	45	0.981	_	45	_	_	_
Confirmation tests	-0.521	56.1	17	0.866	16.7	17		_	_

Table 3.5: Correlation coefficients for conductivity Model PD, Model KM, and the reference model, based on their respective least-squares fit, industrial electrolyte data, and the confirmation tests.

\*Price and Davenport (1981) +Kalliomäki et al. (2021)

## 3.6 LIMITING-CURRENT DENSITY MODEL

#### 3.6.1 Model Selection and Fitting

The general form of the regression models developed for predicting the limiting-current density of electrowinning operations is presented in Equation 3.3. Table 3.6 presents the model coefficients for the limiting-current density model without ("Model A") and with ("Model B") the combined effect of selected variables. Only combined effects with *p*-values less than 0.05 were considered statistically significant and included in Model B. The *p*-values for the included terms, calculated at a confidence level of 95%, are summarised in Appendix D (Table D.8). The coefficients for the limiting-current density model developed by Kalliomäki et al. (2019) ("Model K") are also included. Model K was originally regressed specifically for electrorefining operations. The synthetic electrolyte investigated did not include any deposition controlling additives like glue, thiourea, Avitone or chloride (Kalliomäki et al., 2019). Similarly, for the synthetic electrolytes used in this project these additives were also omitted.

$$\log(i_{\text{lim}}) = a_1 + a_2 x \text{Cu} + a_3 x \text{H}_2 \text{SO}_4 + a_4 x \text{Ni} + a_5 x \text{Fe} + a_6 x \text{Co} + a_7 x \text{As} + a_8 1/T + a_9 \omega^{\frac{1}{2}} + a_n \text{ (combined effect term)}$$
[3.3]

where  $i_{\text{lim}}$  is the limiting-current density (A/m<sup>2</sup>, or A/cm<sup>2</sup> for Model K), *a* is the model coefficient, *x* is the concentration (g/L), *T* is the temperature (°C, or K for Model K), and  $\omega$  is the angular velocity (rad/s).

It is important to note that the developed models do not account for the effect of oxygen evolution at the anode on the mass-transfer conditions at the cathode. This omission results because of limitations associated with the RDE system used to generate the experimental data. Consequently, the models may significantly underestimate the limiting-current density of industrial electrowinning operations (Beukes and Badenhorst, 2009), despite performing satisfactory in the model validation tests conducted in Section 3.6.2. Moreover, the limiting-current density of industrial operations will likely also be site-specific, as factors such as anode age and interelectrode distance will influence oxygen evolution. It is, therefore, acknowledged that the models provide at best conservative estimates of the limiting-current density for actual industrial electrowinning tankhouses.

Industrial copper electrowinning tankhouses commonly operate at current densities of up to 50% of the limiting-current density for copper reduction (Ettel, 1981; Moats and Khouraibchia, 2009). Considering the range of current densities reported for tankhouses surveyed by Sole et al. (2019), a range of typical industrial limiting-current densities can be approximated as between 280 A/m<sup>2</sup> and 996 A/m<sup>2</sup>.

Term	Model A	Model B	Model K
Constant	6.621	5.936	$-2.814 \times 10^{-1}$
<i>x</i> Cu	1.581 × 10 <sup>-2</sup>	1.424 × 10 <sup>-2</sup>	3.146 × 10 <sup>-2</sup>
xH <sub>2</sub> SO <sub>4</sub>	$-1.230 \times 10^{-4}$	-1.240 × 10 <sup>-5</sup>	$-7.999 \times 10^{-4}$
<i>x</i> Ni	-6.482 × 10 <sup>-3</sup>	-6.586 × 10 <sup>-3</sup>	$1.065 \times 10^{-4}$
<i>x</i> Fe	2.784 × 10 <sup>-2</sup>	$3.390 \times 10^{-1}$	_
xCo	-3.152 × 10 <sup>-3</sup>	5.670 × 10 <sup>-2</sup>	_
xAs	_	_	-1.630 × 10 <sup>-2</sup>
1/T	-54.18	-5.524	-322.8
$\omega^{1/2}$	4.357 × 10 <sup>−1</sup>	4.333 × 10 <sup>−1</sup>	1.665 × 10⁻¹
<i>x</i> Cu · <i>x</i> Fe	_	8.746 × 10 <sup>-4</sup>	_
<i>x</i> Ni · <i>x</i> Fe	_	1.359 × 10⁻³	_
<i>x</i> Ni · <i>x</i> Co	-	$-1.961 \times 10^{-3}$	_
<i>x</i> Fe · <i>x</i> Co	-	1.467 × 10 <sup>-2</sup>	_
<i>x</i> Fe · 1/ <i>T</i>	-	-26.63	_
<i>x</i> Cu · <i>x</i> Ni	-	_	$-5.428 \times 10^{-5}$
<i>x</i> Cu · 1/ <i>T</i>	-	_	-7.773
<i>x</i> Ni · <i>x</i> As	-	_	3.668 × 10 <sup>-5</sup>
xAs · 1/T	—	—	4.997

Table 3.6: Terms and their coefficients for the limiting-current density models regressed in this project (Model A and Model B), and Model K.

As before for the conductivity model with interaction terms, the model coefficients could not be assessed individually for the limiting-current density models (except for Model A). Consequently, sensitivity analyses were used to comment on the stability, signs, and magnitudes of the model coefficients.

The sensitivity of the models was tested as outlined previously in literature (Kalliomäki et al., 2021, 2019, 2017; Lehtiniemi et al., 2018). The sensitivity analysis presented in Figure 3.7 shows that the limiting-current densities predicted by Models A, B, and K were affected mainly by changes in the temperature, and changes in the copper and nickel concentrations. The remaining composition parameters were found to have a less substantial effect.

A 15% increase in temperature increased the limiting-current density predicted by the models with between 12.5% and 22.5%. This significant increase in limiting-current density for an increase in temperature corresponds well with what is expected, based on literature (Andersen et al., 1974; Bauer

and Moats, 2020; Jarjoura et al., 2003). Jarjoura et al. (2003) explained that the increase results from the increased velocity of the copper ions, resulting from the increase in temperature. For the case of electrorefining, as investigated by Jarjoura et al. (2003), this means that the copper ions will move faster from the surface of the anode to replenish the depleted area next to the cathode more rapidly. For electrowinning, the same phenomena are expected, with the copper ions originating from the bulk solution and not the anode surface.

A 15% increase in the copper concentration resulted in a predicted increase of 12.8% to 16.7%, whilst a 15% increase in the nickel concentration resulted in a predicted decrease of 3.2% to 4.5%. Bauer and Moats (2020) supported the increase in limiting-current density for an increase in copper concentration. Similarly, both Jarjoura et al. (2003) and Jarjoura and Kipouros (2006) have previously reported that increasing nickel concentrations decrease the limiting-current density. The decrease in limiting-current density has previously been attributed to the increase in electrolyte viscosity resulting from the increase in nickel concentration (Konishi et al., 2003a, 2003b).



Figure 3.7: Effect of changing the variables on the limiting-current density with (a) Model A, (b) Model B, and (c) Model K.

Apart from the sensitivity of Model B to changes in temperature, no excess sensitivity to shifts in the variables were observed. Model A contains exclusively single factors; xCu,  $xH_2SO_4$ , xNi, xFe, xCo, 1/T, and  $\omega^{1/2}$  (Table 3.6). In contrast, Model B contains the additional combined effect terms  $xCu \cdot xFe$ ,  $xNi \cdot xFe$ ,  $xNi \cdot xCo$ ,  $xFe \cdot xCo$ , and  $xFe \cdot 1/T$ . These combined effect terms were statistically significant (*p*-values < 0.05), but inclusion of these terms exacerbated the sensitivity of Model B to shifts in temperature. Nonetheless, the overall sensitivities obtained for Model A and Model B were similar to the sensitivities obtained for Model K (Kalliomäki et al., 2019).

#### 3.6.2 Model Validation

#### 3.6.2.1 Model Adequacy Checking

As previously mentioned in Section 3.2, one of the main functions of model adequacy checking is to diagnose potential violations of the basic regression assumptions. The basic regression assumptions are that the relationship between the dependent variable and independent variables is at least approximately linear, the error term has zero mean and constant variance, the errors are uncorrelated, and that the errors are normally distributed (normality assumption) (Montgomery et al., 2012). Residual analysis, a diagnostic method for assumption violations suggested by Montgomery et al. (2012), is used in this section to assess the models.

Figure 3.8 presents the normality probability plot of the externally studentised residuals for (a) Model A and (b) Model B, developed in this project. The normality assumption is considered to be valid if the points on the graph lie on a straight line (Chibwe, 2020). Both Model A and Model B show flattening at the extremes, typically associated with a distribution with heavier tails than normal. Nonetheless, the deviations are slight, especially for Model A, and there are no indications of a severe problem with the normality assumption for either of the models.



Figure 3.8: Normality plot of the externally studentised residuals for (a) Model A and (b) Model B.

The limiting-current density models were further validated by comparing the predicted values with the measured values for the experiments described in Section 3.3 (the data originally used to regress Model A and Model B) (Figure 3.9 (a)). Figure 3.9 (b) includes a plot of the externally studentised residuals against the modelled limiting-current density values for this set of experiments. Model K is not included in this plot as the original data used to regress the model were not accessible to calculate the associated externally studentised residuals.

Montgomery et al. (2012) explained that if Figure 3.9 (b) indicates that the residuals can be contained in a horizontal band, there are no obvious model defects. The double-bow pattern observed in this plot,

however, indicates that the variance of the errors is not constant. Transformations on the dependent variable are generally used to stabilise the variance. The dependent variable for Models A and B (and Model K), is the log of the limiting-current density. Although alternative transformations were investigated for the dependent variable of Models A and B, the stability of the variance did not markedly improve. Consequently, it was elected to retain the log model form.

Although the non-constant variance indicates that the models could possibly be improved by adding or removing variables, model specification was done based mainly on fundamental theoretical considerations as well as what variables would be typically available to ensure the model is usable for industrial operations. It is important to note that the omission of the effect of oxygen evolution (or current density and other tankhouse-specific factors) are only expected to become relevant when predicting for the limiting-current density of actual electrowinning tankhouses, not experimental-scale data as done here.



Figure 3.9: (a) Measured vs model-predicted limiting-current densities and (b) measured vs externally studentised residuals of model-predicted limiting-current densities, for copper electrowinning electrolytes measured in this project, based on Model A, Model B, and Model K. Error bars denote the SEM, calculated using three independent experiments.

#### 3.6.2.2 Model Predictive Performance

The models were further validated by comparing the predicted values with the measured values for experimental data generated by Chibwe and Tadie (2021) (Figure 3.10). This data are termed the "validation data," as it was previously unseen by all models. Chibwe and Tadie (2021) measured the limiting-current density of synthetic electrolytes containing copper, iron, sulfuric acid, and a polyacrylamide additive (PAM). Model B predicted the limiting-current density of the validation data with more accuracy than Model A and Model K (Table 3.7), confirming the selection of Model B for further use in this project.

Despite the satisfactory performance during validation on experimental data, the models provide at best conservative estimates of the limiting-current density for actual electrowinning tankhouses. As previously discussed in Section 3.6.1, this is because the effect of oxygen evolution and other tankhouse-specific factors are not accounted for. In this project, the main use of the limiting-current density predictions is as a warning mechanism, built into the electrowinning model, to indicate when standard operating conditions might not be applicable. Conservative estimates of the limiting-current densities are, therefore, adequate if not advantageous.



Figure 3.10: (a) Measured vs model-predicted limiting-current densities and (b) measured vs residuals of modelpredicted limiting-current densities, of copper electrowinning electrolytes reported by Chibwe and Tadie (2021), based on Model A, Model B, and Model K. Error bars denote the SEM, calculated using three independent experiments.

Table 3.7. Correlation coefficients for Model A, Model B, and Model K based on their respective least-squares fit, the values measured in this work, and the values reported by Chibwe and Tadie (2021) (validation data).

Description	This Work: Model A			This Work: Model B			Model K*		
Description	R <sup>2</sup>	nRSME (%)	Ν	R <sup>2</sup>	nRSME (%)	Ν	R <sup>2</sup>	nRSME (%)	Ν
Least-squares fit	0.964	12.7	51	0.983	8.85	51	0.969	_	230
This work	_	_	_	_	_	_	-0.469	81.3	51
Validation data+	0.313	21.3	275	0.870	9.28	275	0.676	14.7	275

\*Kalliomäki et al. (2019) †Chibwe and Tadie (2021)

# CHAPTER 4 MODEL DEVELOPMENT

## 4.1 INTRODUCTION

In this chapter, the generic conceptual copper electrowinning model is developed from first principles (Section 4.2), incorporating the physicochemical property correlations discussed in the previous chapter (Chapter 3). The conceptual model is developed using the systematic procedure suggested by Seborg et al. (2011), adapted for the development of a semi-empirical model. This procedure involves first defining the model purpose, required accuracy, and scope. Secondly, the applicable process output and input variables are identified. Finally, the model assumptions are discussed and the appropriate conservation and algebraic equations that form the model basis are introduced. The final part of this chapter details the process of computerising the conceptual model using MATLAB (2023) (Section 4.3).

# 4.2 CONCEPTUAL MODEL DEVELOPMENT

## 4.2.1 Model Purpose and Required Accuracy

The purpose of the high-fidelity dynamic model is to simulate copper electrowinning in an industrial direct electrowinning tankhouse. The model should be sufficiently comprehensive and accurate to enable the development and investigation of improved process control strategies (such as model predictive control, MPC) to ensure pre-emptive control actions are taken for optimal process efficiency. Not only can the model be employed to develop MPC strategies, but it can also be used to compare MPC to conventional controllers, quantifying the advantage of using the more complex strategy (Appl et al., 2020). Moreover, the model can be used for the redevelopment of conventional controllers (Appl et al., 2020).

Various other applications of dynamic models are also possible, including process monitoring and operator training. In this project, the purpose of the dynamic model to be developed is, however, confined to enabling the development and investigation of control strategies. This does not eliminate the model from use for the other potential applications, as application in control will require the most accurate model (Appl et al., 2020). Similarly, developing the model specifically for the worst-case direct electrowinning scenario does not exclude it from use for the ideal-case post-solvent extraction electrowinning case.

A high-fidelity dynamic model must be an accurate representation of the real-life process, representing all phenomena that affect the predicted properties and simulating the current state of the process (Rosen et al., 2015; Wright and Davidson, 2020). Wright and Davidson (2020) suggested, and Gargalo et al. (2020) affirmed, three criteria a high-fidelity model must fulfil:

- 1. The model should be sufficiently fundamental to ensure updating the model parameters based on measured data is meaningful,
- 2. The model should be sufficiently accurate that the updated model parameters will be useful for the intended application of the model, and
- 3. The model should be sufficiently quick to execute so that decisions relevant to the application are possible within the required timescale.

The model developed in this project was qualitatively assessed against the abovementioned criteria during the model validation process (Chapter 9).

## 4.2.2 Model Scope

The scope of the dynamic model is confined to predicting the process performance of direct copper electrowinning operations with sufficient fidelity to enable the development and investigation of advanced control strategies, as elucidated above (Section 4.2.1). In the model, the process performance is quantified by key performance indicators (KPIs). The KPIs included are the current efficiency, copper yield, and specific energy consumption (SEC). The KPI relating to the quality of copper is excluded from the model predictions. Specialised instruments are used to analyse the physical and chemical quality of the copper cathodes after the electrowinning process is completed. This, combined with the fact that the quality is influenced by several variables, reduces the accuracy and usefulness of predicting this performance indicator. This exclusion is supported by Alfantazi and Valic (2003), who stated that the quality of the deposited copper is difficult to incorporate in a model. Multi-physical phenomena, such as fluid dynamics and current distribution, are also excluded from the model as the assumptions required for the inclusion thereof are not in line with developing a tool for process control.

Limiting the scope of the model to direct electrowinning operations does not exclude it from use for post-solvent extraction tankhouses. The electrolytes for post-solvent extraction electrowinning contain similar impurities as those for direct electrowinning, albeit in significantly lower concentrations. Validating the model for the worst-case scenario electrolyte composition (direct electrowinning) should, arguably, support the validity thereof to the ideal-case scenario (post-solvent extraction electrowinning). Moreover, the differences in other operating conditions (such as temperature and current density) are captured by the fundamental part of the semi-empirical model.

The electrolyte components considered in the model are limited to the main constituents typically present in direct copper electrowinning electrolytes; sulfuric acid, copper, nickel, iron, and cobalt

(Robinson et al., 2013; Sole et al., 2019). Although additional impurities, such as manganese, may be present in the electrolyte, the focus is retained on accounting for the impurities that are present in such concentrations that they have a large potential impact on the KPIs of concern (copper yield, current efficiency, and SEC). As the quality of deposited copper is outside the scope of the model, additives, such as chloride and smoothing agents, were also not accounted for. Thiourea, a smoothing agent typically employed by direct electrowinning tankhouses was, however, included at a fixed concentration for validating the empirical density and conductivity correlations used in the model.

The model accounts for changes in the electrolyte density (required for mass balances) and conductivity (required for electrolyte resistance calculation) through the incorporated empirical physicochemical property correlations. Changes in the electrolyte viscosity resulting from changes in the electrolyte composition and temperature are, however, not included in the model scope. The electrolyte viscosity impacts the mass-transfer conditions, and therefore, the mass-transfer limited iron reduction and oxidation. Consequently, changes in the viscosity could impact the KPIs. The impact of the viscosity is included together with other phenomena not directly included in the model scope (such as slime formation and housekeeping) and captured by the online parameter-fitting approach accompanying the model. Similarly, any effect on the energy consumption through changes in the density and viscosity will also be captured by the online parameter-fitting approach and not modelled fundamentally.

Changes in the viscosity could also affect the movement of oxygen bubbles that form at the anode during electrowinning, and as a result, could influence acid mist formation (Shakarji et al., 2011). As will be elaborated during discussion of the model assumptions and simplifications (Section 4.2.4), acid mist formation is not included in the model scope.

The model validation conducted as part of the project is limited to model performance inside the range of standard operating conditions for direct electrowinning operations, as reported by Robinson et al. (2013) and Sole et al. (2019). Bench-scale electrowinning data and industrial data from two tankhouses are used in the validation process to ensure the model is sufficiently robust for use in developing and investigating advanced control strategies.

#### 4.2.3 Model Output and Input Variables

### 4.2.3.1 Output Variables

The KPIs namely, current efficiency, SEC, and copper yield, were identified as the model output variables (Section 4.2.2). Additional intermediary model output variables required to calculate the respective KPIs are given in Table 4.1.

КРІ	Intermediary output variables required
Current efficiency	Current required by copper reduction reaction
SEC	Total potential (including losses) Mass of copper plated (copper concentration in spent electrolyte)
Copper yield	Mass of copper plated (copper concentration in spent electrolyte)

Table 4.1: Electrowinning KPIs and the intermediary model output variables required in their calculation.

## 4.2.3.2 Input Variables

The model was developed based on a current-controlled electrowinning process, therefore, the current applied was selected as an input variable. This approach differs from the potential-controlled approach taken by Tucker (2019). A current-controlled approach was found to be a more accurate representation of the current state-of-the-art in industrial electrowinning process control (Section 2.3.6).

The additional input variables selected need to be readily measured or have the potential to be readily measured (Section 2.3.4) and must be independent of the output variables to ensure a predictive model. The selected input variables were divided into two categories: variables manipulated during operation and variables fixed due to design constraints. The selected input variables are listed in Table 4.2, together with the disturbances that may affect them. The model includes the ability to induce step or pulse disturbances in any one of the manipulated variables. Furthermore, the model allows for the manipulated input variables to be fed into the model as a vector, which enables the inclusion of dynamic input variables.

Category	Input variable	Disturbances in input variable	
	Advance electrolyte copper, iron, nickel, cobalt, and sulfuric acid concentrations	Changes in composition of ore (or matte), or controlled in upstream operation	
Manipulated	Advance electrolyte flow rate	Flow rate controlled by operator	
variables	Temperature	Heat exchanger controlled by operator, Resistive heating of electrolyte	
	Current	Rectifier current controlled by operator	
	Interelectrode distance	Constant	
	Volume of cell	Constant	
Fixed design variables	Electrode area	Constant	
	Number of cathodes	Number of cells in operation	
	Voltage loss over hardware	Degradation, short circuits, housekeeping	

Table 4.2: Selected model input variables and controlled or uncontrolled disturbances that may affect them.

## 4.2.4 Model Assumptions and Simplifications

To simplify the dynamic modelling of the electrowinning process certain assumptions were made:

The components of the electrolyte were assumed to be limited to copper, sulfuric acid, iron, nickel, and cobalt. The effect of nickel and cobalt was, in turn, assumed to be limited to affecting the physicochemical properties of the electrolyte. Since the standard reduction potential of Ni<sup>2+</sup> is 587 mV lower than that of Cu<sup>2+</sup>, nickel is not reduced during copper extraction (Aromaa, 2007). The presence of cobalt has, however, been documented to have various effects on the electrowinning process, including lowering the oxygen overpotential (Bagshaw, 1997; Cachet et al., 1999; Gendron et al., 1975; Kittelty and Mcginnity, 2006; Koch, 1959a, 1959b; Rey et al., 1938; Yu and O'Keefe, 2002).

It has previously been stated that the mechanism for water oxidation is dependent on the presence of cobalt ions. Although various attempts have been made to interpret the mechanism of the observed effect of cobalt (Bagshaw, 1997; Cachet et al., 1999; Gendron et al., 1975; Kittelty and Mcginnity, 2006; Koch, 1959a, 1959b; Rey et al., 1938; Yu and O'Keefe, 2002), no clear mechanism has been established (Nikoloski and Nicol, 2008). Moreover, consensus has not been reached that an alternative pathway for oxygen evolution is indeed the only reason for the decrease in anodic potential in the presence of cobalt. Consequently, fundamental modelling of the effect of cobalt on the oxygen evolution reaction was not plausible. Instead, the effect is captured during calibration of the model parameters, using the accompanying parameter-fitting approach.

Other typical electrolyte components include manganese, selenium, tellurium, bismuth, chloride, and additives such as smoothing agents. All these components were classified as minor components and excluded from the model. Manganese may be present in concentrations below 670 mg/L for copper electrowinning tankhouses situated in Europe and Africa (Robinson et al., 2013; Sole et al., 2019), but the focus is retained on the major electrolyte components. Fundamental modelling of the effect of manganese slime (one of the pertinent consequences of manganese, Section 2.3.4.2) would, furthermore, be dependent on tankhouse-specific factors such as housekeeping, and the composition of the anodes used. Consequently, the effect of the produced slime on the KPIs is accounted for through the current loss parameter (see Assumption 5). As with cobalt, the effect of manganese on the oxygen evolution reaction (Tjandrawan 2010) is also captured by the parameter-fitting approach.

Most tankhouses operate with very low concentrations of chloride (20 mg/L to 30 mg/L) in the electrolyte (Sole et al., 2019). The main impact of chloride on electrowinning operations, if

kept in this range, is on the quality of the deposited copper, which is outside the model scope. Similarly, the low concentrations of additives (such as smoothing agents) and the fact that their main purpose is to influence the quality of the deposited copper, meant that they were not explicitly considered in the model. Any potential effect the additives may have on the electrochemistry of the process was, therefore, not directly accounted for in the model. The additives are likely to be added at a set rate and concentration, without significant disturbances. This means calibration of model parameters for a specific tankhouse is the ideal method to account for any potential effects these additives may have on the considered KPIs.

The combined concentration of tellurium, selenium, and bismuth (if present) must be kept below 1 mg/L in the electrolyte to avoid excessive contamination of the produced cathodes (Mokmeli et al., 2015). Although the presence of tellurium and selenium could potentially affect the current efficiency and energy consumption (Bello, 2014; Ngandu, 2016), fundamental modelling of the effect is not warranted due to the low concentrations and complex mechanisms involved.

2. It was assumed that the copper reduction and water oxidation reactions were reaction-rate-limited. This assumption is supported by the bench-scale electrowinning experiments conducted by Tucker (2019). Therefore, the Butler–Volmer equation, which excludes the effects of mass-transfer kinetics, was used to calculate the current density associated with the copper reduction and water oxidation reactions. The literature review did, however, establish that the Butler–Volmer equation only gives a good approximation of the current density if the operating current density is less than 10% of the diffusion limiting-current density (Bard and Faulkner, 2001).

It is common for industrial copper electrowinning plants to operate at a current density of up to 50% of the limiting-current density for copper reduction (Ettel, 1981; Moats and Khouraibchia, 2009). The Butler–Volmer equation that is modified for the inclusion of mass-transfer effects requires the surface concentration of the respective species, which is not trivial to calculate for the dynamic state. This limits the use of the modified equation in the development of the dynamic model. An assumption was, therefore, made that the current densities associated with the copper reduction and water oxidation could be determined accurately enough, for the purpose of the model, by excluding mass-transfer effects. A warning message was incorporated into the computerised model to notify the model user if the predicted operating current density is more than 10% of the limiting-current density for copper reduction.

Another caveat of the above assumption should be noted; base-metal refineries that utilise direct electrowinning often have this step included as a means of removing copper before the spent

electrolyte is sent for downstream processing, or recycled to the leach circuit (Lamya, 2007; Rademan et al., 1999). Copper is, therefore, produced as a minor by-product in these plants, with the main objective of the electrowinning tankhouse being to produce a spent electrolyte having a composition and flow rate conducive to completing the other processes. Accordingly, if required, the tankhouse may operate closer to the limiting-current or, per occasion, breach the limit and sacrifice the quality of produced copper. Once the limiting-current is exceeded the model might not necessarily reflect the behaviour of the system accurately, as mass-transfer limiting conditions will prevail for copper reduction. Again, the incorporated warning message will provide an indication of when mass-transfer limiting conditions are applicable to the copper deposition.

- The cyclic oxidation and reduction of iron were taken to be mass-transfer limited because the copper electrowinning process is operated above the diffusion-limiting current for iron (Ettel, 1981; Moats and Khouraibchia, 2009).
- 4. The model was developed to be modular i.e., the model was developed to predict the performance of each electrowinning cell in a bank separately, using the resistance network approach (see Section 4.2.5.1). The predictions for each cell in a bank can, therefore, be combined based on the tankhouse configuration, to predict the performance of the bank as a whole. For the purpose of this project, it was assumed that the cells that comprise a bank are identical, due to the limited available measurements.

Moreover, it was assumed that every electrode pair modelled, and the associated hardware and electrolyte resistance was identical (Tucker, 2019). In a real-life plant, the hardware resistance would increase the further away the electrodes are from the voltage source (Loutfy and Leroy, 1978). The hardware resistance, or associated voltage loss, is, however, often not measured in electrowinning tankhouses. The modular nature of the model leaves opportunity for incorporating the current distribution over every bank, if more detailed measurements become available at a later stage. This inclusion would mean the actual current that "reaches" every cell, accounting for hardware losses, could be used in the model.

5. A current loss parameter was included in the model to account for losses caused by any reason other than the reduction of iron, such as ineffective electrode contact, stray currents, short circuits, the effect of sludge, and other side reactions (Tucker et al., 2021). The current loss parameter, therefore, includes the effect of the impurities that were not fundamentally modelled, such as tellurium and selenium. It also follows that this term is of specific importance for capturing the effect of housekeeping practices, such as desludging frequency, that cannot be modelled fundamentally and are known to impact the KPIs significantly.

- 6. Perfect mixing inside the electrowinning cell was assumed, meaning that the composition of the electrolyte within the cell could be taken as identical to the composition of the spent electrolyte leaving the cell. This assumption is supported by an electrowinning tracer test conducted by Aminian et al. (1998). The tests found that, except for a small bypass of 1%, the pilot-plant cell investigated showed perfect mixing.
- 7. A constant volume of electrolyte in the cell was assumed. In a typical industrial electrowinning cell, the electrolyte flows in continuously through a manifold at the bottom and overflows from one of the ends, ensuring a constant volume of electrolyte. This assumption simplifies the mass balances used to develop the dynamic model.
- 8. The effects of acid mist were assumed to be negligible. When conducting the mass balances used to develop the dynamic model it was, therefore, assumed that no electrolyte losses occurred as a result of acid mist generation. Furthermore, similar to the approach taken by Aminian et al. (2000) and Tucker (2019), losses due to evaporation and oxygen formation at the anode were excluded from the mass balances.
- 9. The standard range of operation over which the model should be valid was based on a survey of global electrowinning plants (Robinson et al., 2013; Sole et al., 2019).

#### 4.2.5 Model Basis

The generic conceptual model consists of an electrowinning model (Section 4.2.5.1) and a mass conservation model (Section 4.2.5.2). The electrowinning model is used to predict the current associated with each electrochemical reaction. The individual current densities are in turn used to calculate the rate of generation or consumption for each species present in the electrolyte. The mass conservation model uses the rates of generation or consumption in the respective dynamic mass balances to calculate the spent electrolyte composition.

#### 4.2.5.1 Electrowinning Model

The performance of the electrowinning cell was simulated by assuming that each anode–cathode pair in the cell operates as a resistance network. This assumption infers that the relationships between the electrical components in the resistance network show the relationships between electrochemical equations. This approach was first used by Aminian and Bazin (2000) to model the behaviour of an electrowinning cell consisting of a single anode–cathode pair. A voltage source and resistor were used to represent the reversible potential and overpotential, respectively, for each electrochemical equation in the resistance network (Aminian and Bazin, 2000). Tucker (2019) adapted this approach by replacing the voltage source with a capacitor. The resistance network approach was also used by Blackett and Nicol (2010) to simulate the current distribution in an electrowinning cell consisting of multiple electrode pairs. A voltage source was used to represent the reversible potential, as done by Aminian and Bazin (2000), but a parallel diode combination was used to represent the overpotential, instead of a resistor. Blackett and Nicol (2010) showed that the two diodes in parallel had a voltage–current characteristic similar to the Butler–Volmer equation (Equation 2.20). Furthermore, Blackett and Nicol (2010) reported that the inclusion of mass transfer is also possible by suitable modification of the diode characteristics. Accordingly, in this project, each electrochemical equation is represented in the resistance network by a parallel diode combination, in series with a voltage source (Figure 4.1). As previously mentioned, the model predicts the performance of one electrowinning cell, which can be scaled up to predict the behaviour of an entire tankhouse.



Figure 4.1: Schematic representation of the simplified resistance network diagram for a single anode-cathode pair (adapted from Aminian and Bazin, 2000 and Blackett and Nicol, 2010).

Figure 4.1 shows that the electrochemical reactions that occur at each electrode-side are connected in parallel. The current that flows through each electrode-side was, therefore, calculated by summing the current that was used in each reaction. The current required by each reaction was calculated by multiplying the respective current density by the surface area of the one-sided electrode. The current densities associated with the copper reduction and water oxidation were calculated using the Butler–Volmer equation (Equation 2.20). In contrast, the current densities associated with the iron reduction and oxidation were calculated using the mass-transfer equation (Equation 2.18). The Butler–Volmer equation (Equation 2.20) required the use of the copper reduction and water oxidation overpotentials.

The overpotentials were calculated iteratively, using the constraints that (1) the current flowing through each cathode-side must equal that flowing through the corresponding anode-side, and (2) that the current flowing through each cathode-side must be equal to the current flowing through the individual main branch (Equation 4.1). The first equality constraint is represented by the series connection between each cathode-side and anode-side. The current through each main branch was taken to equal to the total current (excluding the current loss), divided by a scale-up factor (Equation 4.2). The scale-up factor was defined as twice the number of cathodes in the cell, to reflect the two plated sides of each cathode, as represented by the parallel connection between the two main branches (with each branch representing one electrode-side) (Equation 4.3). The scale-up approach will be elucidated later in this section.

$$I_c = I_a = I_B \tag{4.1}$$

$$I_{\rm B} = \frac{1}{S} (I_{\rm T} - I_{\rm L})$$
 [4.2]

$$S = 2 N$$
 [4.3]

where  $I_c$  is the cathodic current (A),  $I_a$  is the anodic current (A),  $I_B$  is the current through each individual main branch (A)  $I_T$  is the total current (A),  $I_L$  is the current loss (A), S is the scale-up factor, and N is the number of cathodes.

For the copper reduction, an initial copper overpotential was estimated and the Butler–Volmer equation (Equation 2.20) was used to calculate the corresponding current density. The copper reduction current density was combined with the current density calculated for iron reduction (Equation 4.4). If the combined cathodic current was not equal to the total current left after accounting for the current loss divided by the scale-up factor (Equation 4.2), the initial estimate was updated. This process was repeated until the currents converged to within an acceptable limit (see Section 4.3.2.4). The same approach was used to determine the overpotential for water oxidation, using the anodic current.

$$I_c = (i_{\rm Cu} + i_{\rm Fe^{3+}}) \left(\frac{1}{2}A\right)$$
 [4.4]

where  $i_{Cu}$  is the copper reduction current density (A/m<sup>2</sup>),  $i_{Fe^{3+}}$  is the iron reduction current density (A/m<sup>2</sup>), and A is the two-sided cathode area (m<sup>2</sup>).

The current loss is calculated per Equation 4.5. The current loss parameter, used to calculate the current loss, was taken to be the difference between unity and the fractional actual average current efficiency, as shown in Equation 4.6. It is acknowledged that the correlation employed in Equation 4.6 could potentially result in the current loss term partially accounting for the effect of iron reduction on the current efficiency of the process.
$$I_{\rm L} = I L_I \qquad [4.5]$$

$$L_I = 1 - \bar{\beta} \qquad [4.6]$$

where  $L_I$  is the current loss parameter (fraction), and  $\bar{\beta}$  is average current efficiency (fraction).

Before implementation of any model, it is good practice to have a good understanding of the parameters that influence the specific system. For example, for a tankhouse having low advance electrolyte iron concentrations (below 1 g/L) the decrease in current efficiency associated with the presence of iron is expected to be below 3% (Das and Gopala, 1996). Losses due to reasons other than the reduction of iron are, therefore, expected to dominate, arguably justifying use of Equation 4.6 in the current form.

Allocating an accurate portion of the overall current losses to iron reduction is expected to result in fitted model parameters that better represent the actual tankhouse being modelled. Consequently, the use of Equation 4.6, and the actual average current efficiency used (for example, for a specific tankhouse it could be the average current efficiency over the previous three months), should be informed based on tankhouse-specific data. If a tankhouse reports high iron concentrations, Equation 4.6 could be replaced with a better suited correlation, based on the tankhouse-specific data, with minimal repercussions for the remainder of the model. In this project, the current loss term was only included for the datasets where it was deemed appropriate (i.e., not experimental-scale systems) and where adequate information was available.

Also shown on Figure 4.1 is that the total potential is equal to the potential over each main branch (Equation 4.7), as the branches are connected in parallel. The potential over each main branch is the sum of the anodic potential, the cathodic potential, and a voltage loss term (Equation 4.8). The anodic potential and cathodic potential were taken to consist of the overpotentials and reduction potentials associated with the water oxidation and copper reduction reactions, respectively. The voltage loss term was calculated as the sum of the loss due to electrolyte resistance and a hardware loss, as shown in Equation 4.9. The electrolyte resistance was calculated using Equation 2.26.

$$U_{\rm T} = U_{\rm B} \qquad [4.7]$$

$$U_{\rm B} = |E_{\rm Cu} + E_{\rm H_2O}| + \eta_{\rm H_2O} + \eta_{\rm Cu} + U_{\rm L}$$
[4.8]

$$U_{\rm L} = R_{\rm s} \, I + U_{\rm h} \tag{4.9}$$

where  $U_{\rm T}$  is the total potential (V),  $U_{\rm B}$  is the potential over an individual branch (V), *E* is the reduction potential (V),  $\eta$  is the overpotential (V),  $U_{\rm L}$  is the voltage loss term (V),  $R_{\rm s}$  is the electrolyte resistance ( $\Omega$ ), *I* is the current (A), and  $U_{\rm h}$  is the hardware loss (V).

The resistance network representing a single anode-cathode pair was scaled up to represent a cell consisting of multiple anode-cathode pairs. This was done by adding one main branch in parallel for

every one-sided anode–cathode pair (Tucker, 2019). A scale-up factor equal to twice the number of cathodes in the cell was previously defined to reflect the two plated sides of each cathode (Equation 4.3). The total scaled current was previously defined as the current for an individual branch multiplied by the scale-up factor, summed with the current loss (Equation 4.2). Similarly, the total current required for each electrochemical reaction was equal to the current required for the reaction in one main branch multiplied by the scale-up factor. The scaled total potential was taken to be equal to the potential over each branch, per Equation 4.7.

The scale-up approach was based on an analysis of the current flow in an industrial electrowinning cell employing the Walker configuration (Tucker, 2019). Superimposition of a scaled-up resistance network on the top view of an electrowinning cell is shown in Figure 4.2. The cell is simplified to contain only a few electrodes, but an actual electrowinning cell will have up to 80 electrodes in the same pattern. The circuit for a single one-sided anode–cathode pair is highlighted in Figure 4.2: electrons flow from the power supply to the first cathode (A), where the reduction reaction occurs and the surface is plated with copper. The charge is carried by the ions in the electrolyte between the cathode and anode. At the surface of the anode (B), which faces the cathode, the oxidation reaction occurs. Next, electrons flow through the busbar on the opposite side and back to the power source, completing the circuit. The current flows in the opposite direction to the electrons in the network.



Figure 4.2: Schematic representation of the top-view of an electrowinning cell, superimposed with a scaled-up resistance network diagram (redrawn from Tucker, 2019).

#### 4.2.5.2 Mass Conservation Model

The conceptual mass conservation model is discussed in this section. It consists of the mass conservation equations required to model the electrowinning process. A simplified representation of the streams around an electrowinning cell, used to formulate the mass conservation equations, is shown in Figure 4.3. An overall conservation of mass equation was formulated over the cell as shown in Equation 4.10. Assuming a constant volume of electrolyte resulted in Equation 4.11. Losses due to evaporation and oxygen formation at the anode were excluded from the overall conservation of mass equation (see Section 4.2.4).



Figure 4.3: Schematic representation of a simplified conservation of mass equation for a copper electrowinning cell containing copper, iron, nickel, cobalt, sulfuric acid, and water.

Conservation equations for copper, sulfuric acid, water, ferric iron, ferrous iron, nickel, and cobalt were formulated in Equations 4.12 through 4.18. For nickel and cobalt, the rate of generation or consumption, used in the conservation equations, was assumed to be zero. The rate of generation or consumption for the remaining species was calculated using the total current required for each electrochemical equation, as per Faraday's law (Equation 2.24).

To render the mass conservation equations solvable, the equations were split into two sets. Firstly, a system of differential-algebraic equations (DAEs) consisting of the conservation equations for copper and sulfuric acid, the overall conservation of mass equation, and the empirical property correlation for the electrolyte density (Model KM, Equation 3.1) was solved to obtain the concentration of sulfuric acid and copper in the spent electrolyte, the spent electrolyte flow rate, and the spent electrolyte density. The equations in this system were simultaneously solved at every time-step (of 1 s). Secondly, the conservation equations for ferric iron, ferrous iron, nickel, cobalt, and water were solved as separate ordinary differential equations (ODEs) to obtain the concentration of the respective species in the spent electrolyte. The ODEs were again solved at every time-step (of 1 s).

Overall conservation of mass equation:

$$\frac{dm}{dt} = m_{\text{electrolyte,in}} - m_{\text{electrolyte,out}} - P_{\text{Cu}} = Q_{\text{in}}\rho_{\text{electrolyte,in}} - Q_{\text{out}}\rho_{\text{electrolyte,out}} - P_{\text{Cu}} [4.10]$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{V\mathrm{d}(\rho_{\mathrm{electrolyte,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}\rho_{\mathrm{electrolyte,in}} - Q_{\mathrm{out}}\rho_{\mathrm{electrolyte,out}} - P_{\mathrm{Cu}} \qquad [4.11]$$

Copper conservation equation:

$$\frac{\mathrm{d}m_{\mathrm{Cu}}}{\mathrm{d}t} = \frac{\mathrm{d}(Vx_{\mathrm{Cu,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Cu,in}} - Q_{\mathrm{out}}x_{\mathrm{Cu,out}} - P_{\mathrm{Cu}} \qquad [4.12]$$

Sulfuric acid conservation equation:

$$\frac{dm_{H_2SO_4}}{dt} = \frac{d(Vx_{H_2SO_4,out})}{dt} = Q_{in}x_{H_2SO_4,in} - Q_{out}x_{H_2SO_4,out} + w_{H_2SO_4}$$
[4.13]

Water conservation equation:

$$\frac{dm_{\rm H_2O}}{dt} = \frac{d(V\rho_{\rm H_2O,out})}{dt} = Q_{\rm in}\rho_{\rm H_2O,in} - Q_{\rm out}\rho_{\rm H_2O,out} + w_{\rm H_2O}$$
[4.14]

Ferric iron conservation equation:

$$\frac{\mathrm{d}m_{\mathrm{Fe}^{3+}}}{\mathrm{d}t} = \frac{\mathrm{d}(vx_{\mathrm{Fe}^{3+},\mathrm{out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Fe}^{3+},\mathrm{in}} - Q_{\mathrm{out}}x_{\mathrm{Fe}^{3+},\mathrm{out}} + w_{\mathrm{Fe}^{3+}} \qquad [4.15]$$

Ferrous iron conservation equation:

$$\frac{dm_{Fe^{2+}}}{dt} = \frac{d(vx_{Fe^{2+},out})}{dt} = Q_{in}x_{Fe^{2+},in} - Q_{out}x_{Fe^{2+},out} + w_{Fe^{2+}}$$
[4.16]

Nickel conservation equation:

$$\frac{\mathrm{d}m_{\mathrm{Ni}}}{\mathrm{d}t} = \frac{\mathrm{d}(Vx_{\mathrm{Ni,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Ni,in}} - Q_{\mathrm{out}}x_{\mathrm{Ni,out}} + w_{\mathrm{Ni}} \qquad [4.17]$$

Cobalt conservation equation:

$$\frac{\mathrm{d}m_{\mathrm{Co}}}{\mathrm{d}t} = \frac{\mathrm{d}(Vx_{\mathrm{Co,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Co,in}} - Q_{\mathrm{out}}x_{\mathrm{Co,out}} + w_{\mathrm{Co}} \qquad [4.18]$$

where *m* is mass (g), *V* is the volume (L), *Q* is the volumetric flow rate (L/s),  $\rho$  is the density (g/L), *x* is the species concentration (g/L), *P* is the copper plating rate (g/s), and *w* is the rate of generation (g/s).

# 4.3 COMPUTERISED MODEL DEVELOPMENT

## 4.3.1 Files

The conceptual model developed in Section 4.2 was computerised using MATLAB (2023) and consists of the following files and main functions, listed in Table 4.3:

File Name	Purpose of File		
data	Accepts input data (can automatically import from Microsoft Excel)		
dataValidated	Calls the data file and validates the input data		
parameterFittingOffline	Calls the dataValidated file and fits offline parameters to validated data		
refitParameters	Calls the dataValidated file and fits online parameters to validated data		
mainModel	Calls other files and generates required output variables		

Table 4.3: List of files that make up the dynamic electrowinning model, with the purpose of each file.

The *data.mlx* file accepts the electrowinning data and can be run independently or called automatically by the *dataValidated.mlx* file. The *dataValidated.mlx* file validates the data, per the discussion to follow in Chapter 6, and can be run independently or called automatically by the *parameterFittingOffline.mlx* file or *refitParameters.mlx* function file. The *parameterFittingOffline.mlx* file regresses for the initial parameters that are to be manually entered into the *mainModel.mlx* file by the user, per the discussion to follow in Chapter 7. The *refitParameters.mlx* function file automatically regresses for the updated parameters based on an evolving set of input data, as discussed in Chapter 8. The *mainModel.mlx* file generates the required predictive output variables, using the specified input variables. The *mainModel.mlx* file is discussed in more detail in Section 4.3.2.

## 4.3.2 Computerised Model

## 4.3.2.1 Overview and Structure

The conceptual model is computerised using three levels of nested *while* loops to form the *mainModel.mlx* file. The three levels consist of the outermost time loop, the concentration loop, and the two innermost current loops. A modelling algorithm for the outermost time loop is shown in Figure 4.4, showing the concentration and current loops as the condensed loop body. Figure 4.5 gives the detailed modelling algorithm for the loop body (concentration and current loops). The conceptual basis of the two innermost current loops is the electrowinning model discussed in Section 4.2.5.1, whilst that of the concentration loop is the mass conservation model discussed in Section 4.2.5.2.

After the loop body converges, the potential is calculated, followed by the KPI calculations. Subsequently, an *if* statement is used to ascertain whether the online parameter-fitting approach is active, whereafter the time loop moves forward to the next time-step. A detailed discussion of the online parameter-fitting approach is deferred to Chapter 8. The outermost time loop repeats all the calculations done in the current and concentration loops at every time-step (of 1 s), for the duration of the electrowinning process.



Figure 4.4: Schematic representation of the modelling algorithm of the *mainModel.mlx* file, showing an overview of the outermost level of the nested *while* loops.



Figure 4.5: Schematic representation of the modelling algorithm of the *mainModel.mlx* file, showing an overview of the two inner levels of nested *while* loops.

## 4.3.2.2 Electrowinning Model Computerisation

The conceptual electrowinning model was computerised using the cathodic and anodic current loops, the innermost *while* loops of the three levels forming the *mainModel.mlx* file (Figure 4.5). The detailed modelling algorithms for the cathodic and anodic current loops are given in Figure 4.6 and Figure 4.7,

respectively. After values have been estimated for the copper and water overpotentials, the cathodic current loop is initiated. Upon its completion the anodic current loop is initiated.

In the cathodic current loop, the cathodic current corresponding to the estimated copper overpotential is determined by calculating the current density for each reaction that occurs at the cathode. The value of the copper overpotential estimate is updated, and the loop is repeated whilst the difference between the calculated cathodic current and the known cathodic current (which is also equal to the current through each individual main branch, Equation 4.1 and 4.2) is more than the user-defined tolerance, defined in Section 4.3.2.5. The anodic current loop functions in an identical manner, with the water overpotential updated after each iteration.



Figure 4.6: Schematic representation of the modelling algorithm of the *mainModel.mlx* file, showing the innermost cathodic current loop.



Figure 4.7: Schematic representation of the modelling algorithm of the *mainModel.mlx* file, showing the innermost anodic current loop.

## 4.3.2.3 Mass Conservation Model Computerisation

The conceptual mass conservation model was computerised in the concentration loop, the middle *while* loop of the three levels forming the *mainModel.mlx* file (Figure 4.5). The equations that form the mass conservation model were solved using an implicit numerical method that assumes the behaviour of the system remains constant over each 1 s time-step. Preceding the start of the concentration loop, values are estimated for the concentrations of the species in the spent electrolyte. At the first time-step (of 1 s) the estimated concentrations of the species in the spent electrolyte are taken to be equal to the concentrations are updated to be equal to the calculated spent electrolyte concentrations at the previous time-step. Upon completion of the current loops and associated scale-up calculations, the concentrations of all species in the spent electrolyte. The loop is repeated while the difference between the estimated and calculated concentrations is more than the user-defined tolerances (see Section 4.3.2.5). After the convergence criteria are satisfied, the estimated concentration values are updated to reflect the calculated concentration values. The innermost current loops are repeated until convergence for each iteration loop.

#### 4.3.2.4 Disturbance Computerisation

The ability to introduce disturbances in operational manipulated variables is essential for ensuring that the model can be used to simulate the impact of changes in operating conditions on performance indicators. The model allows for the introduction of a step or pulse disturbance in the advance electrolyte concentrations, flow rate, and current. The introduction of disturbances in input variables was computerised using multiple *if* statements.

#### 4.3.2.5 Model Convergence and Tolerance

The computerised model requires a series of initial estimates and loop iterations based on convergence criteria set for the current loops (convergence of anodic and cathodic currents) and concentration loop (convergence of estimated and calculated spent electrolyte concentrations). The current loops were set to converge when the difference between the respective calculated and known cathodic or anodic current was less than  $1 \times 10^{-6}$ . Furthermore, a maximum limit on the number of loop iterations was set at 3000 for each current loop, to ensure termination. This maximum limit was selected based on a reasonable number of iterations for meeting the convergence criteria (determined through various model runs), with added contingency.

The concentration loop was set to converge when the difference between the estimated and calculated concentration of each species in the spent electrolyte was less than  $1 \times 10^{-6}$ . At the first time-step (of

1 s) the initial estimate for the composition of the spent electrolyte was set equal to the composition of the advance electrolyte. Thereafter, for each time-step to follow, the spent electrolyte composition at the previous time-step was used as an initial value. This approach was taken to ensure faster convergence of the concentration loop. Furthermore, a maximum limit on the number of loop iterations was set at 6000, to ensure termination of the iterative loop. Again, this maximum limit was selected based on a reasonable number of iterations for meeting the convergence criteria, with added contingency.

#### 4.3.2.6 Built-In MATLAB Functions Used

A built-in MATLAB (2023) solver was used to solve the mass conservation equations that formed the concentration loop. As previously mentioned in Section 4.2.5.2, the mass conservation equations were split into two parts: a system of DAEs and separate ODEs. Both parts were solved using the MATLAB (2023) solver *ode15s*. The solver was selected based on the system stiffness, or how difficult the system is to evaluate. System stiffness remains a difficult concept to define, but a very slow execution speed (when using a non-stiff solver) often indicates stiffness (Moler, 2004). According to Mathworks (2020), the non-stiff solver *ode45* should generally be the first solver attempted, and if a slow execution speed is observed, as was the case for the mass conservation ODEs, the stiff solver *ode15s* should be implemented. Moreover, it is recommended that *ode15s* be used when solving DAEs (Mathworks, 2020).

# CHAPTER 5 DATA GENERATION

# 5.1 INTRODUCTION

In the previous chapter (Chapter 4), a conceptual semi-empirical dynamic electrowinning model was developed and computerised. Dynamic electrowinning data are required to train the model (Chapter 7 and Chapter 8), and for the model validation process (Chapter 9).

In this chapter, the dynamic response of electrowinning to industry-specific disturbances was investigated using a bench-scale setup. Firstly, the experimental designs followed to conduct initial probing screening experiments and final bench-scale electrowinning experiments are discussed (Section 5.2). The experimental design used for the probing screening experiments allowed for characterisation of the effect of initial conditions, as well as possible variable interactions, on the dynamic behaviour of the process. The electrolyte composition used for the screening experiments was limited to copper, iron, and sulfuric acid. For the final bench-scale electrowinning experiments, the electrolyte composition and other operating conditions were updated to better represent the direct electrowinning process. Details pertaining to the employed materials (Section 5.3), equipment (Section 5.4), and methods (Section 5.5), are also provided.

# 5.2 EXPERIMENTAL DESIGN

### 5.2.1 Screening Experiments

The selected experimental design combined the classic design of experiments objective of factor characterisation – determining the influence of factors on the response variables, or key performance indicators (KPIs) – and the additional objective of generating data for use in model validation. A classic design of experiments approach, suggested by Montgomery (2012), was adapted to include guidelines given by Rhinehart (2016) for the generation of model validation data. The first guideline stipulated by Rhinehart (2016) is that sufficient data should be collected to critically test the model throughout the range of the manipulated variables. Secondly, the conditions for the manipulated variables should be sufficiently spaced out so that the effect produced in the response variable is greater than the experimental uncertainty. The third guideline stipulated that the manipulated variables should be controlled so that they remain constant over time. The third guideline contradicts the objective of the experiments conducted during this project (to investigate the effect of industry-specific disturbances on electrowinning) and was, therefore, not considered in the design.

The manipulated variables were selected to be the copper and iron concentrations of the advance electrolyte and the current density. The range of each manipulated variable was based on typical industrial values (Table 5.1). It should be noted that the maximum copper concentration used for the screening experiments was 55 g/L, based on the upper limit of the range typically applicable to post-solvent extraction electrowinning. The remaining variables, such as the temperature and sulfuric acid concentration, were kept constant along with the applicable design specifications (Table 5.2). No additional electrolyte components (such as nickel and cobalt) were considered during the screening experiments.

Table 5.1: Manipulated variables for the screening experiments, with ranges.

Manipulated Variable	Range	Motivation	
Copper concentration in advance electrolyte	25 to 70 g/L	Typical industry range (Beukes and Badenhorst, 2009; Robinson et al., 2013), range for post-solvent extraction electrowinning would typically be narrower (33 to 55 g/L)	
Iron concentration in advance electrolyte	0 to 6 g/L	Typical industry range (Robinson et al., 2013)	
Current density	200 to 375 A/m²	Typical industry range (Beukes and Badenhorst, 2009), but can be as high as 460 A/m <sup>2</sup> (Schlesinger et al., 2011b)	

Table 5.2: Fixed variables for the screening experiments, with setpoints.

Fixed Variable	Setpoint	Motivation		
Initial sulfuric acid concentration	170 g/L	Typical industry average (Davenport et al., 2002)		
Cell temperature	45 °C	Typical industry average (Beukes and Badenhorst, 2009)		
Interelectrode distance	0.025 m	Bench-scale setup (Coetzee, 2018; Tucker, 2019)		
Electrode surface area	0.015 m <sup>2</sup>	Bench-scale setup (Coetzee, 2018; Tucker, 2019)		
Number of cathodes	1	Bench-scale setup (Coetzee, 2018; Tucker, 2019)		
Number of anodes	2	Bench-scale setup (Coetzee, 2018; Tucker, 2019)		
Flow rate	3.5 L/h	Results in interfacial velocity of between 0.05 m/h and 0.1 m/h, typical industry range (Beukes and Badenhorst, 2009).		

Based on the modified approach for developing an experimental design, a small face-centred central composite design was selected using Design Expert (2021). The small face-centred central composite design comprised of the three manipulated variables at three levels, as shown in Table 5.3. The design was repeated three times, with each replicate incorporating a step disturbance (of one level) in a different manipulated variable, as shown in Appendix A (Table A.3 to Table A.5). All experiments in which the step disturbance led to a final coded level of more than one in the respective variable were excluded

from the final design. This experimental design led to a total of eight experiments per face-centred central composite design, for a total of 24 experiments, as per Appendix A (Table A.6).

Manipulated Variable	-1	0	1
Copper concentration (g/L)	25	40	55
Iron concentration (g/L)	1	3	6
Current density (A/m <sup>2</sup> )	200	285	375

Table 5.3: Manipulated variables for the screening experiments as coded variables.

#### 5.2.2 Bench-Scale Electrowinning Experiments

Bench-scale electrowinning experiments, using a synthetic electrolyte that better mimics the composition of that used for direct electrowinning, were conducted to enable more realistic training and validation of the dynamic model. Completion of the screening experiments (Section 5.2.1) confirmed that the initial conditions of the three factors investigated, as well as possible interactions between the factors, did not severely impact the dynamic response of electrowinning to the induced disturbances. Rhinehart (2016), furthermore, acknowledged that an exhaustive experimental design is not necessarily required for the purpose of generating data for model training and validation. Consequently, a one-factor-at-a-time (OFAT) design was selected for conducting the experiments.

Five factors, each at three different levels, were considered for the experiments (Table 5.4). The three manipulated variables investigated in the screening experiments (copper and iron concentrations, and current density) were again varied, alongside two additional major components typically present in direct copper electrowinning electrolytes (nickel and cobalt). The ranges selected for the manipulated variables were informed by typical industrial conditions in direct copper electrowinning tankhouses (Sole et al., 2019). The remaining variables, such as the temperature (60 °C) and sulfuric acid concentration (90 g/L), were kept constant at the typical industry average for direct copper electrowinning. The design specifications associated with the bench-scale setup were identical to those given for the screening experiments (Table 5.2).

Manipulated Variable	Range	Motivation
Copper concentration in advance electrolyte	40 to 70 g/L	Typical industry range (Sole et al., 2019)
Iron concentration in advance electrolyte	1 to 6 g/L	Typical industry range (Sole et al., 2019)
Nickel concentration in advance electrolyte	20 to 65 g/L	Typical industry range (Sole et al., 2019)
Cobalt concentration in advance electrolyte	0.3 to 3 g/L	Typical industry range (Sole et al., 2019)
Current density	140 to 220 A/m <sup>2</sup>	Typical industry range (Sole et al., 2019)

Table 5.4: Manipulated variables for the bench-scale electrowinning experiments, with ranges.

The OFAT design entailed three base synthetic electrolyte compositions, with each base composition being at a coded level (-1, 0, or 1) of the five factors, as shown in Table 5.5. Step disturbances (of one level) in each factor were introduced for each of the three synthetic electrolyte variations. Step increases were induced for the base experiments at level -1 and 0, whilst step decreases were introduced for the experiments at level -1 and 0, whilst step decreases were introduced for the experiments at level 1. This experimental design led to a total of 15 experiments, per Appendix A (Table A.7). This is the minimum number of independent experiments suggested by Rhinehart (2016) to ensure adequate evaluation of the model accuracy. The OFAT design, furthermore, allowed for the change over time in ferric and ferrous iron concentration to be determined at three different electrolyte compositions, with five repeats (if only considering the first four hours of each experiment).

Manipulated Variable	-1	0	1
Copper concentration (g/L)	40	55	70
Iron concentration (g/L)	1	3	6
Nickel concentration (g/L)	20	45	65
Cobalt concentration (g/L)	0.3	1	3
Current density (A/m <sup>2</sup> )	140	160	220

Table 5.5: Manipulated variables for the bench-scale electrowinning experiments as coded variables.

# 5.3 MATERIALS

## 5.3.1 Synthetic Electrolyte

A synthetic electrolyte containing sulfuric acid, copper, and iron was prepared for the screening experiments. Nickel and cobalt were added as electrolyte components for the bench-scale electrowinning experiments. The electrolytes were prepared using analytical grade copper sulfate

pentahydrate, ferric sulfate monohydrate, nickel sulfate heptahydrate (if applicable), cobalt sulfate heptahydrate (if applicable), and sulfuric acid. The electrolyte was prepared according to the component concentrations specified in the experimental designs (Appendix A, Section A.1).

## 5.3.2 Electrodes

Recycled stainless-steel blank cathodes and cold-rolled lead-calcium-aluminium alloy anodes were used for the experiments. The anodes were sourced from Polymer Concrete Industries. Both electrodes had dimensions of 12 cm by 15 cm, with a working surface area of 300 cm<sup>2</sup> and thickness of 0.3 cm (Figure 5.1). The electrodes were riveted to copper hanger bars with dimensions of 2.5 cm by 19 cm, and a thickness of 0.3 cm.



Figure 5.1: Schematic representation of the electrodes used during the experiments, showing the cathode (left) and anode (right). The shaded area shown on the cathode represents the working surface area. Dimensions given in millimetres.

# 5.4 EQUIPMENT

The bench-scale electrowinning setup, originally designed to characterise the role of additives in copper electrowinning (Coetzee, 2018), was previously used to generate steady-state electrowinning data for model training and validation (Tucker, 2019). The setup consists of a 5 L electrowinning cell, a power supply (Manson, SIM-9106 1-15V 60A switching mode power supply), a pump (Blue-White Industries, Flexflo A1N31F-2T peristaltic metering pump), and a heating bath (Julabo, CORIO C heating immersion circulator) (Figure 5.2). The electrowinning cell and all pipes and connections were manufactured using polyvinyl chloride (PVC) due to the material's resistance to acid corrosion at the required operating temperature. The electrolyte entered the cell from the bottom through a perforated horizontal plate and exited by overflowing over the weirs situated on two opposite sidewalls near the top of the cell. The electrolyte leaving the cell was recycled back to the stock solution bottle. The electrodes were inserted into slots cut into the top of the cell (Figure 5.3).



Figure 5.2: Schematic representation of the bench-scale electrowinning setup.



Figure 5.3: Schematic representation of the cell used during the bench-scale electrowinning experiments.

## 5.5 METHODS

### 5.5.1 Experimental Methods

#### 5.5.1.1 Synthetic Electrolyte Preparation

A synthetic electrolyte solution containing the desired concentrations of sulfuric acid, copper, iron, nickel, and cobalt was prepared for use in each experiment. The electrolyte was prepared by adding the required volume of sulfuric acid to 5 L of demineralised water. Thereafter, the required masses of copper sulfate, ferric sulfate, nickel sulfate, and cobalt sulfate were added, and demineralised water was used to top up the electrolyte to 10 L. A detailed procedure for the preparation of the synthetic electrolyte solution is supplied in Appendix A (Section A.2.2).

#### 5.5.1.2 Cathode Preparation

Recycled stainless-steel blank cathodes were prepared by polishing the electrode surface with 22  $\mu$ m (P800) sandpaper, followed by 15  $\mu$ m (P1200) sandpaper, and rinsing sequentially with acetone and water. A new prepared cathode was used for each experiment. The same cold-rolled lead-alloy anodes were re-used for every experiment.

### 5.5.1.3 Bench-Scale Electrowinning

The bench-scale electrowinning experiments were conducted by preparing the synthetic electrolyte solution (Section 5.5.1.1) and cathodes (Section 5.5.1.2) 24 hours in advance. Subsequently, the solution was poured into the stock solution container positioned in the heating bath. The heating bath was switched on and the electrolyte in the stock solution container was allowed to reach the required operating temperature. The cathode and two anodes were placed into the slots of the electrowinning cell. Before the terminals of the power supply were connected to the respective hanger bars, the power supply was switched to current-controlled mode. The positive terminals of the power supply were connected to the cathode, replicating standard industrial cellular connections. Thereafter, the pump was switched on and the electrowinning cell was allowed to fill with the synthetic electrolyte solution. The power supply was switched on when the cell reached capacity and the current setpoint was adjusted to the required value, signifying the start of the experiment.

For the screening experiments, a step disturbance was introduced by adding additional solid copper or ferric sulfate to the stock solution container, or adjusting the value of the current setpoint, four hours into electrowinning. It was elected to induce the disturbance by adding solid salts, instead of a volume of concentrated solution, to ensure that the disturbance was only in the intended variable. The

transparent feed line was monitored to ensure that solids did not deport to the electrowinning cell and become incorporated into the cathode.

For the bench-scale electrowinning experiments increase disturbances were again introduced by adding solid salts to the stock solution container. Decrease disturbances were, however, also introduced by adding a volume of prepared solution to the stock solution container. Any unintended disturbances caused by adding the additional volume could be better captured during the bench-scale electrowinning experiments as more measurements (i.e., conductivity, temperature) were taken during the experiments (compared with the screening experiments).

In each experiment, electrowinning was allowed to take place for an additional four hours after the disturbance was introduced, whereafter the bench-scale electrowinning setup was shut down. A detailed procedure for conducting the bench-scale electrowinning experiments is supplied in Appendix A (Section A.2.2).

#### 5.5.1.4 Sampling

Sampling took place at set intervals during the eight-hour experiments, as specified in the sampling schedule supplied in Appendix A (Section A.2.2). At each sampling interval the current and potential displayed on the power supply were noted, and the potential was measured over each anode–cathode pair using a multimeter (Peakmeter, PM8233B digital multimeter). The advance and spent electrolyte streams were sampled by collecting 50 mL of each, using the valves shown in Figure 5.2. For the bench-scale electrowinning experiments, the conductivity and temperature of the electrolyte sample was measured using a conductivity meter. A 10 mL volume of each sample was extracted and deposited into 15 mL sample vials through syringe filters (nylon, 0.22 µm). For the bench-scale electrowinning experiments, a further 10 mL volume of each sample was extracted for determination of the ferrous iron concentration via titration. The remainder of the sample was returned to the stock solution container.

#### 5.5.2 Analytical Methods

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) performed at the Department of Chemical Engineering at Stellenbosch University, was used to determine the concentrations of copper, iron, nickel, and cobalt in the collected electrolyte samples (see Section 3.3.4.3). For the bench-scale electrowinning experiments, titration was used to determine the concentration of ferrous iron in the electrolyte samples. Titration was selected as it has previously been used for determining the iron speciation specifically in electrowinning electrolytes (Moats and Khouraibchia, 2009). The titration was performed directly after taking each sample to ensure an accurate representation of the iron speciation in the cell, at that point in time. The titration was performed by adding 10 mL of the electrolyte sample into a 250 mL Erlenmeyer flask. Afterwards, 5 mL of 98% sulfuric acid and 5 mL of 98% phosphoric

acid were added to the Erlenmeyer flask to mask the yellow colour of any ferric iron complexes present in the sample, ensuring a clear endpoint (Knop, 1924). Three to five drops of 0.005 M sodium diphenylamine indicator were added, and the content was titrated against a 0.00084 M potassium dichromate standard to a purple (or dark blue–green) endpoint. A detailed procedure for conducting the titration is supplied in Appendix A (Section A.2.3).

# CHAPTER 6 DATA VALIDATION

## 6.1 INTRODUCTION

In the previous chapter (Chapter 5), dynamic experimental electrowinning data were generated for use in model training and validation. As underlined by Eksteen and Reuter (2003), high-quality process data are essential for semi-empirical modelling. Kuhn and Johnson (2013) further commented on the crucial role adequate data preparation plays in ensuring that a model's predictive ability is not compromised. It follows that the implementation of data validation is imperative before a dataset is used as a representation of the electrowinning process suitable for modelling purposes.

In this chapter, the preprocessing and limitations of the four datasets used during this project are discussed, and examples of the raw and validated data are given (Section 6.2). The four datasets consist of the dynamic experimental data generated in this project (screening and bench-scale electrowinning experiments), dynamic industrial tankhouse data, steady-state experimental data generated by Tucker (2019), and steady-state industrial data acquired from a second tankhouse. The chapter further discusses the conceptual methods that formed the building blocks of the data validation approach (Section 6.3) and the process of computerising them for implementation on each dataset (Section 6.4).

It is important to note that the aim of this chapter is limited to developing a data validation approach that ensures the data quality is suitable for use in training and validating the model developed in this dissertation. As will be highlighted throughout the chapter, the developed approach is not conducive to predictive data validation and will, therefore, not be suitable for implementation in an industrial setting. Advanced data validation techniques (such as dynamic data reconciliation), which fall outside the scope of this project, should be investigated for this application. Moreover, the data validation strategy was adapted and tailored to best suit each dataset (based on the available measurements), indicating that the optimal data validation strategy will likely be tankhouse-specific.

# 6.2 DATASETS

## 6.2.1 Dynamic Experimental Data

The dynamic experimental data consists of the probing screening experiments and the bench-scale electrowinning experiments. The experimental procedure used to generate the dynamic data was discussed in detail in Chapter 5. The generated data required processing and validation before they could be used for model training and validation.

## 6.2.1.1 Screening Experiments

Alongside detecting and replacing the outliers (see Section 6.3.2), the main step in processing the screening experiment data was calculating the mass copper plated over each sampling interval. This was done by conducting a copper mass conservation balance over the electrowinning cell, at every sampling interval. The difference between the mass of copper that exited in the spent electrolyte and entered in the advance electrolyte was taken to be the sum of the accumulation in the cell and the mass plated, over the corresponding sampling interval (Equation 6.1).

$$\left(\frac{d(V x_{Cu,out})}{dt} + P_{Cu}\right) = Q_{in} x_{Cu,in} - Q_{out} x_{Cu,out}$$
[6.1]

where V is the volume (L), x is the concentration (g/L), P is the copper plating rate (g/s), and Q is the flow (L/s).

The fraction of this combined term that could be attributed to copper plating was iteratively determined to ensure that the calculated cumulative mass copper plated at the end of the experiment was equal to the corresponding measured mass copper plated. An additional step was required in processing the data for the experiments in which a disturbance in advance electrolyte copper concentration occurred. For these experiments, the assumption was made that the copper reduction was reaction-rate limited. This assumption is supported by literature for standard operating electrowinning conditions (Section 4.2.4). A linear line, with an intercept of y = 0, was fitted to the experimental cumulative mass copper plated over time and used to determine the processed cumulative mass copper plated over time.

Three possible limitations, associated with using the generated screening experiment data to train and validate the model, were identified. The first limitation is the scale of the experimental setup used to generate the data. The bench-scale setup consisted of one cathode and two anodes and would, therefore, not be representative of a full-scale industrial electrowinning cell. This limitation must be considered during the model validation process. The data could, however, be used to comment on the ability of the model to accurately predict dynamic electrowinning behaviour.

The second limitation results from the selected experimental input conditions. The input variables were selected to fall within the standard operating range for electrowinning and would, therefore, not provide information regarding the behaviour of the process under extreme conditions. As the model is assumed to be valid only under standard operating conditions, the impact of this limitation is not significant.

The third limitation associated with the screening dataset is the limited number of variables that were measured during the experiments, as well as the limited number of electrolyte components included. The sulfuric acid concentration in the advance and spent electrolytes, as well as the mass copper plated, were not measured at every sampling interval. Although sulfuric acid is generated during

electrowinning, a simplifying assumption was made that the sulfuric acid concentration remained constant over time, for use in the activity, density, and conductivity calculations required in the parameter-fitting approach (see Chapter 7). Furthermore, it was assumed that all iron was in the ferric form at the start of the electrowinning experiments. This assumption is reinforced, to an extent, by the findings of Moats and Khouraibchia (2009). Moats and Khouraibchia (2009) prepared a synthetic electrolyte similar to the solution used in the dynamic experiments, also using ferric sulfate monohydrate. Using titration, it was confirmed that between 90% and 95% of the iron was in the ferric form at the start of electrowinning (Moats and Khouraibchia, 2009).

The underspecified nature of the system meant that the data reconciliation techniques, which are discussed in Section 6.3.3, could not be used on this dataset. In addition to the preprocessing steps, only incorrect data (outliers) were detected and replaced (see Section 6.3.2), as previously mentioned. An example of the data validation results is given for the copper plating rate and cumulative mass copper plated, for two arbitrary experiments that form part of the screening dataset (Figure 6.1 and Figure 6.2). Figure 6.1 gives the results for an experiment in which a step increase in copper concentration occurred, and Figure 6.2 for an experiment in which a step increase in current density occurred. The complete data validation results for the experimental screening dataset are given in Appendix C (Section C.1.1).



Figure 6.1: Data validation results for the (a) copper plating rate and (b) cumulative mass copper plated of an arbitrary experiment that forms part of the screening experiment dataset. An increase disturbance in copper concentration occurred at t = 4 h.



Figure 6.2: Data validation results for the (a) copper plating rate and (b) cumulative mass copper plated of an arbitrary experiment that forms part of the screening experiment dataset. An increase disturbance in current density occurred at t = 4 h.

### 6.2.1.2 Bench-Scale Electrowinning Experiments

The first step in processing the bench-scale electrowinning experiment data was correcting the concentration measurements for the volume evaporated during the experiments. This step was required because the bench-scale electrowinning experiments were conducted at a significantly higher temperature (60 °C) compared with the screening experiments (45 °C), and the model does not account for evaporation (see Section 4.2.4). In industrial tankhouses mitigation strategies are often employed to limit evaporation and acid mist formation (such as hollow propylene balls), which were not used during the bench-scale experiments. The total volume evaporated during each experiment was determined by assuming that the mass of the three non-plating metals (nickel, iron, and cobalt) stayed constant for the duration of each experiment. The measured start and end concentrations of the metals, in conjunction with their respective mass conservation equations (Equations 4.15 to 4.18), were used to determine the average volume lost due to evaporation. For the experiments in which a disturbance in one of these metals was induced, the metal was not included when determining the volume evaporated.

The first two limitations associated with the bench-scale electrowinning experiment data are identical to those previously given for the screening experiment data (Section 6.2.1.1). The data were generated using a laboratory-scale setup and the input conditions were restricted to within the range of standard operating conditions. The third limitation associated with the screening experiments, the limited availability of measurements and limited electrolyte components, was, however, addressed when conducting the bench-scale electrowinning experiments.

Nickel and cobalt were included as electrolyte components, and the conductivity of the advance and spent electrolytes were measured throughout each bench-scale electrowinning experiment, making it possible to determine the sulfuric acid concentration via the conductivity model (Model KM, Equation

3.2). Furthermore, the iron speciation was measured using titrations, confirming that almost all iron was in the ferric form at the start of the experiments.

The additional measurements introduced redundancy and allowed for data reconciliation to be completed, as elucidated in Section 6.3.3. The data reconciliation was performed after the incorrect data (outliers) were identified and replaced (see Section 6.3.2), and the preliminary values were calculated for the mass copper plated using Equation 4.12 (assuming no accumulation).

A new limitation was, however, introduced by the low current densities at which the bench-scale electrowinning experiments were conducted (140  $A/m^2$  to 220  $A/m^2$ ), compared with the screening experiments (200  $A/m^2$  to 375  $A/m^2$ ). The lower current densities translated to a lower mass of copper plated, and thus, a less pronounced difference between the copper concentrations of the advance and spent electrolytes. The less pronounced difference in copper concentrations was masked by variations in the measurements. Consequently, it was challenging to obtain sensible dynamic copper plating rates by only conducting copper mass conservation balances over the cell. Two separate iterative rounds of data reconciliation were, therefore, incorporated to obtain sensible data.

In the first round of data reconciliation the mass streams entering and leaving the cell were transformed by dividing with the maximum mass flowrate (over the duration of each experiment), for each stream. Owing to the unreasonable preliminary values obtained for the cumulative mass copper plated at the final sampling intervals (compared with the actual weighed differences in cathode mass), the data were transformed to eliminate any potentially unreasonable differences in scale that arouse between the mass streams. The data were transformed back using the same maximum mass flowrate, after reconciliation was completed.

After completion of the first data reconciliation step, the reconciled mass copper plated stream was transformed again, using the cumulative mass copper plated at the end of the experimental duration, and transformed back by multiplying with the actual mass of copper plated at the end of the experiment (as determined by weighing the cathode before and after each experiment). An updated copper plating rate over time was, thereafter, calculated using the updated mass copper plated stream. A second round of data reconciliation was conducted, with the variance of the mass copper plated stream set to an arbitrary, negligibly small value.

This iterative data reconciliation strategy is not practical for industrial implementation and does not allow for predictive online data validation. It is expected that this strategy is only required for the specific case of the bench-scale electrowinning experiments, conducted at lower current densities. Dynamic data reconciliation strategies for online data validation do exist but are outside the scope of this project. As previously mentioned, the goal of the data validation done in this project was limited to ensuring that the quality of the data was not detrimental to the training and validation of the electrowinning model.

An example of the data validation results is given for the copper plating rate and cumulative mass copper plated, for an arbitrary experiment that forms part of the bench-scale electrowinning experiment dataset (Figure 6.3). Despite efforts to conduct rigorous data validation, the quality of the dynamic experimental data means that the data are likely to have limited value for validating the predictive performance of the dynamic model, developed in this project. The dynamic experimental data are, however, useful for commenting on the dynamic trends observed as a result of the induced disturbances. The complete data validation results for the dynamic experimental bench-scale electrowinning dataset are given in Appendix C (Section C.1.2).



Figure 6.3: Data validation results for the (a) copper plating rate and (b) cumulative mass copper plated of an arbitrary experiment that forms part of the bench-scale electrowinning experiment dataset.

#### 6.2.2 Dynamic Industrial Data

The dynamic industrial data were obtained from a base-metal refinery employing direct electrowinning as a final step in the production of copper. The refinery treats Ni-Cu converter matte via hydrometallurgical processing to recover nickel, copper, cobalt, and other metals (Lamya, 2007; Rademan et al., 1999). The first processing step consists of successive stages of acid-oxidation leaching of the converter matte. Nickel and cobalt are first leached, and then recovered via hydrogen pressure reduction in autoclaves (Lamya, 2007). In the second leaching stage, copper is leached, whereafter selenium and tellurium are removed via addition of sulfurous acid. Following, the second-stage leach solution, which is rich in copper, is sent to the electrowinning tankhouse for the recovery of copper. Subsequently, the spent electrolyte is recycled to the leach circuit. The refinery tankhouse consists of multiple electrowinning banks, with one bank selected for use in this project. Figure 6.4 gives a process flow diagram for the relevant section of the electrowinning tankhouse, containing two electrowinning banks (EW-101/2) that share a feed tank (T-102). As mentioned above, only one bank (EW-101) was selected for use in this project. The fresh advance electrolyte (Stream 1), originating from the leaching circuit, enters the advance electrolyte surge tank, T-101. Thereafter, the fresh advance electrolyte is transported to the advance electrolyte feed tank (T-102). The spent electrolyte recycle streams, Streams 6 and 7, originating from the two electrowinning banks (EW-101 and EW-102) also enter T-102. For mass balance purposes, it was assumed that these two streams are first combined, whereafter the spent electrolyte, Stream 5, is extracted for further processing. The remainder of the mixed recycle (combined Streams 6 and 7) is then mixed with the fresh advance electrolyte stream to form the recirculating advance electrolyte (Streams 3 and 4) that is transported to EW-101 and EW-102, respectively. The solid copper cathodes, Stream 8, are harvested from the electrowinning cells (EW-101/2).



Figure 6.4: Process flow diagram of the electrowinning tankhouse from which the dynamic industrial electrowinning data were obtained.

The data obtained from the tankhouse included hourly measurements of the fresh advance and spent electrolyte copper, nickel, and sulfuric acid concentrations, flow rate, temperature, current, and potential (V) for the selected electrowinning bank, which consists of 16 cells. Dynamic measurements of iron and cobalt concentrations were not available. These concentrations were, therefore, assumed to remain constant at their respective approximate values. The design specifications of the electrowinning tankhouse (range of potential (V), flow rate of advance electrolyte, volume of cell, and interelectrode distance) were also provided. The data consisted of measurements taken from May 2022 to September

2022. The data were divided into a training set consisting of three 14-day cycles, and five separate validation sets consisting of a 14-day cycle each.

The copper concentration in the recirculating advance electrolyte (Figure 6.4, Streams 3 and 4) was measured, but not the sulfuric acid and nickel concentrations. Consequently, a simplifying assumption was made that the nickel concentration in the recirculating streams (Streams 3 and 4) could be taken as equal to the nickel concentration in the fresh advance electrolyte stream (Stream 2). The combined mass flow from Stream 6 and Stream 7 was much larger than that of Stream 2, inferring that the assumption is likely not a good representation of the real process. Nonetheless, the assumption was required to obtain estimates of the dynamic nickel concentrations in the relevant streams. The sulfuric acid concentration in the recirculating streams was determined via a mass conservation balance.

The sulfuric acid mass conservation balance was conducted over T-102, with boundaries as shown by the dotted line in Figure 6.4. Firstly, the concentration of sulfuric acid in the spent electrolyte stream, Stream 5, was calculated by mixing Streams 6 and 7. Following, the flowrates of the respective streams entering and exiting T-102 were calculated using an overall mass conservation balance over T-102, with a constant liquid hold up assumed (Equations 6.2 to 6.4). The densities required in the overall mass conservation balance were estimated using the density model developed by Kalliomäki et al. (2021) (Model KM, Equation 3.1). The density of the recirculating electrolyte was assumed to be equal to the combined spent electrolyte density as the concentration of sulfuric acid was not known. Furthermore, a simplifying assumption was made that the flow rate of the streams leaving the electrolyte banks are equal to the flow rate of the streams entering (Equation 6.5).

Overall conservation of mass equation:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = m_{\mathrm{in}} - m_{\mathrm{out}} = Q_{\mathrm{in}}\rho_{\mathrm{in}} - Q_{\mathrm{out}}\rho_{\mathrm{out}} \qquad [6.2]$$

Assuming constant liquid hold up and no accumulation,

$$0 = Q_{\rm in}\rho_{\rm in} - Q_{\rm out}\rho_{\rm out} \qquad [6.3]$$

$$0 = (Q_2\rho_2 + Q_6\rho_6 + Q_7\rho_7) - (Q_3\rho_3 + Q_4\rho_4 + Q_5\rho_5)$$
 [6.4]

But assuming in = out over banks,

$$0 = (Q_2 \rho_2) - (Q_5 \rho_5)$$
 [6.5]

Finally, the concentration of sulfuric acid in the recirculating advance electrolyte streams could be determined by completing the sulfuric acid component conservation balance (Equation 6.6), again assuming that Streams 3 and 4 are identical and that no acid was generated or consumed in T-102, as no reactions occur (Equation 6.7).

Sulfuric acid conservation equation:

$$0 = Q_{in} x_{H_2 SO_4, in} - Q_{out} x_{H_2 SO_4, out} + w_{H_2 SO_4}$$
 [6.6]

Assuming no generation or consumption,

$$0 = Q_{in} x_{H_2 SO_4, in} - Q_{out} x_{H_2 SO_4, out}$$

$$0 = (Q_2 x_{H_2 SO_4, 2} + Q_6 x_{H_2 SO_4, 6} + Q_7 x_{H_2 SO_4, 7}) - (Q_3 x_{H_2 SO_4, 3} + Q_4 x_{H_2 SO_4, 4} + Q_5 x_{H_2 SO_4, 5})$$

Two possible limitations associated with using the industrial dataset were identified: range of operating conditions and missing measurements. The limitations overlap with those identified for the previous two datasets. Firstly, data outside of standard operating conditions were not provided as the plant's control system was in operation. Secondly, measurements of all required variables were not available. Although measurements of all main process variables are becoming commonplace in industrial electrowinning operations (Aqueveque et al., 2015), older and smaller tankhouses are likely to have the minimum data available to effect adequate safety and control (Rhinehart, 2021). The missing measurements are, therefore, not a limitation of this project, but rather the reality of using industrial tankhouse data.

It is important to note that the dynamic model developed in this project should be sufficiently robust to use data of a quality and frequency commonly found in industry. Validation of the model using the dynamic industrial data (see Section 9.4.4) was, therefore, done to (in part) demonstrate the flexibility of the developed model when applied to real-life industrial tankhouse data.

The missing measurements in the dynamic industrial dataset required the use of simplifying assumptions to calculate the values of select variables. Consequently, data reconciliation could not be performed for the dynamic industrial dataset. Incorrect data (outliers) were, however, detected and replaced after completion of the first preprocessing section (determining the required sulfuric acid concentration) (see Section 6.3.2). In the second part of data preprocessing, the copper plating rate was determined by solving Equation 4.12. An example of the data validation results is given for the advance and spent electrolyte copper concentrations, for an arbitrary cycle that forms part of the dynamic industrial dataset (Figure 6.5).



Figure 6.5: Data validation results for the (a) advance and (b) spent electrolyte copper concentrations of an arbitrary cycle that forms part of the dynamic industrial dataset.

## 6.2.3 Steady-State Experimental Data

Tucker (2019) generated bench-scale electrowinning data to train a steady-state semi-empirical electrowinning model. This experimental steady-state dataset was also used in this project for model training and validation. The data were generated using a full factorial design consisting of four factors: the copper, iron, and sulfuric acid concentration of the advance electrolyte, and the potential (Tucker, 2019). Measurements of the relevant variables were taken at the start and end of four-hour experiments. Tucker (2019) approximated the initial ferric-to-ferrous iron ratio using an average of the ratio in the spent electrolyte of industrial tankhouses, surveyed by Robinson et al. (2013). For use in this project, it was, however, assumed that all iron was in the ferric form at the start of electrowinning.

Three possible limitations for using the steady-state experimental dataset in this project were identified: the scale of the experimental setup, the range of operating conditions, and the steady-state nature of the data. The first two limitations overlapped with those identified for previous datasets. The steady-state nature of the data means that they were used only for limited conceptual and operational validation of the model (see Section 9.4.2).

#### 6.2.4 Steady-State Industrial Data

Industrial electrowinning data from a second full-scale copper electrowinning tankhouse were also made available for use in this project. The tankhouse was commissioned in 1992 and has a nameplate cathode capacity of 4400 t/a. The available data consisted of measurements taken once every 24 hours from January to June 2019. The measurements consisted of the compositions of the advance and spent electrolytes, as well as the applied current. The average number of cells online per month were provided, as well as design specifications of the electrowinning tankhouse (range of potential, flow rate of advance electrolyte, volume of cell, and interelectrode distance).

Figure 6.6 gives a process flow diagram for the relevant section of the electrowinning tankhouse. The fresh advance electrolyte, Stream 1, enters the advance electrolyte feed tank, T-101, where it is mixed with a recycle stream of spent electrolyte, Stream 4, to result in the recirculating advance electrolyte, Stream 2, which is fed to the electrowinning cells, EW-101. The provided concentration measurements were for the fresh electrolyte stream, Stream 1, and the combined spent electrolyte, Stream 3.

Data filling techniques (see Section 6.3.1) were used to fill any missing measurements. Thereafter, mass conservation balances were conducted over T-101 to determine the concentrations of Stream 2 (Equations 4.10 to 4.18). The densities used in the mass conservation balances were estimated using the density model developed by Kalliomäki et al. (2021) (Equation 3.1). The flowrates of the respective streams were not measured and were, therefore, estimated based on information provided by Sole et al. (2019). The combined spent electrolyte, Stream 3, splits up into the spent electrolyte recycle, Stream 4, and the bleed, Stream 5. Plated copper cathodes are removed via Stream 6.



Figure 6.6: Process flow diagram of the electrowinning tankhouse from which the steady-state industrial electrowinning data were obtained.

Four possible limitations associated with using the industrial dataset were identified: range of operating conditions, missing measurements, lack of dynamic characteristics, and the use of an empirical model to estimate key performance indicators (KPIs). The first three limitations overlap with those identified for the previous datasets. Firstly, data outside of standard operating conditions were not provided as the plant's control system was in operation. Secondly, measurements of all required variables were not available. The potential (V), for example, was not measured, but rather provided as a once-off design value. Thirdly, dynamic process characteristics were not included in the acquired data, due to the low-frequency sampling rate (once every 24 hours).

The final limitation results from the empirical steady-state model used to estimate the current efficiency and specific energy consumption (SEC). The model developed by Khouraibchia and Moats (2010) was used to estimate these performance indicators because the mass of copper plated and the potential were

not measured online during the electrowinning process. The ranges of these variables were provided in the design specifications of the tankhouse.

To use the empirical model, an assumption was made that all iron present in the advance electrolyte was in the ferric form at the start of electrowinning. A higher ferric iron concentration corresponded to a lower current efficiency and higher SEC, according to the empirical model. Nonetheless, the average estimated current efficiency of 94.3%, calculated using the empirical model, was well above the 80% given in the design specifications. The copper plating rate was calculated using the predicted current efficiency. Consequently, the system was overspecified and data reconciliation could be done. The estimated SEC, using the empirical model, resulted in an average potential of 1.4 V, which was outside the range of 1.8 V to 2.2 V given in the design specifications. The empirical model also assumed that the SEC was independent of the applied current density.

Taking into consideration the identified limitations, the steady-state industrial data were used for limited operational validation of the model (see Section 9.4.2). An example of the data validation results is given for the advance and spent electrolyte copper concentrations of the steady-state industrial dataset (Figure 6.7).



Figure 6.7: Data validation results for the (a) advance and (b) spent electrolyte copper concentrations of the steady-state industrial dataset.

## 6.3 CONCEPTUAL DATA VALIDATION

Data validation involves performing mass balances to identify any possible internal inconsistencies resulting from, for example, faulty instrument readings (Knoblauch, 2015). This objective was already partially met by the work described during preprocessing of the datasets (Section 6.2). As an extension of the data validation process, missing data were filled, and incorrect and incomplete data were detected and replaced (where applicable) before data reconciliation was performed (for the datasets where possible).

#### 6.3.1 Filling Missing Data

Filling missing data is important to ensure optimal utilisation of datasets, increased sample size, and overall improved model performance by training on complete data. In an industrial setting data may be missing for various reasons, including faulty sensors. In this project, missing data in incomplete measurement sets were filled using a moving window mean. The window was selected to contain the current measurement, six measurements backward, and six measurements forward. Again, this method does not allow for predictive data filling. Although Roffel and Betlem (2006) suggested removing both missing and zero values, only missing values were filled to avoid introducing gross errors into the model training data. Unreasonable zero values were addressed when detecting and replacing outliers.

## 6.3.2 Detecting and Replacing Incorrect Data

Incorrect data include high- and low-frequency disturbances, unexplained outliers, and drift or offset. Incorrect data were detected and replaced for the dynamic experimental data (generated as part of this project), and the acquired dynamic industrial data. It was not done for the two steady-state datasets because each set of measurements was taken as a separate run, limiting the use of detection and replacement of incorrect data.

The measurements that formed the dynamic datasets were divided into three groups to process for incorrect data. The first group was made up of data obtained from direct measurements, including the applied current, potential, and temperature. For the dynamic experimental dataset, this group was not processed for incorrect data as the values were continuously monitored during the experiments. For the dynamic industrial dataset, unexplained outliers, defined as values below the 10<sup>th</sup> percentile and above the 90<sup>th</sup> percentile for each sampling interval, were detected. The outliers were filled using linear interpolation of neighbouring, non-outlier values.

The second group was made up of data obtained from indirect measurements, including the concentration data obtained from Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), or titrations. This group also included the flow rate, which was obtained by measuring the time

taken to fill a container of known volume (for the experimental data), or using flowmeters (for the industrial data). For this group, unexplained outliers, defined as values more than three local scaled median absolute deviations from the local median over a window of the five preceding and succeeding values, were detected. These outliers were also replaced using linear interpolation of neighbouring non-outlier values.

The third group was made up of the mass of copper plated, which was calculated using other measured variables (see Section 6.2). As outliers were already detected and replaced for the variables used to calculate the mass copper plated, this group was not processed for incorrect data.

#### 6.3.3 Data Reconciliation

Using reconciled data for model training and validation adds robustness and credibility to the data (Eksteen et al., 2002). Consequently, data reconciliation was done to address the internal inconsistencies identified by the mass balances performed for the two steady-state datasets, and the dynamic experimental data (bench-scale electrowinning experiments only). It was possible for these three datasets because they were overspecified (there were redundant measurements available). The data reconciliation process used in this project does not allow for predictive online data validation.

The data reconciliation process entailed solving for a least-squares error objective function, to minimise the weighted sum of the measurement adjustments for each run (steady-state case) or point in time (dynamic case), as shown in Equation 6.8 (Luttrell, 2004). The process consisted of adjusting the mass fractions of each stream to create a unique and self-consistent dataset for every run (steady-state case) or point in time (dynamic case). The adjustments were made so that the overall conservation of mass equation (Equation 4.11) and the conservation of mass equation for each species (Equations 4.12 to 4.18) were satisfied. The constraints applicable to the overall conservation of mass equation and conservation of mass equation for each species are given in Equations 6.9 and 6.10, respectively. Eksteen and Reuter (2003) highlighted the use of a proper once-off sampling campaign to determine the variability associated with the measured streams. For the purposes of the project, the variances were, however, taken as estimates based on the expected sensor or measurement errors.

$$\min\phi = \sum_{k=1}^{c} \sum_{i=1}^{m} \left( \frac{A_i^{k*} - A_i^k}{\sigma_i^{2k}} \right)^2 + \sum_{i=1}^{m} \left( \frac{M_i^* - M_i}{\sigma_i^{2}} \right)^2$$
 [6.8]

s.t. 
$$\sum_{i=1}^{m} C_i M_i = 0$$
 [6.9]

$$\sum_{i=1}^{m} C_i A_i^k M_i = 0$$
 [6.10]

where  $\phi$  is the objective function,  $\sigma_i^{2k}$  and  $\sigma_i^{2}$  are the variances of the measured concentrations and flow rates, respectively, \* refers to estimated values,  $C_i$  refers to the direction of each stream *i*,  $M_i$  is the mass flow rate of each stream *i*, and  $A_i^k$  is the fraction for each species *k* in stream *i*.

## 6.4 COMPUTERISED DATA VALIDATION

### 6.4.1 Overview and Structure

The modelling algorithm for the general computerised data validation process is given in Figure 6.8. The first step in the modelling algorithm entails loading the applicable raw dataset. The next step, filling any missing data, was only required for the steady-state industrial data. The experimental data consisted of measurements taken on a set schedule for the purpose of model training and are, therefore, complete. The time period for the industrial dynamic data was selected so as to not contain any missing data, and zero data were dealt with when detecting and replacing outliers, if required.



Figure 6.8: Schematic representation of the modelling algorithm of the *dataValidation.mlx* file, showing an overview of the general computerised data validation process.

The first part of data preprocessing varied for each dataset, as shown on Figure 6.8. Outliers were detected and replaced for the dynamic datasets, but not for the two steady-state datasets. The copper plating rate, determined in the second part of the data preprocessing, was calculated differently for each dataset, as discussed in Section 6.2. Finally, the data reconciliation process, the computerised structure of which is discussed in Section 6.4.2, was implemented for the two steady-state datasets and the dynamic bench-scale electrowinning data.

# 6.4.2 Data Reconciliation

The conceptual data reconciliation process is computerised in the function *dataReconciliation.mlx*, as shown in the modelling algorithm given in Figure 6.9. A *while* loop is used to reconcile each run (steady-state case) or point in time (dynamic case) by minimising the objective function given in Equation 6.8. The output of the *dataReconciliation.mlx* function, namely the reconciled compositions of the advance and spent electrolytes, the electrolyte flow rate, and the mass of copper plated, are automatically imported into the *mainModel.mlx* file or the *parameterFittingOffline.mlx* file, as discussed in Chapter 4 and Chapter 7, respectively.


Figure 6.9: Schematic representation of the modelling algorithm of the dataReconciliation.mlx function.

## 6.4.3 Built-In MATLAB Functions Used

A built-in MATLAB (2023) solver was used to minimise the least-squares objective function for the data reconciliation process, whilst ensuring that the overall mass conservation and mass conservation equations for all species were satisfied. The nonlinear solver *fmincon* was used to minimise the equation, subject to the specified equality constraints. The built-in MATLAB function *fillmissingdata* was used to fill missing data, per the methods discussed in Section 6.3.1. Furthermore, the built-in MATLAB (2023) function *filloutliers* was used to detect and replace outliers, per the selected find and fill methods discussed in Section 6.3.2.

# CHAPTER 7 OFFLINE PARAMETER FITTING

#### 7.1 INTRODUCTION

As stated by Hedengren and Edgar (2006), fitting of model parameters from acquired data bridges the gap between the theoretical realm of mathematical models and the realistic processes they represent. Parameter-fitting can be done using both offline and online methods (Robertson et al., 1996). For copper electrowinning, the semi-empirical model developed in this project will benefit from the implementation of online parameter-fitting. Nonetheless, offline parameter-fitting is required for fitting the parameters that are not included in the online method, as well as the initial states of those parameters that are (Robertson et al., 1996). Moreover, offline parameter-fitting enables additional model applications (such as operator training), for tankhouses where limited data are available. Offline parameter-fitting will be discussed in this chapter, and online parameter-fitting in the following chapter (Chapter 8).

In the previous chapter (Chapter 6), the available datasets were validated for use in training and validating the developed model. In this chapter, the offline parameter-fitting approach, used to determine the model parameters included in the semi-empirical model, is considered. The conceptual offline parameter-fitting approach was first developed (Section 7.2), whereafter it was computerised using MATLAB (2023) (Section 7.3). Lastly, parameter sensitivity and variability analyses were conducted to investigate the effect of altering the fitted parameters on the model-predicted output variables, and to motivate the necessity of online parameter-fitting (Section 7.4).

# 7.2 CONCEPTUAL PARAMETER FITTING

### 7.2.1 Parameters

The parameters required in the model included the Butler–Volmer equation parameters (Equation 2.20), the mass-transfer equation coefficients (Equation 2.18), and the current loss parameter (Equation 4.5). The Butler–Volmer equation parameters were fitted for the reduction of copper and oxidation of water. The mass-transfer equation coefficients were fitted for the reduction and oxidation of iron. The current loss parameter was fitted to account for losses caused by any reason other than the reduction of iron, such as ineffective electrode contact, stray currents, short circuits, the effect of sludge, and other side reactions (Moats, 2018; Schlesinger et al., 2022; Tucker et al., 2021). An overview of the offline approach used to fit each parameter, together with the applicable constraints, is given in Table 7.1.

Parameter	Туре	Constraint	Approach
$i_{0,Cu} lpha_{Cu}$	Exchange current density Charge-transfer coefficient	$i_{0,Cu} > 0$ $0 < \alpha_{Cu} < 2$	Nonlinear regression based on calculated overpotential and current density
$i_{0,\mathrm{H_2O}} lpha_{\mathrm{H_2O}}$	Exchange current density Charge-transfer coefficient	$i_{0,H_2O} > 0$ $0 < \alpha_{H_2O} < 2$	Nonlinear regression based on calculated overpotential and current density
m <sub>Fe<sup>3+</sup></sub>	Mass-transfer coefficient	$m_{\mathrm{Fe}^{3+}} > 0$	Nonlinear regression based on calculated ferric iron concentration and current density
m <sub>Fe<sup>2+</sup></sub>	Mass-transfer coefficient	$m_{\mathrm{Fe}^{2+}} > 0$	Nonlinear regression based on calculated ferrous iron concentration and current density
$L_I$	Current loss parameter	$0 < L_I < 1$	$L_I = 1 - \bar{\beta}$

Table 7.1: Parameters required in the model, the applicable constraints, and the approach used to fit them.

## 7.2.2 Resampling Method

Cross validation, a type of resampling method, was used to estimate the model errors associated with the offline parameter-fitting approach (James et al., 2017). This enabled evaluation of the developed approach's performance and assessment of the fitted parameters when confronted with previously unseen data, as discussed in Section 7.4. The specific resampling method selected was *k*-fold cross validation, an algorithm of which is shown in Figure 7.1. This method entails randomly dividing the set of data points, or observations, into *k* groups, or folds, of equal size (James et al., 2017). The first fold is treated as the validation set, with the remaining k - 1 folds used to train the model. A model error term is then calculated for each fold.

This resampling method was selected due to its computational advantage over methods such as leaveone-out-cross validation (LOOCV), which would require significantly more iterations. Furthermore, although LOOCV gives approximately unbiased estimates of the model error term, it has a higher variance than k-fold cross validation, with k smaller than the number of observations (James et al., 2017). James et al. (2017) suggested using k = 5 or k = 10, as these values have been empirically shown to yield model error term estimates that have neither excessively high bias, nor high variance.



Figure 7.1: Simplified algorithm showing the training and validation folds used in *k*-fold cross validation, for a case where k = 5.

The model error term for each  $i^{th}$  fold was quantified using the residual mean square error (RMSE), calculated using Equation 7.1. This was repeated k - 1 times with a different group of observations treated as the validation set each time. The *k*-fold cross validation estimate of the RMSE was calculated by taking the average of the RMSEs calculated for every  $i^{th}$  fold, as shown in Equation 7.2 (James et al., 2017; Knoblauch, 2015).

$$\text{RMSE}_{i} = \sqrt{\left(y_{i} - \hat{f}(x_{i})\right)^{2}}$$
[7.1]

where RMSE<sub>i</sub> is the RMSE of the  $i^{th}$  fold,  $y_i$  is the  $i^{th}$  observation of the variable to be predicted, and  $\hat{f}(x_i)$  is the prediction that the model gives for the  $i^{th}$  observation.

$$RMSE_{CV} = \frac{1}{k} \sum_{i=1}^{k} RMSE_i$$
 [7.2]

where  $\text{RMSE}_{\text{CV}}$  is the k-fold cross validation estimate of the RMSE and k is the number of folds.

Following this, the RMSE was normalised using Equation 7.3, resulting in the normalised residual mean square error (nRSME).

$$nRMSE = \frac{RMSE}{\bar{y}}$$
[7.3]

where nRMSE is the normalised RMSE and  $\bar{y}$  is the mean of the variable to be predicted (also referred to as the actual real-life value).

## 7.2.3 Approach

This section details the conceptual approach followed to fit offline model parameters to each of the four sets of electrowinning data used in this project. To fit for the Butler–Volmer equation parameters (Equation 2.20), the overpotentials and current densities associated with the respective electrochemical reactions are required. Likewise, fitting for the mass-transfer coefficients required the current densities and concentrations of the respective species involved in the reactions (Equation 2.18). The approach to

fitting for the parameters is, therefore, divided into calculating the required intermediary variables using the input variables provided, and then determining the respective parameters.

The input variables used to train the model consisted of the validated current, potential (V), advance and spent electrolyte compositions, and mass of copper plated. The current efficiency and total overpotential were calculated at the end of the process for the steady-state datasets and at every available time-step for the dynamic dataset. The current efficiency was calculated by dividing the actual mass copper plated by the theoretical mass copper plated (Equation 2.23), calculated from Faraday's law (Equation 2.24). The current loss parameter was taken as the difference between unity and the mean of the fractional current efficiency over the dataset (Equation 4.6). The total overpotential was calculated by taking the difference between the actual potential and the potential associated with the reactions and losses (Equation 7.4). The calculated current efficiency and total overpotential were used to calculate the required intermediary variables for the copper reduction, water oxidation, and iron reduction and oxidation.

$$\eta_{\rm T} = U - (|E_{\rm Cu} + E_{\rm H_2O}| + U_{\rm L})$$
[7.4]

where  $\eta_{\rm T}$  is the total overpotential (V), U is the actual measured potential (V), E is the reduction potential (V), and  $U_{\rm L}$  is the voltage loss term (V).

For the copper reduction, the current density, overpotential, and copper mass plating rate were calculated as intermediary variables. The current density associated with the copper reduction reaction was calculated using the actual total current, calculated current efficiency, and two-sided cathode area (Equation 7.5).

$$i_{\rm Cu} = \frac{I \frac{\beta}{100}}{SA}$$
 [7.5]

where *i* is the current density (A/m<sup>2</sup>), *I* is the current (A),  $\beta$  is the current efficiency (%), *S* is the scaleup factor (Equation 4.3), and *A* is the cathode area (m<sup>2</sup>).

The overpotential associated with copper reduction was determined by specifying a ratio according to which the calculated total overpotential was divided between the copper reduction and water oxidation (Equation 7.6). A ratio of 0.3 was specified, meaning that 30% of the total overpotential calculated is associated with copper reduction. The ratio is based on the theoretical cell reactor developed by Beukes and Badenhorst (2009) and is within the range given by Schlesinger et al. (2011b) for a typical industrial electrowinning tankhouse. Finally, the copper mass plating rate was determined from the copper reduction current density using Faraday's law (Equation 2.21).

$$b = \frac{\eta_{\rm Cu}}{\eta_{\rm T}} = \frac{\eta_{\rm Cu}}{\eta_{\rm Cu} + \eta_{\rm H_2O}} = 0.3$$
 [7.6]

where *b* is the ratio,  $\eta_{Cu}$  is the overpotential associated with copper reduction (V), and  $\eta_{H_2O}$  is the overpotential associated with water oxidation (V).

The concentrations of ferric and ferrous iron in the advance electrolyte, and current densities associated with iron reduction and oxidation were also calculated as intermediary variables. The calculated current efficiency was used to determine the current required for iron reduction (Equation 7.7). From this, the rate at which ferric iron was reduced to ferrous iron was calculated using Faraday's law (Equation 2.21). The intermediary variables associated with the iron oxidation were, thereafter, calculated using a system of ordinary differential equations (ODEs). The system consisted of the mass conservation equations for ferric and ferrous iron (Equation 4.15 and Equation 4.16, respectively).

$$i_{\rm Fe^{3+}} = \frac{I\left(1 - \frac{\beta}{100}\right) - I_L}{SA}$$
[7.7]

where  $I_L$  is the current loss (A).

Lastly, for water oxidation the overpotential and current density were also determined as intermediary variables. The current density was calculated by assuming that all the current not required for the oxidation of iron (or lost via the current loss term), was required for the oxidation of water (Equation 7.8). The overpotential was calculated by applying the ratio previously specified (Equation 7.6).

$$i_{\rm H_2O} = \frac{I - I_{\rm Fe^{2+}} - I_{\rm L}}{SA}$$
[7.8]

Upon calculating all the required intermediary variables, the respective parameters were determined. A different set of fitted parameters was obtained for each of the available datasets validated in Chapter 6. The resampling method, discussed in Section 7.2.2, was implemented to train the model using the available datasets, with different *k*-values, or number of folds, specified for each of the datasets. The dynamic experimental screening dataset consisted of 24 experiments, or observations, with 25 timesteps, or points, associated with each experiment. Therefore, eight folds were selected containing three observations each. Similarly, eight folds were selected for the 16 steady-state experiments conducted by Tucker (2019). Tests done using k = 5, as suggested by James et al. (2017), yielded nearly identical parameters to those completed using k = 8. In both cases, k = 8 was selected to ensure an equal number of observations, with 25 points associated with each observation. Three folds were selected as k = 5 yielded similar parameters but resulted in too few observations in each fold. The dynamic industrial data consisted of 1000 points, with k = 10 selected. The steady-state industrial data consisted of 1000 observations and, therefore, ten folds were, again, selected. The two industrial datasets were not divided

into observations containing separate points, as the tankhouses ran continuously over the respective time periods, unlike the distinctly separate experiments.

# 7.3 COMPUTERISED PARAMETER FITTING

#### 7.3.1 Overview and Structure

The offline parameter-fitting approach was computerised in the MATLAB (2023) file *parameterFittingOffline.mlx*, as indicated in Chapter 4 (Table 4.3). The modelling algorithm for the parameter-fitting approach is given in Figure 7.2. The parameter-fitting approach required the *dataValidated.mlx* file to be imported as an initial step. The loaded data were next used to fit for the current loss parameter. Thereafter, the copper and iron reduction data-processing calculations for determining the relevant intermediary variables were completed. A *for* loop was used to solve the system of ODEs, discussed in Section 7.2.3, for each run (steady-state case) or point in time (dynamic case). Upon completion of the water oxidation data-processing calculations, a *for* loop was used to implement the resampling method. The output of the *parameterFittingOffline.mlx* file was the model parameters corresponding to the smallest nRMSE for the respective dataset.



Figure 7.2: Schematic representation of the modelling algorithm of the parameterFittingOffline.mlx file.

#### 7.3.2 Built-In MATLAB Functions Used

A built-in MATLAB (2023) function was used to fit the model parameters using nonlinear regression. The Statistical Toolbox function *fitnlm* and the Optimisation Toolbox function *lsqcurvefit* were both investigated as options. The functions gave comparable results and execution times, however, *lsqcurvefit* was selected as it accepts constraints on the parameters. This was useful as the parameters were able to be constrained to the ranges given in Table 7.1.

## 7.4 PARAMETER VALIDATION

#### 7.4.1 Sensitivity Analysis

Sensitivity analyses were conducted to study the effect of varying the fitted parameters on the modelpredicted output variables. Parameters fitted to the dynamic bench-scale electrowinning experiment dataset were independently increased or decreased to investigate their effect on the respective calculated current densities. Thereafter, the varied parameters were used as inputs to the electrowinning model and the sensitivity of the model-predicted key performance indicators (KPIs) to changes in the parameters was observed.

Figure 7.3 shows the Butler–Volmer equation for copper reduction, incorporating parameters that were fit for the dynamic bench-scale electrowinning experiment dataset. The graph shows the current density for the copper reduction reaction plotted as a function of the overpotential, as per the Butler–Volmer equation. The results of increasing and decreasing the charge-transfer coefficient ( $\alpha_{Cu}$ ) and exchange current density ( $i_{0,Cu}$ ) by 10%, are shown. The charge-transfer coefficient had the largest effect on the calculated current density. Both an increase in the charge-transfer coefficient and an increase in the exchange current density resulted in a steeper gradient, meaning that a less negative overpotential would result in a higher current density. At lower values of the charge-transfer coefficient the resulting current density would, therefore, be less sensitive to changes in overpotential, enabling more accurate model predictions.



Figure 7.3: Sensitivity of the current density, calculated using the Butler–Volmer equation for copper reduction, to changes in its parameters.

Similarly, Figure 7.4 shows the Butler–Volmer equation for water oxidation, incorporating parameters that were fit for the dynamic experimental bench-scale electrowinning dataset. As above, the results of a 10% increase and decrease in the charge-transfer coefficient ( $\alpha_{H_20}$ ) and exchange current density ( $i_{0,H_20}$ ), are shown. The current density demonstrated the highest sensitivity to a decrease in the charge-transfer coefficient resulted in higher current densities obtained at lower overpotentials. Consequently, the resulting current density would be less sensitive to changes in the overpotential at higher values of the charge-transfer coefficient. As above for the copper reduction reaction, a current density that is less sensitive to changes in overpotential would enable more accurate dynamic model predictions.



Figure 7.4: Sensitivity of the current density, calculated using the Butler–Volmer equation for water oxidation, to changes in its parameters.

Sensitivity analyses were also conducted using the mass-transfer equations (Equation 2.18) for iron reduction and oxidation (Figure 7.5). The current density for iron reduction is plotted as a function of the ferric iron concentration, whilst that for iron oxidation is plotted as a function of the ferrous iron concentration. From the graph, the mass-transfer equation for iron reduction  $(m_{\text{Fe}^{3+}})$  has a much steeper gradient than that for iron oxidation  $(m_{\text{Fe}^{2+}})$ . The mass-transfer equation for iron reduction is also more sensitive to a change in the corresponding parameter than is the equation for iron oxidation. These findings are relevant specifically to the case of the dynamic experimental bench-scale electrowinning dataset. Refitting the parameters for a different dataset could result in, for example, similar gradients for the two mass-transfer equations, depending on the effect of iron in the system.



Figure 7.5: Sensitivity of the mass-transfer equations for iron reduction and oxidation kinetics to changes in their parameters.

After determining to what parameters the copper reduction, water oxidation, iron reduction, and iron oxidation current densities were most sensitive to, the parameters were used as inputs to the electrowinning model. The parameters were used together with the input variables associated with an arbitrary experiment (forming part of the dynamic bench-scale electrowinning dataset), to generate model-predicted KPIs. The parameters were again independently increased and decreased to ascertain the effect on the predicted performance indicators. Only parameters that were identified to have a significant effect on the corresponding current densities (see Figure 7.3, Figure 7.4, Figure 7.5), were varied when the model-predicted performance indicators were generated. This included the charge-transfer coefficients for copper reduction and water oxidation, as well as the mass-transfer coefficient for iron reduction. The current loss parameter was also included.

The copper plating rate and current efficiency predicted for the arbitrary run, with 10% increases and decreases in parameters, are shown in Figure 7.6 and Figure 7.7, respectively. The graphs show that both the copper plating rate and the current efficiency are sensitive only to changes in the mass-transfer

coefficient for iron reduction, and the current loss parameter. A decrease in the mass-transfer coefficient for iron reduction increases the copper plating rate and current efficiency, and vice versa for an increase in the parameter. In the electrowinning model, the predicted copper reduction current is constrained by the predicted current required for iron reduction. It is, therefore, expected that the copper plating rate should be sensitive to changes in the mass-transfer coefficient for iron reduction. For real-life operations, it is similarly expected that changes in the mass-transfer conditions for iron reduction would affect the current available for copper reduction and, therefore, current efficiency.



Figure 7.6: Sensitivity of the model-predicted copper plating rate, for an arbitrary dynamic bench-scale electrowinning experiment, to changes in the model parameters.



Figure 7.7: Sensitivity of the model-predicted current efficiency, for an arbitrary dynamic bench-scale electrowinning experiment, to changes in the model parameters.

The specific energy consumption (SEC) and potential predicted for the arbitrary run, with 10% increases and decreases in parameters, are shown in Figure 7.8 and Figure 7.9, respectively. The graph shows that both the potential and SEC are very sensitive to an increase in the charge-transfer coefficient for water oxidation. The significant impact of this parameter results from the contribution of the water oxidation overpotential to the predicted potential, which is in turn used to predict the SEC. An increase

in the charge-transfer coefficient for the anodic water oxidation reaction results in the relationship between the overpotential and current density remaining a horizontal line, even at higher overpotentials, as observed from Figure 7.4. The relationship will eventually start showing a gradual increase at overpotentials significantly higher than those shown on Figure 7.4. This means that a significantly higher overpotential is required to give a high current density when the charge-transfer coefficient is increased. Conversely, it is shown that the SEC is not sensitive to changes in the charge-transfer coefficient for copper reduction. Unlike for water oxidation, the copper reduction current density plotted as a function of the overpotential has a steep gradient, regardless of the change in charge coefficient, as shown in Figure 7.3.



Figure 7.8: Sensitivity of the model-predicted SEC, for an arbitrary dynamic bench-scale electrowinning experiment, to changes in the model parameters.



Figure 7.9: Sensitivity of the model-predicted potential, for an arbitrary dynamic bench-scale electrowinning experiment, to changes in the model parameters.

## 7.4.2 Variability Analysis

Variability analyses were conducted to assess the time-varying nature of the model parameters. As will be elucidated in the next section (Section 7.4.3), the model parameters are known to be dependent on time-varying process conditions (such as the electrolyte composition and temperature). In the next chapter (Chapter 8), an online parameter-fitting approach is proposed to complement the developed model, by ensuring the fitted model parameters are up to date. In order to ensure a robust and efficient design, it is, however, important to include the parameters to which the model predictions are sensitive, and those that exhibit significant variation during the electrowinning process. Consequently, the variability analysis, in conjunction with the sensitivity analysis (Section 7.4.1), was used to inform the selection of parameters for the online parameter-fitting approach developed in Chapter 8.

Resampling with replacement, or bootstrap as it is sometimes referred to (Effron and Tibshirani, 1993), was used to estimate the variability of the parameters fitted for the dynamic experimental bench-scale electrowinning dataset. The dataset was divided into six separate subsets over time in order to assess the time-varying nature of the parameters. Each subset contained 60 samples, four from each of the 15 experiments. The subsets were not evenly spaced over time as an increased number of measurements were taken during experimental start-up and just after inducing the disturbance (after four hours). Each subset was resampled 10 000 times, with replacement, to generate bootstrap parameter estimates. Consequently, some samples were represented multiple times in the bootstrap sample (Kuhn and Johnson, 2013). The bootstrap sample taken was the same size as the corresponding original subset. The number of resamples (repetitions) was selected to be large enough to ensure meaningful statistics, whilst not resulting in computationally prohibitive calculations. The bootstrap approach is illustrated in Figure 7.10.



Figure 7.10: Graphical representation of the bootstrap approach.

The results of the variability analysis are visualised using boxplots (Figure 7.11 to Figure 7.15). The boxplots are discussed in the context of assessing the time-varying nature of the parameters (variation between boxes), as well as the variability of the fitted parameters within each subset (variation within each box). The charge-transfer coefficients for copper reduction and water oxidation remained constant at 0.2 and 0.9, respectively, and were, therefore, not included.

Figure 7.11 and Figure 7.12 show the variability associated with the exchange current densities for copper reduction and water oxidation, respectively. With the exception of the boxplot for the exchange current density for copper reduction fitted at t = 0.6 h, the median lines of the boxplots for this parameter all fall within the box of the comparison plots, signifying that the median parameters are similar over the timespan of the experiments (Figure 7.11). The same is true for the exchange current density for water oxidation (Figure 7.12). The interquartile ranges (box lengths) show that the data are similarly dispersed for each parameter, over the experimental time. Additionally, the outliers (values more than 1.5 interquartile range away from the top or bottom of the box), are almost exclusively located above the upper quartile, indicating that the parameter-fitting approach was inclined to overestimate, rather than underestimate, the exchange current densities for the dynamic experimental bench-scale electrowinning dataset.



Figure 7.11: Boxplot visualisation showing the variability of the fitted exchange current density for copper reduction over time. The line inside each box represents the median, the lower and upper box represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the sample, and outliers are defined as values more than 1.5 times the interquartile range away from the lower or upper box.



Figure 7.12: Boxplot visualisation showing the variability of the fitted exchange current density for water oxidation over time. The line inside each box represents the median, the lower and upper box represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the sample, and outliers are defined as values more than 1.5 times the interquartile range away from the lower or upper box.

Figure 7.13 and Figure 7.14 show the variability associated with the mass-transfer coefficients for iron reduction and iron oxidation, respectively. The medians for both mass-transfer coefficients differ significantly over time. The interquartile ranges for the mass-transfer coefficient for iron reduction show that the data become less dispersed over time (Figure 7.13). It is possible that this results from the method used to calculate the actual copper plating rates (mass conservation balance over cell, Equation 4.12), as the copper plating rate has an influence on the fitted mass-transfer coefficient for iron reduction in the model.

As previously explained during discussion of the parameter-fitting approach (Section 7.2.3), the current required for iron reduction, alongside the ferric iron concentration, was used to fit for the mass-transfer coefficient for iron reduction (Equation 2.18). The current required for iron reduction was determined using the calculated current efficiency. The current efficiency was calculated using the actual and theoretical mass copper plated (Equation 2.23). The actual mass copper plated was, in turn, calculated using the actual copper plating rate.

As time passed during the experiment, the difference between the measured advance and spent electrolyte copper concentrations, used to calculate the copper plating rate, became more pronounced. This lessened the impact of uncertainty on the copper plating rate calculation. Consequently, the dispersion of the fitted mass-transfer coefficients within each subset (each subset contained four samples from each of the 15 experiments) is theorised to decrease over time, because the calculated copper plating rates became less dispersed.



Figure 7.13: Boxplot visualisation showing the variability of the fitted mass-transfer coefficient for iron reduction over time. The line inside each box represents the median, the lower and upper box represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the sample, and outliers are defined as values more than 1.5 times the interquartile range away from the lower or upper box.



Figure 7.14: Boxplot visualisation showing the variability of the fitted mass-transfer coefficient for iron oxidation over time. The line inside each box represents the median, the lower and upper box represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the sample, and outliers are defined as values more than 1.5 times the interquartile range away from the lower or upper box.

Figure 7.15 shows the variability associated with the current loss parameter. As with the mass-transfer coefficients, the median for the current loss parameter also differs significantly over time. The dispersion of data (box lengths) also decreased with time, as shown before for the mass-transfer coefficient for iron reduction (Figure 7.13). Again, this is theorised to be because the calculated actual copper plating rates became less dispersed. The copper plating rate, calculated using a mass conservation balance over the cell (Equation 6.3), was used to determine the current efficiency, which was in turn used to fit for the current loss parameter (Equation 4.6). The current loss parameter was only included as a fitted parameter for the dynamic experimental bench-scale data for the purpose of the variability analysis, it was not included as a final fitted parameter (see Section 7.4.3).



Figure 7.15: Boxplot visualisation showing the variability of the fitted current loss parameter over time. The line inside each box represents the median, the lower and upper box represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles of the sample, and outliers are defined as values more than 1.5 times the interquartile range away from the lower or upper box.

### 7.4.3 Summary of Fitted Parameters

A summary of the final offline parameters fitted for all the datasets considered in this project is given in Table 7.2, alongside the parameters reported by Aminian et al. (2000) and Tucker et al. (2021), for their respective steady-state models.

Datasot	$\alpha_{Cu}$	<b>i</b> <sub>0,Cu</sub>	$\alpha_{\rm H_20}$	<i>i</i> <sub>0,H2</sub> 0	$m_{\rm Fe^{3+}}$	$m_{\rm Fe^{2+}}$	L <sub>I</sub>
Dataset	_	A/m <sup>2</sup>	_	A/m <sup>2</sup>	m/s	m/s	_
Dynamic exp (Screening)	0.20	0.116	0.89	9.40	8.69 × 10 <sup>-6</sup>	3.67 × 10 <sup>-7</sup>	0
Dynamic exp (bench-scale electrowinning)	0.20	16.7	0.89	51.1	6.20 × 10 <sup>-6</sup>	2.27 × 10 <sup>-7</sup>	0
Dynamic industrial	0.20	0.0226	0.89	0.591	2.61 × 10 <sup>-7</sup>	3.40 × 10 <sup>-8</sup>	0.44
Steady-state exp	0.20	16.7	0.89	55.9	4.10 × 10 <sup>-6</sup>	3.52 × 10⁻ <sup>7</sup>	0
Steady-state industrial	0.20	21.6	0.80	16.1	6.76 × 10 <sup>-6</sup>	2.25 × 10 <sup>-6</sup>	0
Tucker et al. (2021)*	0.26	0.839	0.57	0.105	2.89 × 10 <sup>-6</sup>	4.47 × 10 <sup>-6</sup>	_
Aminian et al. (2000)*	0.62	23	0.2	$2.06 \times 10^{-4}$	3.21 × 10 <sup>-9</sup>	4.17 × 10 <sup>-9</sup>	—

Table 7.2: Summary of the fitted parameters for each dataset.

\*Tucker et al. (2021) and Aminian et al. (2000) used a different form of the mass-transfer equation (Equation 2.18), where the stoichiometric coefficient (*n*) and Faraday's constant (*F*) were included in the definition of the mass-transfer coefficient (*m*). Consequently, in order to directly compare the mass-transfer coefficients, the reported mass-transfer coefficients for these two sources were divided by  $(n \times F)$ .

The parameters are dependent on the individual electrowinning system being modelled, as shown by the variability in the fitted values for each dataset. As discussed in Chapter 2, the charge-transfer coefficient is the fraction of the electrostatic potential energy affecting the reduction rate in an electrode reaction, with the remaining fraction affecting the corresponding oxidation rate (Guidelli et al., 2014).

All the charge-transfer coefficient values reported in Table 7.2 are within the range specified by Newman and Thomas-Alyea (2004) (between 0.2 and 2).

The exchange current density is dependent on the concentrations of reactants and products, temperature, the electrolyte–electrode interface, and impurities on the electrode surface (Barbir, 2013). Additionally, Cifuentes and Simpson (2005) reported that the kinetic parameters obtained in previous studies on copper electrodeposition also varied with cell geometry and cathode material. Each of these factors can change the value of the exchange current density by several orders of magnitude ( $1 \times 10^{-8}$  A/m<sup>2</sup> to more than 100 000 A/m<sup>2</sup>) (Newman and Thomas-Alyea, 2004).

The fitted mass-transfer coefficients for iron reduction and oxidation exhibit notable disparities between the different datasets used in the project. Nonetheless, it is important to acknowledge that mass-transfer coefficients are also influenced by system-specific factors. Factors that could possibly have contributed to the observed variations in coefficient values include the fluid flow, cell geometry, temperature, electrolyte composition, and formation of oxygen gas (Cifuentes et al., 2004; Ettel et al., 1974; Free et al., 2013; Moats and Khouraibchia, 2009). System-specific mass-transfer coefficients could be substantiated using empirical correlations, or using suitably designed experiments. Beukes and Badenhorst (2009), however, indicated that these methods may not necessarily be representative of the conditions in industrial tankhouses.

Inclusion of the resampling method enabled evaluation of the parameter-fitting approach's performance, and assessment of the fitted parameters when confronted with previously unseen validation data. Table 7.3 gives the average nRMSE for the fold from which the fitted parameters were selected for each dataset (nRMSE<sub>*i*,avg</sub>). The average *k*-fold cross validation estimate of the nRMSE over all the folds is also given for each dataset (nRMSE<sub>CV,avg</sub>). The nRMSE<sub>*i*,avg</sub> was determined by averaging the nRMSE<sub>*i*</sub> for the copper reduction, water oxidation, iron reduction, and iron oxidation reactions, within each fold. The parameters corresponding to the fold having the lowest nRMSE<sub>*i*,avg</sub>, for each dataset, were then selected for use in the dynamic model. The nRMSE<sub>CV,avg</sub> was determined by averaging the nRMSE<sub>*i*,avg</sub> for all the folds, for each dataset.

Datasat	nRMSE <sub><i>i</i>,avg</sub>	nRMSE <sub>CV,avg</sub>	
Dataset	%	%	
Dynamic exp (screening)	58.4	186	
Dynamic exp (bench-scale electrowinning)	55.7	61.0	
Dynamic industrial	71.3	73.6	
Steady-state exp	47.6	62.0	
Steady-state industrial	58.3	73.3	

Table 7.3: Summary of the RMSEs for each dataset, corresponding to fitted parameters as per Table 7.2.

The nRMSE<sub>*i*,avg</sub> and nRMSE<sub>CV,avg</sub> for all datasets are high. For the steady-state industrial dataset the low data quality, the empirical models used to determine the actual real-life KPIs, and the steady-state assumption likely resulted in the high error when fitting for parameters. For the dynamic datasets the high error values are likely the result of the time-varying nature of the fitted parameters. Alongside the high error values, the results of the variability analysis (see Section 7.4.2) and sensitivity analysis (see Section 7.4.1) motivate the inclusion of an online parameter-fitting approach to enable more accurate model predictions, where data availability allows.

# CHAPTER 8 ONLINE PARAMETER FITTING

# 8.1 INTRODUCTION

Online parameter-fitting, also known as dynamic parameter estimation, is often required to obtain a model that is sufficiently accurate for use in advanced predictive control applications (Hedengren and Eaton, 2017). As process conditions are continuously changing, the model, specifically the model parameters, may become outdated and will no longer enable satisfactory control performance (Hedengren and Eaton, 2017). The impact of time-varying process conditions is specifically relevant to the parameters fitted for the electrowinning model, as they are influenced by factors such as the electrolyte composition and temperature.

The offline parameter-fitting approach developed in the previous chapter (Chapter 7), requires manual intervention when refitting for updated model parameters. An online parameter-fitting approach that can automatically fit and implement updated parameters, based on an evolving dataset is, therefore, developed in this chapter. The conceptual online parameter-fitting approach was first developed (Section 8.2), whereafter it was computerised using MATLAB (2023) (Section 8.3). Lastly, the online parameter-fitting approach was validated to ensure it contributes to a high overall model fidelity (Section 8.4).

Refitting for parameters online requires a large dataset, containing frequent measurements. As seen with the oil and gas industry previously (Hedengren and Eaton, 2017), data availability for electrowinning operations is expected to continuously increase due to advances in technology, improved networking, and regulatory requirements that mandate additional monitoring. Recent advances in Internet of Things (IoT) technology are also enabling a connected network of low-cost, highly capable sensors to capture evolving datasets in real-time (Klein and Walsh, 2017). Nonetheless, due to the data limitations discussed in Chapter 6, the online parameter-fitting approach was only considered for the dynamic industrial dataset in this dissertation.

# 8.2 CONCEPTUAL PARAMETER FITTING

### 8.2.1 Dynamic Estimation Approach

## 8.2.1.1 Method

Methods for dynamic parameter estimation include filtered bias update, implicit dynamic feedback, Kalman filtering, and moving horizon estimation (MHE). In this project, MHE was selected for use in the online parameter-fitting approach. MHE is an optimisation approach that typically entails the minimisation of a least-squares objective function to align the process model with available measurements by adjusting certain model parameters (Hedengren and Eaton, 2017; Hedengren and Edgar, 2006; Sun et al., 2015; Yin and Gao, 2019). The selected objective function is further discussed in Section 8.2.2, and the system models in Sections 8.2.3 and 8.2.4.

The advantage of MHE over methods such as the Kalman filter is the ability to include various types of physical constraints in the optimisation problem (Gatzke and Doyle, 2002; Sun et al., 2015). This ability proved useful for modelling the electrowinning system due to the reliance on constraints such as mass conservation balances. Previously, the greater computational expense required to solve the iterative MHE optimisation problem proved to be a barrier to use (Hedengren and Eaton, 2017; Hedengren and Edgar, 2006; Sun et al., 2015). Recent advances in computational capability and methods have, however, all but eliminated this barrier and have improved the application of MHE to fast (Lambert et al., 2013) and industrial-scale systems (Ramlal et al., 2007). MHE is, for example, widely used in many industrial applications, such as process monitoring in the oil and gas industry (Hedengren and Eaton, 2017).

MHE uses a receding window of prior measurements to adjust time-varying parameters and model predictions, over a past horizon (with the parameters assumed to be constant over the horizon) (Robertson et al., 1996; Sun et al., 2015). In this project, a sliding window was used, meaning that for each new measurement included in the horizon, the oldest measurement is excluded, ensuring the horizon window remains a constant size. It is, however, necessary to find a compromise between choosing a sufficiently small horizon so that all parameters can be assumed constant and errors in the state equations are not significant, and a large enough size so that the measurements contain enough information to fit the parameters (Robertson et al., 1996). The dynamic industrial dataset, used for online fitting in this project, consisted of hourly measurements (Section 6.2.2). Consequently, a horizon of 12 hours was selected for use with this dataset as a compromise between having a sufficiently small horizon so that the model parameters could be assumed constant, whilst having enough measurements to fit the parameters.

If higher frequency data are used, the 12-hour horizon might, however, become computationally prohibitive for online parameter-fitting, and would require reassessment. For this case, Robertson et al. (1996) suggested using as large a horizon size as is computationally feasible. This statement is supported by the fact that as the horizon size increases, the influence of the initial state and weighting matrix is reduced (Hedengren and Eaton, 2017; Robertson et al., 1996). For sufficiently long horizons, it is only the model parameters that have a significant effect on the current model state (Hedengren and Eaton, 2017). The lag in model prediction induced by the online parameter-fitting approach could,

however, become significant for larger horizon sizes. This is an important consideration as it could affect the use of the model for control applications.

## 8.2.1.2 Selected Parameters

The copper plating rate is not only a key performance indicator (KPI) in itself, but is also used as an intermediate variable, alongside the potential (V), for calculating the remaining KPIs of current efficiency (Equation 2.23) and specific energy consumption (SEC) (Equation 2.25). In order to minimise the difference between the model-predicted and actual KPIs it is, therefore, necessary to minimise the difference between the model-predicted and actual versions of these two intermediate variables (Figure 8.1). The copper plating rate and potential are affected by different parameters, meaning that the two variables are described by two distinct system models, and defined by separate objective functions.

The model parameters that significantly impacted the model-predicted potential and mass copper plating rate had to be identified for inclusion in the respective system models. The included parameters were selected based on previously conducted parameter sensitivity and variability analyses, as suggested by Xu et al. (2017). Per the sensitivity analysis conducted in Chapter 7 (Section 7.4.1), the copper plating rate was most sensitive to changes in the mass-transfer coefficient for iron reduction. The model-predicted potential was most sensitive to changes in the Butler–Volmer equation parameters for water oxidation.



Figure 8.1: Graphical representation of the online parameter-fitting approach, used to minimise the difference between the modelled and actual outputs.

The current loss parameter was also updated online as it accounts for time-varying process conditions such as additional electrolyte impurities, short circuits, and the effect of sludge and housekeeping. These factors were previously identified as having a significant effect on the performance of real-life electrowinning tankhouses (Section 2.3.4), alongside the presence of iron, but cannot yet be fundamentally modelled. A separate objective function was not minimised for updating the current loss parameter; instead, it was recalculated using Equation 4.6, over the previous horizon.

#### 8.2.2 Objective Function

The objective function, along with the system model, is an important consideration for ensuring desirable results when implementing an online parameter-fitting approach (Hedengren et al., 2014). The intuitive least-squares error objective function was selected for use in this project (Equation 8.1). Although the sensitivity to outliers may be exacerbated by the squared error objective, it is simple to implement and computationally inexpensive (Hedengren et al., 2014; Hedengren and Eaton, 2017). If the sensitivity to outliers presents a problem, an alternative objective function, such as the  $l_1$ -norm objective function can be investigated for use in future work. The  $l_1$ -norm optimisation problem includes increased complexity and size, and requires the use of specialised software to solve (Hedengren et al., 2014; Hedengren and Eaton, 2017).

$$\min \phi = W_m (y_x - y)^2 \qquad [8.1]$$
  
s.t. 
$$0 = f\left(\frac{dx}{dt}, x, y, p, d, u\right)$$
$$0 = g(x, y, p, d, u)$$
$$0 \le h(x, y, p, d, u)$$

where  $\phi$  is the objective function,  $W_m$  is the measurement deviation penalty,  $y_x$  is the measurements, y is the model values, f, g, h are the equation residuals, output function, and inequality constraints that form a general system model, x is the states, u the inputs, p the parameters, and d the unmeasured disturbances.

Multiple methods have been developed for selecting the measurement deviation penalties ( $W_m$ ) (Garriga and Soroush, 2010). It is, however, commonly assumed that the penalty is time-invariant and available from the manufacturer of the measurement device used (Schneider and Georgakis, 2013). Alternatively, a dedicated once-off sampling campaign could be conducted to determine the measurement device accuracies (Eksteen and Reuter, 2003). In the absence of data relating to the penalties, the inverse of the variance of the measurements were used as the measurement deviation penalties in this project, as motivated by Schneider and Georgakis (2013).

A penalty for movement from prior parameter values was investigated for inclusion in the objective function to penalise unnecessary parameter adjustments and aid noise-rejection (Hedengren et al., 2014). Inclusion of this term, however, negatively affected the performance of the approach. Instead, it was elected to include hard-coded dead-bands to ensure that the respective parameters were left unchanged if the mean difference (over the previous horizon) between the measurement and model value was less than 5%.

#### 8.2.3 Fundamental System Models

## 8.2.3.1 Copper Plating Rate System Model

The copper plating rate is correlated to the current available for copper reduction via Faraday's law (Equation 2.24). In the electrowinning model, the current available for copper reduction is constrained by the current used in iron reduction. In other words, the current density associated with iron reduction can be adjusted to minimise the difference between the model-predicted and actual copper plating rate, by refitting for the applicable mass-transfer coefficient. The fundamental system model for the copper plating rate, therefore, consisted of the mass-transfer equation for ferric iron (Equation 8.2), as well as the constraint specified in Equation 8.3. The imposed constraint ensured that the mass-transfer coefficient remained positive, but did not exceed the limit where the current available for copper reduction was below the arbitrarily low selected value of 0.25 A.

$$i = n F m Fe^{3+} (C_{Fe^{3+}, bulk})$$
 [8.2]

$$0 < m F e^{3+} < \min\left(\frac{I - I L_I - 0.25}{n C_{F e^{3+}, bulk} F A}\right)$$
 [8.3]

where  $mFe^{3+}$  is the mass-transfer coefficient (cm/s), *I* is the current (A),  $L_I$  is the current loss parameter (fraction), *n* is stoichiometric coefficient (dimensionless), *F* is Faraday's constant (96 485 C per equivalent mol),  $C_{i,bulk}$  is the bulk molar concentration (mol/cm<sup>3</sup>), and *A* is the electrode area (m<sup>2</sup>).

#### 8.2.3.2 Potential System Model

The potential (V) calculation includes a term for the overpotential of the water oxidation reaction (Equation 4.8). Consequently, the overpotential for water oxidation can be manipulated, by refitting the parameters of the Butler–Volmer equation (Equation 2.20), to minimise the difference between the model-predicted and actual potential. The fundamental system model for potential, therefore, consisted of the Butler–Volmer equation for water oxidation (Equation 2.20) and the constraints specified in Equation 8.4. The specified constraints are based on the ranges of the fitted offline parameters, for the datasets considered in this project (Table 7.2). As previously established (Section 7.4), the parameters are expected to be system-specific. Consequently, the constraints can be adapted based on the acceptable variability for the refitted parameters of the specific system being modelled.

$$0 < \alpha_{\rm H_2O} < 0.9$$
 [8.4]  
 $0 < i_{0,\rm H_2O} < 200$ 

where  $\alpha_{H_2O}$  is the charge-transfer coefficient for water oxidation (dimensionless) and  $i_{0,H_2O}$  is the exchange current density for water oxidation (A/m<sup>2</sup>).

The actual real-life overpotential for water oxidation was not directly measured, but also calculated using Equation 4.8. This method required specification of the copper reduction overpotential, which can be calculated using the Butler–Volmer equation (Equation 2.20). The current density for copper reduction, required in this calculation, was taken as the difference between the total current density (after accounting for the current loss) and the updated current density for iron reduction (Equations 4.1) to 4.4).

### 8.2.4 Surrogate System Models

#### 8.2.4.1 Background

Surrogate models are used to reduce the computational cost by substituting high-fidelity fundamental or semi-empirical models with fast executing black-box models (Frangos et al., 2010). Surrogate models are, therefore, mathematically simple models that regress the input–output relationships of a more complex model (Bárkányi et al., 2021). The review done by Bárkányi et al. (2021) detailed the use of surrogate models in a wide range of engineering applications, including digital twinning. In this section, the technique is, however, investigated for use in parameter estimation by replacing the fundamental system models (discussed in Section 8.2.3) with appropriate surrogate models.

Although the fundamental system models are computationally inexpensive for the dataset used in this project, surrogate modelling is investigated as a future-orientated strategy for online parameter-fitting using computationally intensive datasets (i.e., datasets with high-frequency measurements). Furthermore, it serves as an introduction for the development of a surrogate model of the dynamic electrowinning model, should this be required for industrial applications, such as the development of digital twins, at a later stage.

The process for developing a surrogate model discussed by Bárkányi et al. (2021), was used in this dissertation (Figure 8.2). The process aims to develop a surrogate model that is as accurate as possible, whilst using as few simulations as possible. Two separate surrogate system models were developed; one for the copper plating rate and one for the potential. The surrogate models were constructed using repeated simulations that were performed in an offline phase, as described by (Frangos et al., 2010). Details pertaining to the simulation design are provided in Section 8.2.4.2. Furthermore, the model adequacy checks incorporated in the regression model building process (Figure 3.1) were interweaved with the validation step shown in Figure 8.2.



Figure 8.2: Process for development of surrogate model (adapted from Bárkányi et al., 2021).

#### 8.2.4.2 Design of Experiments and Sampling

The sampling step entails the generation of data to be used in surrogate model development (Bárkányi et al., 2021). The quality of the surrogate model is significantly affected by the quality and number of samples (McBride and Sundmacher, 2019). It is important to obtain sufficient samples to give the surrogate model the ability to interpret the behaviour of the original model accurately (Galeazzi et al., 2023), whilst keeping the number of required simulations realistic. Consequently, the design of sampling experiments, also described as the sampling method used to obtain samples from the detailed model, is an important consideration.

Bárkányi et al. (2021) differentiated between two types of sampling methods for use in surrogate modelling: stationary sampling and adaptive sampling. Stationary sampling methods, including space-filling designs such as Latin Hypercube Sampling (LHS), rely on geometry or patterns (Bárkányi et al., 2021). Shang and Apley (2021) explained that LHS designs are the most popular approach for designing simulations for surrogate modelling. Adaptive methods, on the other hand, start out by generating a lower number of samples (using stationary methods). Thereafter, new sample locations are determined serially (Bárkányi et al., 2021). Bárkányi et al. (2021) explained that the aim of the adaptive method is to decrease the sampling requirements by obtaining more samples that actively improve the quality of the surrogate model.

In this dissertation, the adaptive method was selected, and implemented using a Nearly Orthogonal Latin Hypercube (NOLH) design as starting point. The design was generated for nine factors (six manipulated variables, three parameters) at two levels (low, high) using a spreadsheet developed by Sanchez (2011). The six manipulated variables included the component concentrations in the advance electrolyte, and the applied current. The temperature and flow rate of the advance electrolyte were not included in the design, as the impact of these two variables were found to be limited during initial screening simulations. The three parameters consisted of the same parameters included in the fundamental system models (mass-transfer coefficient for iron reduction, exchange current density for water oxidation, and charge-transfer coefficient for water oxidation).

The low and high levels selected for each factor are given in Table 8.1, where the factors are represented as coded variables. The ranges for the manipulated variables were based on typical industry conditions, as discussed in Chapter 5 (Table 5.4). The ranges for the parameters were informed from initial screening simulations and the constraints given in Chapter 7 (Table 7.1).

Manipulated Variable	-1	1
Copper concentration (g/L)	40	70
Iron concentration (g/L)	1	6
Nickel concentration (g/L)	20	65
Cobalt concentration (g/L)	0.3	3
Sulfuric acid concentration (g/L)	70	200
Current density (A/m <sup>2</sup> )	140	220
i <sub>0,H2</sub> O (A/m²)	5	100
$\alpha_{ m H_{2}O}$ (dimensionless)	0.2	0.9
$m_{ m Fe^{3+}}$ (m/s)	2.20 × 10 <sup>-6</sup>	5.00 × 10 <sup>-5</sup>

Table 8.1: Manipulated variables for computerised experiments as coded variables.

For some of the initial 33 samples generated in the NOLH design, the simulation results indicated a copper plating rate of zero. This occurred when certain combinations of factors were used. For example, when the current was at the low level, but the mass-transfer coefficient for iron reduction was at the high level, no current was available for copper reduction. Consequently, an additional 17 samples were generated randomly, per the adaptive method. Another 35 random confirmation samples were also generated for use in validating the surrogate system models.

#### 8.2.4.3 Model Selection and Fitting

Surrogate models can be categorised into three main classes: data-fit models, reduced-order models, and hierarchical models (Eldred et al., 2004). The most popular surrogate model types, as reviewed by Bárkányi et al. (2021), fall into the data-fit model class. Frangos et al. (2010) defined data-fit models as models that are generated using interpolation or regression of simulation data from the input–output relationships in the detailed model. Data-fit model types include polynomial regression models, Kriging models, and nonlinear regression models of machine learning (such as artificial neural networks). In this dissertation, the polynomial regression data-fit model type was selected for use in developing the surrogate system models. As this is the simplest surrogate model type, the associated computational requirements are small, making them ideal for real-time online applications.

The general form of the system surrogate models for predicting the copper plating rate and potential (V) is presented in Equation 8.5. The corresponding model coefficients are given in Table 8.2.

 $f(x) = a_1 + a_2 xCu + a_3 xH_2SO_4 + a_4 xNi + a_5 xFe + a_6 xCo + a_7 l + a_8 m_{Fe^{3+}} + a_9 \alpha_{H_2O} + a_{10} i_{0,H_2O} + a_n \text{ (combined effect term)} + a_p \text{ (polynomial term)}$ 

where *a* is the model coefficient, *x* is the concentration (g/L), *I* is the current (A),  $m_{\text{Fe}^{3+}}$  is the mass-transfer coefficient for iron reduction (m/s),  $\alpha_{\text{H}_2\text{O}}$  is the charge-transfer coefficient for water oxidation (dimensionless), and  $i_{0,\text{H}_2\text{O}}$  is the exchange current density for water oxidation (A/m<sup>2</sup>).

Term	Model <i>P</i> Cu	Model Potential
Constant	2.993 × 10⁻⁵	3.589 × 10⁻¹
xCu	_	3.871 × 10⁻³
xH2SO4	_	$-6.010 \times 10^{-4}$
xNi	_	6.878 × 10 <sup>-3</sup>
<i>x</i> Fe	7.256 × 10 <sup>-6</sup>	$-2.420 \times 10^{-2}$
хСо	_	1.275 × 10 <sup>-1</sup>
1	3.256 × 10 <sup>−4</sup>	9.618 × 10 <sup>-2</sup>
$m_{ m Fe^{3+}}$	-8.095	-3.304 × 10 <sup>3</sup>
α <sub>H20</sub>	_	2.483
i <sub>0,H2</sub> 0	_	2.307 × 10 <sup>−3</sup>
<i>x</i> Ni xCo	_	-2.658 × 10 <sup>-3</sup>
$\alpha_{ m H_2O} \cdot i_{0, m H_2O}$	_	$-8.601 \times 10^{-3}$
m <sub>Fe³+</sub> ∙ xFe	-11.83	-
$(m_{\rm Fe^{3+}})^2$	2.034 × 10 <sup>5</sup>	_
xFe <sup>2</sup>	-5.452 × 10 <sup>-6</sup>	_
$\left(\alpha_{\rm H_2O}\right)^2$	-	-4.260
$\left( lpha_{\mathrm{H_{2}O}} \right)^{3}$	-	2.996

Table 8.2: Terms	and corresponding coeffic	ients for the copper	plating rate and	potential system s	urrogate models.
	1 8	11	1 0 1		0

The copper plating rate model included the squared, linear, and interaction terms that were determined to be statistically significant (*p*-values < 0.05). The potential model form is cubic with interactions, but again only the interaction terms determined to be statistically significant (*p*-values < 0.05) were included. The *p*-values for the included terms, calculated at a confidence level of 95%, are summarised in Appendix D (Table D.9). Amongst the terms determined to be statistically significant for the potential model was the mass-transfer coefficient for iron reduction. Consequently, as with the fundamental

system models, the mass-transfer coefficient for iron reduction must first be refitted using the copper plating rate model, before the remaining parameters in the potential model can be refitted.

#### 8.2.4.4 Model Validation

The model validation process, as it pertains to regression modelling, was discussed extensively in Chapter 3. As before, the distinction is made between model adequacy testing and model validation for the surrogate system models. Model adequacy testing is concerned with investigating the fit of the regression model to available training data, testing for lack of fit, and diagnosing violations of the basic regression assumptions. Model validation, on the other hand, is concerned with assessing the model performance on previously unseen validation data.

#### Model Adequacy Checking

Figure 8.3 presents the normality probability plots of the externally studentised residuals for the (a) copper plating rate surrogate system model and (b) potential (V) surrogate system model. The normality assumption is considered to be valid if the points on the plots lie on the respective straight lines (Chibwe, 2020). Montgomery et al. (2012), however, explained that the straight line is determined with emphasis on the central values (i.e., the 0.33 and 0.67 cumulative probability points) rather than the extremes. Even though the probability plot for the copper plating rate model seems to be linear for the central values, per visual inspection, the distribution is heavy-tailed. The deviation seems to be mainly the result of possible outliers. The plot for the potential system surrogate model also shows negative skewness, again seemingly resulting from possible outliers.



Figure 8.3: Normality plot of the externally studentised residuals for the (a) copper plating rate and (b) potential systems surrogate models.

Figure 8.4 shows the parity plots of the (a) modelled versus measured values and (b) externally studentised residuals versus the modelled values, for the copper plating rate surrogate system model. Figure 8.4 (b) shows that the residuals can be contained in a horizontal band for the copper plating rate

model, indicating that there are no obvious model defects (Montgomery et al., 2012). Two points do, however, again present as possible outliers.



Figure 8.4: Parity plots of the (a) modelled versus measured values and (b) externally studentised residuals versus the modelled values, for the copper plating rate surrogate system model.

Figure 8.5 shows the parity plots of the (a) modelled versus measured values and (b) externally studentised residuals versus the modelled values, for the potential (V) surrogate system model. Figure 8.5 (b) shows that the residuals for the potential model decreased slightly for an increase in modelled potential, implying that the variance is a decreasing function of the measured data. The largest residual also occurred at the extreme of the modelled values and may, therefore, support that the variance is not constant (Montgomery et al., 2012).

Transformations on the dependent variable are generally used to stabilise the variance in practice (Montgomery et al., 2012). The common variance-stabilising transformations suggested by Montgomery et al. (2012) did, however, not markedly improve the residual pattern. Additional strategies, such as applying a suitable transformation to the independent variables or using the weighted least-squares method, are also described. It was, however, elected to use the model as is because the observed decrease in residuals for increasing modelled potential was not severe.



Figure 8.5: Parity plots of the (a) modelled versus measured values and (b) externally studentised residuals versus the modelled values, for the potential surrogate system model.

The correlation coefficients for both models show a good fit on the training data (Table 8.3). As expected, based on the residual analysis, the copper plating rate model is shown to have a better overall fit than the potential model.

Table 8.3: Correlation coefficients for the copper plating rate and potential system surrogate models, based on their respective least-squares fit.

Correlation coefficient	<i>P</i> Cu Model	Potential Model
Least-squares fit R <sup>2</sup>	0.999	0.909
Adjusted R <sup>2</sup>	0.999	0.875
Prediction $R^2$ (calculated via PRESS <sup>*</sup> )	0.998	0.778
nRMSE (%)	1.25	3.32

\*Prediction sum of squares.

### Model Predictive Performance

The main goal of surrogate modelling is predictive modelling; therefore, the focus is shifted to model validation using previously unseen data. In the context of surrogate modelling, model validation is used to confirm that the outputs of the surrogate model have such a fidelity to the outputs of the detailed model that the objectives of the investigation can be achieved (Bárkányi et al., 2021). In this dissertation, the objective being investigated is the online refitting of model parameters to enhance the predictive capabilities of the dynamic electrowinning model. The 35 confirmation samples, referred to in Section 8.2.4.2, were used to assess the predictive performance of the two surrogate system models. The number of samples used in the validation step is more than the minimum of 20 suggested by Montgomery et al. (2012), to give a reliable assessment of the model's performance.

Figure 8.6 shows the parity plot of the modelled versus measured values for the (a) copper plating rate and (b) potential (V) surrogate system models. The corresponding correlation coefficients are given in Table 8.4. The performance of the models required further assessment for use in online parameter-fitting, as provided during the conceptual validation completed in Section 8.4.



Figure 8.6: Parity plot of the modelled versus measured values for the (a) copper plating rate and (b) potential surrogate system models.

Table 8.4: Correlation coefficients for the copper plating rate and potential surrogate system models, based on the validation data.

Correlation coefficient	<i>P</i> Cu Model	Potential Model
Confirmation R <sup>2</sup>	0.998	0.652
nRMSE (%)	1.49	4.68

It should be noted that neither surrogate model is expected to be sufficiently accurate for replacing the detailed model in applications such as digital twinning, regardless of the performance during model validation. Surrogate models for use in this application would likely require a more complex model structure, such as the artificial network type that has previously been applied in the petroleum industry specifically for digital twinning (Örs et al., 2020).

### 8.3 COMPUTERISED PARAMETER FITTING

#### 8.3.1 Overview and Structure

The online parameter-fitting approach was partially computerised in the MATLAB (2023) file *mainModel.mlx*. The section of the computerised approach contained in the *mainModel.mlx* file is shown in the modelling algorithm given in Figure 8.7. In this file, an *if* statement was used to ensure that the refitting of parameters did not commence until the time-step was equal to or greater than the sum of the selected horizon and sampling frequency. Adding the sampling frequency here ensured that

the first sampling instance was not included when refitting for the parameters; mitigating for any possible process start-up irregularities. A second *if* statement activated the necessary preprocessing calculations and called the *refitParameters.mlx* function file if the sampling frequency was a factor of the current time-step. The bulk of the computerised approach was contained in the *refitParameters.mlx* function file (Table 4.3).



Figure 8.7: Schematic representation of the modelling algorithm of the *mainModel.mlx* file, showing an overview of the parameter refitting section.

The modelling algorithm for the *refitParameters.mlx* function file is given in Figure 8.8. The function used nested *if* statements to determine whether the fundamental or surrogate system models had to be used in refitting for the parameters, based on user selection. The output of the *refitParameters.mlx* function file is the refitted parameters to be used until the next sample instance was available.



Figure 8.8: Schematic representation of the modelling algorithm of the refitParameters.mlx function file.

## 8.3.2 Built-In MATLAB Functions Used

A built-in MATLAB (2023) function, *lsqnonlin*, was used to refit the model parameters by minimising the selected least-squares objective function (Equation 8.1). Another Optimisation Toolbox function, *lsqcurvefit*, was also investigated as a possible solver. Although both solvers could be implemented successfully (*lsqcurvefit* was used to fit for the offline parameters), it was elected to use *lsqnonlin* as it was more intuitive for use in minimising the selected objective function.

# 8.4 CONCEPTUAL VALIDATION

The goal of the conceptual validation performed in this section was to not only evaluate the performance of the online parameter-fitting approach, but also further assess the accuracy of the surrogate system models when implemented for this purpose. Conceptual validation of the online parameter-fitting approach was conducted at the operating conditions of an arbitrary experiment that formed part of the dynamic experimental bench-scale electrowinning dataset. The validation entailed generating three separate eight-hour baselines (one for each parameter that is included in the approach) that could be sampled and used as the "desired values" when the online parameter-fitting approach was activated.

Each baseline was generated by inducing disturbances in one of the respective parameters to be refitted (mass-transfer coefficient for iron reduction, exchange current density for water oxidation, and charge-transfer coefficient for water oxidation). The disturbances consisted of a 75% decrease after two hours, 45% increase after four hours, and a 50% increase after 6 hours. Following, the online parameter-fitting approach was activated, and the performance thereof assessed. The approach was implemented with a time horizon of 1 hour and the baseline was sampled every 15 minutes. Online refitting of the current loss parameter was deactivated. The validation process was repeated for both the fundamental and surrogate system models, for each baseline.

Figure 8.9 and Figure 8.10 show the mass-transfer coefficient for iron reduction and the copper plating rate, respectively, for the baseline in which disturbances were introduced in the mass-transfer coefficient for iron reduction. The graphs also include the online parameter-fitting results using the fundamental and surrogate system models. The approach was able to successfully correct for the effect of the disturbance in the mass-transfer coefficient, regardless of what system model was used. The approach using the fundamental system model is, however, shown to have superior fidelity, despite the good fit of the surrogate model, shown previously in Section 8.2.4.



Figure 8.9: Baseline response showing disturbances in the mass-transfer coefficient, with the online parameter-fitting results using the fundamental and surrogate system models.


Figure 8.10: Baseline response showing the effect of disturbances in the mass-transfer coefficient on the copper plating rate, with the online parameter-fitting results using the fundamental and surrogate system models.

Figure 8.11 shows the charge-transfer coefficient and exchange current density for water oxidation, for the case where the disturbances were induced in the charge-transfer coefficient. Again, the baseline, as well as results for the online parameter-fitting approach incorporating the respective fundamental and surrogate system models, are shown. The figure shows that the online approach does not refit for the charge-transfer coefficient in order to adjust the predicted potential, but rather refits the exchange current density. The objective of the approach is to enable more accurate predictions of the potential, regardless of the exact parameter refitted to achieve this. This finding is also consistent with the results presented in the parameter-sensitivity analysis, conducted in Chapter 7. Overall, as shown in Figure 8.12, the online parameter-fitting approach improved the model predictions for the potential. Again, the performance of the approach using the fundamental system model was shown to be superior.



Figure 8.11: Baseline response of the (a) charge-transfer coefficient and (b) exchange current density, showing disturbances in the charge-transfer coefficient, with the online parameter-fitting results using the fundamental and surrogate system models.



Figure 8.12: Baseline response showing the effect of disturbances in the charge-transfer coefficient on the potential, with the online parameter-fitting results using the fundamental and surrogate system models.

Figure 8.13 shows the charge-transfer coefficient and exchange current density for water oxidation, for the case where disturbances were induced in the exchange current density. As before, the baseline and results for the online parameter-fitting approach incorporating both the fundamental and surrogate system models are included. For the approach using the surrogate system models, the exchange current density was reduced to 0 after being refitted for the first disturbance (Figure 8.13 (b)). The model-predicted potential (Figure 8.14) reflects this behaviour; the predicted potential drastically overshoots after t = 2 h and does not recover. This behaviour confirmed that the polynomial model regressed for the potential is not necessarily adequate for use as a surrogate system model in online parameter-fitting applications. The online parameter-fitting approach that implemented the fundamental system models is, however, shown to adequately correct for the predicted potential by adjusting the corresponding parameter.



Figure 8.13: Baseline response of the (a) charge-transfer coefficient and (b) exchange current density, showing disturbances in the exchange current density, with the online parameter-fitting results using the fundamental and surrogate system models.



Figure 8.14: Baseline response showing the effect of disturbances in the exchange current density on the potential, with the online parameter-fitting results using the fundamental and surrogate system models.

Up until this point an important consideration for implementing the surrogate system models has been left unaddressed. The surrogate models were regressed using sample data specific to the dynamic experimental dataset. The development process (shown in Figure 8.2), with the exception of the design of experiments step, will need to be repeated for each unique dataset in order to obtain a case-specific surrogate model. This is necessary because the fixed design variables, unique to each tankhouse or experimental setup, were not taken as input variables to the surrogate models, to retain a simple model structure. Owing to the empirical nature of the selected data-fit class type, the models cannot be extrapolated beyond the conditions used to develop them, and they will require refitting or additional validation before being applied to a different system.

The conceptual validation performed in this section showed that the proposed surrogate system models are not necessarily adequate for use in online parameter-fitting. It is, therefore, recommended that more advanced model structures (such as artificial neural networks), are investigated for this purpose in future work. Consequently, it was elected to not regress separate surrogate system models for each dataset used in this project. Instead, the robust fundamental system models, which were validated for use in the online parameter-fitting approach, were selected for use in this project.

# CHAPTER 9 MODEL VALIDATION

## 9.1 INTRODUCTION

In the previous two chapters (Chapter 7 and Chapter 8), parameter-fitting approaches were developed to accompany the semi-empirical dynamic electrowinning model, developed in Chapter 4. In this chapter, the model, combined with the parameter-fitting approaches, is validated using a combination of qualitative consistency checks and quantitative model accuracy indicators, using the datasets previously validated in Chapter 6. Model validation is required to determine the extent to which the model matches the real-life electrowinning process. The iterative validation process described by Sargent (1984) is considered. It consists of conceptual model validation (Section 9.2), computerised model verification (Section 9.3), and operational validation (Section 9.4). The industrial application of the model, given the validation results, is also considered in this chapter (Section 9.5).

# 9.2 CONCEPTUAL MODEL VALIDATION

## 9.2.1 Background

The conceptual model validation considered in this project consists of two components. The first component involves testing that the fundamental theory and assumptions underlying the conceptual model are correct. This component was limited to an evaluation of the assumptions made during the conceptual model development (Section 4.2.4). The second component pertains to the causal descriptive nature and internal structure of the model. For this component, Barlas (1996) stipulated that the model should not only reproduce the behaviour of the real-life process, but also explain how the behaviour is generated.

Barlas (1996) suggested two types of tests for validating the model structure: direct structure tests and structure-orientated behaviour tests. Direct structure tests evaluate the validity of the structure by direct comparison with knowledge about the real-life system. This involves taking each mathematical equation that forms the conceptual model and individually comparing it with available knowledge about the real-life system (Barlas, 1996). Structure-orientated behaviour tests indirectly evaluate the structure of the model by applying tests on model-generated behaviour (Forrester and Senge, 1980). Structure-orientated behaviour tests are selected for use in this project due to their structure-orientated and quantifiable nature. This is in contrast with the qualitative and informal nature of the direct structure tests (Barlas, 1996). The three structure-orientated behaviour tests listed by Barlas (1996) are used in this project: the indirect extreme-condition test, the behaviour sensitivity test, and the phase behaviour test.

## 9.2.2 Structure-Orientated Behaviour Tests

### 9.2.2.1 Extreme-Condition Tests

Extreme-condition tests involve assigning extreme conditions to the model input variables and comparing the model-predicted output behaviour to the observed or anticipated behaviour of the reallife system. The electrowinning model developed in this project is only valid under standard operating conditions (Section 4.2.4). The value of conducting the extreme-condition tests is, therefore, limited to identifying possible limitations of the model if it is used outside of this standard operating range. The baseline for the extreme-condition tests used the design variables and initial parameters as specified for the bench-scale electrowinning experiments, and a current density of 180 A/m<sup>2</sup>. The baseline advance electrolyte contained 55 g/L Cu, 3.5 g/L Fe, 42.5 g/L Ni, 1.65 g/L Co, and 90 g/L H<sub>2</sub>SO<sub>4</sub>. The selected conditions represent the mean values for the typical industrial ranges given in Chapter 5 (Table 5.4). The tests consisted of introducing an extreme step disturbance in one model input variable at a time, two hours into the eight-hour run. The disturbance involved either increasing the variable by 200% or decreasing it to 1% of the original value.

## *Current efficiency*

Figure 9.1 shows the current efficiency predicted by the model for the extreme disturbances induced in the various input variables. Disturbances in the current density are shown to have the most pronounced effects on the predicted current efficiency. An increase in current density corresponds to an increase in current efficiency, and vice versa. This corresponds to the behaviour anticipated for the real-life system, under standard operating conditions (Alfantazi and Valic, 2003; Moats and Khouraibchia, 2009). The assumed reaction-rate-limited nature of the copper reduction, verified in the experiments conducted by Tucker (2019), dictates that any additional current applied would increase the rate of copper reduction.



Figure 9.1: Model-predicted current efficiency showing the effect of the disturbances in input variables induced as part of the extreme-condition tests.

The current efficiency considers the actual mass copper plated relative to the theoretical mass copper plated (Equation 2.23). Although an increase in current density results in an increase in the theoretical mass copper plated (as per Faraday's law, Equation 2.24), a larger fraction of the overall applied current is allocated for copper reduction, increasing the actual mass copper plated. Under extreme conditions, where the limiting-current density for the copper reduction reaction is approached, it is, however, expected that a further increase in current density would result in a decrease in current efficiency for the real-life system (Alfantazi and Valic, 2003). This is because the quality of the deposited copper decreases when the electrowinning process is operated in excess of the limiting-current density, generating a powder product instead of plated copper cathodes (Gopala and Das, 1992).

The model-predicted current efficiency shows a significant, but gradual, decrease for the decrease in current density. This is because the current efficiency is calculated using the cumulative mass copper plated, not the instantaneous copper plating rate. Therefore, even though the copper plating rate will decrease to zero upon the decrease in current density (because all available current will be allocated to iron reduction), the current efficiency will not immediately decrease to zero.

The model will likely not accurately predict the behaviour of the real-life system for a substantial decrease in current density. During model development, it was assumed that the iron reactions are mass-transfer limited. However, if the current density decreases well below the standard operating minimum (the lowest operating current density reported by Sole et al. (2019) was 45 A/m<sup>2</sup>), these reactions may

become reaction-rate limited. A further implication of the mass-transfer-limited iron reduction is also shown on Figure 9.1; disturbances in the iron concentration have a substantial effect on the current efficiency. The rule of thumb for copper electrowinning is that the current efficiency decreases by between 2% and 3% for every 1 g/L increase in iron (Das and Gopala, 1996). This is reflected by the model-predicted behaviour.

The substantial effect of iron on the system also has an impact through changes in other variables, such as the electrolyte flow rate. The model-predicted current efficiency shows a small increase of 5.3% (at the end of the eight-hour test) for the decrease disturbance in advance electrolyte flow rate. The current efficiency shows a 2.0% decrease after eight hours for the increase disturbance in flow rate. The observed behaviour for the current efficiency originated from changes in the ferric iron concentration, which, in turn, resulted from the changing flow rate. For the extreme-condition tests a ferric-to-ferrous iron ratio of 0.8 was assumed for the advance electrolyte. An increase in flow rate would, therefore, increase the ferric-to-ferrous iron ratio in the bulk electrowinning cell, resulting in a decrease in the current efficiency, and vice versa.

As previously discussed in Chapter 2 (Section 2.3.4.5), the electrolyte flow rate determines the interfacial cathode velocity which, in turn, affects the boundary layer at the cathode surface and, therefore, the mass-transfer rates of ions (Beukes and Badenhorst, 2009). This dependency highlights a potential shortcoming of the model; the effect of flow rate on the boundary layer is not fundamentally modelled. It is, however, expected that disturbances in the flow rate, within the range of standard operating conditions (unlike for the extreme-condition tests conducted in this section), should minimally affect the interfacial cathode velocity.

Disturbances in the copper, nickel, and cobalt concentrations are shown to have no effect on the modelpredicted current efficiency. The lack of effect for a change in the copper concentration is due to the assumed reaction-rate-limited nature of the copper reduction, as previously mentioned. It is, however, anticipated that a substantial decrease in copper concentration, below the standard operating minimum, would result in a decrease in the current efficiency for a real-life system. This is because the system will likely reach a point where the copper reduction becomes mass-transfer limited if the concentration is significantly decreased (Tucker, 2019). Similarly, circulation of the electrolyte, and correspondingly the flow rate, influences the mass-transfer conditions in the cell. At a flow rate below the standard operating minimum, it is expected that the copper reduction would also become mass-transfer limited for the real-life system.

Overall, the model-predicted response of the current efficiency to changes in input conditions is anticipated to be more reasonable for disturbances within standard operating conditions, as extremecondition tests are indicative of extreme faults.

# Copper plating rate and SEC

Figure 9.2 and Figure 9.3 show, respectively, the model-predicted copper plating rate and specific energy consumption (SEC) corresponding to the induced extreme disturbances. Despite the increase in the copper plating rate shown for an increased current density disturbance, it was not enough to offset the additional power consumption, as shown by the increase in SEC. This increase in SEC for an increase in current density is supported by literature (Das and Gopala, 1996; Khouraibchia and Moats, 2010; Panda and Das, 2001). The model-predicted SEC for the decrease in current density could not be calculated, as it entailed division by zero (Equation 2.25). This is because the SEC is calculated using the instantaneous copper plating rate, which drops to zero for the extreme decrease in current density.



Figure 9.2: Model-predicted copper plating rate showing the effect of the disturbances in input variables induced as part of the extreme-condition tests.



Figure 9.3: Model-predicted SEC showing the effect of the disturbances in input variables induced as part of the extreme-condition tests.

Also shown on the graphs is that an extreme increase in iron results in a moderate decrease in the predicted copper plating rate (Figure 9.2), but a severe increase in the SEC (Figure 9.3). Not only does an increase in iron concentration result in less copper plated (because less current is available for copper reduction), but it also increases the electrolyte resistance (see Section 3.5). The increase in SEC for an increase in iron concentration is supported by Moats and Khouraibchia (2009). Although a slight increase in electrolyte viscosity was reported, Moats and Khouraibchia (2009) suggested that the increase in SEC resulted from the observed decrease in current efficiency as the potential was found to be independent of the iron concentration (Moats and Khouraibchia, 2009). Despite the effect of iron on the electrolyte resistance (through the conductivity, see Section 3.5), the model-predicted potential increased by only 2.3% after eight hours, for the extreme increased disturbance in iron, confirming that the increase in SEC is mainly the result of a decrease in current efficiency.

The change in electrolyte resistance is, however, responsible for the changes in the model-predicted SEC corresponding to the disturbances in the nickel, copper, and sulfuric acid concentrations. The effect of nickel on the electrolyte conductivity and, therefore, electrolyte resistance and potential, has been previously elucidated in Chapter 3. From this discussion it follows that the increase in SEC for the increase disturbance in nickel corresponds well with what is expected from the real-life system.

Similarly, an increase in copper concentration is known to increase the electrolyte resistance, lending credence to the increase in SEC observed for the increase in copper concentration. Nonetheless, both Das and Gopala (1996) and Moats and Khouraibchia (2009) reported a decrease in SEC resulting from

an increase in copper concentration (when working with concentrations below 40 g/L). Moats and Khouraibchia (2009) did, however, suggest that the energy consumption might increase with an increase in copper at concentrations greater than 40 g/L. The extreme-condition tests were conducted at a base copper concentration of 55 g/L. Panda and Das (2001), on the other hand, found energy consumption to be independent of copper concentration during bench-scale electrowinning experiments. This is in line with the relatively moderate increase in SEC for the extreme increase in copper concentration.

An increase in sulfuric acid concentration increases the electrolyte conductivity and decreases the electrolyte resistance. This leads to a decrease in the model-predicted potential and, therefore, the SEC. This behaviour is supported by Das and Gopala (1996) and Owais (2009) who reported a decrease in SEC resulting from an increase in sulfuric acid in the range of 50 g/L to 150 g/L, and 50 g/L to 300 g/L, respectively. Owais (2009) also observed a corresponding decrease in potential. Similarly, Panda and Das (2001) reported a marginal decrease in potential corresponding to an increase in sulfuric acid in the range of 30 g/L to 150 g/L. However, no change in the SEC was reported. Likewise, Moats and Khouraibchia (2009) reported no change in SEC with an increase in sulfuric acid concentration from a higher initial concentration of 160 g/L to 220 g/L. The extreme-condition tests were conducted at a base concentration of 90 g/L sulfuric acid, and the model-predicted behaviour is, therefore, supported by the available literature.

#### 9.2.2.2 Behaviour Sensitivity Tests

Behaviour sensitivity tests involve determining to what variables the model is sensitive, and establishing whether the real-life system will exhibit similar sensitivity to the corresponding variables. The tests were conducted within the range of standard operating conditions. The baseline used for the behaviour sensitivity tests is identical to that used for the extreme-condition tests in Section 9.2.2.1. The tests involved introducing disturbances consisting of a 30% increase or decrease, two hours into the eighthour run.

#### Current efficiency and copper plating rate

Figure 9.4 and Figure 9.5 show, respectively, the current efficiency and copper plating rate predicted by the model in response to the induced disturbances. The graphs show that the two model-predicted key performance indicators (KPIs) are very sensitive to disturbances in the current density. This corresponds well with the anticipated sensitivity of a real-life electrowinning system. Moats and Khouraibchia (2009) explained that since iron is at its limiting-current density, an increase in current density should result in a noteworthy increase in the current efficiency. It is, however, expected that both the real-life current efficiency and model-predicted current efficiency will be less sensitive to increases in current density if the initial current efficiency is already very high. For example, Alfantazi and Valic (2003) reported a very subtle increase in current efficiency from 98.1% to 98.5% for an

increase in current density from 180  $A/m^2$  to 300  $A/m^2$ , with an advance electrolyte copper concentration of 25 g/L and temperature of 60 °C.



Figure 9.4: Model-predicted current efficiency showing the effect of the disturbances in input variables induced as part of the behaviour sensitivity tests.



Figure 9.5: Model-predicted copper plating rate showing the effect of the disturbances in input variables induced as part of the behaviour sensitivity tests.

The graphs also show that the two model-predicted KPIs are sensitive to disturbances in the advance electrolyte iron concentration. As previously mentioned, the presence of iron in the electrolyte is one of the main factors that affect the current efficiency of a real-life system (Moats, 2012; Schlesinger et al., 2011b). The significant decrease in current efficiency for an increase in iron concentration has been well-documented (Das and Gopala, 1996; Moats and Khouraibchia, 2009; Moats, 2012), and the sensitivity of the model-predicted KPIs are, therefore, expected to align well with what is expected for real-life systems.

As previously mentioned for the extreme-condition tests (Section 9.2.2.1), the sensitivity of the system to iron also results in the sensitivity of the two model-predicted KPIs to disturbances in the electrolyte flow rate. This is because an increase in flow rate results in an increase in the ferric-to-ferrous iron ratio in the bulk electrowinning cell (for the conditions investigated). The work conducted by Das and Gopala (1996) seems to support this statement. They investigated the effect of increasing the electrolyte flow rate for a system containing different concentrations of ferric iron. Although the interfacial cathode velocities investigated were much higher (between 0.6 and 9.6 m<sup>3</sup>/h/(m<sup>2</sup> of available cathode surface area), the trends they observed for the experimental-scale system were similar to those observed for the model-predicted KPIs. At a ferric iron concentration of 0.5 g/L an approximately 4% decrease in current efficiency was observed for an increase in interfacial cathode velocity from 0.6 to 9.6 m<sup>3</sup>/h/(m<sup>2</sup> of available cathode surface area). However, for a ferric iron concentration of 6 g/L the same change in interfacial cathode velocity resulted in an approximately 15% decrease in current efficiency.

It is important to note that the baseline interfacial cathode velocity for the behaviour sensitivity tests was  $0.12 \text{ m}^3/\text{h}/(\text{m}^2 \text{ of available cathode surface area})$ . The disturbances resulted in interfacial cathode velocities of  $0.08 \text{ m}^3/\text{h}/(\text{m}^2 \text{ of available cathode surface area})$  for the decrease disturbance and  $0.15 \text{ m}^3/\text{h}/(\text{m}^2 \text{ of available cathode surface area})$  for the increase disturbance, respectively. The values are close to the range for industrial operations specified by Beukes and Badenhorst (2009) (between 0.05 and 0.1 m<sup>3</sup>/h/(m<sup>2</sup> of available cathode surface area)). The disturbances are, therefore, not expected to influence the mass-transfer of ions.

The graphs further show that the model-predicted current efficiency and copper plating rate are independent of the sulfuric acid, copper, nickel, and cobalt concentrations. The sensitivity of the current efficiency to changes in the sulfuric acid concentration reported in literature is temperature-dependent. Das and Gopala (1996) and Panda and Das (2001) reported the current efficiency to be independent of the sulfuric acid concentration for experiments conducted at 30 °C. Das and Gopala (1996), however, reported a slight increase in current efficiency for an increase in the sulfuric acid concentration, for experiments conducted at 40 °C and 50 °C. Likewise, Moats and Khouraibchia (2009) reported an approximate 1% increase in current efficiency for an increase in sulfuric acid from 160 g/L to 220 g/L, for a system at 40 °C. The baseline experiment used for the behaviour sensitivity tests was conducted

at 60 °C. Although a slight increase in current efficiency would, therefore, be expected for an increase in acid concentration for the real-life system, according to available literature, this increase is expected to be very small. Consequently, the model-predicted independence is not expected to severely impact the accuracy of the model.

A slight sensitivity of the current efficiency to a change in copper concentration is supported by literature, with only one study supporting the complete independence of current efficiency from copper concentration. Panda and Das (2001) found no significant effect on the current efficiency upon increasing the copper concentration from 10 g/L to 50 g/L, supporting the model-predicted independence of the current efficiency from the copper concentration. Alfantazi and Valic (2003), however, reported increases of between 0.2% and 2.3% in current efficiency for increases in copper concentration from 25 g/L to 65 g/L. The effect of copper concentration on current efficiency was determined to be statistically significant, despite the very subtle increases (Alfantazi and Valic, 2003). Furthermore, Das and Gopala (1996) and Moats and Khouraibchia (2009) reported a marginal increase in current efficiency for an increase in the advance electrolyte copper concentration from 17 g/L to 37 g/L, and from 30 g/L to 45 g/L, respectively. Das and Gopala (1996) attributed the slight increase in current efficiency to the increase in viscosity caused by the increase in copper concentration. The increase in viscosity leads to a thicker boundary layer and lower iron mass transfer, slightly increasing the current efficiency.

Both Moats (2012) and Moats and Khouraibchia (2009) reported that a change in cobalt concentration had no effect on the current efficiency. It should be noted that Moats and Khouraibchia (2009) investigated cobalt concentrations between 0.1 and 0.2 g/L, which is significantly lower than the baseline concentration of 1.65 g/L used for the behaviour sensitivity tests. Panda et al. (2009), however, confirmed that cobalt additions ranging from 0.01 g/L to 2 g/L also had little effect on the current efficiency. Consequently, it is expected that the model-predicted behaviour will reflect the behaviour of the real-life electrowinning system.

No literature could be found detailing the effect of nickel concentration on the current efficiency of copper electrowinning systems. As discussed in Chapter 2 (Section 2.3.4.2) nickel is not reduced during copper electrowinning. It is, therefore, unlikely that the presence of nickel will have a significant influence on the current efficiency. Nickel may, however, influence the mass-transfer conditions (due to the increase in viscosity). Similar to the effect of copper, this may lead to a thicker boundary layer and lower iron mass transfer, possibly increasing the current efficiency.

# SEC and potential

Figure 9.6 and Figure 9.7 show, respectively, the SEC and potential predicted by the model in response to the induced disturbances. The graphs show that although the disturbances in iron concentration did not markedly influence the potential, a significant change in SEC is observed. As explained for the extreme-condition tests (Section 9.2.2.1) this is because of the severe effect iron has on the current efficiency. An increase in iron decreases the current efficiency and, consequently, increases the SEC. This model-predicted behaviour is supported by literature sources for the real-life electrowinning system (Das and Gopala, 1996; Moats and Khouraibchia, 2009).



Figure 9.6: Model-predicted SEC showing the effect of the disturbances in input variables induced as part of the behaviour sensitivity tests.



Figure 9.7: Model-predicted potential showing the effect of the disturbances in input variables induced as part of the behaviour sensitivity tests.

As with the current efficiency and copper plating rate previously, the SEC is also sensitive to disturbances in the current density. Both an increase and decrease in current density resulted in an increase in the model-predicted SEC. This behaviour corresponds well with the expected behaviour of the real-life electrowinning system. Various literature sources support the increase in SEC as a result of an increase in current density (Das and Gopala, 1996; Moats and Khouraibchia, 2009; Panda and Das, 2001). Moats and Khouraibchia (2009) further explained that the increase in potential results in the increase in SEC for a higher current density, despite more copper being plated. They add that the increase in potential is likely the result of higher electrode potentials and an increase in the electrolyte resistance. Panda and Das (2001) supported this statement, adding that the increase in SEC may be attributed to the increase in both cathodic and anodic polarisations.

Unlike the current efficiency and copper plating rate, the potential and, therefore, SEC exhibits moderate sensitivity to the sulfuric acid, copper, and nickel concentrations. Although the moderate sensitivity of the SEC to changes in the sulfuric acid concentration is supported by most literature sources, some did report it to be independent of the acid concentration (Das and Gopala, 1996; Moats and Khouraibchia, 2009; Owais, 2009; Panda and Das, 2001). The sulfuric acid concentration was, however, shown to have a significant effect on the conductivity of the electrolyte, and consequently the electrolyte resistance (see Section 3.5). Following, the decrease in model-predicted SEC observed for an increase in sulfuric acid concentration, and consequently conductivity is, therefore, expected to align with the behaviour of the real-life system.

The model-predicted SEC shows a subtle increase for an increase in the copper concentration. The increase in model-predicted SEC results from the increase in potential, which is in turn a result of the decrease in conductivity caused by the increase in copper concentration (see Section 3.5). As discussed during the extreme-condition tests (Section 9.2.2.1), both Das and Gopala (1996) and Moats and Khouraibchia (2009) reported a decrease in SEC resulting from an increase in copper concentration when working with concentrations below 40 g/L. Moats and Khouraibchia (2009), however, suggested that the energy consumption might increase with an increase in copper at concentrations greater than 40 g/L. The baseline for the behaviour sensitivity test had a copper concentration of 55 g/L. It is, therefore, plausible that the model-predicted behaviour could correspond to the real-life system behaviour.

Again, no information could be found regarding the effect of nickel on the SEC of a copper electrowinning system. It has, however, been established that an increase in nickel concentration negatively affects the conductivity of the electrolyte (see Section 3.5) and, consequently, increases the potential. The model-predicted behaviour aligns with this statement. It is, therefore, expected that the model-predicted increase in SEC corresponding to an increase in nickel concentration will correspond with the behaviour of the real-life system.

The increase disturbance in cobalt concentration shows a very subtle increase in the model-predicted SEC. This increase is a result of the decrease in conductivity caused by the increase in cobalt concentration (see Section 3.5). Various experimental-scale studies have, however, confirmed a decrease in anode potential, and corresponding decrease in SEC, for increases in cobalt concentration of up to 0.6 g/L (Nikoloski and Nicol, 2008; Panda et al., 2009; Sole et al., 2019). Nonetheless, an increase of approximately 1% in potential for an increase in cobalt from 0.6 g/L to 2 g/L was observed by Panda et al. (2009). The baseline cobalt concentration for the behaviour sensitivity tests was 1.65 g/L. The developed model will, regardless, only capture the effect of cobalt on the anodic overpotential when the parameters are refitted by the online parameter-fitting approach, based on changes observed in the measured potential.

#### 9.2.2.3 Phase Relationship Tests

Phase relationship tests compare the relationships between model-predicted variables and the expected or observed relationships of the corresponding variable pairs in real life (Forrester and Senge, 1980). The steady-state experimental dataset generated by Tucker (2019) was used to complete the phase behaviour tests. Tucker (2019) selected the step sizes to have a high and low level of each variable, based on typical industry ranges (Robinson et al., 2013). The relationships between variables are noted only as an increase or decrease, to verify that the model responds as expected. Table 9.1 and Table 9.2 show the results of the phase relationship tests done using the experiments conducted at 200 A/m<sup>2</sup> and

 $300 \text{ A/m}^2$ , respectively. The tables show that all the model-predicted variables change in the same direction as the experimental response variables, with two exceptions discussed below.

Table 9.1: Stepped input variables, with step sizes given, and the response of output variables per the experimental data (Tucker, 2019) and model developed in this project, for a current density of 200  $A/m^2$ . The grey shading indicates a difference between the experimental and model responses.

Step	Step Size (%)	Experimental Response (Tucker, 2019)			Model Response		
		Current efficiency	Plating rate	SEC	Current efficiency	Plating rate	SEC
хCu	+57.1	v	^	٨	^	^	٨
xH₂SO₄	+12.1	^	^	v	^	^	V
<i>x</i> Fe	+3	v	v	٨	v	v	^
i	+47.3	^	^	٨	^	^	^

x =Concentration (g/L), i =Current density (A/m<sup>2</sup>)

Table 9.2: Stepped input variables, with step sizes given, and the response of output variables per the experimental data (Tucker, 2019) and model developed in this project, for a current density of 300  $A/m^2$ . The grey shading indicates a difference between the experimental and model responses.

Step	Step Size (%)	Experimental Response (Tucker, 2019)			Model Response		
		Current efficiency	Plating rate	SEC	Current efficiency	Plating rate	SEC
хCu	+57.1	Λ	^	v	Λ	۸	^
<i>x</i> H₂SO₄	+12.1	^	^	V	^	٨	V
<i>x</i> Fe	+3	v	v	۸	v	v	^
i	-47.3	v	v	V	v	v	v

x =Concentration (g/L), i =Current density (A/m<sup>2</sup>)

The first exception is observed in Table 9.1, for the experiments conducted at 200 A/m<sup>2</sup>. The model predicted an increase in current efficiency for an increase in advance electrolyte copper concentration. Conversely, the experimental data show a decrease in current efficiency. The experimental response contradicts available literature sources (Das and Gopala, 1996; Moats and Khouraibchia, 2009). The literature sources reported a marginal increase in current efficiency resulting from an increase in copper concentration.

The second exception is observed in Table 9.2, for the experiments conducted at 300 A/m<sup>2</sup>. The model predicted an increase in SEC for an increase in copper concentration. This contradicts the decrease observed for the experimental response. Both Das and Gopala (1996) and Moats and Khouraibchia

(2009) reported a decrease in SEC for increases in copper concentration below 40 g/L. Moats and Khouraibchia (2009), however, suggested that the energy consumption might increase with an increase in copper concentration greater than 40 g/L, as previously mentioned for the extreme-condition (Section 9.2.2.1) and behaviour sensitivity tests (Section 9.2.2.2). No explanation is reported for the suggested increase. The empirical model developed by the same authors also shows an increase in SEC for an increase in copper concentration above approximately 40 g/L (Khouraibchia and Moats, 2010). The baseline experiment had an advance electrolyte copper concentration of 35 g/L, and was compared with an experiment having a copper concentration of 55 g/L. Regardless, the model-predicted increase in SEC for an increase in copper concentration is further elucidated as a model limitation in Section 9.5.1.

# 9.3 COMPUTERISED MODEL VERIFICATION

# 9.3.1 Background

Computerised model verification is the process of ensuring that the computerised version of the conceptual model is implemented correctly (Sargent, 2013). Fairley (1976) suggested combining static and dynamic testing for computerised model verification. Static testing, consisting of structured walkthroughs, was used to debug the computerised model developed in this project. Dynamic testing involves executing the computerised model and using the predicted output variables to determine whether the model works correctly. This method was used to ensure that no internal consistency limitations were violated during the execution of the computerised model, as discussed in Section 9.3.2.

#### 9.3.2 Hardcoded Limits and Warnings

Several hardcoded limits were incorporated when the conceptual model was computerised. This was done to ensure that no internal consistency limitations are violated when the model is used. If the concentration or flow rate of any species decreases to below zero, a corresponding error message is generated, and execution of the code is halted. Additionally, error messages are included to ensure that user inputs are entered in the correct format. Warning messages are also generated when assumptions made during model development are violated, where possible. This ensures that the violations are considered when interpreting the model results. A warning message would, for example, be generated if the operating current density increases to more than 10% of the limiting-current density for copper reduction. A list of all incorporated hardcoded limits and warnings is supplied in Appendix E (Section E.3).

## 9.4 OPERATIONAL VALIDATION

## 9.4.1 Background

Operational validation is the process of ensuring that the model-predicted behaviour has a satisfactory range of accuracy for the intended model purpose (Sargent, 2013). Knoblauch (2015) maintained that this is the most important part of model validation because the majority of model errors are detectable in this step. During operational validation, the model-predicted output variables are compared with those of the real-life system being modelled. Numerous methods are available for conducting the comparison required in operational validation, but Sargent (2013) suggested using a combination of qualitative and quantitative methods. Knoblauch (2015) agreed but stated that the qualitative method is arguably the more important of the two, as the model's validity (with regards to the purpose) is evaluated. Still, Knoblauch (2015) added that the quantitative method should be used to support the subjective qualitative method, even though it only evaluates an absolute measure of accuracy.

In this project, the qualitative method suggested by Sargent (2013) is used in combination with a quantitative method to compare the model-predicted and validated real-life KPIs. The qualitative method consists of graphically comparing the model-predicted and real-life KPIs. The quantitative method consists of quantifying the difference between the predicted and actual variables. This was done using the normalised residual mean square errors (nRMSEs), alongside the mean absolute percentage errors (MAPEs), where applicable.

The residual mean square error (RMSE) was calculated using Equation 7.1. Following this, the RMSE was normalised using Equation 7.3. Schmee and Opperlander (2010) stated that the RMSE can be interpreted as the standard deviation of the residuals between two datasets. This implies that a reference value for the RMSE could be set at the standard deviations of the model and real-life values. Knoblauch (2015), however, added that RMSEs larger than this setpoint would not necessarily indicate a bad correlation, and suggested a crude baseline of 30% for the nRMSEs. This baseline was selected for use in this project, meaning nRMSEs larger than 30% would indicate a bad correlation.

The MAPE was calculated using Equation 9.1. Owing to its scale-independency and interpretability the MAPE is one of the most widely used measures of prediction accuracy (Kim and Kim, 2016). It does, however, have a notable disadvantage: because of how it is calculated, it is not suitable for use when the variables to be predicted are close to 0. This is because the calculation will result in division by 0, giving infinite or undefined MAPE values. This inadequacy is addressed by using the MAPE values to supplement the nRMSE values, only where appropriate. Allwright (2022) suggested that in general MAPE values below 20% are indicative of a good model fit.

MAPE = 
$$\frac{100}{n} \sum_{i=1}^{n} \left| \frac{y_i - \hat{f}(x_i)}{y_i} \right|$$
 [9.1]

where *n* is number of data points,  $y_i$  is the *i*<sup>th</sup> observation of the variable to be predicted, and  $\hat{f}(x_i)$  is the prediction that the model gives for the *i*<sup>th</sup> observation.

## 9.4.2 Steady-State Experimental and Industrial Data

Figure 9.8 compares the model-predicted current efficiency and the real-life current efficiency for the two steady-state datasets. All the experiments conducted by Tucker (2019) are shown, but only the ten validation runs that were not used during parameter fitting are shown for the industrial dataset. The model predicted the current efficiencies for the steady-state experiments to a high degree of accuracy, with a MAPE of 2.2%. The model overpredicted the current efficiency by a maximum error of 7.8% and did not underpredict any of the current efficiencies. Also shown on the graph is that the experimental data are divided into three distinct groups. The group with the lowest current efficiencies (Group a) consisted of the experiments conducted at a low current density and high advance electrolyte iron concentration. The group in the middle (Group b) had a high iron concentration and high current density. The group having the highest current efficiencies (Group c) were the experiments conducted at both low and high current densities, but with low iron concentrations. This corresponds well with the results of the behaviour sensitivity tests conducted in Section 9.2.2.2.



Figure 9.8: Actual versus model-predicted current efficiency for steady-state experimental and industrial data.

As previously mentioned, the empirical model developed by Khouraibchia and Moats (2010) was used to estimate the real-life industrial current efficiencies (Section 6.2.4). Although Khouraibchia and Moats (2010) reported that the empirical model predicted the current efficiencies of seven real-life industrial plants with a maximum difference of 2.9%, the average empirical model estimate of 92.4% (for the tankhouse from which the industrial dataset was acquired), is significantly higher than the 80% given in the design specifications. This discrepancy is further emphasised by the fact that the bulk of

the estimated real-life industrial current efficiencies, obtained from the empirical model, are shown to be on the higher end of the current efficiencies obtained by Tucker (2019) on a bench-scale setup. This is counterintuitive as the bench-scale setup is an idealised version of the electrowinning process.

The accuracy of the electrowinning model predictions is, therefore, expected to be lower because the model was trained using, and is being compared with, the predictions of the empirical model. The electrowinning model overpredicted the current efficiency by a maximum error of 4.4%, and underpredicted it by a maximum error of 5.7%. The MAPE of 3.1% shows that the model was, however, still able to predict the current efficiencies with a reasonable degree of accuracy.

Figure 9.9 compares the model-predicted copper plating rates and the corresponding real-life values for the two steady-state datasets. Again, only the ten validation runs that were not used during parameter fitting are shown for the industrial data. The MAPE for the steady-state experimental copper plating rate was 2.4%, indicating a good model fit for the experimental data. The model overpredicted the copper plating rate by a maximum error of 7.8%. The graph shows that the experimental copper plating rates are divided into two distinct groups based on their values. The lower group (Group a) consisted of the experiments conducted at a low current density, and the higher group (Group b) the experiments which were conducted at a high current density. Again, this corresponds with the behaviour sensitivity tests (Section 9.2.2.2), which showed that the model KPIs are most sensitive to fluctuations in the applied current density. The steady-state industrial data fall close to the x = y line, with a MAPE of 3.1%. The model overpredicted the copper plating rate for the industrial data by a maximum error of 4.4% and underpredicted it by a maximum error of 5.6%.



Figure 9.9: Actual versus model-predicted copper plating rate for steady-state experimental and industrial data

Figure 9.10 compares the model-predicted SEC and the corresponding real-life value for the two steadystate datasets. Once more, only the ten validation runs are shown for the industrial data. The MAPE of 3.5% for the experimental dataset indicates a good degree of accuracy. Overall, the model overpredicted the experimental SEC with a maximum error of 5.4% and underpredicted it with a maximum error of 8.2%.



Figure 9.10: Actual versus model-predicted SEC for steady-state experimental and industrial data.

The model predicted the industrial SEC with a MAPE of 24.2%, which is just above the 20% baseline set for a good fit. The model overpredicted the industrial energy consumption with a maximum error of 41.5% and did not underpredict any of the values. Similar to the current efficiency, the real-life industrial SEC was also estimated using the empirical model developed by Khouraibchia and Moats (2010).

Figure 9.10 shows that the actual industrial SEC values were consistently lower than those for the ideal bench-scale experiments conducted by Tucker (2019). Furthermore, the average SEC for the tankhouse from which the industrial dataset was acquired is reported to be approximately 2300 kWh/t (according to the design specifications). This value is significantly higher than the empirical model estimate average of approximately 1280 kWh/t. In the same vein, the average SEC for 17 industrial electrowinning tankhouses (employing direct and post-solvent extraction electrowinning), as reported by Tucker (2019), is approximately 1990 kWh/t.

Khouraibchia and Moats (2010) confirmed that the empirical model will predict energy consumption values lower than those observed industrially. They explained that this is because of the non-standard anode material (IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> coated titanium mesh) and small cell (1 L) used to generate the experimental data from which the empirical model was regressed. The overprediction of the SEC values by the electrowinning model is likely also exacerbated by the fact that it accounts for the effect of additional electrolyte impurities such as nickel, not included in the empirical model, on the electrolyte resistance.

Overall, the semi-empirical electrowinning model predicted the current efficiency, copper plating rate, and SEC for the steady-state experimental dataset to a high degree of accuracy. The model predicted the same KPIs for the steady-state industrial dataset with reasonable accuracy. This supports use of the developed model for predicting the behaviour of a full-scale industrial copper electrowinning tankhouse. All experimental and industrial model predictions, MAPEs, and accuracy evaluations of other process outputs (potential and spent electrolyte composition) are provided in Appendix D (Section D.1 and Section D.2).

#### 9.4.3 Dynamic Experimental Data

The dynamic response of electrowinning to the introduction of industry-specific disturbances was investigated using a bench-scale setup, as discussed in Chapter 5. In this section, the actual and model-predicted responses to disturbances in the copper, iron, nickel, and cobalt concentrations, and current density are discussed, for the respective screening and bench-scale electrowinning validation experiments. The transient start-up period (defined as the first two hours of each experiment) was excluded when calculating the respective quantitative error indicators. The start-up conditions are likely to be outside the range of standard operating conditions (for which the model is to be validated).

For the bench-scale electrowinning experiments, the selected experimental design allowed for the uncertainty relating to the calculated actual copper plating rate to be quantified. The first four hours of five experiments were conducted at similar base conditions (see Section 5.2.2). Upper and lower uncertainty limits were determined as the final reconciled copper plating rate at the respective sampling times,  $\pm$  one standard deviation. The average standard deviation for the sampling times for which repeats were available (up to four hours into the eight hour runs) was used for the remainder of the sampling times in the respective runs.

It was elected to quantify the uncertainty associated with the final reconciled copper plating rate instead of the measured advance and spent electrolyte copper concentrations, and subsequently propagating the error to the copper plating rate. This method was used in an attempt to account for deviations inserted via the preprocessing and reconciliation of data. The quantified error in the copper plating rate was propagated through to the calculation of the SEC, but not the current efficiency. It was not possible to propagate the error to the current efficiency as it was calculated using the cumulative mass copper plated, and not the instantaneous copper plating rate, as was the SEC. Sample calculations for the uncertainty calculations are provided in Appendix C (Section C.2.1).

As previously elucidated during the data validation process (Section 6.2.1.2), the low current densities used for the bench-scale electrowinning experiments introduced a significant limitation to the dataset. The low current densities  $(140 \text{ A/m}^2 \text{ to } 220 \text{ A/m}^2)$  were selected to replicate the conditions for direct

electrowinning in industrial tankhouses. The lower values, however, translated to a lower mass of copper plated, and thus, a less pronounced difference between the copper concentration of the advance and spent electrolytes. The less pronounced difference in copper concentrations was masked by variations in the measurements and other variables. Consequently, it was more challenging to obtain a sensible copper plating rate by conducting a copper mass conservation balance over the cell.

In this section, the experimental data are compared with available literature data to assess whether it is an acceptable representation of the expected behaviour of the copper electrowinning process. The dynamic experimental data are, therefore, discussed as a limited fundamental analysis of the behaviour of the bench-scale electrowinning setup, and the performance of the model for predicting the behaviour of the bench-scale system. Comparing the model predictions to both the experimental data and literature data will be useful for commenting on the robustness of the model (without implementation of the online parameter-fitting approach) to bad training data. Regardless, there is expected to be limited value in using the experimental bench-scale electrowinning data for the purpose of predictive model validation.

As mentioned, the operational validation of the model entails comparing the model-predicted output variables with those of the real-life system it is intended to represent. For the dynamic electrowinning model, the system to be modelled is an industrial electrowinning tankhouse. The validation completed using the industrial electrowinning data (Section 9.4.4) is, therefore, seen as the crucial part of the model validation process.

## 9.4.3.1 Effect of Copper Concentration

#### *Copper plating rate and current efficiency*

Figure 9.11 shows the effect of the increase disturbance in advance electrolyte copper concentration on the (a) copper plating rate and (b) current efficiency, of the respective screening validation experiment. Figure 9.11 shows that both the experimental copper plating rate and current efficiency remained constant over time, even initially during start-up. This behaviour stems from the method followed to process the experimental data. It was assumed that the copper reduction reaction was reaction-rate limited and a linear line was, therefore, used to represent the cumulative mass copper plated over time (See Section 6.2.1.1). This assumption resulted in an experimental current efficiency that is independent of both time and copper concentration. The nRMSE values for the copper plating rate and current efficiency of the validation screening experiment were calculated to be 0.1% and 0.3%, respectively. Per the selected baseline, this indicates good correlation.



Figure 9.11: Actual versus predicted (a) copper plating rate and (b) current efficiency for the screening validation experiment in which an increase disturbance in advance electrolyte copper concentration occurred four hours into the eight-hour run (Initial conditions: 25 g/L Cu, 1 g/L Fe, 200 A/m<sup>2</sup>. Disturbance final: 40 g/L Cu).

Figure 9.12 shows the effect of the decrease disturbance in advance electrolyte copper concentration on the (a) copper plating rate and (b) current efficiency of the respective bench-scale electrowinning validation experiment. Figure 9.12 shows that the experimental copper plating rate and current efficiency decreased for the decrease disturbance in advance electrolyte copper concentration, whilst the model-predicted values remained constant. The nRMSE values for the copper plating rate and current efficiency of the validation bench-scale electrowinning experiment were calculated to be 36.1% and 28.9%, respectively. It is noteworthy that the experimental current efficiency is consistently above 100%, likely exacerbating the model error.



Figure 9.12: Actual versus predicted (a) copper plating rate and (b) current efficiency for the bench-scale electrowinning validation experiment in which a decrease disturbance in advance electrolyte copper concentration occurred four hours into the eight-hour run (Initial conditions: 70 g/L Cu, 6 g/L Fe, 65 g/L Ni, 3 g/L Co, 220 A/m<sup>2</sup>. Disturbance final: 55 g/L Cu).

Literature supports the reaction-rate-limited nature of the copper reduction reaction. It does, however, not necessarily mean complete independence of the copper plating rate and current efficiency from the advance electrolyte copper concentration, as indicated by the model, is supported. This limitation should, therefore, also be noted when considering the method used to process the screening experiment data (Section 6.2.1.1).

Das and Gopala (1996) observed increases in current efficiency of 1.95% to 5.8% for increases in copper concentration from 17 g/L to 37 g/L, at different iron concentrations and temperatures. The increase in current efficiency was more pronounced at 50 °C compared with 30 °C. Das and Gopala (1996) speculated that the increase in current efficiency was due to the increase in electrolyte viscosity caused by the increase in copper concentration. The increase in viscosity impeded the mass transfer of the ferric ions present in the electrolyte. Both Khouraibchia and Moats (2010) and Moats (2012) also supported the slight increase of current efficiency for an increase in copper concentration.

The bench-scale electrowinning experiment was conducted at a higher baseline copper concentration and temperature (60 °C), than the available literature sources. It is, therefore, possible that the decrease disturbance in copper concentration resulted in the very pronounced decrease in current efficiency (Figure 9.12 (b)). The specific validation experiment, however, likely overstated the trend. The current efficiency was significantly higher than 100% for almost the full duration of the experiment. Per Chapter 6, the copper plating rate was transformed to ensure the final mass copper plated corresponded to the change in mass of the copper cathode. This means that the decrease in current efficiency could also possibly be attributed to the selected method for data preprocessing. Nevertheless, the model will not directly capture the effect of disturbances in the advance electrolyte copper concentration on the electrolyte viscosity. The online parameter-fitting approach will, however, capture the change in masstransfer conditions, if it is implemented.

#### SEC and potential

Figure 9.13 shows the effect of the increase disturbance in advance electrolyte copper concentration on the (a) SEC and (b) potential of the screening experiment. The model-predicted SEC shows a slight increase for the increase in copper concentration. The model predicted an increase in the SEC because the predicted electrolyte resistance increased, due to the decrease in conductivity associated with an increase in copper concentration. Conversely, the experimental potential, and SEC, showed a decrease when the copper concentration was increased. The increase in model-predicted potential and SEC, for an increase in copper concentration, is discussed as a model limitation In Section 9.5.1. The calculated nRMSE value for both the SEC and potential was 28.7%. Per the selected baseline this indicates a good overall model fit. The corresponding MAPE value for the SEC was 28.7%.



Figure 9.13: Actual versus predicted (a) SEC and (b) potential for the screening validation experiment in which an increase disturbance in advance electrolyte copper concentration occurred four hours into the eight-hour run. (Initial conditions: 25 g/L Cu, 1 g/L Fe, 200 A/m<sup>2</sup>. Disturbance final: 40 g/L Cu).

Figure 9.14 shows the effect of the decrease disturbance in advance electrolyte copper concentration on the (a) SEC and (b) potential of the bench-scale electrowinning validation experiment. The modelpredicted potential shows a very slight decrease whilst the SEC remained unaffected. Both the experimental potential and SEC show an increase as a result of the decrease in copper concentration. The calculated nRMSE values for the SEC and potential were 42.2% and 4.2%, respectively. The MAPE for the SEC was 32.2%. The model-predicted potential shows a good fit, per the selected baselines. The nRMSE and MAPE values for the SEC are similar in size, with both values being higher than desired. The high SEC error is suggested to result from the error in the model-predicted plating rate, which is exacerbated when calculating the SEC (Equation 2.25).



Figure 9.14: Actual versus predicted (a) SEC and (b) potential for the bench-scale electrowinning validation experiment in which a decrease disturbance in advance electrolyte copper concentration occurred four hours into the eight-hour run (Initial conditions: 70 g/L Cu, 6 g/L Fe, 65 g/L Ni, 3 g/L Co, 220 A/m<sup>2</sup>. Disturbance final: 55 g/L Cu).

Literature regarding the effect of the copper concentration on the SEC provides some insights but is largely inconclusive. It is important to note that the literature sources also refer to results generated on experimental-scale setups. Moats and Khouraibchia (2009) reported an approximately 3% decrease in SEC for a copper increase from 30 g/L to 40 g/L. However, an increase in SEC of 0.4% was reported when the copper was increased from 40 g/L to 45 g/L. As previously mentioned during conceptual model validation, Moats and Khouraibchia (2009) argued that the energy consumption would increase for an increase in copper concentration above 40 g/L. This argument is supported, in theory, by Panda and Das (2001) who reported a decrease in potential for an increase in copper concentration from 10 g/L to 35 g/L, but reported a slight increase in potential for a copper concentration increase from 35 g/L to 50 g/L. No significant change in SEC is reported by Panda and Das (2001) for the increases in copper concentration.

Overall, the inclusion of the electrolyte resistance in the prediction of the potential and SEC for the bench-scale experiments resulted in behaviour that contradicted the experimental observations. Literature supports the model-predicted behaviour, but only for copper concentrations above approximately 40 g/L, and the findings are not definitive. The screening validation experiment had an initial copper concentration of 25 g/L, which was increased to a final value of 40 g/L. The copper concentration did, however, increase to approximately 60 g/L directly after the disturbance was induced, and gradually decreased to the expected 40 g/L after mixing occurred in the system. The bench-scale electrowinning validation experiment had an initial copper concentration of 70 g/L that was decreased to 55 g/L. No literature was found regarding the effect of increasing the copper concentration on the SEC in an industrial electrowinning tankhouse. If the electrolyte resistance, however, accounts for a significant portion of the energy consumption, as discussed in Chapter 2, it is expected that an increase in copper concentration would increase the energy consumption. This statement would need to be verified using appropriate industrial data.

## 9.4.3.2 Effect of Iron Concentration

## *Copper plating rate and current efficiency*

Figure 9.15 shows the effect of the increase disturbance in advance electrolyte iron concentration on the (a) copper plating rate and (b) current efficiency of the respective validation screening experiment. The experimental copper plating rate and current efficiency both showed a decrease followed by an increase in response to the disturbance. This behaviour is possibly the result of the method used to induce the disturbance during the experiment. The additional ferric sulfate hydrate required to reach the final iron concentration was added to the stock solution bottle that fed the cell. The ferric iron concentration was, therefore, very high in the advance electrolyte just after the disturbance was induced. Gradually, through mixing with the recycled spent electrolyte stream, and to a lesser extent reduction

of iron, the ferric iron concentration in the advance electrolyte decreased. The model-predicted current efficiency and copper plating rate decreased slightly as a result of the disturbance, before showing a subtle increase. The calculated nRMSE was 7.2% for the copper plating rate and 4.5% for the current efficiency.



Figure 9.15: Actual versus predicted (a) copper plating rate and (b) current efficiency for the screening validation experiment in which an increase disturbance in advance electrolyte iron concentration occurred four hours into the eighthour run. (Initial conditions: 40 g/L Cu, 3 g/L Fe, 375 A/m<sup>2</sup>. Disturbance final: 6 g/L Fe).

Figure 9.16 shows the effect of the increase disturbance in advance electrolyte iron concentration on the (a) copper plating rate and (b) current efficiency, for the bench-scale electrowinning validation experiment. The experimental copper plating rate showed a decrease as a result of the disturbance. The experimental current efficiency showed a delayed decrease, likely as it was calculated using the cumulative mass copper plated. The experimental KPIs did not show the secondary increase, observed for the screening experiments, as the ferric iron concentration for the specific bench-scale electrowinning validation experiment was significantly lower. The model-predicted values also showed a decrease, as expected. The calculated nRMSE was 42.4% for the copper plating rate and 5.6% for the current efficiency.

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Figure 9.16: Actual versus predicted (a) copper plating rate and (b) current efficiency for the bench-scale electrowinning validation experiment in which an increase disturbance in advance electrolyte iron concentration occurred four hours into the eight-hour run. (Initial conditions: 40 g/L Cu, 1 g/L Fe, 20 g/L Ni, 0.3 g/L Co, 140 A/m<sup>2</sup>. Disturbance final: 3 g/L Fe).

## SEC and potential

Figure 9.17 shows the experimental and model-predicted response of the (a) SEC and (b) potential to the increase disturbance in advance electrolyte iron concentration, for the screening validation experiment. Both the experimental SEC and potential remained constant after the disturbance occurred. The model-predicted potential also remained constant, but the SEC showed an increase after the disturbance occurred. The nRMSE calculated for the potential was 34.1%. The nRMSE for the SEC was 41.2%, whilst the corresponding MAPE value was 40.8%.



Figure 9.17: Actual versus predicted (a) SEC and (b) potential for the screening validation experiment in which an increase disturbance in advance electrolyte iron concentration occurred four hours into the eight-hour run (Initial conditions: 40 g/L Cu, 3 g/L Fe, 375 A/m<sup>2</sup>. Disturbance final: 6 g/L Fe).

Figure 9.18 shows the experimental and model-predicted response of the (a) SEC and (b) potential to the increase disturbance in advance electrolyte iron concentration, for the bench-scale electrowinning validation experiment. Both the experimental SEC and potential showed an increase after the disturbance occurred. The model-predicted SEC showed a slight increase whilst the model-predicted potential showed a very subtle decrease.

For the bench-scale electrowinning validation experiment the nRMSE value for the potential was 0.7%. The nRMSE value for the SEC was 302.7%, whilst the MAPE value was 37.9%. A large discrepancy is observed between the two quantitative error indicators for the SEC, with the nRMSE value being very high. As a result of the square term used when calculating the RMSE (Equation 7.1), this metric penalises larger errors (or outliers) more, compared to smaller errors. In contrast, the MAPE understates the effect of large, infrequent errors. It follows that the high SEC nRMSE value (and noteworthy difference between the calculated nRMSE and MAPE values), indicates the presence of large but infrequent discrepancies between the model-predicted and actual SEC. The SEC is calculated using two model-predicted variables (copper plating rate and potential), meaning that any abnormal behaviour from the real-life system is exacerbated. The zero values for the actual copper plating rate (Figure 9.16 (a), t = 4 h to t = 6 h) likely resulted in the high nRMSE value for the SEC.



Figure 9.18: Actual versus predicted (a) SEC and (b) potential for the bench-scale electrowinning validation experiment in which an increase disturbance in advance electrolyte iron concentration occurred four hours into the eight-hour run (Initial conditions: 40 g/L Cu, 1 g/L Fe, 20 g/L Ni, 0.3 g/L Co, 140 A/m<sup>2</sup>. Disturbance final: 3 g/L Fe).

Das and Gopala (1996) found that increasing the iron concentration up to 1 g/L from 0.5 g/L rapidly increased the SEC. The increase in SEC was, however, slower when increasing the iron concentration beyond 1 g/L, up to 6 g/L. Khouraibchia and Moats (2010) found a 19.7% increase in SEC when increasing the iron concentration from 0 g/L to 6 g/L. As previously mentioned, they determined the potential to be independent of the iron concentration and attributed the change in SEC to the decrease in current efficiency.

## 9.4.3.3 Effect of Nickel Concentration

## Copper plating rate and current efficiency

Figure 9.19 shows the experimental and model-predicted response of the (a) copper plating rate and (b) current efficiency to the increase disturbance in advance electrolyte nickel concentration, for the bench-scale electrowinning validation experiment. Both the experimental copper plating rate and current efficiency showed a significant decrease after the disturbance occurred. The model-predicted values, however, remained constant. The nRMSE value was 32.7% for the copper plating rate and 17.0% for the current efficiency.



Figure 9.19: Actual versus predicted (a) copper plating rate and (b) current efficiency for the bench-scale electrowinning validation experiment in which an increase disturbance in advance electrolyte nickel concentration occurred four hours into the eight-hour run. (Initial conditions: 40 g/L Cu, 1 g/L Fe, 20 g/L Ni, 0.3 g/L Co, 140 A/m<sup>2</sup>. Disturbance final: 45 g/L Ni).

Nickel is known to have an adverse effect on the mass-transfer conditions and limiting-current density of the copper electrodeposition process (see Section 2.3.4.2). For the bench-scale electrowinning validation experiment the operating current density was, however, under 14% of the predicted limiting-current density, for the duration of the run. Although this is higher than the preferred 10% specified for the approximation of the Butler–Volmer equation that excludes the mass-transfer kinetics, it is sufficiently low that the effect of nickel on the mass-transfer conditions should, arguably, not affect the copper reduction reaction. It would, however, be expected for changes in the mass-transfer conditions to be reflected in the reduction and oxidation of iron (see Section 9.4.3.1). It is argued that the adverse effect of nickel on the mass-transfer conditions should, therefore, result in an increase in current efficiency, for an increase in nickel. This, however, contradicts the behaviour of the dynamic bench-scale electrowinning experiment. It is also noteworthy that the experimental current efficiency is above 100% for almost the entire duration. Consequently, it is suggested that the dynamic bench-scale electrowinning experiment has limited value for use in model validation. Regardless, any possible

changes in the mass-transfer conditions will only be accounted for by the model if the online parameterfitting approach is implemented.

## SEC and potential

Figure 9.20 shows the experimental and model-predicted response of the (a) SEC and (b) potential to the increase disturbance in advance electrolyte nickel concentration, for the bench-scale electrowinning validation experiment. Both the experimental SEC and potential showed an increase after the disturbance occurred. The model-predicted potential also showed an increase, but the model-predicted SEC, on the other hand, remained constant. Owing to the small observed increase in experimental potential, the bulk of the change in the experimental SEC is attributed to the previously observed change in the copper plating rate (Figure 9.19 (a)). Regardless, literature supports the increase in potential resulting from the increase in nickel concentration. As discussed in Chapter 3, nickel reduces the conductivity, which increases the electrolyte resistance and in turn, the potential. The nRMSE value calculated for the SEC was 34.2%, whilst the value for the potential was 1.4%. The MAPE value for the SEC was 27.2%.



Figure 9.20: Actual versus predicted (a) SEC and (b) potential for the bench-scale electrowinning validation experiment in which an increase disturbance in advance electrolyte nickel concentration occurred four hours into the eight-hour run. (Initial conditions: 40 g/L Cu, 1 g/L Fe, 20 g/L Ni, 0.3 g/L Co, 140 A/m<sup>2</sup>. Disturbance final: 45 g/L Ni).

#### 9.4.3.4 Effect of Cobalt Concentration

#### Copper plating rate and current efficiency

Figure 9.21 shows the experimental and model-predicted response of the (a) copper plating rate and (b) current efficiency to the increase disturbance in advance electrolyte cobalt concentration, for the bench-scale electrowinning validation experiment. Both the experimental copper plating rate and current efficiency showed a decrease after the disturbance occurred. The model-predicted values, however,

remained unchanged. Khouraibchia and Moats (2010) found that cobalt had no notable effect on the current efficiency in concentrations of between 0.1 g/L and 0.2 g/L. The concentrations used in the bench-scale electrowinning experiments were, however, significantly higher (up to 3 g/L). Nevertheless, the two training experiments in which a disturbance in cobalt concentration occurred also showed no significant change in the copper plating rate and current efficiency, supporting the model-predicted behaviour. The nRMSE value was 22.8% for the copper plating rate and 10.2% for the current efficiency.



Figure 9.21: Actual versus predicted (a) copper plating rate and (b) current efficiency for the bench-scale electrowinning validation experiment in which a disturbance in advance electrolyte cobalt concentration occurred four hours into the eight-hour run. (Initial conditions: 40 g/L Cu, 1 g/L Fe, 20 g/L Ni, 0.3 g/L Co, 140 A/m<sup>2</sup>. Disturbance final: 1 g/L Co).

#### SEC and potential

Figure 9.22 shows the experimental and model-predicted response of the (a) SEC and (b) potential to the increase disturbance in advance electrolyte cobalt concentration, for the bench-scale electrowinning experiment. The experimental SEC showed an increase after the disturbance occurred. The experimental potential showed no change. The model-predicted SEC and potential remained constant. The nRMSE value calculated for the potential was 2.4%, showing a good model fit. The nRMSE value for the SEC was 30.1%. The corresponding MAPE value was 17.7%.

As discussed in Chapter 2 (Section 2.3.4.2), the presence of cobalt is expected to decrease the water oxidation overpotential, resulting in a decreased potential. Khouraibchia and Moats (2010), however, found no notable effect on the SEC for changes in cobalt concentrations ranging from 0.1 g/L to 0.2 g/L. In the validation bench-scale electrowinning experiment the cobalt was increased from 0.3 g/L to 1 g/L. Nonetheless, the model will only capture the effect of cobalt concentration on potential, and any possible accompanying effect on the SEC, when the online parameter-fitting approach is implemented.



Figure 9.22: Actual versus predicted (a) SEC and (b) potential for the bench-scale electrowinning validation experiment in which a disturbance in advance electrolyte cobalt concentration occurred four hours into the eight-hour run. (Initial conditions: 40 g/L Cu, 1 g/L Fe, 20 g/L Ni, 0.3 g/L Co, 140 A/m<sup>2</sup>. Disturbance final: 1 g/L Co).

# 9.4.3.5 Effect of Current Density

# Copper plating rate and current efficiency

Figure 9.23 shows the effect of the increase disturbance in current density on the (a) copper plating rate and (b) current efficiency, for the screening validation experiment. The experimental copper plating rate and current efficiency showed, as expected, an increase in response to the increase in current density. Similarly, the model-predicted copper plating rate and current efficiency also showed an increase. The model-predicted increase in current efficiency was, however, very subtle, as the current efficiency was already close to 100%. The observed behaviour supports the assumption that the copper reduction reaction was reaction-rate-limited. The nRMSE value was 30.6% for the copper plating rate, and 18.5% for the current efficiency.


Figure 9.23: Actual versus predicted (a) copper plating rate and (b) current efficiency for the screening experiment in which an increase disturbance in current density occurred four hours into the eight-hour run. (Initial conditions: 40 g/L Cu, 1 g/L Fe, 285 A/m<sup>2</sup>. Disturbance final: 375 A/m<sup>2</sup>).

Figure 9.24 shows the effect of the decrease disturbance in current density on the (a) copper plating rate and (b) current efficiency, for the bench-scale electrowinning validation experiment. The experimental copper plating rate and current efficiency showed a decrease followed by an increase in response to the disturbance. The increase following the initial decrease is suggested to be an artifact from the data preprocessing method (see Section 6.2.1.2). The model-predicted copper plating rate and current efficiency showed a decrease, as expected from literature (Moats et al., 2012). The nRMSE value was 47.5% for the copper plating rate, and 8.8% for the current efficiency.



Figure 9.24: Actual versus predicted (a) copper plating rate and (b) current efficiency for the bench-scale electrowinning validation experiment in which a decrease disturbance in current density occurred four hours into the eight-hour run. (Initial conditions: 70 g/L Cu, 6 g/L Fe, 65 g/L Ni, 3 g/L Co, 220 A/m<sup>2</sup>. Disturbance final: 160 A/m<sup>2</sup>).

## SEC and potential

Figure 9.25 shows the response of the experimental and model-predicted (a) SEC and (b) potential to the increase in current density, for the screening validation experiment. The experimental potential (and SEC) showed a sharp increase as a result of the induced disturbance. The model-predicted potential showed an increase of roughly the same magnitude as the corresponding experimental increase. The predicted SEC, however, showed a much smaller increase compared with the observed experimental increase. It is possible that the increase in experimental SEC was amplified by the approximately 30-minute deadtime before the mass copper plated showed an increase, observed in Figure 9.23 (a). The nRMSE value for the SEC was 14.8%, whilst the corresponding MAPE value was 18.8%. This indicates a good fit. The nRMSE value for the potential was 31.2%.



Figure 9.25: Actual versus predicted (a) SEC and (b) potential for the screening validation experiment in which an increase disturbance in current density occurred four hours into the eight-hour run. (Initial conditions: 40 g/L Cu, 1 g/L Fe, 285 A/m<sup>2</sup>. Disturbance final: 375 A/m<sup>2</sup>).

Figure 9.26 shows the experimental and model-predicted response of the (a) SEC and (b) potential to the decrease disturbance in current density, for the bench-scale electrowinning validation experiment. The experimental SEC showed a slight increase after the disturbance occurred, whilst the potential showed a decrease. Similarly, the model-predicted SEC showed a subtle increase, whilst the potential showed a decrease. The increase in SEC despite the decrease in potential is, as expected, a result of the decrease in the copper plating rate for the decrease in current density (Figure 9.24 (a)). The calculated nRMSE value was 3.9% for the potential. The nRMSE for the SEC was 41.6%, and the corresponding MAPE value was 45.6%.



Figure 9.26: Actual versus predicted (a) SEC and (b) potential for the validation experiment in which a decrease disturbance in current density occurred four hours into the eight-hour run. (Initial conditions: 70 g/L Cu, 6 g/L Fe, 65 g/L Ni, 3 g/L Co, 220 A/m<sup>2</sup>. Disturbance final: 160 A/m<sup>2</sup>).

#### 9.4.4 Dynamic Industrial Data

In this section, the dynamic industrial data obtained from a base-metal refinery tankhouse (see Section 6.2.2) are used to validate the electrowinning model developed in this project. The refinery tankhouse consists of multiple electrowinning banks, with one bank selected for use in evaluation of the model. It was assumed that each cell in the bank is identical, with every cell being modelled individually. The actual and model-predicted KPIs for one cell over five 14-day cycles (Cycle a to Cycle e), previously unseen by the model, are used to discuss the electrowinning model performance. The model performance with and without the implementation of the online parameter-fitting approach (developed in Chapter 8), is included. Only the online parameter-fitting approach using the fundamental system models is considered, as the surrogate system models were shown to be inadequate during conceptual validation (see Section 8.4).

# Current efficiency

Figure 9.27 shows the actual and model-predicted current efficiency for the five validation cycles (Cycle a to Cycle e). The current efficiency was calculated using the cumulative mass copper plated. As such, even with the online parameter-fitting approach implemented, the model-predicted current efficiency shows a response lag, before eventually converging to a point close to the corresponding actual current efficiency. Nevertheless, Figure 9.27 shows that including the online parameter-fitting approach resulted in a notable improvement in the model's ability to predict the current efficiency of the industrial tankhouse. Quantitative indicators for the model performance are discussed later in this section (Table 9.3).



Figure 9.27: Actual and model-predicted current efficiency for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting.

# Copper plating rate

Figure 9.28 shows the actual and model-predicted copper plating rate for the five validation cycles (Cycle a to Cycle e). The copper plating rate varied significantly over time for all five of the validation cycles. The considered tankhouse produces copper as a minor by-product, meaning that the main objective is to produce a spent electrolyte having a composition and flow rate conducive to downstream processing. Variability in the copper plating rate is, therefore, expected. Overall, the figure shows that

the model fits the data well, with minimal sensitivity to possible outliers, even with inclusion of the online parameter-fitting approach. The insensitivity to possible outliers is particularly clear for Cycle c (Figure 9.28 (c), t = 300 h) and Cycle d (Figure 9.28 (d), t = 140 h). The use of the least-squares objective function, as discussed in Chapter 8 (Section 8.2.2), is, therefore, supported. Quantitative indicators for the model performance are discussed later in this section (Table 9.3).



Figure 9.28: Actual and model-predicted copper plating rate for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting.



Figure 9.28 Actual and model-predicted copper plating rate for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting (continued).

#### SEC and potential

Figure 9.29 and Figure 9.30 show the actual and model-predicted SEC and potential, respectively, for the five validation cycles (Cycle a to Cycle e). Although the average model-predicted SEC for each cycle is in the correct range, the dynamic SEC fluctuated noticeably less than the corresponding actual data. As the model-predicted potential, shown on Figure 9.30, is a very good fit to the actual data, it is suggested that the lack of fluctuations in the model-predicted SEC resulted from the model-predicted copper plating rate. Although the model-predicted copper plating rates showed a good fit, the model-predicted fluctuations were less severe than those for the actual data (Figure 9.28). The damped model-predictions still result in acceptable predicted copper plating rates, but because of how the SEC is calculated (Equation 2.25), the damped responses are accentuated.

The behaviour observed for Cycle a (with fitting, t = 20 h,

Figure 9.29 (a)), further confirms the limitations associated with the model-predicted SEC values. A sharp increase in the model-predicted SEC is observed, corresponding to the decrease in model-predicted copper plating rate (Figure 9.28 (a)). Although the model-predicted copper plating rate

corrected soon after, it emphasises the sensitivity of the SEC to changes in the copper plating rate. The model performance for predicting the SEC is quantified later in this section (Table 9.3).

Notwithstanding, the goal of the developed model is to enable the investigation of advanced control strategies that are likely to be based on predictions of the copper plating rate, spent electrolyte concentration, and/or potential. Consequently, high-fidelity predictions of the SEC would likely not be required for this application.



Figure 9.29: Actual and model-predicted SEC for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting.



Figure 9.29 Actual and model-predicted SEC for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting (continued).

Figure 9.30 confirms that the model-predicted potential is not sensitive to suspected outliers, even with the online parameter-fitting approach implemented. Cyle d (t = 200 h to 350 h) and Cycle e (t = 55 h and 210 h) are emphasised to support this statement.



Figure 9.30: Actual and model-predicted potential for one cell of the industrial electrowinning tankhouse over five 14day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting.



Figure 9.30 Actual and model-predicted potential for one cell of the industrial electrowinning tankhouse over five 14day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting **(continued)**.

#### Spent electrolyte copper concentration

Figure 9.31 shows the actual and model-predicted spent electrolyte copper concentration for the five validation cycles (Cycle a to Cycle e). The spent electrolyte copper concentration, although not a KPI, is an important variable for use in the investigation and development of advanced control strategies. Moreover, the spent electrolyte composition is also of concern for refineries that send this stream for further processing. Overall, the figure shows that the model fits the data well, with quantitative indicators for the model fit discussed later in this section (Table 9.3).



Figure 9.31: Actual and model-predicted spent electrolyte copper concentration for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting.



Figure 9.31 Actual and model-predicted spent electrolyte copper concentration for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e), with (w) and without (w/o) online parameter-fitting (continued).

#### Limiting-current density

Finally, the operating current density of the industrial tankhouse was compared with the limiting-current density predicted by the regression model that included the combined effect terms (Model B), developed in Chapter 3 (Section 3.6). The operating current density fluctuated between 4% and 14% of the predicted limiting-current density, well below the acceptable limit for operation (Figure 9.32). Moreover, the predicted limiting-current densities fall within the range of typical industrial limiting-current densities (between approximately 280 A/m<sup>2</sup> and 996 A/m<sup>2</sup>, see Section 3.6), supporting that the predicted values are realistic.

It is important to note that the operating current densities were, however, above the limit suggested by Bard and Faulkner (2001) for use of the Butler–Volmer equation that excludes the effects of mass-transfer kinetics (10% of the limiting-current density). As discussed in Chapter 3 (Section 3.6), the regression model used to predict the limiting-current densities does not account for the effect of oxygen evolution at the anode on mass-transfer kinetics at the cathode. Consequently, the model may significantly underestimate the limiting-current density of industrial copper electrowinning operations

(Beukes and Badenhorst, 2009). Regardless, the validation performed for the dynamic electrowinning model showed that the form of the Butler–Volmer equation used remained an adequate approximation of the current densities associated with copper reduction and water oxidation. A warning was, nonetheless, included in the model to alert the user when the 10% limit is breached (see Section 9.3.2).



Figure 9.32: Operating current density and limiting-current density (predicted by Model B (Section 3.6)) for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e).



Figure 9.32 Operating current density and limiting-current density (predicted by Model B (Section 3.6)) for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e) (continued).

#### Quantitative indicators

The MAPE and nRMSE values for the predicted variables are given in Table 9.3, for the five validation cycles with (w) and without (w/o) the online parameter-fitting approach implemented. As previously discussed, the dynamic model was developed to predict the performance of industrial electrowinning tankhouses for use in the development and investigation of advanced control strategies (Section 4.2.1). Consequently, the validation completed using the dynamic industrial data is of utmost importance to ensure the model is sufficiently accurate for its intended purpose.

Table 9.3: MAPE and nRMSE values for the prediction of KPIs and intermediary variables for one cell of the industrial case-study tankhouse over the five 14-day validation cycles, for the model with (w) and without (w/o) the online parameter-fitting approach implemented. The grey shading indicates where indicators are above the selected baselines (20% for MAPE values and 30% for nRMSE values).

Indicator	Cycle a		Cycle b		Cycle c		Cycle d		Cycle e	
	w	w/o								
MAPE (%)										
Current efficiency	14.9	21.8	6.36	21.1	6.11	26.2	5.79	22.7	6.48	24.7
Cu plating rate	-	_	-	-	-	-	-	-	-	-
SEC	47.2	56.2	23.3	42.2	18.1	43.6	21.4	40.4	21.9	40.2
Potential	4.76	9.68	2.40	6.32	1.74	6.65	2.10	5.84	2.76	5.87
Spent <i>x</i> Cu	6.29	6.56	4.50	5.91	4.78	7.36	5.06	6.91	5.19	7.45
nRMSE (%)										
Current efficiency	16.6	20.2	10.0	23.0	7.73	26.7	6.95	23.3	8.59	25.3
Cu plating rate	45.5	44.5	25.8	28.6	23.8	31.0	24.9	31.1	26.3	31.1
SEC	225	224	30.7	38.9	48.2	55.0	49.5	53.3	42.5	45.4
Potential	6.91	11.4	3.18	6.90	2.28	7.34	3.10	6.45	4.19	6.82
Spent <i>x</i> Cu	7.64	8.02	5.72	7.15	6.31	8.47	6.23	8.26	7.05	8.44

Overall, the MAPE values for the majority of the predictions are below the 20% baseline set in this project, and the nRMSE values below the 30% baseline. The SEC predictions are a notable exception. As already mentioned during qualitative analysis of the results, it is expected that the model-predicted SEC values will, therefore, hold limited value.

The nRMSE values for the copper plating rate predicted for Cycle a (with and without fitting) are also above the selected threshold of 30%. For Cycle a, the model-predicted values, both with and without the online parameter-fitting approach, were not well-aligned with the actual real-life values for the first 50 hours of the cycle (see Figure 9.28 (a)). Although it is difficult to ascertain the exact reason for the misalignment, it is hypothesised that it could be the result of unusual operating conditions, or other unexpected disturbances not fully captured by the electrowinning model. Additionally, the quality of data captured for the initial stages of Cycle a could also necessitate more rigorous data validation.

Nonetheless, the favourable performance, as supported by the remainder of the quantitative indicators in Table 9.3, lends credence to the application of the model for predicting the performance of the direct copper electrowinning tankhouse from which the data were obtained.

#### 9.5 INDUSTRIAL APPLICATION

#### 9.5.1 Model Limitations

Certain limitations of the developed model were highlighted in this chapter, but ultimately it was shown to be sufficiently comprehensive and accurate for the model purpose. As discussed throughout this dissertation, the main purpose of the model is to enable the development and investigation of improved control strategies (such as model predictive control, MPC) for industrial direct copper electrowinning tankhouses. Other possible applications of the model also include process monitoring for early-fault detection and operator training.

The first noteworthy model limitation, already identified during the development process, is that the model is only valid under standard operating conditions. This is mainly due to the assumptions of mass-transfer-limited iron reduction and oxidation, and reaction-rate-limited copper reduction. The limitation also extends to the fact that phenomena such as the effect of the flow rate on mass-transfer conditions were not fundamentally modelled. Within the range of standard operating conditions, changes in the flow rate should, however, not have a significant effect on the interfacial cathode velocity.

As the electrolyte viscosity is also known to impact the mass-transfer conditions, the second limitation results from the exclusion of viscosity from the model scope. The effect of this limitation was observed during model validation for the behaviour resulting from disturbances in the experimental copper and nickel concentrations (Section 9.4.3.1 and Section 9.4.3.3, respectively). According to the available literature, an increase in copper concentration (and the corresponding increase in viscosity) results in a slight increase in the current efficiency. This is because the resulting change in mass-transfer conditions impacts the mass-transfer limited iron reduction. Similar behaviour is expected for an increase in nickel concentrations. The model may not directly include for the effect of disturbances in the mass-transfer conditions on the iron reduction reaction, but if the accompanying online parameter-fitting approach is implemented, the behaviour will be accounted for. This is because the online parameter-fitting approach refits for the applicable mass-transfer coefficient in order to accurately represent the current mass-transfer conditions.

Inclusion of the online parameter-fitting approach also mitigates the impact of the third limitation; fundamental modelling of the effect cobalt has on the overpotential for water oxidation is not included in the model. Consequently, the model will only capture the effect of cobalt on the anodic overpotential when the Butler–Volmer equation parameters for water oxidation are refitted, based on changes in the measured potential. The importance of implementing the online parameter-fitting approach is, therefore, further motivated in order to ensure the model predictions remain representative of the current state of the actual process.

The final limitation is the model-predicted increase in potential, and SEC, observed for an increase in advance electrolyte copper concentration. Although the model-predicted increases in the two variables are seemingly supported by literature for copper concentrations greater than 40 g/L, the generated experimental data contradict the model behaviour, even at high copper concentrations (Moats and Khouraibchia, 2009; Panda and Das, 2001). Furthermore, the model predicted an increase in the two variables regardless of the initial or final copper concentration. The effect of the electrolyte resistance may, however, be more significant on an industrial-scale than it is for the bench-scale electrowinning experiments. If this is the case, it would render the model-predicted increases accurate, regardless of the initial or final copper concentration. Historical plant data should be reviewed to determine the applicability of the model to predict the dynamic response of the SEC, for a specific tankhouse, to changes in the advance electrolyte copper concentration.

Notwithstanding the above limitations, model validation showed that the developed model (with the accompanying online parameter-fitting approach) is a sufficiently accurate representation of the reallife industrial electrowinning process. The model further fulfils the three criteria for a high-fidelity model listed in Chapter 4 (Section 4.2.1). The model is sufficiently fundamental to ensure that updating the model parameters based on measured data is meaningful, as shown by the validation conducted in Section 9.4.4 for the model and online parameter-fitting approach. Next, the model was shown to be sufficiently accurate so that the updated parameters were useful for the intended application of the model, as motivated throughout this chapter. Finally, the model was computerised in such a manner to ensure that it is sufficiently quick to execute for the intended application.

#### 9.5.2 Requirements for Industrial Application

Electrowinning data are required to train the model for application in a specific tankhouse. Real-time online data are further required for implementation of the accompanying online parameter-fitting approach, for the model to be sufficiently accurate for use in control applications. Table 9.4 outlines the measured variables required for the implementation of the developed model in industry. The only non-critical measurement listed in Table 9.4 is the mass copper plated during electrowinning. It is expected that measuring the mass copper plated during electrowinning will be difficult, if not impossible. The model and the data-processing methods followed require only the steady-state mass copper plated, which can easily be determined by weighing the cathode after electrowinning is completed. Again, the impact of data quality is emphasised. Bad quality training data will have a significant impact on the performance of the semi-empirical model developed in this project.

Category	Requirement	Details					
	Advance electrolyte composition	Includes sulfuric acid, copper, nickel, cobalt, and iron concentrations Will vary significantly and require regular monitoring					
Input variables to be measured regularly	Cell current and voltage	Will vary significantly and require regular monitoring					
	Cell temperature	Should stay relatively constant, require less regular monitoring					
	Electrolyte flow rate	Should stay relatively constant, require less regular monitoring					
Once-off measurements	Hardware loss	Should stay constant, maintenance checks suggested					
	Electrode surface area	Constant (design specification)					
	Interelectrode distance	Constant (design specification)					
	Number of cathodes	Constant (design specification)					
Output variables to be measured regularly	Spent electrolyte composition	Includes sulfuric acid, copper, nickel, cobalt, and iron concentrations Will vary significantly and require regular monitoring					
	Mass copper plated	Dynamic measurements not critical, only for use in data reconciliation					
Electrowinning model	Model	Developed as part of this project					
	Software	Modelling software and user interface					
	Operator/ automated procedure	Operator required to monitor actual versus predicted plant performance and for entering relevant variables, automation is possible					
Parameter fitting	Methodology	Developed as part of this project					
	Software	Required to conduct nonlinear regression, with a user interface					

Table 9.4: Requirements for industrial application of the model (adapted from Tucker, 2019).

# 9.5.3 Recommended Applications

The main industrial application recommended for the electrowinning model, based on the defined model purpose (Section 4.2.1), is to aid in the investigation and development of improved control strategies (such as MPC) for direct copper electrowinning tankhouses. The model can also be used to compare the improved control strategies to conventional strategies and controllers, quantifying the advantage of using the more complex strategy (Appl et al., 2020). As discussed in the introduction of this dissertation (Section 1.1), development of the model specifically for direct copper electrowinning applications does, also, not exclude it from use by post-solvent extraction operations.

Additional industrial applications for the model are also recommended. Firstly, it is recommended that the electrowinning model, with specific fitted parameters, be used as a tool for operator training. The model could be used as a "sandbox" environment that accurately mimics the dynamic behaviour of the real-life electrowinning process. This would enable operators to study the impact of changes in operating conditions on the KPIs. Use in this application would also not necessarily require the implementation of the online parameter-fitting approach, if only limited tankhouse data are available.

Secondly, the electrowinning model, with specific fitted parameters, could be used for continuous process monitoring and early-fault detection. The model has the potential to, for example, complement continuous online voltage measurements to identify possible problems. If the actual plant performance is below the predicted plant performance, operators could locate faults, such as short circuits, quicker than in current industrial practice. The model-predicted spent electrolyte composition could also be used to identify if the current operating conditions would lead to, for example, low copper concentration in the spent electrolyte, which is one of the root causes for short circuits. Retaining the central role of an experienced plant operator is key, but as discussed above, accurate model predictions can provide valuable data for the operator to act upon (Crooks et al., 2023).

In conclusion, although the commercialisation and implementation of the abovementioned technologies are not trivial, they are gradually gaining acceptance across the mineral processing and extractive metallurgical industries (Crooks et al., 2023; Schlesinger et al., 2022).

# CHAPTER 10 CONCLUSIONS AND RECOMMENDATIONS

# **10.1 CONCLUSIONS**

In this project the understanding developed in previous studies (Aminian et al., 2000; Tucker, 2019) was extended to develop a dynamic semi-empirical model for copper electrowinning operations, with a specific focus on the direct electrowinning process. The developed high-fidelity model represents a first step towards the investigation and development of improved control strategies for copper electrowinning tankhouses. The main conclusions from this project are discussed based on the objectives specified in Chapter 1 (Section 1.3), alongside the associated original scientific contributions (Section 1.4).

# i. Evaluation and development of physicochemical property correlations

The physicochemical correlations for density and conductivity, originally developed by Kalliomäki et al. (2021), were validated for use over the full range of operating conditions applicable to typical direct copper electrowinning operations, using experimental data generated in this project. The experimental data were generated by measuring the densities and conductivities of heated synthetic electrolytes containing copper, sulfuric acid, nickel, cobalt, iron, and thiourea. It was confirmed that the density model could be extrapolated to predict the densities of typical direct copper electrowinning electrolytes, as supported by the obtained  $R^2$  (0.97) and normalised residual mean square error (nRMSE) (1.1%), Similarly, the  $R^2$  (0.87) and nRMSE (16.7%) of the conductivity model confirmed the goodness of fit for use in predicting the conductivity of typical direct copper electrolytes. In this vein, the project extended the literature by providing validation of the previously developed correlations for the full range of conditions applicable to typical industrial copper electrowinning operations. The correlations formed an integral component of the dynamic electrowinning model developed in this project.

Changes in the physicochemical properties of the electrolyte due to the presence of impurities also affect the limiting-current density (Subbaiah and Das, 1994). Although a correlation for predicting the limiting-current density for electrorefining applications has previously been developed and validated by Kalliomäki et al. (2019), no such model is known to exist for predicting the limiting-current density of electrowinning operations. This project, therefore, introduced a validated regression model for predicting the limiting-current density associated with direct copper electrowinning electrolytes. The model was developed using experimental linear sweep voltammetry test data, generated in this project.

The model form including the effect of combined terms (Model B) was determined to be more accurate than the model form excluding these effects (Model A). This was confirmed by the respective correlation coefficients for the validation data. The  $R^2$  was 0.31 for Model A and 0.87 for Model B. Similarly, the nRMSE for Model A was 21.3% and 9.3% for Model B.

It is important to note that the developed limiting-current density models did not account for the effect of oxygen evolution at the anode on the mass-transfer conditions at the cathode. Accordingly, the models may significantly underestimate the limiting-current density of industrial electrowinning operations (Beukes and Badenhorst, 2009), despite having acceptable performance during model validation using the experimental data. It is, therefore, acknowledged that the models provide at best conservative estimates of the limiting-current density for actual industrial electrowinning tankhouses. For the application of the limiting-current density model in this project (i.e., the inclusion of a warning message), the conservative nature of the predicted estimates was satisfactory.

#### ii. Development of a semi-empirical dynamic model

A semi-empirical dynamic model for predicting the performance of direct copper electrowinning operations was developed and computerised using MATLAB (2023). The developed model used a conceptual resistance network consisting of parallel electrode pairs to represent an electrowinning cell, as previously done by Aminian et al. (2000) and Tucker (2019), for steady-state models. The network was combined with reaction-rate kinetics (for copper reduction and water oxidation), mass-transfer kinetics (for iron reduction and oxidation), property correlations, and mass conservation equations to form the dynamic model.

The electrowinning performance was quantified using the key performance indicators (KPIs), namely, the copper plating rate, current efficiency, and specific energy consumption (SEC). The model input variables are readily measured in tankhouses or have the potential to be readily measured with the technology currently available. The manipulated input variables required are the current, advance electrolyte composition (including nickel, cobalt, and iron as impurities), and electrolyte flow rate. The model includes the ability to specify a step or pulse disturbance in any one manipulated variable at a time. This feature allows for the response of the KPIs to changes in the input variables to be investigated; fostering an understanding of how process variables interact. Following, the original scientific contribution established in this objective is a dynamic copper electrowinning model that is sufficiently accurate so as to enable the investigation and development of improved control strategies. It is expected that the developed dynamic model for copper electrowinning operations has the potential to be a valuable tool, specifically for African operations employing resource-intensive direct copper electrowinning.

#### iii. Development of online parameter-fitting approach

The semi-empirical nature of the model necessitated the inclusion of an appropriate parameter-fitting approach to calibrate the model parameters for specific applications. The model parameters included the Butler–Volmer equation parameters (for copper reduction and water oxidation), the mass-transfer coefficients (for iron reduction and oxidation), and a current loss parameter.

Two parameter-fitting approaches were developed in this project: an offline and an online parameterfitting approach. The offline parameter-fitting approach was developed in order to fit for the parameters that were not included in the online method, as well as for the initial states of those parameters that were included in the online method. Moreover, inclusion of the offline approach enables alternative model applications (such as operator training) for tankhouses where only limited data are available. The offline approach entailed calibrating the model to each of the datasets used in this project, through a series of nonlinear regressions. A resampling method, *k*-fold cross validation, was incorporated to extract maximum usage out of the limited data available for each training set.

Parameter sensitivity analyses showed the model-predicted KPIs were most sensitive to changes in the coefficients for the water oxidation reaction, and the mass-transfer coefficient for iron reduction. The sensitivity of the model-predicted outputs to changes in the parameters bode well for the application of the parameter-fitting approach in calibrating the model to diverse datasets. Further, variability analyses, conducted using resampling with replacement, confirmed the time-varying nature of the model parameters.

The developed online parameter-fitting approach ensured that the time-varying model parameters did not become outdated as process conditions changed. The online approach is, therefore, crucial for ensuring that the model fidelity is sufficiently high for use in control applications. Based on the conducted sensitivity and variability analyses, four parameters were selected for inclusion in the online approach (charge-transfer coefficient for water oxidation, exchange current density for water oxidation, mass-transfer coefficient for iron reduction, and current loss parameter).

The moving horizon estimation (MHE) method, using the least-squares error objective function, was selected for use in developing the online approach. Two types of system models were investigated for use: fundamental system models and surrogate system models. The fundamental models utilised similar equations and procedures as used in the offline parameter-fitting approach. The surrogate models were investigated mainly as a future-orientated strategy for online parameter-fitting using computationally intensive datasets. The simple model form selected (polynomial regression) was, however, determined to be inadequate during conceptual validation. Consequently, it was elected to use the fundamental

system models for the remainder of the project. It is recommended that more advanced surrogate model structures, such as artificial neural networks, are investigated for use in future work.

The implementation of MHE for online parameter-fitting is not novel; it has been consistently used in the oil and gas industry for applications such as process monitoring (Hedengren and Eaton, 2017). As far as could be ascertained, MHE has, however, not previously been used to develop an online parameter-fitting approach to accompany a model for copper electrowinning operations. The original scientific contribution associated with the developed approach is, therefore, the implementation of an online parameter-fitting approach to continuously refit for electrowinning model parameters, based on evolving input data.

As alluded above, refitting for parameters online requires a large dataset, containing frequent, good quality measurements. Although the developed online parameter-fitting approach was validated in principle, industrial application will require the availability of good quality real-time data. It should, therefore, be noted that the data validation conducted in this dissertation was limited to offline validation, in order to ensure the data quality was not detrimental to the performance of the electrowinning model. As the quality of the training data has a significant impact on model performance, it is recommended that online data validation strategies should be investigated in future work for specific application to electrowinning operations.

# iv. Validation of the developed model

The developed electrowinning model was validated using an iterative process consisting of conceptual model validation, computerised model verification, and operational validation. The conceptual validation was completed using three types of structure-orientated behaviour tests: extreme-condition tests, behaviour sensitivity tests, and phase behaviour tests. The extreme-condition tests confirmed that the model should be used with caution outside the standard range of operation for electrowinning tankhouses. The behaviour sensitivity tests showed that the model-predicted output variables were most sensitive to the applied current density, followed by the iron concentration in the advance electrolyte. This was determined to align well with the expected sensitivity of a real-life electrowinning tankhouse to changes in the input conditions. Lastly, the phase behaviour tests confirmed that the model was able to predict most phase relationships between electrowinning variables. The only noteworthy exception was the increase predicted in SEC for an increase in advance electrolyte copper concentration. Overall, during the conceptual model validation process the assumptions underlying the model, as well as the internal structure thereof, were found to be adequate for the model purpose.

After computerised verification, which entailed incorporating relevant warning and error messages in the code, operational validation of the model was considered. The model was able to predict the KPIs for both the steady-state experimental and industrial data with reasonable accuracy. The current efficiency was predicted with a mean absolute percentage error (MAPE) of 2.1% for the experimental data and 3.1% for the industrial data. Likewise, the MAPEs for the copper plating rates were 2.1% and 3.1%, for the experimental and industrial data, respectively. The SEC was predicted with a MAPE of 3.4% for the experimental data and 24.4% for the industrial data. The high error value for the prediction of the industrial SEC is likely the result of the empirical models used to estimate the actual real-life values, as the required measurements were not available for the tankhouse.

Operational validation of the model using the dynamic experimental data had limited value due to the quality of the data. Experimental data was also compared with available literature data, and it was determined that the data were not necessarily a good representation of the expected behaviour of the copper electrowinning process. Recommendations for future work to improve the quality of the generated experimental data are included Section 10.2. Nonetheless, experimental and literature data proved useful for commenting on the robustness of the model (excluding online fitting) for use with bad training data.

Overall, the model performance for the dynamic experimental data was acceptable, given the constraints on data quality. The only exception was the model-predicted increase in SEC for an increase in advance electrolyte copper concentration, as also noted during conceptual model validation. Although literature alludes to increases in copper concentration above approximately 40 g/L resulting in increases in the SEC, more research is required to better understand this phenomenon. Caution is, therefore, advised when interpreting the dynamic response of this KPI to changes in copper concentration, until the dependency is better characterised with data relevant to a specific application.

The most crucial section of the operational validation was the work conducted using the dynamic industrial tankhouse data. The favourable performance of the model extended credibility to the use thereof for predicting the performance of the direct copper electrowinning tankhouse from which the data was obtained. Overall, implementation of the online parameter-fitting approach resulted in a model having good fidelity. The average MAPE for the current efficiency over the five 14-day cycles investigated for the selected cell was 23.3% when the online parameter-fitting approach was deactivated, and 7.9% when it was activated. Similarly, the nRMSE values for the current efficiency was 23.7% and 10.0%, for the online parameter-fitting approach excluded and included, respectively. The nRMSE for the average copper plating rate over the five validation cycles was 33.3% without online parameter-fitting, and 29.3% with. The MAPE for the SEC and potential over the five validation cycles was 33.3% for the SEC and 7.8% for the potential. With the online parameter-fitting activated the MAPE for the SEC and 3.9% for the potential 2.8%. The corresponding nRMSE values were 79.2% for the SEC and 3.9% for the potential.

The goal of the developed model is to enable the investigation of advanced control strategies that are likely to be based on predictions of the copper plating rate, spent electrolyte concentration, and/or potential. The high-fidelity model predictions for the beforementioned variables, therefore, bode well for application of the model, despite the error values for the SEC being consistently above the thresholds selected in this project for acceptable model fit.

Key limitations associated with the model were established and discussed during the validation process. Again, the model is only valid under standard operating conditions. Furthermore, activation of the online parameter-fitting approach is required to capture the effect of changing mass-transfer conditions resulting from changes in copper and nickel concentrations, on the mass-transfer-limited iron reduction reaction. Moreover, the online approach also accounts for the effect of cobalt on the anodic overpotential; a phenomenon that could not be fundamentally modelled.

In conclusion, the validation process showed that the model, and accompanying parameter-fitting approach, had a satisfactory range of accuracy, for the intended purpose of the model. Although rigorous conceptual and operational validation confirmed the model is an adequate representation of the electrowinning system, it is acknowledged that successful application of the model to one tankhouse does not necessarily imply that it could be used on another. It is, therefore, recommended that the operational validation step be repeated to verify the model performance for other copper electrowinning tankhouses.

Based on the recommended applications, the model developed and validated as part of this project has the potential to make a meaningful contribution to the field of copper electrowinning. This contribution includes assisting in operator training, process monitoring, and early-fault detection, as well as in the investigation and development of improved control strategies.

# **10.2 RECOMMENDATIONS AND FUTURE WORK**

Although the model has been found sufficiently accurate and comprehensive for the intended purpose described in this project, it is acknowledged that improvements could be made to further advance model predictions. The first recommendation pertains to the model-predicted response for the SEC when a disturbance in copper concentration occurs, which contradicts the expected behaviour. It is recommended that experiments be conducted to better characterise the relationship between the copper concentration and the SEC. This is required to ensure that the fundamental model can be updated to fully describe the mechanisms underlying the relationship. If this is not possible, it is recommended that historical plant data are analysed before the model is applied to a specific industrial tankhouse. Secondly, it is recommended that the effect of deadtime be investigated for inclusion in the model.

Barring the recommendations made for improving model predictions, it is also possible to expand the scope of the model to include additional inputs or outputs. The scope of the model could be expanded to include the performance indicator for the quality of copper as an additional output variable. This could be done by employing computational fluid dynamics to, for example, determine the effect of electrolyte flow rate on the deposited copper quality. Nevertheless, the accuracy and usefulness of predicting the quality will likely be limited due to the large number of variables affecting it. It would, however, be trivial to include pre-emptive warning messages in the model, based on the input variables, if the copper quality is expected to be outside the acceptable range. The prediction of localised growths, resulting in short circuits, could, for example, be included. This would require the generation of experimental data to investigate the relationships between input variables and copper quality, if no such data already exist. Clear, quantifiable ranges, within which the cathode quality is acceptable, would need to be determined for each input variable. The effect of smoothing agents on the quality of copper could also be incorporated as a separate feature of the model, using empirical correlations.

The scope of the model could also be expanded to include the prediction of performance outside the range of standard operating conditions. This would entail including mass-transfer effects for the copper reduction and water oxidation, as well as reaction-rate effects for the iron reduction and oxidation. The limiting-current density, already calculated in the model, could be used to reflect the system boundaries beyond standard conditions for copper reduction. Although the additional complexity associated with including non-standard operating conditions in the model will be useful for operator training, it might not necessarily be warranted. This is because operation outside standard operating conditions for industrial tankhouses is rare. If the process is operating outside the range of standard operating conditions, it is likely because a fault occurred. Therefore, it would possibly be more useful to incorporate warning messages or alarms in the model, based on various input and intermediate variables, to indicate when the process is operating outside of the expected operating conditions. The above discussion assumes that the reaction-rate-limited nature of copper reduction and water oxidation, as well as the mass-transfer-limited nature of iron, which is well reported in literature, applies to the majority of tankhouses. If this is not the case, the model could easily be adapted to use the correct mechanism as applicable to the specific tankhouse.

The effect of water losses due to evaporation and the production of acid mist could also be incorporated. Although the prediction of acid mist generation might not necessarily greatly improve the model accuracy, it does hold potential for predicting an increase in acid mist generation based on input variables. This would aid in creating a safer environment in the tankhouse. The bottleneck for implementation of such a feature will likely be the generation or acquisition of data for use in training the model to accurately predict acid mist generation. Next, the dynamic model could be combined with existing electronic circuit simulation software to predict the distribution of current in an electrowinning cell. The resistance network used as a basis for the dynamic model would allow for easy integration. It is likely that only the scale-up approach would need to be changed. This is because the individual current density associated with each electrode pair would be available, instead of assuming that every electrode pair is identical, as is currently done. The integrated model could be used to predict the effect of poor electrode alignment, short circuits, poor cathode contact, and the removal of electrodes on the current distribution in the cell, as well as the effect thereof on the KPIs.

The remainder of the recommendations is not directly applicable to the model itself, but rather to the data used to train and validate it. The generation of acceptable dynamic experimental data for use in model training and validation, having sufficiently large responses in output variables to eliminate experimental uncertainty, whilst keeping the input variables within the narrow range of standard operating conditions, proved challenging. Although limited options are available for addressing this challenge, as the model will always need to be trained and validated for input variables within a standard range, extending the duration of the experiments could result in more discernible trends. This is specifically relevant to the direct copper electrowinning bench-scale electrowinning experiments, where the lower current densities translated to a lower mass of copper plated.

Extended run-times were not possible for the experiments conducted during this project, as it would require an enlarged bench-scale setup. This is to ensure the advance electrolyte, which is continuously mixed with the spent electrolyte, is not depleted of copper. Alternatively, the bench-scale setup could be adapted to ensure either a continuous fresh stream of advance electrolyte or to replenish the advance electrolyte. This would be a very resource-intensive approach due to the large volume of electrolyte required. It is acknowledged that there is limited value in conducting future electrowinning tests if appropriate dynamic industrial tankhouse data are available for training the model in a specific application.

The final recommendation entails the investigation of online data validation strategies, as previously mentioned (Section 10.1). The performance of the electrowinning model is significantly affected by the quality of the data used for training and validation. Specifically for advanced control applications where online real-time data are required, the inclusion of an appropriate data validation strategy would complement the developed model.

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# APPENDIX A EXPERIMENTAL PROCEDURE

Appendix A provides additional information pertaining to the generation of the experimental data required in this project, as discussed in Chapter 3 (Property Correlations) and Chapter 5 (Data Generation). Detailed information is provided on the experimental designs (Section A.1) and experimental procedures (Section A.2). Furthermore, sample calculations are provided for the mass of chemicals used and flow rate required (Section A.3).

#### A.1 DETAILED EXPERIMENTAL DESIGN

#### A.1.1 Electrolyte Properties

The  $2^{k-2}$  fractional factorial design of experiments for the property correlation experiments is given below in Table A.1 with coded variables, and Table A.2 with the actual values for the variables. The 19 experiments were repeated three times at different angular velocities (1.6 rad/s, 3.1 rad/s, and 10.5 rad/s) for the limiting-current density measurements, resulting in 57 experiments.

Run	Factr 1: xCu	Factr 2: xFe	Factr 3: <i>x</i> Ni	Factr 4: <i>x</i> Co	Factr 5: xH <sub>2</sub> SO <sub>4</sub>	Factr 6: <i>T</i>
1	-1	-1	-1	-1	-1	-1
2	1	-1	-1	-1	1	-1
3	-1	1	-1	-1	1	1
4	1	1	-1	-1	-1	1
5	-1	-1	1	-1	1	1
6	1	-1	1	-1	-1	1
7	-1	1	1	-1	-1	-1
8	1	1	1	-1	1	-1
9	-1	-1	-1	1	-1	1
10	1	-1	-1	1	1	1
11	-1	1	-1	1	1	-1
12	1	1	-1	1	-1	-1
13	-1	-1	1	1	1	-1
14	1	-1	1	1	-1	-1
15	-1	1	1	1	-1	1
16	1	1	1	1	1	1

Table A.1: The  $2^{k-2}$  fractional factorial design of experiments for the property correlation experiments.

Run	Factr 1: <i>x</i> Cu	Factr 2: xFe	Factr 3: <i>x</i> Ni	Factr 4: xCo	Factr 5: xH <sub>2</sub> SO <sub>4</sub>	Factr 6: T
17 (CP)	0	0	0	0	0	0
18 (CP)	0	0	0	0	0	0
19 (CP)	0	0	0	0	0	0

where xCu is the copper concentration (g/L), xFe is the iron concentration (g/L), xNi is the nickel concentration (g/L), xCo is the cobalt concentration (g/L),  $xH_2SO_4$  is the sulfuric acid concentration, and T is the temperature (°C).

Table A.2: The  $2^{k-2}$  fractional factorial design of experiments for the property correlation experiments, with conditions for the manipulated variables.

Run	<i>x</i> Cu (g/L)	xFe (g/L)	xNi (g/L)	<i>x</i> Co (g/L)	<i>x</i> H₂SO₄ (g/L)	<i>Т</i> (°С)
1	30	0.5	20	0	20	50
2	90	0.5	20	0	120	50
3	30	6	20	0	120	70
4	90	6	20	0	20	70
5	30	0.5	65	0	120	70
6	90	0.5	65	0	20	70
7	30	6	65	0	20	50
8	90	6	65	0	120	50
9	30	0.5	20	3	20	70
10	90	0.5	20	3	120	70
11	30	6	20	3	120	50
12	90	6	20	3	20	50
13	30	0.5	65	3	120	50
14	90	0.5	65	3	20	50
15	30	6	65	3	20	70
16	90	6	65	3	120	70
17 (CP)	60	3.3	42.5	1.5	70	60
18 (CP)	60	3.3	42.5	1.5	70	60
19 (CP)	60	3.3	42.5	1.5	70	60

where xCu is the copper concentration (g/L), xFe is the iron concentration (g/L), xNi is the nickel concentration (g/L), xCo is the cobalt concentration (g/L), xH<sub>2</sub>SO<sub>4</sub> is the sulfuric acid concentration, and T is the temperature (°C).

## A.1.2 Screening Experiments

The three separate small face-centred central composite designs for the screening experiments, each incorporating a disturbance in a different manipulated variable, are given below. Table A.3 gives the design for a disturbance in factor 1, the advance electrolyte copper concentration. Table A.4 gives the design for a disturbance in factor 2, the advance electrolyte iron concentration. Table A.5 gives the design for a disturbance in factor 3, the current density. All runs in which the step disturbance led to a final level of more than one in the respective variable, were excluded from the design as shown by the grey shading. The experimental conditions for all 24 runs are given in Table A.6.

Table A.3: Small face-centred central composite design for a disturbance in factor 1 (advance electrolyte copper concentration).

Run	Factr 1: <i>x</i> Cu	Factr 2: <i>x</i> Fe	Factr 3: <i>i</i>	Final Value: Factr 1
1	0	0	1	1
2	0	1	0	1
	1	-1	1	2
	1	0	0	2
3	-1	0	0	0
4	0	0	0	1
5	-1	-1	-1	0
	1	1	-1	2
6	0	-1	0	1
7	0	0	-1	1
8	-1	1	1	0

where xCu is the copper concentration (g/L), xFe is the iron concentration (g/L), and *i* is the current density  $(A/m^2)$ .

Table A.4: Small face-centred central composite design for a disturbance in factor 2 (advance electrolyte iron concentration).

Run	Factr 1: <i>x</i> Cu	Factr 2: <i>x</i> Fe	Factr 3: <i>i</i>	Final Value: Factr 2
9	0	0	1	1
	0	1	0	2
10	1	-1	1	0
11	1	0	0	1
12	-1	0	0	1
13	0	0	0	1

Run	Factr 1: <i>x</i> Cu	Factr 2: <i>x</i> Fe	Factr 3: <i>i</i>	Final Value: Factr 2
14	-1	-1	-1	0
	1	1	-1	2
15	0	-1	0	0
16	0	0	-1	1
	-1	1	1	2

where xCu is the copper concentration (g/L), xFe is the iron concentration (g/L), and *i* is the current density  $(A/m^2)$ .

Table A.5: Small face-centred central composite design for a disturbance in factor 3 (current density).

Run	Factr 1: <i>x</i> Cu	Factr 2: <i>x</i> Fe	Factr 3: <i>i</i>	Final Value: Factr 3
	0	0	1	2
17	0	1	0	1
	1	-1	1	2
18	1	0	0	1
19	-1	0	0	1
20	0	0	0	1
21	-1	-1	-1	0
22	1	1	-1	0
23	0	-1	0	1
24	0	0	-1	0
	-1	1	1	2

where xCu is the copper concentration (g/L), xFe is the iron concentration (g/L), and i is the current density (A/m<sup>2</sup>).

Run	<i>x</i> Cu (g/L)	<i>x</i> Fe (g/L)	<i>i</i> (A/m²)	Fina	al Value
1	40	3	375	55	
2	40	6	285	55	
3	25	3	285	40	
4	40	3	285	55	Stop in vCv
5	25	1	200	40	step in xcu
6	40	1	285	55	
7	40	3	200	55	
8	25	6	375	40	

Table A.6: Combined design of experiments for the screening experiments, with conditions for manipulated variables.

Run	<i>x</i> Cu (g/L)	<i>x</i> Fe (g/L)	<i>i</i> (A/m²)	Final Value	
9	40	3	375	6	
10	55	1	375	3	
11	55	3	285	6	
12	25	3	285	6	Chan in vEa
13	40	3	285	6	Step in xre
14	25	1	200	3	
15	40	1	285	3	
16	40	3	200	6	
17	40	6	285	375	
18	55	3	285	375	
19	25	3	285	375	
20	40	3	285	375	Chan in i
21	25	1	200	285	Step in <i>i</i>
22	55	6	200	285	
23	40	1	285	375	
24	40	3	200	285	

where *x*Cu is the copper concentration (g/L), *x*Fe is the iron concentration (g/L), and *i* is the current density (A/m<sup>2</sup>).

# A.1.3 Bench-Scale Electrowinning Experiments

The OFAT design of experiments for the bench-scale electrowinning experiments is given below in Table A.7 with coded variables, and Table A.8 with the actual values for the variables.

Table A.7: The OFAT design of experiments for the bench-scale electrowinning experiments.

Run	Base Level	Step Factor	Final Value
1	-1	хCu	0
2	-1	<i>x</i> Fe	0
3	-1	<i>x</i> Ni	0
4	-1	хСо	0
5	-1	i	0
6	0	хCu	1
7	0	<i>x</i> Fe	1
8	0	хNi	1
9	0	<i>х</i> Со	1

Run	Base Level	Step Factor	Final Value
10	0	i	1
11	1	хCu	0
12	1	<i>x</i> Fe	0
13	1	хNi	0
14	1	<i>х</i> Со	0
15	1	i	0

where *x*Cu is the copper concentration (g/L), *x*Fe is the iron concentration (g/L), *x*Ni is the nickel concentration (g/L), *x*Co is the cobalt concentration (g/L),  $xH_2SO_4$  is the sulfuric acid concentration, and *i* is the current density (A/m<sup>2</sup>).

Table A.8: The OFAT	design of experiments	for the bench-scale	electrowinning	experiments,	with conditions	for the
manipulated variables.						

Run	Base Level	Step Factor	Final Value
1	40 g/L	хCu	55 g/L
2	1 g/L	<i>x</i> Fe	3 g/L
3	20 g/L	хNi	45 g/L
4	0.3 g/L	<i>х</i> Со	1 g/L
5	140 A/m <sup>2</sup>	i	160 A/m <sup>2</sup>
6	55 g/L	<i>x</i> Cu	70 g/L
7	3 g/L	<i>x</i> Fe	6 g/L
8	45 g/L	хNi	65 g/L
9	1 g/L	<i>х</i> Со	3 g/L
10	160 A/m <sup>2</sup>	i	220 A/m <sup>2</sup>
11	70 g/L	<i>x</i> Cu	55 g/L
12	6 g/L	<i>x</i> Fe	3 g/L
13	65 g/L	xNi	45 g/L
14	3 g/L	<i>х</i> Со	1 g/L
15	220 A/m <sup>2</sup>	i	160 A/m²

#### A.2 DETAILED PROCEDURE

#### A.2.1 Electrolyte Properties

#### A.2.1.1 Pycnometer Calibration

A detailed procedure for calibrating the pycnometer is outlined below, adapted from Chibwe (2020):

- 1. Select a pycnometer and the corresponding stopper (lid). Ensure that the lid fits properly on the pycnometer.
- 2. Clean the pycnometer with distilled water and allow to dry completely.
- 3. Weigh the empty pycnometer (with the lid) and record the mass as  $m_1$ .
- 4. Pour distilled water into a beaker and record the temperature thereof as  $T_1$ . Carefully pour the distilled water into the pycnometer to just above the neck (only leave space for the lid to fit).
- 5. Place the lid on the pycnometer. A small amount of water must flow out of the capillary hole on the lid. Ensure that there is no entrapped air in the pycnometer.
- 6. Wipe any excess water from the pycnometer using a lint-free tissue until it is completely dry.
- 7. Weigh the full pycnometer (with the lid) and record the mass as  $m_2$ .
- 8. Determine the mass of distilled water in the pycnometer by subtracting the mass of the empty pycnometer  $(m_1)$  from the mass of the full pycnometer  $(m_2)$ .
- 9. Using the temperature–density data given below in Table A.9, determine the density of the distilled water at the measured temperature  $(T_1)$ .

Temp. (°C)	Density (g/mL)	Temp. (°C)	Density (g/mL)	Temp. (°C)	Density (g/mL)	Temp. (°C)	Density (g/mL)
14	0.99925	18	0.99860	22	0.99777	26	0.99679
15	0.99910	19	0.99841	23	0.99754	27	0.99652
16	0.99895	20	0.99821	24	0.99730	28	0.99624
17	0.99878	21	0.99800	25	0.99705	29	0.99595

Table A.9: Density of distilled water at different temperatures, taken at 1 atm (NIST, 2023).

10. Determine the volume of the pycnometer  $(V_1)$  using Equation A.1.

$$V_1 = \frac{m_2 - m_1}{\rho_{water}}$$
 [A.1]

where *m* is the mass (g), *V* is volume (mL), and  $\rho$  is density (g/mL).

11. Repeat steps 1 through 10 three times and take the average pycnometer volume to determine the calibrated volume for the pycnometer/lid set.

#### A.2.1.2 Synthetic Electrolyte Preparation

A detailed procedure for preparing the 250 mL synthetic electrolyte solution is outlined below:

- 1. Clean a 600 mL beaker with demineralised water.
- 2. Add 100 mL of demineralised water to the container.
- 3. Slowly add the required volume of sulfuric acid to the container in approximately 5 mL intervals, allowing the mixture to cool down to the touch in between intervals.
- 4. Weigh the required mass of copper sulfate, ferric sulfate, nickel sulfate, cobalt sulfate, and thiourea and slowly add to the sulfuric acid/water mixture.
- 5. Stir the synthetic electrolyte solution with a glass rod until the solid crystals are completely dissolved.
- Decant the mixture into a volumetric flask and fill with demineralised water up to the 250 mL mark.

#### A.2.1.3 Conductivity and Density Measurements

A detailed procedure for measuring the conductivity and density of an electrolyte with known composition is outlined below:

- 1. Clean a 250 mL bottle with demineralised water and allow to dry completely.
- 2. Slowly pour the prepared 250 mL synthetic electrolyte solution (Section A.2.1.2) into the clean bottle.
- 3. Place the filled bottle into the heating bath and insert the bottle stopper.
- 4. If more than one experiment is conducted simultaneously repeat steps 1 to 3 for all experiments.
- 5. Fill the heating bath with tap water up to the level indicated by the float meter on the heater.
- 6. Set the heating bath to 5 °C above the desired temperature for the experiment.
- 7. Allow the heating bath to reach the desired temperature, stirring the synthetic electrolyte in the bottle/s every 15 minutes.
- 8. Once the heating bath reaches temperature, stir the solution/s and confirm the temperature inside the bottle/s using the conductivity meter.

- 9. Measure the conductivity and temperature of the solution/s using the conductivity meter. Rinse the conductivity probe with distilled water and dry using a lint-free tissue in between samples.
- 10. Use a syringe to extract 10 mL of the solution/s and deposit the samples in 15 mL sample vials through syringe filters (nylon, 0.45 μm).
- 11. Use a syringe to extract 50 mL of each solution and deposit the sample in the clean, calibrated, and weighed empty pycnometer.
- 12. Place the lid on the pycnometer. A small amount of solution must flow out of the capillary hole on the lid. Ensure that there is no entrapped air in the pycnometer.
- 13. Wipe any excess solution from the pycnometer using a lint-free tissue until it is completely dry.
- 14. Weigh the full pycnometer (with the lid) and record the final mass.
- 15. Clean the pycnometer with distilled water and allow to dry completely.
- 16. Repeat steps 11 to 14 three times for each solution.

#### A.2.1.4 Limiting-Current Density Measurements

A detailed procedure for measuring the limiting-current density of an electrolyte with known composition using linear sweep voltammetry is outlined below:

- 1. Prepare the synthetic electrolyte solution (Section A.2.1.2) and working electrode (Section A.2.1.5) in advance.
- 2. Use a syringe to extract 10 mL of the solution and deposit the sample in a 15 mL sample vial through a syringe filter (nylon,  $0.45 \mu m$ ).
- 3. Slowly pour the prepared synthetic electrolyte solution into a clean 250 mL Erlenmeyer flask. Place the flask on a magnetic stirrer and heat to the desired temperature for the experiment.
- 4. Fill the heating bath with tap water up to the level indicated by the float meter on the heater. This step is only required for the first experiment.
- 5. Set the heating bath to 10 °C above the desired temperature for the experiment.
- 6. Slowly pour 150 mL of the heated synthetic electrolyte solution into the jacketed reactor vessel connected to the heating bath. Plug all ports on the jacketed reactor vessel using bottle stoppers.
- 7. Once the heating bath reaches the desired temperature, confirm the temperature inside the jacketed reactor vessel using a glass temperature probe.
- 8. Insert the counter electrode and reference electrode, both must be equidistant to the working electrode.

- 9. Screw in the working electrode. The motor unit should be positioned so that the working electrode tip is immersed approximately 1.0 cm into the test solution. Excessive immersion may corrode the shaft or tip if the solution seeps into the joint between the shaft and tip (Cohen, 2018).
- 10. Connect the cell cable to the electrodes per the Gamry manual (Cohen, 2018).
- 11. Switch on the motor unit. Rotation should be carried out for at least 5 minutes before commencing the linear sweep voltammetry test to ensure steady-state hydrodynamic conditions at the electrode (Chibwe, 2020).
- 12. Confirm the temperature of the synthetic electrolyte solution using a glass temperature probe.
- 13. Switch on the interface unit and conduct the linear sweep voltammetry test as instructed by Cohen (2018).

#### A.2.1.5 Working Electrode Preparation

A detailed procedure for preparing the working electrode is outlined below, adapted from Chibwe (2020):

- 1. Attach an appropriate micro-cloth on the bench-top using its adhesive back.
- 2. Apply five drops of 3 µm diamond suspension polishing solution to the micro-cloth.
- 3. Rinse the electrode surface with distilled water.
- 4. Place the electrode face down on the micro-cloth and polish using a smooth figure-eight movement for 5 minutes, or until a mirror-finish is reached. The pressure applied during polishing should be uniform.
- 5. Rinse the electrode surface with acetone, followed by distilled water.
- 6. Leave the working electrode to air dry.

#### A.2.2 Bench-Scale Electrowinning Experiments

#### A.2.2.1 Synthetic Electrolyte Preparation

A detailed procedure for preparing the 10 L synthetic electrolyte solution is outlined below:

- 1. Clean a 10 L glass container with demineralised water.
- 2. Add 5 L of demineralised water to the container.
- 3. Slowly add the required volume of sulfuric acid to the container in 100 mL intervals, allowing the mixture to cool down to the touch in between intervals.
- 4. Weigh the required mass of copper sulfate, ferric sulfate, nickel sulfate, and cobalt sulfate and slowly add to the sulfuric acid/water mixture.
- 5. Fill the container with demineralised water up to the 10 L mark.
- 6. Stir the synthetic electrolyte solution with a PVC paddle until the solid crystals are completely dissolved.
- 7. The prepared synthetic electrolyte can be stored overnight by sealing the top of the container loosely with plastic wrap.

#### A.2.2.2 Blank Cathode Preparation

A detailed procedure for preparing the blank cathodes is outlined below:

- 1. Remove all previously deposited copper using an angle grinder and chisel.
- 2. Polish the cathode surface with 22  $\mu$ m (P800) sandpaper, followed by 15  $\mu$ m (P1200) sandpaper.
- 3. Rinse the cathode surface with acetone.
- 4. Rinse the cathode surface with demineralised water.
- 5. Ensure that the cathode surface is visually bright and clean.
- 6. Leave the cathode to air dry overnight.
- 7. Weigh the prepared blank cathode.

#### A.2.2.3 Bench-Scale Electrowinning

A detailed procedure for executing the bench-scale electrowinning experiments is outlined below:

1. Prepare the synthetic electrolyte solution (Section A.2.2.1) and blank cathode (Section A.2.2.2) in advance.

- 2. Place an empty 10 L glass container (stock solution container) in the heating bath.
- 3. Slowly pour the prepared 10 L synthetic electrolyte solution into the stock solution container.
- 4. Fill the heating bath with tap water up to the level indicated by the float meter on the heater.
- 5. Set the heating bath to 10 °C above the desired temperature of the synthetic electrolyte solution in the stock solution container.
- 6. Insert the prepared blank cathode in the middle slot of the electrowinning cell (Figure A.1).
- 7. Insert two anodes, one on each side of the cathode, 25 mm away from the cathode.
- 8. Switch on the power supply (whilst the terminals are not connected to the electrodes) and set the voltage to the maximum setting and the current to the minimum setting. This is required to operate the power supply in current-controlled mode. Switch off the power supply.
- 9. Bolt the negative terminal of the power supply to the cathode hanger bar and the positive terminals to the anode hanger bars.
- 10. Set the pump to 75% of the maximum speed, prime it by using a 50 mL syringe to fill the feed pipe with electrolyte and switch on the pump. Allow at least 30 minutes for the 5 L cell to fill up and the electrolyte to reach the desired temperature.
- 11. Take a 10 mL sample of the synthetic advance electrolyte solution.
- 12. Set the pump to a speed that corresponds to the desired flow rate. Allow at least 5 minutes for the flow rate to reach steady state. Take three measurements of the time it takes to fill a 100 mL volume to ensure to pump speed translates to the correct flow rate.
- 13. Switch on the power supply and set the current setpoint. Start the timer.
- 14. After 4 hours of electrowinning induce a step disturbance.
  - a. If the step disturbance is in the concentration of an electrolyte component: Add the desired amount of either the applicable solid sulfate salt (for an increase disturbance), or the volume of concentrated solution (for a decrease disturbance). Stir the solution with a PVC paddle until all solids are dissolved.
  - b. If the step disturbance is in the current density: Change the current setpoint on the power supply.
- 15. Allow electrowinning to take place for an additional 4 hours.
- 16. Switch off the power supply and pump, and remove the electrodes (Figure A.2).



Figure A.1: Photographic representation of the cell used during the bench-scale electrowinning experiments.



Figure A.2: Photographic representation of the electrodes used during the experiments, showing the plated cathode (left) and anode (right).

#### A.2.2.4 Sampling

A detailed procedure for sampling the required variables, as per the intervals given in the sampling schedule (Table A.10), is outlined below:

- 1. Note the potential and current values displayed on the power supply.
- 2. Measure the potential over each anode-cathode pair using a multi-meter.
- 3. Take 50 mL samples of both the advance and spent electrolytes (valves as per Figure 5.2).
- 4. Measure the conductivity and temperature of the respective 50 mL advance and spent electrolyte samples using a calibrated conductivity meter (not for screening experiments).
- 5. Use a syringe to extract 10 mL of the respective 50 mL advance and spent electrolyte samples and deposit the samples in 15 mL sample vials through syringe filters (nylon, 0.45 μm).
- 6. Titrate against a potassium dichromate standard to determine the amount of ferrous iron in the respective advance and spent electrolyte samples (Section A.2.3) (not for screening experiments).
- 7. Empty the remainder of both 50 mL samples into the stock solution container.
- 8. Use the bucket-and-stopwatch method to determine the flow rate using a 100 mL beaker and measuring cylinder.

Duration (h)	Potential (V)	Current (A)	Concentrations (g/L)	Flow rate (mL/s)	Conductivity (S/m)	Titration
0	x	х	х	х	x	х
0.125	x	x	x		x	
0.25	x	x	x		x	
0.5	x	x	x		x	х
0.625	x	x	x		x	
0.75	x	x	x		x	
1	x	x	x	x	x	х
1.5	x	x	x		x	
2	x	x	x	x	x	х
2.5	x	x	x		x	
3	x	x	x	x	x	х
3.5	x	x	х		x	

Table A.10: Sampling schedule showing intervals at which variables were sampled or measured. The duration refers to the time passed from the start of the experiment (taken from when power supply was switched on).

Duration (h)	Potential (V)	Current (A)	Concentrations (g/L)	Flow rate (mL/s)	Conductivity (S/m)	Titration
4	х	х	х	х	х	х
4.125	x	x	x		x	
4.25	x	x	x		x	
4.5	x	x	x		x	x
4.75	x	x	x		x	
5	x	x	x	x	x	x
5.5	x	x	x		x	
6	x	x	x	x	x	x
6.5	x	x	x		x	
7	x	x	x	x	x	x
7.5	x	x	x		x	
8	x	х	x	х	x	x

#### A.2.2.5 Sample Preparation

A detailed procedure for preparing the samples for ICP-OES analysis is outlined below:

- Calculate the expected maximum total dissolved solids (TDS) and concentration of copper, iron, nickel, and cobalt for each experimental run. The quantification range for the concentrations is 0.05 mg/L to 100 mg/L and the TDS must be below 2 mass per cent. A suitable dilution factor is, therefore, required.
- 2. The accuracy of the pipettes and pipetting technique is verified before each set of dilutions are conducted. This is done by setting the pipette to the desired volume and taking the mass of demineralised water pipetted at this setting. Every time the setting is changed this is repeated five times.
- The samples are first diluted 10 times by adding 9 mL demineralised water to 1 mL sample. Following, the 10 times diluted samples are diluted a further 101 times by adding 10 mL of demineralised water to 100 μL sample. This gives a total dilution factor of 1010.

#### A.2.3 Titration

#### A.2.3.1 Potassium Dichromate Standard Preparation

A detailed procedure for preparing the potassium dichromate standard is outlined below:

- 1. Clean a 5 L container with demineralised water.
- 2. Add 2.5 L of demineralised water to the container.
- 3. Weigh the required mass of potassium dichromate and add to the container.
- 4. Fill the container with demineralised water up to the 5 L mark.
- 5. Stir the standard with a PVC paddle until the potassium dichromate crystals are completely dissolved.
- 6. Confirm the potassium dichromate concentration of the standard by titrating against a solution with a known concentration of ferrous iron. Repeat the titration a total of three times.
- 7. The potassium dichromate standard is sensitive to light and must be stored in an opaque bottle.

#### A.2.3.2 Titration for Ferrous Iron

A detailed procedure for determining the amount of ferrous iron in an electrolyte sample, via titration, is outlined below, adapted from Masambi (2015):

- 1. Clean a 250 mL Erlenmeyer flask with demineralised water and allow to dry completely.
- 2. Add 10 mL of the electrolyte sample into the dry Erlenmeyer flask using a pipette.
- Add 5 mL of 98% sulfuric acid and 5 mL of 98% phosphoric acid to the Erlenmeyer flask to mask any ferric iron present in the sample.
- Add three to five drops of 0.005 M sodium diphenylamine indicator to the Erlenmeyer flask, using a 1 mL syringe.
- 5. Place the Erlenmeyer flask on a magnetic stirrer and stir at 20 rad/s.
- 6. Set a 50 mL burette with 0.00084 M potassium dichromate standard (Section A.2.3.1).
- Titrate the content of the Erlenmeyer flask against the potassium dichromate standard to a purple (or dark blue–green) endpoint. The endpoint is taken when the colour change persists for 30 seconds.
- 8. Calculate the concentration of ferrous iron in the electrolyte sample per the balanced chemical reaction (Equation A.2), using Equation A.3.

$$Cr_2O_7^{-2} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$
 [A.2]

$$x_{\rm Fe^{2+}} = \frac{6 M_{\rm K_2 Cr_2 O_7} V_{\rm K_2 Cr_2 O_7} M_{\rm Fe}}{V_{\rm sample}}$$
[A.3]

where  $x_i$  is the concentration (g/L),  $M_i$  is the molecular mass (g/mol), and V is volume (mL).

#### A.3 SAMPLE CALCULATIONS

#### A.3.1 Electrolyte Composition

#### Copper sulfate

The mass of copper sulfate (CuSO<sub>4</sub> $\cdot$ 5H<sub>2</sub>O) that is required to give a certain copper concentration in the electrolyte is calculated using Equation A.4.

$$m_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}} = x_{\text{Cu}} V\left(\frac{M_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}}{M_{\text{Cu}}}\right) \left(\frac{\nu_{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}}}{\nu_{\text{Cu}}}\right)$$
[A.4]

where *M* is the mass (g), *x* is the concentration (g/L), *V* is volume (L), *M* is the molar mass (g/mol), and *v* is the stoichiometric coefficient ( $v_{Cu} = 1, v_{CuSO_4} = 1$ ).

#### Ferric sulfate

The mass of ferric sulfate ( $Fe_2(SO_4)_3 \cdot xH_2O$ ) that is required to give a certain iron concentration in the electrolyte is calculated using Equation A.5.

$$m_{\rm Fe_2(SO_4)_3:xH_2O} = x_{\rm Fe} V \left(\frac{M_{\rm Fe_2(SO_4)_3:xH_2O}}{M_{\rm Fe}}\right) \left(\frac{v_{\rm Fe_2(SO_4)_3:xH_2O}}{v_{\rm Fe}}\right)$$
[A.5]

where *M* is the mass (g), *x* is the concentration (g/L), *V* is volume (L), *M* is the molar mass (g/mol), and *v* is the stoichiometric coefficient ( $v_{\text{Fe}} = 2$ ,  $v_{\text{Fe}_2(\text{SO}_4)_3:x\text{H}_2\text{O}} = 1$ ).

#### Nickel sulfate

The mass of nickel sulfate (NiSO<sub>4</sub> $\cdot$ 7H<sub>2</sub>O) that is required to give a certain nickel concentration in the electrolyte is calculated using Equation A.6.

$$m_{\rm NiSO_4·7H_2O} = x_{\rm Ni} V \left(\frac{M_{\rm NiSO_4·7H_2O}}{M_{\rm Ni}}\right) \left(\frac{v_{\rm NiSO_4·7H_2O}}{v_{\rm Ni}}\right)$$
[A.6]

where *M* is the mass (g), *x* is the concentration (g/L), *V* is volume (L), *M* is the molar mass (g/mol), and *v* is the stoichiometric coefficient ( $v_{\text{Ni}} = 1, v_{\text{NiSO}_4 \cdot 7\text{H}_2 0} = 1$ ).

#### Cobalt sulfate

The mass of cobalt sulfate ( $CoSO_4 \cdot 7H_2O$ ) that is required to give a certain cobalt concentration in the electrolyte is calculated using Equation A.7.

$$m_{\rm CoSO_4·7H_2O} = x_{\rm Co} V \left( \frac{{\rm CoS}_{-4}·7H_2O}{M_{\rm Co}} \right) \left( \frac{v_{\rm CoSO_4·7H_2O}}{v_{\rm Co}} \right)$$
[A.7]

where *M* is the mass (g), *x* is the concentration (g/L), *V* is volume (L), *M* is the molar mass (g/mol), and *v* is the stoichiometric coefficient ( $v_{Co} = 1, v_{CoSO_4 \cdot 7H_2O} = 1$ ).

#### Sulfuric acid

The volume of sulfuric acid ( $H_2SO_4$ ) that is required to give a certain sulfuric acid concentration in the electrolyte is calculated using Equation A.8.

$$V_{\rm H_2SO_4} = \frac{x_{\rm H_2SO_4}V}{\text{grade }\rho}$$
 [A.8]

where *V* is the volume (L), *x* is the concentration (g/L), grade is the purity of sulfuric acid (fraction), and  $\rho$  is the density (g/L).

#### A.3.2 Flow Rate

The electrolyte flow rate was calculated based on the desired interfacial velocity of 0.1  $m^{3}/(h \cdot m^{2})$  over the electrode surface. The volumetric flow rate was calculated using Equation A.9.

$$Q = uA$$
 [A.9]

where Q is the flow rate (m<sup>3</sup>/h), u interfacial velocity m<sup>3</sup>/(h·m<sup>2</sup>), and A is the electrode surface area (m<sup>2</sup>).

# **APPENDIX B**

# **EXPERIMENTAL RESULTS**

Appendix B provides the generated experimental physicochemical property data, as discussed in Chapter 3 (Property Correlations). Detailed experimental results are provided (Section B.1), alongside relevant sample calculations (Section B.2).

# **B.1 ELECTROLYTE PROPERTIES**

Table B.1: Experimental results for the density and conductivity of synthetic electrolytes, per the experimental design in Table A.1.

Run	хCu	хFe	хNi	хСо	xH₂SO₄	Т	Density (g/L)	Conductivity (S/m)
1	32.1	0.3	21.2	0	20	51.2	1125.0	11.6
2	92.6	0.5	20.8	0	120	52.2	1300.2	33.4
3	31.1	3.6	20.1	0	120	70.1	1180.6	46.4
4	96.2	1.7	20.6	0	20	70.0	1260.0	16.3
5	32.3	0.4	68.0	0.1	120	71.4	1282.4	36.0
6	94.2	0.5	67.8	0.1	20	70.6	1361.4	15.5
7	30.0	1.6	64.2	0.1	20	53.1	1248.8	13.1
8	68.0	4.1	72.7	0.1	120	51.8	1385.6	27.9
9	32.5	0.4	21.1	3.0	20	71.4	1124.7	13.1
10	96.6	0.5	21.7	3.1	120	71.1	1301.1	36.5
11	34.2	4.0	22.3	3.2	120	53.2	1196.3	41.5
12	102.3	1.7	22.6	3.3	20	53.1	1278.4	14.1
13	33.6	0.4	72.1	3.2	120	53.5	1297.3	35.0
14	97.3	0.5	71.1	3.2	20	53.8	1374.7	12.8
15	33.6	2.0	71	3.2	20	70.2	1254.4	15.5
16	74.0	4.2	73.8	3.3	120	71.4	1415.6	28.8
17	66.1	2.3	46.3	1.6	70	61.4	1278.4	24.3
18	65.8	2.3	46.2	1.6	70	61.5	1274.7	23.9
19	66.7	2.3	46.4	1.6	70	61.2	1280.1	24.3

where *x*Cu is the copper concentration (g/L), *x*Fe is the iron concentration (g/L), *x*Ni is the nickel concentration (g/L), *x*Co is the cobalt concentration (g/L),  $xH_2SO_4$  is the sulfuric acid concentration, and *T* is the temperature (°C).

Run	хCu	хFe	хNi	хСо	<i>x</i> H₂SO₄	Т	ω	<i>i</i> lim (A/m²)
1	33.1	0.4	21.6	0	20	51	10.5	1863.4
						52	3.1	1034.8
						52	1.6	789.8
2	97.7	0.6	21.3	0	120	52	10.5	4612.4
						50	3.1	2385.1
						52	1.6	1831.7
3	33.7	3.8	22.2	0	120	68	10.5	2046.9
						68	3.1	1116.4
						68	1.6	832.7
4	101.6	2.5	22.2	0	20	70	10.5	5725.8
						70	3.1	3570.1
						69	1.6	2598.8
5	33.2	0.4	70.3	0	120	66	10.5	1475.3
						69	3.1	795.9
						70	1.6	578.6
6	98.8	0.5	70.7	0	20	65	10.5	3680.4
						66	3.1	2204.1
						69	1.6	1701.1
7	32.6	2.0	69.9	0	20	51	10.5	1202.6
						52	3.1	684.0
						52	1.6	491.4
8	73.5	4.3	77.0	0	120	51	10.5	2206.7
						52	3.1	1259.1
						52	1.6	968.8
9	33.8	0.4	22.3	3.2	20	68	10.5	2170.9
						68	3.1	1136.6
						67	1.6	825.1
10	99.3	0.5	21.5	3.1	120	65	10.5	5746.0
						66	3.1	3065.5
						70	1.6	2290.3

Table B.2: Experimental results for the limiting-current density measurements of synthetic electrolytes, per the experimental design in Table A.1.

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Run	хCu	хFe	хNi	хСо	xH₂SO₄	Т	ω	<i>i</i> lim (A/m²)
11	33.3	3.8	21.3	3.1	120	53	10.5	1606.4
						52	3.1	874.5
						52	1.6	619.0
12	99.9	2.7	21.1	3.0	20	52	10.5	4332.2
						50	3.1	2752.5
						52	1.6	2085.7
13	33.1	0.4	71.6	3.2	120	48	10.5	1024.7
						48	3.1	554.4
						52	1.6	439.8
14	97.1	0.5	69.5	3.1	20	50	10.5	2430.4
						50	3.1	1709.7
						49	1.6	1135.1
15	34.1	2.9	73.6	3.3	20	68	10.5	1529.7
						69	3.1	848.8
						68	1.6	590.2
16	78.7	4.2	76.4	3.3	120	67	10.5	3853.3
						68	3.1	2177.4
						70	1.6	1655.7
17	66.7	2.3	47.1	1.5	70	58	10.5	2843.2
						62	3.1	1867.9
						62	1.6	1147.7
18	68.1	2.4	47.7	1.6	70	59	10.5	3084.2
						59	3.1	1680.4
						58	1.6	1116.9
19	65.9	2.2	45.9	1.5	70	60	10.5	3124.0
						60	3.1	1688.5
						62	1.6	1179.4

where *x*Cu is the copper concentration (g/L), *x*Fe is the iron concentration (g/L), *x*Ni is the nickel concentration (g/L), *x*Co is the cobalt concentration (g/L),  $xH_2SO_4$  is the sulfuric acid concentration, *T* is the temperature (°C),  $\omega$  is the angular velocity (rad/s), and *i*lim is the limiting-current density.

### **B.2 SAMPLE CALCULATIONS**

### **B.2.1** Experimental Limiting-Current Density

The linear sweep voltammetry voltammograms generated using the RDE setup were used to determine the limiting-current density as described by Chibwe (2020) (Figure B.1).



Figure B.1: Linear sweep voltammetry voltammogram for the RDE showing limiting-current density.

# APPENDIX C DATA VALIDATION RESULTS

Appendix C provides additional information pertaining to the experimental datasets generated (Chapter 5) and validated (Chapter 6), in this project. The validated datasets are provided for the screening experiments and the bench-scale electrowinning experiments (Section C.1).

### C.1 VALIDATED DYNAMIC EXPERIMENTAL DATA

#### C.1.1 Screening Experiments

Table C.1: Validated dynamic electrowinning data for the screening experiment corresponding to Run 1 in Table A.6.

Time (h)	(())		Advance electrolyte (g/L)		Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	хCu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	11.36	3.05	46.02	2.43	46.02	2.43	0	3.43
0.125	11.35	3.03	46.37	2.40	46.05	2.32	1.6	3.43
0.25	11.35	2.95	47.25	2.43	46.08	2.50	3.21	3.43
0.5	11.35	2.89	46.74	2.46	46.77	2.54	6.42	3.43
0.625	11.35	2.83	47.67	2.52	47.46	2.59	8.02	3.43
0.75	11.35	2.79	46.07	2.42	46.29	2.54	9.63	3.43
7	11.35	2.74	47.80	2.59	45.83	2.74	12.84	3.57
1	11.35	2.71	45.27	2.45	44.01	2.48	19.25	3.71
1.5	11.35	2.66	45.11	2.48	43.45	2.53	25.67	3.65
2	11.35	2.66	46.51	2.71	43.24	2.62	32.09	3.54
2.5	11.35	2.66	45.01	2.52	41.34	2.59	38.51	3.66
3	11.35	2.61	44.01	2.59	42.93	2.64	44.93	3.78
3.5	11.35	2.62	43.56	2.62	40.45	2.59	51.34	3.78
4	11.35	2.59	69.34	2.38	40.57	2.65	52.95	3.78
4.125	11.35	2.60	72.86	2.49	40.16	2.57	54.55	3.78
4.25	11.35	2.60	73.33	2.52	41.90	2.55	57.76	3.78
4.625	11.35	2.55	73.66	2.53	44.18	2.50	59.37	3.78
4.75	11.35	2.55	69.46	2.47	47.73	2.60	60.97	3.78
5	11.35	2.55	66.08	2.52	56.34	2.59	64.18	3.78
5.5	11.36	2.54	59.42	2.55	57.43	2.54	70.60	3.78
6	11.35	2.44	56.78	2.56	56.02	2.59	77.02	3.43

Time (h)	Time (h) / (A)	/ (A) U (V)	Advance electrolyte (g/L)		Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)			<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
6.5	11.36	2.63	55.46	2.56	54.83	2.63	83.43	3.53
7	11.35	2.64	55.53	2.56	53.87	2.58	89.85	3.39
7.5	11.36	2.65	54.81	2.56	51.88	2.56	96.27	3.49
8	11.35	2.64	53.49	2.59	50.59	2.59	102.69	3.60

Table C.2: Validated dynamic electrowinning data for the screening experiment corresponding to Run 2 in Table A.6.

<b>T</b> ime (h)	( ( ) )		Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	mCu (g)	(L/h)
0	8.64	2.20	49.04	6.47	49.04	6.47	0	3.64
0.125	8.64	2.12	48.42	5.87	47.99	6.49	1.04	3.64
0.25	8.64	2.19	47.54	6.17	47.22	6.22	2.08	3.64
0.5	8.64	2.17	49.10	6.43	47.25	6.42	4.17	3.64
0.625	8.64	2.16	48.23	6.49	45.78	6.25	5.21	3.64
0.75	8.64	2.15	47.16	6.31	46.52	6.31	6.25	3.64
7	8.64	2.14	47.31	6.31	46.07	6.35	8.34	3.81
1	8.64	2.12	48.02	6.49	46.22	6.46	12.51	3.64
1.5	8.64	2.11	47.80	6.45	45.11	6.26	16.68	3.46
2	8.64	2.10	45.25	6.22	45.69	6.53	20.85	3.62
2.5	8.64	2.09	46.82	6.51	45.96	6.61	25.01	3.78
3	8.64	2.08	43.57	6.12	43.75	6.39	29.18	3.86
3.5	8.64	2.08	44.86	6.42	43.52	6.55	33.35	3.93
4	8.64	2.08	74.56	6.28	44.31	6.73	34.40	4.26
4.125	8.64	2.08	78.25	6.20	42.05	6.34	35.44	4.26
4.25	8.64	2.07	78.95	6.19	43.67	6.36	37.52	4.26
4.625	8.64	2.06	73.62	5.80	47.74	6.51	38.56	4.26
4.75	8.64	2.06	81.86	6.47	50.65	6.34	39.61	4.26
5	8.64	2.05	71.34	6.08	58.76	6.27	41.69	4.58
5.5	8.64	2.05	63.44	6.18	62.77	6.20	45.86	4.58
6	8.64	2.05	59.36	6.45	60.97	6.30	50.03	4.58
6.5	8.64	2.05	59.94	6.45	56.52	6.17	54.20	4.73
7	8.64	2.06	56.09	6.10	56.83	6.10	58.37	4.89

Time (h)	n) / (A) U (V)		Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)		<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)	
7.5	8.64	2.06	58.21	6.24	57.04	6.29	62.54	4.78
8	8.63	2.07	59.27	6.53	55.01	6.02	66.71	4.67

Table C.3: Validated dynamic electrowinning data for the screening experiment corresponding to Run 3 in Table A.6.

			Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.63	2.29	29.03	2.49	29.03	2.49	0	3.53
0.125	8.63	2.48	29.73	2.43	29.31	2.53	1.23	3.53
0.25	8.63	2.42	30.43	2.66	28.82	2.43	2.46	3.53
0.5	8.63	2.36	29.95	2.61	29.37	2.54	4.91	3.53
0.625	8.63	2.37	30.18	2.60	29.13	2.59	6.14	3.53
0.75	8.63	2.30	32.71	2.64	28.25	2.50	7.37	3.53
7	8.63	2.33	30.04	2.66	28.83	2.62	9.83	3.51
1	8.63	2.26	29.25	2.66	28.25	2.69	14.74	3.49
1.5	8.63	2.30	29.46	2.66	27.41	2.59	19.65	3.00
2	8.63	2.27	28.64	2.58	26.97	2.61	24.57	3.57
2.5	8.63	2.26	28.70	2.49	25.96	2.59	29.48	4.14
3	8.63	2.26	28.03	2.64	24.79	2.59	34.40	4.20
3.5	8.63	2.25	27.13	2.57	24.03	2.60	39.31	4.26
4	8.63	2.24	58.13	2.60	24.81	2.60	40.54	4.57
4.125	8.63	2.25	61.63	2.57	25.48	2.60	41.77	4.57
4.25	8.63	2.18	60.88	2.50	26.91	2.60	44.22	4.57
4.625	8.63	2.15	61.28	2.55	30.03	2.61	45.45	4.57
4.75	8.63	2.14	60.61	2.59	34.25	2.61	46.68	4.57
5	8.63	2.13	54.53	2.64	41.51	2.58	49.14	4.88
5.5	8.63	2.14	45.13	2.66	45.33	2.59	54.05	4.76
6	8.63	2.15	40.31	2.55	43.38	2.63	58.96	4.76
6.5	8.63	2.14	42.80	2.63	42.85	2.62	63.88	4.76
7	8.63	2.15	42.41	2.71	40.88	2.61	68.79	4.64
7.5	8.64	2.15	41.24	2.70	40.43	2.68	73.70	4.68
8	8.63	2.15	41.00	2.56	39.73	2.69	78.62	4.72

Time (h)	/ (A)	<i>U</i> (V)	Advance electrolyte (g/L)		Spent electrolyte (g/L)		Cumulative	Q
			xCu	<i>x</i> Fe	хCu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.65	2.18	49.75	2.52	49.75	2.52	0	3.23
0.125	8.65	2.22	48.68	2.62	47.78	2.62	1.24	3.63
0.25	8.65	2.22	48.65	2.57	45.8	2.48	2.49	3.63
0.5	8.65	2.20	48.68	2.61	46.96	2.54	4.97	4.02
0.625	8.65	2.19	50.48	2.67	46.51	2.51	6.22	3.94
0.75	8.65	2.18	49.18	2.56	47.42	2.69	7.46	3.94
7	8.65	2.17	49.36	2.63	46.74	2.55	9.95	3.85
1	8.65	2.15	47.83	2.64	45.78	2.46	14.92	3.78
1.5	8.65	2.14	48.63	2.69	47.69	2.66	19.89	3.71
2	8.65	2.12	47.18	2.62	44.94	2.54	24.87	4.07
2.5	8.65	2.12	46.50	2.69	44.88	2.61	29.84	4.43
3	8.65	2.11	45.97	2.63	44.50	2.69	34.81	4.46
3.5	8.65	2.11	45.06	2.69	43.45	2.59	39.78	4.48
4	8.65	2.11	78.10	2.49	43.52	2.59	41.03	4.78
4.125	8.65	2.11	80.11	2.56	42.55	2.59	42.27	4.78
4.25	8.65	2.10	79.40	2.52	46.71	2.56	44.76	4.78
4.625	8.65	2.09	78.97	2.60	48.56	2.71	46.00	4.78
4.75	8.65	2.08	77.91	2.57	53.24	2.69	47.24	4.78
5	8.65	2.07	68.75	2.55	64.52	2.59	49.73	5.09
5.5	8.65	2.08	65.16	2.57	63.45	2.55	54.70	5.13
6	8.65	2.08	59.92	2.68	61.88	2.67	59.68	5.18
6.5	8.65	2.08	59.77	2.64	59.58	2.60	64.65	5.19
7	8.65	2.09	59.03	2.63	58.72	2.70	69.62	5.20
7.5	8.65	2.09	60.08	2.66	58.13	2.61	74.60	4.95
8	8.65	2.09	57.96	2.61	55.64	2.58	79.57	4.69

Table C.4: Validated dynamic electrowinning data for the screening experiment corresponding to Run 4 in Table A.6.
			Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (h)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	6.06	2.14	30.25	0.86	30.25	0.86	0	3.24
0.125	6.06	2.16	31.71	0.86	29.64	0.88	0.85	3.53
0.25	6.06	2.16	30.84	0.87	29.28	0.86	1.71	3.81
0.5	6.06	2.14	31.29	0.88	30.07	0.87	3.41	3.69
0.625	6.06	2.13	30.49	0.86	29.85	0.86	4.27	3.69
0.75	6.06	2.13	29.92	0.86	29.17	0.86	5.12	3.69
7	6.06	2.12	30.34	0.92	29.00	0.88	6.83	3.57
1	6.06	2.10	29.43	0.88	29.11	0.87	10.24	3.60
1.5	6.06	2.10	29.36	0.88	27.54	0.86	13.65	3.63
2	6.06	2.09	28.97	0.88	26.27	0.82	17.07	4.02
2.5	6.06	2.08	28.35	0.86	27.92	0.89	20.48	4.41
3	6.06	2.08	27.97	0.86	26.80	0.89	23.89	4.05
3.5	6.06	2.09	28.29	0.88	27.03	0.86	27.31	3.69
4	6.06	2.09	58.49	0.86	26.22	0.86	28.16	3.89
4.125	6.06	2.08	62.69	0.85	27.52	0.88	29.01	3.89
4.25	6.06	2.06	63.79	0.86	30.22	0.89	30.72	4.08
4.625	6.06	2.06	62.11	0.87	32.49	0.84	31.57	4.20
4.75	6.06	2.05	61.26	0.88	36.37	0.88	32.43	4.20
5	6.06	2.03	55.04	0.86	42.59	0.87	34.13	4.31
5.5	6.06	2.03	45.82	0.85	45.74	0.88	37.55	4.11
6	6.06	2.03	43.07	0.90	44.28	0.89	40.96	3.90
6.5	6.06	2.04	43.16	0.88	44.00	0.91	44.37	4.24
7	6.06	2.03	43.15	0.88	43.32	0.88	47.79	4.58
7.5	6.06	2.03	41.64	0.84	42.18	0.90	51.20	4.41
8	6.06	2.03	41.80	0.93	42.64	0.91	54.62	4.25

Table C.5: Validated dynamic electrowinning data for the screening experiment corresponding to Run 5 in Table A.6.

<b>T</b> ime = (1-)	()	11/50	Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.64	2.20	47.03	0.84	47.03	0.84	0	4.90
0.125	8.64	2.22	48.78	0.86	48.37	0.85	1.24	4.90
0.25	8.64	2.22	49.64	0.85	47.29	0.85	2.48	4.90
0.5	8.63	2.21	47.26	0.85	46.59	0.85	4.97	4.90
0.625	8.64	2.21	48.91	0.86	46.59	0.85	6.21	4.90
0.75	8.64	2.21	48.75	0.86	46.57	0.86	7.45	4.90
7	8.63	2.2	47.73	0.83	47.06	0.84	9.93	5.27
1	8.63	2.19	46.50	0.82	45.95	0.86	14.90	4.66
1.5	8.63	2.18	46.83	0.83	45.13	0.85	19.86	4.04
2	8.64	2.18	47.04	0.86	45.13	0.87	24.83	3.93
2.5	8.64	2.18	46.24	0.88	45.25	0.89	29.80	3.82
3	8.63	2.18	45.70	0.88	41.90	0.84	34.76	4.26
3.5	8.63	2.18	45.17	0.87	42.57	0.85	39.73	4.20
4	8.63	2.19	69.53	0.81	43.16	0.86	40.97	4.14
4.125	8.63	2.19	76.05	0.89	43.09	0.88	42.21	4.14
4.25	8.63	2.18	72.44	0.84	45.20	0.83	44.69	4.14
4.625	8.63	2.17	72.67	0.84	49.99	0.88	45.93	4.14
4.75	8.63	2.16	72.36	0.86	55.93	0.91	47.18	4.14
5	8.63	2.16	70.17	0.87	58.92	0.87	49.66	4.16
5.5	8.63	2.16	62.73	0.88	59.09	0.88	54.62	4.18
6	8.63	2.16	59.12	0.87	59.26	0.87	59.59	4.71
6.5	8.63	2.17	59.00	0.88	58.37	0.88	64.56	4.78
7	8.63	2.17	59.29	0.90	59.22	0.90	69.52	4.85
7.5	8.63	2.17	61.03	0.93	59.33	0.92	74.49	4.62
8	8.64	2.21	59.55	0.91	57.43	0.91	79.45	4.39

Table C.6: Validated dynamic electrowinning data for the screening experiment corresponding to Run 6 in Table A.6.

			Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (h)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	6.06	2.18	47.28	2.45	47.28	2.45	0	3.61
0.125	6.06	2.34	49.47	2.50	48.43	2.60	0.80	3.61
0.25	6.06	2.38	47.63	2.52	48.75	2.57	1.60	3.61
0.5	6.06	2.59	48.12	2.44	48.03	2.65	3.21	3.61
0.625	6.06	2.23	47.89	2.56	46.94	2.53	4.01	3.61
0.75	6.06	2.24	49.21	2.63	46.85	2.56	4.81	3.61
7	6.06	2.57	48.60	2.56	47.58	2.64	6.42	3.53
1	6.06	2.67	48.72	2.66	47.78	2.59	9.62	3.96
1.5	6.06	2.22	48.58	2.67	47.51	2.64	12.83	4.39
2	6.06	2.20	48.57	2.61	46.61	2.63	16.04	3.90
2.5	6.06	2.20	47.07	2.60	46.67	2.58	19.25	3.41
3	6.06	2.21	47.03	2.61	46.00	2.68	22.46	3.42
3.5	6.06	2.22	47.70	2.61	46.37	2.70	25.67	3.42
4	6.06	2.24	77.55	2.64	44.71	2.57	26.47	3.56
4.125	6.06	2.53	81.87	2.75	45.32	2.68	27.27	3.56
4.25	6.06	2.82	77.79	2.48	47.07	2.70	28.87	3.56
4.625	6.06	2.58	79.05	2.46	46.02	2.54	29.68	3.56
4.75	6.06	2.70	77.97	2.43	46.51	2.55	30.48	3.56
5	6.06	2.58	78.40	2.48	54.50	2.56	32.08	3.71
5.5	6.06	2.65	70.20	2.59	64.79	2.54	35.29	3.76
6	6.06	2.65	64.75	2.58	65.80	2.62	38.50	3.81
6.5	6.06	2.76	61.01	2.62	62.24	2.60	41.71	3.85
7	6.06	2.65	60.47	2.49	63.24	2.80	44.91	3.90
7.5	6.06	2.61	62.46	2.52	60.92	2.71	48.12	3.91
8	6.06	2.73	62.52	2.55	59.88	2.68	51.33	3.92

Table C.7: Validated dynamic electrowinning data for the screening experiment corresponding to Run 7 in Table A.6.

			Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (h)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	11.35	2.95	30.54	5.00	30.54	5.00	0	2.81
0.125	11.35	2.72	30.73	5.40	26.25	4.76	1.53	2.81
0.25	11.35	2.63	29.21	5.01	28.30	5.10	3.05	2.81
0.5	11.35	2.35	29.87	5.27	27.77	4.91	6.10	2.81
0.625	11.35	2.37	28.89	4.83	26.78	5.03	7.63	2.99
0.75	11.35	2.32	29.50	5.10	27.55	5.16	9.15	2.81
7	11.35	2.29	29.39	5.11	28.10	5.21	12.21	2.63
1	11.35	2.22	29.06	5.49	27.62	5.08	18.31	2.73
1.5	11.35	2.21	27.97	5.18	25.35	4.96	24.41	3.67
2	11.35	2.21	27.12	5.13	24.87	5.14	30.51	3.82
2.5	11.35	2.21	26.06	4.91	23.58	5.04	36.62	3.98
3	11.35	2.19	25.21	5.26	23.64	5.24	42.72	3.88
3.5	11.35	2.20	24.82	5.06	22.92	5.14	48.82	3.79
4	11.35	2.19	53.08	4.98	24.97	5.24	50.35	4.02
4.125	11.35	2.17	55.99	4.89	23.77	5.11	51.87	4.02
4.25	11.35	2.12	58.89	4.80	26.57	5.17	54.92	4.02
4.625	11.35	2.10	56.66	4.89	30.37	5.27	56.45	4.02
4.75	11.35	2.09	59.14	5.20	33.37	5.01	57.97	4.02
5	11.35	2.08	50.55	5.10	40.40	5.30	61.03	4.24
5.5	11.35	2.08	45.79	5.22	42.33	5.07	67.13	4.49
6	11.35	2.10	37.51	5.08	38.66	4.97	73.23	4.74
6.5	11.35	2.11	36.84	4.90	36.01	4.70	79.33	3.90
7	11.35	2.12	35.79	4.96	37.2	5.11	85.44	4.51
7.5	11.35	2.12	36.93	5.16	34.56	5.00	91.54	4.34
8	11.35	2.13	35.71	5.14	35.31	4.88	97.64	4.18

Table C.8: Validated dynamic electrowinning data for the screening experiment corresponding to Run 8 in Table A.6.

Time of (h)	( ( ^ )	11/10	Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	хCu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	11.36	2.35	46.79	2.61	46.79	2.69	0	3.88
0.125	11.36	2.41	46.38	2.67	46.68	2.69	-0.07	3.88
0.25	11.36	2.38	47.08	2.66	46.82	2.70	-0.08	3.88
0.5	11.36	2.35	49.10	2.84	46.18	2.68	2.15	3.88
0.625	11.36	2.33	47.41	2.64	46.03	2.68	3.66	3.88
0.75	11.36	2.32	47.19	2.69	45.72	2.68	4.66	3.88
7	11.36	2.30	46.24	2.60	44.98	2.73	6.47	3.85
1	11.36	2.28	48.72	2.82	42.83	2.55	15.86	3.82
1.5	11.36	2.26	45.34	2.74	43.17	2.63	27.53	4.20
2	11.36	2.25	43.57	2.65	43.14	2.74	31.56	4.37
2.5	11.36	2.25	45.83	2.78	43.14	3.77	36.57	4.53
3	11.36	2.24	44.28	4.02	43.14	4.80	42.95	4.72
3.5	11.36	2.24	44.28	5.14	43.14	5.37	46.67	4.46
4	11.36	2.23	42.73	7.24	40.34	2.73	48.03	4.20
4.125	11.36	2.24	40.93	7.81	40.49	2.98	49.10	4.20
4.25	11.36	2.22	41.95	8.05	39.53	3.80	51.27	4.20
4.625	11.36	2.22	43.25	8.28	39.30	4.42	53.68	4.20
4.75	11.36	2.22	41.26	7.75	39.27	4.85	55.94	4.20
5	11.36	2.23	41.77	7.07	39.56	5.44	59.08	4.07
5.5	11.36	2.23	41.28	5.68	39.04	5.72	65.57	4.02
6	11.36	2.23	40.67	5.40	37.67	5.56	73.13	3.97
6.5	11.36	2.25	39.97	5.62	37.35	5.65	80.82	3.59
7	11.36	2.26	39.75	5.69	36.56	5.69	87.95	3.76
7.5	11.36	2.27	37.40	5.56	35.77	5.65	93.70	3.93
8	11.36	2.27	38.79	5.69	36.86	5.61	98.52	4.10

Table C.9: Validated dynamic electrowinning data for the screening experiment corresponding to Run 9 in Table A.6.

r			1				T	
Time (b)	/ (Δ)		Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
	, (A)		<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	11.36	3.18	62.67	0.83	60.63	0.92	0	3.51
0.125	11.36	3.00	63.03	0.92	63.12	0.91	-0.87	3.51
0.25	11.36	3.15	63.39	0.88	62.55	0.91	-0.63	3.51
0.5	11.36	3.20	62.61	0.87	60.27	0.89	1.46	3.51
0.625	11.36	3.11	63.51	0.88	61.95	0.90	2.74	3.51
0.75	11.36	3.15	64.06	0.92	61.80	0.90	4.00	3.51
7	11.36	3.05	63.11	0.95	61.18	0.91	6.65	3.44
1	11.36	2.97	63.89	0.95	59.98	0.89	13.92	3.37
1.5	11.36	3.02	62.52	0.91	59.82	0.92	22.27	3.37
2	11.36	3.08	60.57	0.89	57.91	0.90	29.03	3.37
2.5	11.36	3.02	60.20	0.92	58.43	0.93	34.70	3.47
3	11.36	2.94	60.02	0.92	56.04	0.90	42.08	3.37
3.5	11.36	3.13	59.21	0.90	56.72	0.90	50.12	3.27
4	11.36	2.81	57.20	3.77	54.54	0.90	51.66	3.13
4.125	11.36	2.80	56.41	4.28	54.30	0.93	53.06	3.13
4.25	11.36	2.82	57.24	4.04	53.97	1.25	56.21	3.13
4.625	11.36	2.82	57.96	3.96	55.25	1.55	57.96	3.13
4.75	11.36	2.82	58.26	3.85	55.41	1.74	59.59	3.13
5	11.36	2.77	58.95	3.54	54.29	2.17	63.99	3.13
5.5	11.36	2.75	56.32	2.77	53.02	2.44	73.30	3.13
6	11.36	2.79	56.22	2.70	53.85	2.68	79.79	2.98
6.5	11.36	3.60	55.78	2.91	53.14	2.71	85.69	3.31
7	11.36	2.79	53.95	2.64	52.49	2.78	91.03	3.65
7.5	11.36	2.78	54.93	2.72	51.93	2.73	96.87	3.34
8	11.36	2.79	53.50	2.73	50.63	2.64	103.87	3.02

Table C.10: Validated dynamic electrowinning data for the screening experiment corresponding to Run 10 in Table A.6.

Time (1)		1160	Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.65	2.15	67.36	2.84	67.36	2.84	0	4.14
0.125	8.65	2.21	64.38	2.83	65.49	2.81	0.25	3.86
0.25	8.65	2.18	67.79	2.81	63.07	2.75	1.37	3.86
0.5	8.65	2.15	65.65	2.74	63.83	2.78	5.30	3.58
0.625	8.65	2.14	64.14	2.77	64.65	2.77	5.66	3.34
0.75	8.65	2.12	65.40	2.69	64.84	2.79	5.68	3.34
7	8.65	2.11	66.38	2.76	65.26	2.78	6.55	3.10
1	8.65	2.08	66.41	2.78	64.04	2.81	10.06	3.15
1.5	8.65	2.07	65.29	2.82	61.91	2.74	15.93	3.19
2	8.65	2.06	63.95	2.77	61.67	2.78	22.21	3.69
2.5	8.65	2.03	64.36	2.84	62.67	2.82	27.24	4.20
3	8.65	2.03	63.69	2.84	60.28	2.73	34.07	4.11
3.5	8.64	2.02	62.80	2.79	61.70	2.83	39.99	4.02
4	8.64	2.02	62.21	7.93	60.87	2.83	40.77	3.97
4.125	8.64	2.02	61.75	8.20	61.78	2.95	41.19	3.97
4.25	8.65	2.01	62.10	8.41	60.82	4.00	41.99	3.97
4.625	8.64	2.01	61.62	8.38	59.80	4.65	42.98	3.97
4.75	8.64	2.01	59.45	7.63	58.55	5.10	43.85	3.97
5	8.65	2.01	61.22	6.10	58.99	5.72	45.84	3.92
5.5	8.64	2.01	60.40	5.42	58.86	5.80	50.62	3.95
6	8.64	2.01	60.18	5.58	59.75	5.85	53.13	3.99
6.5	8.65	2.00	59.36	5.53	58.80	5.81	54.47	4.42
7	8.65	2.01	60.33	5.78	58.84	5.75	57.54	4.86
7.5	8.65	2.01	60.37	5.74	58.31	5.72	66.09	4.88
8	8.65	2.01	60.40	5.70	57.77	5.7	73.66	4.90

Table C.11: Validated dynamic electrowinning data for the screening experiment corresponding to Run 11 in Table A.6.

			Advance ele	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	0
Time (h)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	mCu (g)	(L/h)
0	8.64	2.20	32.83	2.61	32.08	2.61	0	3.27
0.125	8.64	2.53	31.63	2.52	29.43	2.44	4.01	3.27
0.25	8.64	2.43	30.43	2.44	26.78	2.49	8.11	3.27
0.5	8.64	2.36	29.44	2.37	30.12	2.54	9.8	3.27
0.625	8.64	2.35	29.21	2.38	29.31	2.49	9.58	3.27
0.75	8.64	2.33	29.67	2.45	28.71	2.46	9.82	3.27
7	8.64	2.32	31.00	2.46	28.64	2.50	11.70	3.31
1	8.64	2.25	28.95	2.45	28.14	2.53	15.75	4.12
1.5	8.64	2.27	29.46	2.53	26.73	2.43	19.98	2.80
2	8.64	2.24	28.36	2.52	26.73	2.50	26.00	5.21
2.5	8.64	2.21	26.73	2.42	26.50	2.57	29.15	4.60
3	8.64	2.23	27.94	2.54	25.60	2.50	33.00	4.08
3.5	8.64	2.23	27.67	2.61	26.05	2.66	38.21	3.56
4	8.64	2.20	26.71	7.49	25.19	2.60	39.23	3.96
4.125	8.64	2.23	26.08	7.88	25.03	2.72	40.11	3.96
4.25	8.64	2.19	25.87	7.85	24.76	4.08	41.65	4.36
4.625	8.64	2.21	23.11	6.82	24.39	4.69	41.59	4.72
4.75	8.64	2.21	26.76	7.04	25.10	5.35	41.74	4.72
5	8.64	2.20	24.62	5.46	24.67	5.59	43.10	5.09
5.5	8.64	2.21	25.23	5.36	23.93	5.49	45.18	4.59
6	8.64	2.21	24.33	5.31	23.96	5.64	47.69	4.09
6.5	8.63	2.22	24.39	5.52	22.82	5.46	50.47	4.15
7	8.63	2.22	24.72	5.69	21.93	5.40	56.77	4.22
7.5	8.63	2.21	23.30	5.58	20.51	5.18	64.90	4.24
8	8.63	2.21	23.27	5.66	21.59	5.62	71.44	4.26

Table C.12: Validated dynamic electrowinning data for the screening experiment corresponding to Run 12 in Table A.6.

			Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	хCu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.65	2.66	50.04	2.57	48.46	2.57	0	3.72
0.125	8.65	2.62	47.91	2.56	48.27	2.62	0.38	3.72
0.25	8.65	2.57	49.06	2.54	48.08	2.53	0.55	3.72
0.5	8.65	2.45	48.63	2.51	47.71	2.59	1.62	3.72
0.625	8.65	2.42	47.72	2.51	47.43	2.50	1.96	3.72
0.75	8.65	2.40	49.05	2.56	45.88	2.46	2.94	3.72
7	8.65	2.38	47.47	2.52	48.28	2.67	4.30	3.93
1	8.65	2.34	48.49	2.56	46.21	2.51	6.09	4.14
1.5	8.65	2.31	46.07	2.40	44.35	2.43	11.24	4.34
2	8.65	2.31	46.31	2.52	43.97	2.42	16.49	4.20
2.5	8.65	2.31	44.66	2.46	43.51	2.44	20.85	4.06
3	8.65	2.31	47.11	2.66	43.99	2.55	26.32	4.39
3.5	8.65	2.31	44.78	2.56	43.78	2.62	32.00	4.71
4	8.65	2.31	44.38	7.21	43.12	2.63	32.78	4.53
4.125	8.65	2.32	43.81	7.38	42.36	2.55	33.71	4.53
4.25	8.65	2.31	43.77	7.49	42.96	3.68	35.26	4.53
4.625	8.65	2.30	43.77	7.14	42.53	4.29	35.97	4.53
4.75	8.65	2.28	44.61	7.55	42.31	4.59	37.97	4.53
5	8.65	2.27	44.07	6.70	42.08	5.37	44.29	4.34
5.5	8.65	2.29	43.53	5.09	42.14	5.36	52.32	4.26
6	8.65	2.29	43.23	5.20	41.73	5.29	56.02	4.17
6.5	8.65	2.28	42.51	5.29	40.39	5.09	60.58	4.14
7	8.65	2.29	41.87	5.26	41.70	5.57	63.45	4.11
7.5	8.65	2.29	41.80	5.23	40.44	5.08	67.39	4.33
8	8.65	2.30	42.17	5.39	39.18	5.29	75.31	4.56

Table C.13: Validated dynamic electrowinning data for the screening experiment corresponding to Run 13 in Table A.6.

Time of (h)	(())		Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	6.05	2.08	29.35	0.76	29.35	0.76	0	3.57
0.125	6.05	2.13	29.51	0.77	28.82	0.76	0.69	3.57
0.25	6.05	2.13	29.66	0.77	28.39	0.74	1.62	3.99
0.5	6.05	2.13	29.58	0.78	28.92	0.77	2.74	3.99
0.625	6.05	2.12	29.54	0.77	28.48	0.77	3.24	3.99
0.75	6.05	2.12	30.06	0.80	28.47	0.76	4.06	4.41
7	6.05	2.10	29.34	0.78	28.71	0.78	5.53	4.67
1	6.05	2.09	29.07	0.78	27.91	0.77	7.97	4.67
1.5	6.05	2.08	28.59	0.78	27.41	0.77	11.24	4.93
2	6.05	2.08	27.71	0.76	27.26	0.78	13.60	4.97
2.5	6.05	2.07	27.97	0.78	26.42	0.76	16.51	5.02
3	6.05	2.06	26.87	0.77	26.55	0.77	19.27	5.12
3.5	6.05	2.07	27.99	0.80	25.80	0.77	23.06	5.21
4	6.05	2.07	27.40	3.74	26.63	0.80	24.20	5.27
4.125	6.05	2.07	26.58	3.49	25.62	0.83	24.86	5.27
4.25	6.05	2.06	27.03	2.94	25.78	1.46	26.56	5.27
4.625	6.05	2.06	26.06	2.65	25.98	1.67	27.07	5.27
4.75	6.05	2.06	26.33	2.53	24.59	1.82	27.78	5.27
5	6.05	2.06	26.26	2.48	25.58	2.17	29.65	5.33
5.5	6.05	2.04	25.57	2.32	24.86	2.28	31.80	5.17
6	6.05	2.05	25.30	2.31	24.89	2.36	33.47	5.19
6.5	6.05	2.06	27.26	2.37	23.51	2.25	39.68	5.21
7	6.05	2.06	24.35	2.33	23.47	2.35	46.72	5.21
7.5	6.05	2.06	23.62	2.29	22.59	2.25	49.68	5.40
8	6.05	2.07	23.22	2.28	21.42	2.18	53.96	4.97

Table C.14: Validated dynamic electrowinning data for the screening experiment corresponding to Run 14 in Table A.6.

Time - (la)	(())	1160	Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (h)	/ (A)	U (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.65	2.66	46.88	0.82	46.88	0.82	0	3.40
0.125	8.65	2.63	47.36	0.90	47.13	0.88	0	3.40
0.25	8.65	2.66	47.87	0.97	47.50	0.87	0.28	3.40
0.5	8.65	2.66	47.94	0.92	46.29	0.91	2.14	3.40
0.625	8.64	2.68	47.43	0.86	45.92	0.89	3.59	3.40
0.75	8.65	2.67	46.60	0.84	45.41	0.83	4.84	3.40
7	8.64	2.63	46.19	0.82	44.98	0.90	7.07	3.45
1	8.64	2.67	47.17	0.87	44.44	0.86	14.13	3.14
1.5	8.65	2.63	47.03	0.85	46.81	0.95	18.97	2.88
2	8.65	2.61	47.56	0.90	43.97	0.86	25.27	3.20
2.5	8.65	2.64	45.98	0.86	44.36	0.86	34.79	3.51
3	8.65	2.63	45.10	0.85	44.74	0.89	38.62	3.58
3.5	8.65	2.62	44.06	0.86	42.33	0.87	42.75	3.66
4	8.65	2.62	42.64	3.89	42.06	0.91	43.90	3.70
4.125	8.65	2.68	43.29	3.95	42.85	0.94	44.42	3.70
4.25	8.65	2.68	44.44	3.51	41.46	1.48	47.86	3.70
4.625	8.65	2.68	42.72	3.12	40.81	1.75	50.32	3.70
4.75	8.65	2.69	43.11	3.01	41.79	2.01	51.94	3.70
5	8.65	2.68	43.02	2.96	41.08	2.25	55.24	3.70
5.5	8.65	2.67	42.93	2.68	40.93	2.41	62.98	3.70
6	8.65	2.67	41.54	2.62	41.44	2.61	66.93	3.70
6.5	8.65	2.68	41.13	2.63	41.10	2.61	67.15	3.70
7	8.65	2.63	39.75	2.50	39.56	2.73	67.54	3.70
7.5	8.65	2.69	40.09	2.60	38.86	2.65	70.38	3.69
8	8.65	2.70	40.53	2.68	37.84	2.63	78.24	3.69

Table C.15: Validated dynamic electrowinning data for the screening experiment corresponding to Run 15 in Table A.6.

Time (h)	(())	11/10	Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	6.05	2.20	50.42	2.70	50.42	2.70	0	3.97
0.125	6.05	2.23	42.43	2.74	46.98	2.76	-0.28	3.97
0.25	6.05	2.20	46.87	2.78	47.52	2.76	-1.57	3.97
0.5	6.05	2.18	45.46	2.65	49.15	2.74	-3.73	3.97
0.625	6.05	2.16	47.42	2.78	47.38	2.80	-4.63	3.97
0.75	6.05	2.15	50.71	2.84	46.15	2.71	-3.49	3.97
7	6.05	2.13	40.98	2.37	47.01	2.83	-4.21	3.96
1	6.05	2.12	47.56	2.83	44.39	2.69	-7.02	3.94
1.5	6.05	2.11	42.93	2.53	45.16	2.75	-6.10	3.97
2	6.05	2.10	45.32	2.74	45.39	2.80	-8.42	4.09
2.5	6.05	2.09	44.53	2.70	45.61	2.61	-6.01	4.21
3	6.05	2.08	43.30	2.64	45.84	2.86	-6.15	4.28
3.5	6.05	2.08	45.23	2.83	44.68	2.76	-8.29	4.35
4	6.05	2.08	46.23	7.84	44.93	2.92	-7.79	4.35
4.125	6.05	2.08	45.66	8.32	44.84	3.12	-7.21	4.35
4.25	6.05	2.08	45.69	8.43	44.53	3.98	-6.13	4.35
4.625	6.05	2.07	42.66	7.50	44.60	4.88	-6.35	4.44
4.75	6.05	2.07	46.44	7.56	43.79	5.30	-6.15	4.44
5	6.05	2.07	44.02	6.01	46.73	6.00	-6.18	4.53
5.5	6.05	2.07	44.89	5.58	43.75	5.87	-8.01	4.78
6	6.05	2.07	45.59	5.81	42.18	5.41	-2.44	5.03
6.5	6.05	2.08	41.49	5.35	43.84	5.79	-1.15	4.83
7	6.05	2.08	44.31	5.88	43.43	5.81	-2.89	4.63
7.5	6.05	2.08	41.70	5.34	42.01	5.70	-2.21	4.82
8	6.05	2.08	43.97	5.91	41.74	5.67	0.15	5.00

Table C.16: Validated dynamic electrowinning data for the screening experiment corresponding to Run 16 in Table A.6.

		Advance electrolyte (g/L)		Spont alact	roluto (g/l)			
Time (h)	/ (A)	<i>U</i> (V)	Auvalice elec		Spent elect		Cumulative	Q (I/h)
			xCu	<i>x</i> Fe	xCu	xFe		(_//
0	8.65	2.13	48.29	4.95	47.67	4.95	0	3.85
0.125	8.65	2.16	46.94	4.91	46.65	4.98	0.69	3.85
0.25	8.65	2.16	48.23	4.99	45.63	4.83	1.74	3.85
0.5	8.65	2.14	47.07	5.01	46.17	4.88	4.29	3.85
0.625	8.65	2.14	47.27	4.88	45.83	4.92	5.15	3.85
0.75	8.65	2.13	46.44	4.93	46.59	5.10	5.62	3.85
7	8.65	2.12	47.80	4.88	45.37	4.98	7.30	3.92
1	8.65	2.11	47.45	5.00	45.52	5.13	13.86	3.99
1.5	8.65	2.10	47.17	5.00	45.45	4.97	19.37	4.00
2	8.65	2.10	45.96	4.98	45.42	5.18	22.75	3.90
2.5	8.65	2.10	45.16	4.96	45.20	5.18	23.49	3.92
3	8.65	2.09	45.05	4.98	43.30	4.99	25.96	3.94
3.5	8.65	2.09	44.67	5.03	43.25	5.05	30.60	3.96
4	11.36	2.22	44.85	4.97	42.54	4.95	31.99	3.98
4.125	11.36	2.22	44.36	5.02	43.03	5.24	33.36	3.98
4.25	11.36	2.22	44.10	5.23	42.21	5.15	35.79	3.98
4.625	11.36	2.22	44.66	5.11	42.43	5.04	37.33	3.98
4.75	11.36	2.22	44.24	5.18	41.92	5.05	39.05	3.98
5	11.36	2.21	43.30	5.10	41.71	5.06	42.02	4.05
5.5	11.36	2.22	42.60	4.96	39.76	5.06	48.86	4.10
6	11.36	2.21	41.55	5.17	39.75	5.06	56.12	4.15
6.5	11.36	2.21	41.20	5.10	39.67	5.06	61.64	4.57
7	11.36	2.21	40.58	5.11	39.80	5.03	65.85	4.99
7.5	11.36	2.21	40.42	5.21	39.93	5.01	73.38	4.92
8	11.36	2.21	40.32	5.19	40.06	4.93	85.96	4.84

Table C.17: Validated dynamic electrowinning data for the screening experiment corresponding to Run 17 in Table A.6.

Time (h) / (A)	<i>I</i> (A) <i>U</i> (V)	Auvance electrolyte (g/L)		Spent electrolyte (g/L)		Cumulative	Q	
			<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	mCu (g)	(L/n)
0	8.64	2.40	65.63	2.54	65.63	2.46	0	3.64
0.125	8.64	2.42	60.03	2.31	61.98	2.44	0.9	3.64
0.25	8.64	2.37	62.40	2.41	62.01	2.42	0.02	3.64
0.5	8.64	2.28	63.78	2.46	63.81	2.47	0.42	3.64
0.625	8.64	2.24	60.99	2.35	62.38	2.44	-0.38	3.64
0.75	8.64	2.22	64.47	2.43	63.82	2.46	-0.79	3.64
7	8.64	2.19	65.80	2.58	63.2	2.49	3.09	4.07
1	8.63	2.16	64.06	2.54	64.00	2.59	9.66	3.90
1.5	8.64	2.16	62.76	2.42	62.00	2.50	11.60	3.73
2	8.64	2.14	63.70	2.53	62.73	2.48	15.77	4.03
2.5	8.63	2.13	63.61	2.58	62.37	2.56	21.30	4.03
3	8.63	2.12	61.74	2.50	61.67	2.60	24.69	4.33
3.5	8.63	2.12	63.26	2.62	62.15	2.57	27.83	4.27
4	11.37	2.25	61.90	2.53	60.05	2.56	29.85	4.55
4.125	11.37	2.25	62.01	2.49	60.87	2.61	31.95	4.55
4.25	11.37	2.24	62.41	2.68	59.73	2.51	37.34	4.55
4.625	11.38	2.25	60.12	2.60	59.00	2.54	40.02	4.55
4.75	11.38	2.25	59.83	2.52	59.54	2.59	41.01	4.55
5	11.37	2.25	60.13	2.48	59.50	2.62	42.36	4.53
5.5	11.38	2.25	60.88	2.62	57.83	2.64	53.01	4.50
6	11.38	2.24	58.14	2.56	57.64	2.62	62.53	4.54
6.5	11.37	2.25	59.81	2.60	57.15	2.59	71.06	4.57
7	11.38	2.24	58.24	2.59	56.24	2.63	84.84	4.98
7.5	11.38	2.25	56.67	2.58	56.73	2.59	90.62	4.63
8	11.38	2.25	56.57	2.67	56.79	2.64	89.86	4.29

Table C.18: Validated dynamic electrowinning data for the screening experiment corresponding to Run 18 in Table A.6.

Time (b) ((A)			Advance electrolyte (g/L)		Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	хCu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.64	2.29	28.92	2.48	28.14	2.48	0	2.92
0.125	8.64	2.59	28.97	2.66	28.11	2.45	2.53	2.92
0.25	8.64	2.50	29.02	2.53	28.07	2.55	4.88	2.92
0.5	8.64	2.35	28.95	2.51	28.04	2.50	5.92	2.92
0.625	8.64	2.34	29.51	2.56	28.07	2.62	6.57	2.92
0.75	8.64	2.26	29.24	2.55	27.96	2.55	7.32	2.92
7	8.64	2.24	29.22	2.70	27.53	2.56	8.93	2.75
1	8.64	2.2	27.62	2.61	26.72	2.57	11.58	2.64
1.5	8.64	2.21	27.95	2.53	26.22	2.59	14.17	2.53
2	8.64	2.20	28.12	2.64	25.38	2.57	18.53	2.59
2.5	8.64	2.18	27.21	2.57	24.40	2.58	24.08	2.65
3	8.64	2.18	26.41	2.50	24.24	2.58	29.28	2.82
3.5	11.37	2.21	26.18	2.62	22.96	2.52	35.07	2.82
4	11.37	2.44	25.10	2.53	23.08	2.56	36.48	2.82
4.125	11.37	2.39	25.44	2.61	22.91	2.55	37.71	2.82
4.25	11.37	2.36	24.17	2.59	21.92	2.47	40.28	2.82
4.625	11.37	2.35	24.85	2.56	21.99	2.54	41.65	2.82
4.75	11.37	2.35	25.25	2.56	21.88	2.59	43.32	2.82
5	11.37	2.34	24.13	2.61	21.32	2.56	46.75	3.00
5.5	11.37	2.34	23.52	2.56	20.96	2.64	52.81	2.93
6	11.37	2.34	23.41	2.64	18.58	2.47	60.97	2.86
6.5	11.37	2.34	23.04	2.67	18.81	2.51	72.03	3.53
7	11.37	2.32	21.71	2.67	18.78	2.60	82.61	4.21
7.5	11.37	2.32	19.65	2.53	18.16	2.66	89.32	3.76
8	11.37	2.34	19.92	2.65	17.49	2.61	94.61	3.32

Table C.19: Validated dynamic electrowinning data for the screening experiment corresponding to Run 19 in Table A.6.

			Advance electrolyte (g/L)		Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.64	2.46	48.15	2.57	48.15	2.57	0	3.71
0.125	8.64	2.48	46.41	2.55	47.67	2.51	-0.29	3.71
0.25	8.64	2.49	50.46	2.53	48.33	2.58	0.05	3.71
0.5	8.64	2.46	49.08	2.57	48.26	2.61	2.35	3.71
0.625	8.64	2.46	48.58	2.56	48.34	2.62	2.76	3.71
0.75	8.64	2.45	48.21	2.45	47.09	2.57	3.29	3.71
7	8.64	2.43	49.09	2.57	48.14	2.61	4.97	3.69
1	8.64	2.41	47.93	2.62	46.04	2.56	9.55	3.67
1.5	8.64	2.41	47.56	2.62	45.63	2.61	15.10	3.75
2	8.64	2.46	46.64	2.63	45.34	2.58	19.88	3.82
2.5	8.64	2.51	47.13	2.60	44.50	2.57	26.15	3.82
3	8.64	2.51	46.50	2.65	44.23	2.57	33.98	3.82
3.5	8.64	2.53	45.45	2.52	42.98	2.58	42.07	4.36
4	11.36	2.60	44.59	2.55	42.50	2.55	44.05	4.00
4.125	11.37	2.63	44.63	2.66	43.20	2.57	45.52	4.00
4.25	11.36	2.56	44.49	2.54	43.16	2.73	47.81	4.00
4.625	11.36	2.55	43.41	2.54	43.46	2.63	48.35	4.00
4.75	11.37	2.56	45.89	2.55	44.43	2.73	48.94	4.00
5	11.37	2.58	44.07	2.64	41.57	2.63	52.09	3.63
5.5	11.37	2.58	43.02	2.64	41.67	2.65	58.32	4.11
6	11.37	2.62	43.43	2.61	40.7	2.61	65.76	4.59
6.5	11.37	2.51	41.09	2.61	40.01	2.65	72.99	4.47
7	11.36	2.60	41.65	2.63	39.50	2.60	78.94	4.34
7.5	11.36	2.59	39.99	2.60	38.91	2.69	84.78	4.31
8	11.37	2.58	39.16	2.58	37.79	2.69	89.17	4.27

Table C.20: Validated dynamic electrowinning data for the screening experiment corresponding to Run 20 in Table A.6.

			Advance electrolyte (g/L)		Spent elect	rolyte (g/L)	Cumulative	Q
Time (n)	7 (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	хCu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	6.06	1.85	30.06	0.84	30.06	0.84	0	4.19
0.125	6.06	2.04	28.90	0.84	29.51	0.86	-0.02	4.19
0.25	6.06	2.04	29.85	0.85	29.71	0.86	-0.24	4.19
0.5	6.06	2.04	29.99	0.86	29.64	0.87	0.22	4.19
0.625	6.06	2.04	29.54	0.87	28.61	0.85	0.8	4.19
0.75	6.06	2.03	29.38	0.84	29.35	0.87	1.24	4.19
7	6.06	2.03	29.34	0.84	28.91	0.85	1.66	4.19
1	6.06	2.02	29.18	0.85	28.56	0.88	3.61	4.20
1.5	6.06	2.01	29.03	0.85	28.05	0.86	6.53	4.16
2	6.06	2.01	28.82	0.87	27.94	0.87	9.94	4.30
2.5	6.06	2.00	28.71	0.87	26.86	0.86	15.13	4.44
3	6.06	2.01	28.00	0.87	27.18	0.87	20.16	4.23
3.5	6.06	2.01	28.08	0.89	26.92	0.88	23.71	4.02
4	8.65	2.16	27.18	0.86	26.22	0.87	24.64	4.07
4.125	8.65	2.17	26.87	0.85	26.34	0.88	25.29	4.07
4.25	8.65	2.18	27.52	0.88	25.88	0.87	27.20	4.07
4.625	8.65	2.19	26.99	0.87	25.67	0.88	28.51	4.07
4.75	8.65	2.19	27.25	0.85	25.73	0.88	29.77	4.07
5	8.65	2.18	26.61	0.87	25.07	0.87	32.50	4.11
5.5	8.65	2.18	25.72	0.86	24.53	0.89	37.37	4.09
6	8.65	2.15	25.39	0.89	23.67	0.86	42.54	4.08
6.5	8.65	2.14	25.07	0.89	22.99	0.86	49.31	4.09
7	8.65	2.19	24.71	0.90	23.06	0.89	55.98	4.11
7.5	8.65	2.18	23.82	0.89	22.38	0.91	61.60	4.12
8	8.65	2.19	23.40	0.92	21.69	0.88	67.50	4.14

Table C.21: Validated dynamic electrowinning data for the screening experiment corresponding to Run 21 in Table A.6.

Time (h) / (A)		(A) U(V)	Advance electrolyte (g/L)		Spent elect	rolyte (g/L)	Cumulative	Q
	. ,		<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	mCu (g)	(L/h)
0	6.06	1.93	64.54	5.34	64.54	5.34	0	4.07
0.125	6.06	2.06	64.33	5.44	62.14	5.33	1.23	4.07
0.25	6.06	2.05	63.40	5.36	61.4	5.28	2.41	4.07
0.5	6.06	2.04	64.07	5.48	60.37	5.11	5.62	4.07
0.625	6.06	2.02	64.08	5.52	61.27	5.19	7.45	4.07
0.75	6.06	2.02	63.60	5.38	63.85	5.51	8.17	4.07
7	6.06	2.00	63.59	5.28	62.95	5.40	7.00	4.29
1	6.06	1.99	63.59	5.38	62.71	5.58	5.93	4.51
1.5	6.06	1.98	63.95	5.56	59.39	5.21	12.78	4.61
2	6.06	1.97	61.85	5.33	61.12	5.39	19.29	4.32
2.5	6.06	1.97	63.03	5.45	60.88	5.42	22.60	4.03
3	6.06	1.97	63.12	5.16	61.05	5.46	21.72	3.71
3.5	6.06	1.97	63.21	5.67	58.80	5.34	23.18	3.58
4	8.64	2.10	62.91	5.71	58.88	5.36	25.36	3.91
4.125	8.64	2.16	62.33	5.41	61.61	5.51	26.65	3.91
4.25	8.64	2.11	62.13	5.53	60.41	5.57	27.96	3.91
4.625	8.64	2.13	63.14	5.63	61.81	5.51	28.79	3.91
4.75	8.64	2.14	63.14	5.62	62.41	5.67	29.34	3.91
5	8.64	2.09	62.62	5.70	59.84	5.45	31.32	3.88
5.5	8.64	2.08	62.49	5.67	58.92	5.54	38.43	3.86
6	8.64	2.09	61.25	5.63	59.29	5.68	44.02	3.46
6.5	8.64	2.09	60.87	5.66	60.08	5.77	46.74	3.69
7	8.64	2.09	61.23	5.74	59.29	5.67	49.62	3.92
7.5	8.64	2.13	60.48	5.82	56.98	5.53	55.74	4.21
8	8.64	2.10	59.73	5.70	58.64	5.74	60.57	4.50

Table C.22: Validated dynamic electrowinning data for the screening experiment corresponding to Run 22 in Table A.6.

			Advance elec	ctrolyte (g/L)	Spent elect	rolyte (g/L)	Cumulative	Q
Time (h)	/ (A)	U (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	8.65	2.30	46.95	0.86	46.95	0.86	0	3.55
0.125	8.65	2.30	43.27	0.87	46.75	0.88	-1.36	3.55
0.25	8.65	2.28	49.90	0.91	46.78	0.86	-1.51	3.55
0.5	8.65	2.25	47.70	0.88	46.53	0.88	2.08	3.55
0.625	8.65	2.24	48.76	0.90	46.60	0.86	3.47	3.55
0.75	8.65	2.23	46.39	0.85	47.78	0.89	3.79	3.55
7	8.65	2.21	47.64	0.88	44.77	0.83	5.04	3.60
1	8.65	2.17	47.50	0.88	47.22	0.91	10.60	3.92
1.5	8.65	2.16	47.59	0.89	46.10	0.90	13.98	4.24
2	8.65	2.15	47.43	0.92	46.49	0.91	18.90	4.41
2.5	8.65	2.16	45.41	0.89	44.60	0.88	22.60	4.58
3	8.65	2.15	45.82	0.93	45.79	0.93	24.47	4.85
3.5	8.65	2.14	44.60	0.89	42.76	0.91	28.86	4.65
4	11.36	2.29	44.05	0.90	41.23	0.88	31.55	4.44
4.125	11.36	2.29	44.32	0.91	41.79	0.89	34.36	4.24
4.25	11.36	2.29	43.78	0.90	42.36	0.90	38.31	4.27
4.625	11.36	2.29	44.69	0.92	41.94	0.89	40.40	4.27
4.75	11.36	2.28	45.03	0.89	41.33	0.90	43.64	4.27
5	11.36	2.29	43.25	0.91	39.57	0.87	51.09	4.29
5.5	11.36	2.28	43.51	0.94	40.90	0.91	63.42	4.04
6	11.36	2.29	41.78	0.90	40.08	0.91	71.35	3.78
6.5	11.36	2.29	40.06	0.90	39.73	0.92	74.99	3.83
7	11.36	2.29	40.17	0.87	38.07	0.92	79.42	3.88
7.5	11.36	2.30	39.94	0.91	37.60	0.91	87.16	3.51
8	11.36	2.31	37.96	0.88	37.02	0.90	92.29	3.14

Table C.23: Validated dynamic electrowinning data for the screening experiment corresponding to Run 23 in Table A.6.

		1150	Advance electrolyte (g/L)		Spent elect	rolyte (g/L)	Cumulative	Q
Time (h)	/ (A)	<i>U</i> (V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Cu	<i>x</i> Fe	<i>m</i> Cu (g)	(L/h)
0	6.06	3.07	49.62	2.54	49.62	2.54	0	3.08
0.125	6.06	2.60	49.34	2.46	47.27	2.51	0.52	3.08
0.25	6.06	2.58	49.07	2.54	47.73	2.46	0.81	3.08
0.5	6.06	2.62	49.29	2.51	48.68	2.50	1.87	3.08
0.625	6.06	2.68	49.80	2.59	48.93	2.58	2.28	3.08
0.75	6.06	2.67	50.39	2.58	47.18	2.51	3.39	3.08
7	6.07	2.64	48.61	2.55	48.08	2.55	5.57	3.51
1	6.06	2.61	48.83	2.59	48.04	2.55	7.17	3.35
1.5	6.06	2.45	47.90	2.55	47.81	2.64	8.19	3.18
2	6.06	2.76	48.33	2.56	45.03	2.60	12.02	3.19
2.5	6.07	2.77	48.59	2.58	46.08	2.57	18.59	3.20
3	6.06	2.79	48.15	2.61	45.22	2.52	24.74	3.19
3.5	6.07	2.99	46.99	2.57	46.09	2.59	29.07	3.18
4	8.64	2.95	47.93	2.64	45.39	2.59	30.14	3.86
4.125	8.65	2.92	46.34	2.56	45.46	2.57	31.31	3.86
4.25	8.65	2.82	46.81	2.59	44.35	2.51	33.60	3.86
4.625	8.65	2.78	46.74	2.53	44.56	2.65	35.19	3.86
4.75	8.65	2.67	46.05	2.65	45.24	2.64	36.22	3.86
5	8.65	2.73	46.28	2.57	44.78	2.64	37.93	4.55
5.5	8.65	2.62	45.69	2.59	43.36	2.61	43.99	4.40
6	8.65	2.80	44.82	2.61	42.67	2.56	50.85	4.26
6.5	8.65	2.77	44.35	2.58	42.94	2.56	56.09	4.05
7	8.65	2.82	44.12	2.67	44.40	2.57	57.72	4.05
7.5	8.65	2.58	43.14	2.67	41.19	2.58	60.13	4.05
8	8.65	2.69	43.22	2.62	41.53	2.65	65.21	3.85

Table C.24: Validated dynamic electrowinning data for the screening experiment corresponding to Run 24 in Table A.6.



Figure C.1: Comparison between raw and validated cumulative mass copper plated for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure C.1 (continued)



Figure C.1 (continued)



Figure C.1 (continued)



Figure C.2: Comparison between raw and validated copper plating rate for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure C.2 (continued)



Figure C.2 (continued)



Figure C.2 (continued)



Figure C.3: Comparison between raw and validated advance and spent electrolyte copper concentrations for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure C.3 (continued)



Figure C.3 (continued)



Figure C.3 (continued)



Figure C.4: Comparison between raw and validated advance and spent electrolyte iron concentrations for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure C.4 (continued)



Figure C.4 (continued)



Figure C.4 (continued)


Figure C.5: Comparison between raw and validated flow rate for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure C.5 (continued)



Figure C.5 (continued)



Figure C.5 (continued)

## C.1.2 Bench-scale Electrowinning Experiments

Table C.25: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 1 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	rolyte (g	/L)	Cumulative	Q	
(h)	7 (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	<i>х</i> Со	<i>m</i> Cu (g)	(L/h)
0	4.24	1.83	43.62	0.73	21.82	0.31	43.63	0.73	21.82	0.31	0	5.91
0.125	4.24	1.83	43.49	0.73	21.53	0.32	43.44	0.73	21.62	0.32	0.03	5.91
0.25	4.24	1.83	44.11	0.74	21.92	0.32	43.77	0.74	21.87	0.32	0.03	6.40
0.5	4.24	1.83	44.32	0.74	22.00	0.32	42.80	0.73	21.53	0.32	0.35	6.40
0.625	4.24	1.82	43.92	0.74	21.70	0.32	41.66	0.71	21.03	0.30	0.61	6.40
0.75	4.24	1.83	44.14	0.74	21.99	0.33	42.07	0.71	21.28	0.32	0.83	7.05
7	4.24	1.81	44.42	0.75	22.23	0.32	43.01	0.73	21.54	0.31	1.11	7.05
1	4.24	1.80	44.61	0.77	22.54	0.33	41.61	0.71	21.16	0.30	2.47	6.60
1.5	4.24	1.79	45.02	0.77	22.66	0.34	40.69	0.72	20.92	0.30	4.18	6.24
2	4.24	1.80	44.26	0.76	22.63	0.33	39.61	0.69	20.47	0.30	6.41	6.49
2.5	4.24	1.80	44.10	0.77	22.65	0.34	41.12	0.73	21.33	0.32	7.98	6.76
3	4.24	1.80	43.07	0.74	21.92	0.31	41.18	0.72	21.40	0.31	9.26	6.37
3.5	4.24	1.80	57.78	0.78	21.56	0.32	41.00	0.70	20.72	0.30	10.87	6.01
4	4.24	1.82	59.40	0.82	21.92	0.32	38.55	0.69	20.35	0.29	11.59	6.01
4.125	4.24	1.82	58.79	0.78	22.46	0.33	39.41	0.70	20.59	0.30	12.55	6.51
4.25	4.24	1.81	61.40	0.86	23.54	0.35	37.10	0.62	17.89	0.28	15.25	6.51
4.625	4.24	1.79	56.41	0.84	23.68	0.35	41.77	0.65	18.48	0.27	16.70	6.51
4.75	4.24	1.79	52.90	0.85	23.61	0.35	45.14	0.68	19.16	0.28	18.04	7.02
5	4.24	1.80	51.37	0.80	23.35	0.34	44.58	0.68	19.17	0.28	20.43	7.02
5.5	4.24	1.81	50.78	0.81	22.74	0.34	44.57	0.69	19.80	0.30	24.25	7.16
6	4.24	1.81	51.00	0.81	22.79	0.33	44.79	0.72	20.17	0.30	27.54	7.33
6.5	4.24	1.81	50.28	0.78	22.39	0.32	44.81	0.70	20.20	0.29	30.56	7.25
7	4.24	1.81	50.47	0.80	22.81	0.34	45.67	0.74	20.78	0.30	33.17	7.18
7.5	4.24	1.81	49.53	0.79	22.31	0.33	45.6	0.75	20.64	0.31	35.52	6.83
8	4.24	1.81	48.4	0.81	22.12	0.33	44.99	0.73	20.65	0.3	37.65	6.5

Time (b) / (A)		Adva	nce ele	ctrolyte	(g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	7 (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	<i>х</i> Со	<i>m</i> Cu (g)	(L/h)
0	4.24	1.79	42.01	0.69	20.42	0.31	41.98	0.69	20.41	0.31	0	6.81
0.125	4.24	1.77	42.08	0.69	20.14	0.30	42.47	0.73	21.09	0.31	0	6.81
0.25	4.24	1.77	42.68	0.7	20.65	0.31	42.55	0.72	20.86	0.31	0	6.66
0.5	4.24	1.76	45.10	0.74	22.04	0.32	39.82	0.67	19.8	0.28	0.66	6.66
0.625	4.24	1.75	46.87	0.78	23.02	0.35	37.34	0.62	18.55	0.27	1.42	6.66
0.75	4.24	1.74	45.40	0.76	22.10	0.33	41.01	0.69	20.24	0.3	1.82	6.51
7	4.24	1.74	45.91	0.77	22.70	0.33	38.35	0.65	19.14	0.28	3.05	6.51
1	4.24	1.73	44.38	0.74	21.98	0.33	40.52	0.68	20.03	0.30	4.37	6.59
1.5	4.24	1.72	45.88	0.78	22.93	0.34	37.47	0.64	18.75	0.28	7.11	6.68
2	4.24	1.72	46.05	0.81	23.18	0.35	36.11	0.61	18.15	0.27	10.75	7.08
2.5	4.24	1.72	44.90	0.76	22.29	0.32	38.69	0.65	19.18	0.27	13.11	7.49
3	4.24	1.72	45.77	0.79	22.88	0.33	35.74	0.63	18.33	0.27	16.52	7.02
3.5	4.24	1.72	44.52	1.87	22.98	0.33	35.68	0.63	18.36	0.28	19.98	6.58
4	4.24	1.73	44.6	2.11	22.70	0.33	35.36	0.64	18.43	0.28	20.81	6.58
4.125	4.24	1.73	44.09	1.92	22.85	0.34	35.92	0.67	18.57	0.28	21.61	6.81
4.25	4.24	1.73	44.03	1.64	22.72	0.34	35.59	0.97	18.48	0.28	23.15	6.81
4.625	4.24	1.72	43.85	1.57	22.85	0.33	35.44	1.14	18.69	0.28	23.92	6.81
4.75	4.24	1.72	43.54	1.52	22.55	0.33	36.46	1.20	18.78	0.27	23.92	7.08
5	4.24	1.72	43.80	1.48	22.78	0.33	36.06	1.20	18.97	0.27	25.34	7.08
5.5	4.24	1.73	43.31	1.46	22.68	0.32	34.97	1.20	18.63	0.27	25.34	6.49
6	4.24	1.73	43.33	1.51	22.97	0.34	34.64	1.20	18.59	0.27	28.22	6.01
6.5	4.24	1.73	41.97	1.42	22.62	0.32	35.65	1.25	19.01	0.29	30.76	6.47
7	4.24	1.73	40.92	1.43	22.15	0.32	36.38	1.28	19.54	0.29	32.81	6.93
7.5	4.24	1.73	40.71	1.43	22.01	0.32	36.12	1.29	19.70	0.29	34.64	6.98
8	4.24	1.73	39.81	1.40	21.73	0.32	36.18	1.30	19.96	0.29	37.17	7.04

Table C.26: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 2 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	/ (A)	0(0)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	4.24	1.84	43.83	0.72	20.98	0.30	43.86	0.72	20.99	0.31	0	6.04
0.125	4.24	1.82	47.49	0.81	23.38	0.35	38.92	0.65	19.14	0.28	0.77	6.04
0.25	4.24	1.81	45.45	0.78	22.55	0.33	41.84	0.71	20.86	0.31	1.09	6.03
0.5	4.24	1.8	46.57	0.79	23.04	0.33	40.93	0.70	20.31	0.29	1.98	6.03
0.625	4.24	1.79	45.62	0.78	22.64	0.35	42.05	0.71	20.65	0.30	2.35	6.03
0.75	4.24	1.79	46.85	0.80	23.16	0.34	40.70	0.69	20.49	0.30	2.79	6.02
7	4.24	1.78	48.54	0.82	24.05	0.36	38.4	0.67	19.49	0.29	4.43	6.02
1	4.24	1.77	48.67	0.85	24.45	0.37	36.50	0.63	18.52	0.27	9.01	6.24
1.5	4.24	1.77	46.77	0.80	23.55	0.35	38.97	0.66	19.74	0.29	12.15	6.47
2	4.24	1.77	46.84	0.80	23.38	0.35	38.61	0.68	19.72	0.29	15.03	6.15
2.5	4.24	1.77	46.44	0.82	23.85	0.35	38.16	0.67	19.65	0.29	17.99	5.82
3	4.24	1.77	46.28	0.83	23.94	0.35	37.73	0.66	19.57	0.29	20.92	5.79
3.5	4.24	1.77	41.01	0.74	52.56	0.34	39.11	0.71	20.72	0.30	24.15	5.76
4	4.24	1.78	40.78	0.71	50.51	0.33	39.19	0.70	20.66	0.31	24.85	5.76
4.125	4.24	1.78	41.09	0.72	50.64	0.32	39.44	0.72	21.31	0.31	25.49	6.12
4.25	4.24	1.77	40.93	0.76	46.2	0.32	39.66	0.73	24.29	0.32	26.52	6.12
4.625	4.24	1.77	41.79	0.73	41.45	0.33	39.14	0.73	29.19	0.32	26.95	6.12
4.75	4.24	1.77	43.23	0.79	38.22	0.34	37.44	0.68	35.62	0.30	27.27	6.58
5	4.24	1.78	42.19	0.74	34.52	0.33	38.03	0.71	37.01	0.32	28.04	6.58
5.5	4.24	1.78	41.55	0.77	35.74	0.33	38.13	0.70	34.76	0.32	29.61	6.96
6	4.24	1.78	41.21	0.76	36.50	0.33	38.25	0.71	34.63	0.32	31.09	7.38
6.5	4.24	1.78	40.94	0.76	36.52	0.33	36.54	0.70	33.39	0.31	33.04	7.19
7	4.24	1.78	40.24	0.75	36.15	0.34	37.47	0.69	33.92	0.31	34.71	7.04
7.5	4.24	1.78	41.01	0.75	37.08	0.33	37.08	0.70	34.47	0.31	36.31	7.17
8	4.24	1.78	39.44	0.74	36.32	0.33	37.23	0.71	34.02	0.32	37.94	7.33

Table C.27: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 3 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte	(g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	/ (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	4.24	2.03	43.79	0.74	21.45	0.31	43.89	0.74	21.49	0.31	0	6.70
0.125	4.24	1.90	44.4	0.73	21.44	0.31	43.79	0.73	21.48	0.31	0.02	6.70
0.25	4.24	1.88	45.28	0.78	22.28	0.32	43.35	0.73	21.25	0.31	0.16	6.90
0.5	4.24	1.85	49.20	0.83	24.18	0.35	37.34	0.63	18.90	0.27	2.05	6.90
0.625	4.24	1.84	48.42	0.82	23.83	0.35	39.13	0.66	19.33	0.28	2.83	6.90
0.75	4.24	1.83	46.29	0.78	23.62	0.34	40.20	0.68	19.77	0.29	3.47	7.12
7	4.24	1.81	46.60	0.78	22.74	0.33	41.82	0.72	20.77	0.30	4.10	7.12
1	4.24	1.79	48.10	0.82	23.85	0.35	38.22	0.65	19.00	0.28	7.33	6.73
1.5	4.24	1.79	47.46	0.82	23.70	0.34	38.80	0.68	19.56	0.29	10.05	6.36
2	4.24	1.79	47.03	0.80	23.31	0.34	38.62	0.67	19.38	0.28	12.79	6.86
2.5	4.24	1.79	46.47	0.81	23.40	0.34	38.04	0.66	19.18	0.27	15.84	7.43
3	4.24	1.78	46.00	0.81	23.39	0.34	37.60	0.67	19.36	0.28	18.87	7.09
3.5	4.24	1.78	46.19	0.81	23.70	1.12	37.17	0.66	19.03	0.30	21.85	6.78
4	4.24	1.78	45.88	0.81	23.41	1.05	37.65	0.69	19.63	0.43	22.57	6.78
4.125	4.24	1.78	45.74	0.82	23.42	0.98	38.45	0.69	19.88	0.50	23.24	6.58
4.25	4.24	1.78	45.16	0.79	22.99	0.85	38.18	0.69	19.83	0.56	24.48	6.58
4.625	4.24	1.78	45.47	0.80	23.24	0.82	38.26	0.68	19.76	0.58	25.09	6.58
4.75	4.24	1.78	45.54	0.83	23.63	0.81	39.40	0.68	19.78	0.60	25.65	6.39
5	4.24	1.78	45.12	0.81	23.34	0.76	37.32	0.67	19.34	0.60	26.86	6.39
5.5	4.24	1.78	44.26	0.79	22.94	0.75	37.44	0.68	19.66	0.62	29.23	6.52
6	4.24	1.78	44.31	0.82	23.42	0.75	38.00	0.70	20.21	0.65	31.35	6.65
6.5	4.24	1.78	43.10	0.78	22.73	0.72	38.92	0.71	20.63	0.66	33.11	6.37
7	4.24	1.78	42.71	0.80	22.83	0.74	37.48	0.7	20.15	0.65	34.84	6.09
7.5	4.24	1.78	42.46	0.79	22.90	0.73	38.00	0.73	20.78	0.67	36.36	6.13
8	4.24	1.78	41.51	0.78	22.64	0.72	38.69	0.73	21.24	0.67	37.61	6.18

Table C.28: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 4 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	/ (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	4.24	1.82	44.39	0.75	22.19	0.33	44.42	0.75	22.21	0.33	0	5.35
0.125	4.24	1.82	44.7	0.75	22.17	0.33	44.82	0.77	22.47	0.33	0	5.35
0.25	4.24	1.82	44.24	0.77	21.95	0.32	43.77	0.75	21.81	0.32	0.09	5.67
0.5	4.24	1.81	45.14	0.77	22.37	0.32	41.54	0.73	21.16	0.30	0.78	5.67
0.625	4.24	1.80	45.41	0.78	22.70	0.33	41.84	0.73	21.41	0.32	1.08	5.67
0.75	4.24	1.80	45.15	0.78	22.54	0.33	43.45	0.75	21.81	0.32	1.24	6.08
7	4.24	1.80	44.68	0.79	22.29	0.33	41.98	0.72	21.22	0.31	1.95	6.08
1	4.24	1.79	42.52	0.72	21.39	0.31	43.25	0.76	22.07	0.32	1.95	5.45
1.5	4.24	1.79	42.75	0.73	21.55	0.31	43.12	0.77	22.12	0.33	1.95	4.75
2	4.24	1.78	43.47	0.76	22.13	0.33	43.17	0.76	22.23	0.32	1.95	5.96
2.5	4.24	1.79	42.68	0.77	22.01	0.33	42.85	0.76	22.24	0.33	1.95	7.24
3	4.24	1.79	44.17	0.81	23.00	0.34	40.42	0.73	21.19	0.31	3.16	7.06
3.5	4.86	1.83	46.76	0.84	24.38	0.36	37.09	0.68	20.14	0.29	6.86	6.88
4	4.86	1.84	46.61	0.86	25.13	0.37	38.82	0.71	20.47	0.30	7.80	6.88
4.125	4.86	1.84	46.82	0.85	24.36	0.36	37.64	0.69	19.89	0.29	8.78	6.88
4.25	4.86	1.84	46.87	0.84	24.37	0.36	38.64	0.70	20.43	0.30	10.68	6.88
4.625	4.86	1.84	46.41	0.84	24.45	0.36	37.59	0.68	19.88	0.29	11.67	6.88
4.75	4.86	1.84	46.71	0.88	24.75	0.36	38.85	0.71	20.74	0.31	12.61	6.88
5	4.86	1.84	45.87	0.86	24.42	0.35	39.52	0.74	20.76	0.31	14.29	6.88
5.5	4.86	1.84	45.47	0.84	24.34	0.36	37.99	0.69	20.42	0.30	17.83	6.79
6	4.86	1.84	46.09	0.85	24.84	0.36	37.43	0.70	20.39	0.30	21.53	6.71
6.5	4.86	1.84	46.09	0.87	25.00	0.37	36.47	0.68	19.93	0.29	25.83	6.75
7	4.86	1.84	45.61	0.87	24.98	0.37	35.40	0.68	19.50	0.28	30.65	6.79
7.5	4.86	1.84	45.28	0.87	25.11	0.37	34.96	0.69	19.63	0.29	35.73	7.13
8	4.86	1.85	43.95	0.87	24.53	0.38	35.79	0.70	19.94	0.30	40.51	7.55

Table C.29: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 5 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	/ (A)	0(V)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	4.86	2.28	56.18	2.00	47.97	1.06	56.17	2	49.53	1.06	0	6.39
0.125	4.86	2.26	57.35	1.99	48.64	1.05	57.26	2.05	49.61	1.09	0	6.39
0.25	4.86	2.25	59.31	2.04	49.29	1.07	58.22	2.03	49.66	1.07	0	6.89
0.5	4.86	2.24	64.39	2.19	53.45	1.15	51.79	1.87	44.10	0.98	1.80	6.89
0.625	4.86	2.23	63.59	2.17	52.45	1.14	51.75	1.79	44.17	0.94	2.74	6.89
0.75	4.86	2.23	63.82	2.20	52.17	1.16	53.29	1.91	45.27	1.00	3.58	7.48
7	4.86	2.21	65.52	2.20	53.50	1.16	54.85	1.93	45.95	1.02	5.17	7.48
1	4.86	2.19	65.66	2.22	53.51	1.15	53.30	1.90	45.78	0.99	5.17	7.46
1.5	4.86	2.19	63.17	2.15	51.90	1.14	55.49	1.91	46.22	1.00	8.15	7.43
2	4.86	2.20	63.90	2.18	52.71	1.15	54.57	1.92	45.69	1.00	10.93	7.06
2.5	4.86	2.21	62.87	2.18	52.26	1.14	52.79	1.87	44.00	0.98	14.15	6.75
3	4.86	2.21	63.41	2.19	53.29	1.15	55.00	1.93	46.57	1.01	16.76	6.97
3.5	4.86	2.22	71.09	2.13	49.74	1.09	54.92	1.96	46.74	1.03	19.50	7.19
4	4.86	2.23	78.63	2.17	50.43	1.11	54.82	1.92	46.57	1.01	20.38	7.19
4.125	4.86	2.23	66.83	2.24	53.04	1.15	52.76	1.85	44.53	0.97	21.40	7.19
4.25	4.86	2.22	77.18	2.19	51.67	1.12	55.37	1.91	44.35	0.99	23.49	7.19
4.625	4.86	2.21	72.66	2.23	52.22	1.15	58.32	1.86	43.58	0.96	24.54	7.19
4.75	4.86	2.22	70.38	2.21	53.18	1.15	59.19	1.78	43.18	0.92	24.54	7.19
5	4.86	2.24	69.53	2.25	52.43	1.17	60.09	1.83	43.96	0.94	26.39	7.19
5.5	4.86	2.25	69.77	2.17	52.11	1.13	59.27	1.84	44.15	0.96	29.76	7.14
6	4.86	2.24	68.33	2.15	51.04	1.12	57.69	1.78	42.86	0.93	33.17	7.09
6.5	4.86	2.22	68.74	2.18	51.62	1.13	60.91	1.92	45.87	1.00	35.95	7.35
7	4.86	2.23	68.47	2.20	51.44	1.13	61.33	1.97	46.39	1.03	38.46	7.61
7.5	4.86	2.27	67.29	2.13	50.85	1.11	61.48	1.98	46.74	1.02	40.76	7.64
8	4.86	2.27	66.09	2.13	50.52	1.11	61.56	2.00	47.37	1.04	42.72	7.68

Table C.30: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 6 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	7 (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	<i>х</i> Со	<i>m</i> Cu (g)	(L/h)
0	4.86	1.86	59.07	1.91	47.81	1.01	59.20	1.92	47.91	1.01	0	5.40
0.125	4.86	1.87	59.46	1.94	48.35	1.03	60.08	1.98	49.11	1.05	0	5.40
0.25	4.86	1.87	61.33	2.01	48.83	1.06	60.41	2.19	49.44	1.15	0	6.20
0.5	4.86	1.85	66.99	2.17	54.05	1.14	52.44	1.75	42.99	0.98	2.27	6.20
0.625	4.86	1.84	64.36	2.15	52.70	1.15	54.85	1.85	44.98	0.97	3.10	6.20
0.75	4.86	1.84	61.58	2.03	49.62	1.05	60.03	2.04	49.02	1.07	3.26	7.30
7	4.86	1.83	61.09	2.03	49.76	1.07	61.17	2.05	50.08	1.08	3.26	7.30
1	4.86	1.82	61.95	2.10	50.47	1.11	58.86	2.00	48.48	1.06	4.35	7.28
1.5	4.86	1.81	62.70	2.13	51.72	1.12	55.18	1.91	46.02	1.01	7.22	7.26
2	4.86	1.81	64.54	2.18	53.04	1.15	53.04	1.82	44.32	0.95	10.81	6.65
2.5	4.86	1.81	64.27	2.10	52.15	1.11	53.82	1.83	44.10	0.96	14.13	6.03
3	4.86	1.81	62.61	2.11	52.48	1.12	53.86	1.85	45.43	0.99	17.23	6.52
3.5	4.86	1.82	61.59	4.27	51.93	1.11	50.91	1.75	43.47	0.92	21.30	7.02
4	4.86	1.83	62.55	3.89	51.86	1.12	49.84	1.74	43.71	0.91	22.36	7.02
4.125	4.86	1.82	63.55	3.60	53.10	1.14	51.82	2.20	43.98	0.96	23.37	6.64
4.25	4.86	1.82	62.25	3.44	52.52	1.15	51.64	2.53	44.18	0.95	25.33	6.64
4.625	4.86	1.82	61.51	3.36	52.44	1.14	50.85	2.63	43.93	0.93	26.30	6.64
4.75	4.86	1.82	61.50	3.27	52.27	1.11	52.83	2.70	45.00	0.97	26.30	6.31
5	4.86	1.82	60.44	3.22	51.81	1.12	53.73	2.72	45.81	0.97	27.64	6.31
5.5	4.86	1.82	59.75	3.21	51.72	1.13	52.18	2.78	45.25	0.98	30.25	6.31
6	4.86	1.82	59.47	3.12	51.62	1.10	51.49	2.75	44.27	0.98	32.99	6.31
6.5	4.86	1.81	60.54	3.15	51.92	1.11	50.52	2.69	44.58	0.95	35.71	5.37
7	4.86	1.81	59.84	3.18	52.36	1.12	50.80	2.73	44.15	0.96	38.20	4.62
7.5	4.86	1.81	59.06	3.19	52.16	1.12	51.46	2.79	45.50	0.99	40.37	5.09
8	4.86	1.82	57.70	3.13	50.08	1.09	53.48	2.84	46.85	1.01	41.94	5.58

Table C.31: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 7 in Table A.8.

Time (b) / (A)		Adva	ince ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	7 (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	<i>х</i> Со	<i>m</i> Cu (g)	(L/h)
0	4.86	1.91	57.62	2.04	48.77	1.05	57.82	2.05	48.94	1.05	0	5.82
0.125	4.86	1.92	60.66	2.24	51.24	1.13	53.53	1.98	46.1	1.01	0.43	5.82
0.25	4.86	1.93	61.85	2.16	50.82	1.10	54.84	1.97	46.86	1.00	0.81	6.30
0.5	4.86	1.9.0	65.19	2.15	52.37	1.09	53.73	1.95	45.25	1.00	2.05	6.30
0.625	4.86	1.93	67.15	2.22	52.22	1.13	54.25	1.91	44.80	0.98	2.74	6.30
0.75	4.86	1.93	67.06	2.27	53.23	1.15	53.20	1.84	44.32	0.94	3.61	6.87
7	4.86	1.89	66.86	2.22	53.56	1.12	53.23	1.84	43.82	0.94	5.47	6.87
1	4.86	1.87	67.61	2.29	54.15	1.16	51.61	1.80	42.40	0.91	9.64	6.73
1.5	4.86	1.87	66.98	2.32	54.44	1.14	54.80	1.94	45.16	0.98	13.02	6.61
2	4.86	1.88	67.29	2.34	55.17	1.19	54.12	1.92	44.96	0.99	16.43	6.49
2.5	4.86	1.88	65.48	2.31	54.10	1.17	52.98	1.88	44.37	0.96	19.91	6.35
3	4.86	1.88	65.04	2.23	53.78	1.13	53.64	1.95	45.25	1.00	23.11	6.73
3.5	4.86	1.88	58.92	2.10	71.55	1.07	56.29	2.02	47.37	1.03	26.23	7.11
4	4.86	1.89	59.74	2.11	72.23	1.08	57.25	2.07	48.13	1.06	26.95	7.11
4.125	4.86	1.89	60.34	2.12	72.05	1.09	56.88	2.03	49.06	1.02	27.65	7.24
4.25	4.86	1.89	59.68	2.27	72.49	1.07	56.45	2.08	53.00	1.06	28.96	7.24
4.625	4.86	1.88	60.36	2.13	64.55	1.08	54.77	1.93	57.20	0.99	29.52	7.24
4.75	4.86	1.88	61.26	2.15	61.05	1.10	54.97	1.98	59.90	1.01	30.01	7.38
5	4.86	1.90	61.23	2.24	61.49	1.15	54.53	1.95	58.31	1.00	31.03	7.38
5.5	4.86	1.91	60.50	2.20	62.74	1.13	52.85	1.92	55.77	0.99	33.49	7.54
6	4.86	1.91	60.28	2.19	63.19	1.12	54.63	2.03	57.85	1.04	35.66	7.72
6.5	4.86	1.92	59.65	2.18	63.21	1.12	54.06	1.97	57.18	1.00	37.70	6.96
7	4.86	1.92	59.86	2.16	63.46	1.11	53.77	1.99	57.69	1.01	39.64	6.38
7.5	4.86	1.92	60.45	2.23	63.59	1.14	54.71	2.03	58.81	1.03	41.40	6.58
8	4.86	1.89	59.91	2.17	64.01	1.12	55.57	2.06	59.83	1.05	42.98	6.80

Table C.32: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 8 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	7 (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	<i>х</i> Со	<i>m</i> Cu (g)	(L/h)
0	4.86	1.88	58.41	2.10	50.00	1.11	58.62	2.11	50.18	1.11	0	5.19
0.125	4.86	1.88	60.82	2.16	51.90	1.13	55.79	2.05	48.41	1.07	0.31	5.19
0.25	4.86	1.88	59.71	2.15	51.07	1.10	57.34	2.01	49.95	1.06	0.49	5.64
0.5	4.86	1.86	61.12	2.09	51.39	1.09	59.77	2.14	51.33	1.11	0.49	5.64
0.625	4.86	1.85	61.84	2.16	51.91	1.13	57.90	2.03	50.75	1.07	0.68	5.64
0.75	4.86	1.85	64.09	2.16	52.34	1.13	57.33	2.01	49.30	1.05	1.01	6.14
7	4.86	1.83	65.30	2.30	54.19	1.19	52.75	1.88	45.21	0.98	2.77	6.14
1	4.86	1.81	65.95	2.35	55.65	1.21	51.68	1.80	44.83	0.94	7.24	6.81
1.5	4.86	1.80	66.87	2.29	54.95	1.19	53.49	1.88	45.52	0.98	11.22	7.60
2	4.86	1.79	64.79	2.27	55.06	1.19	53.29	1.84	44.99	0.96	15.21	6.84
2.5	4.86	1.79	64.13	2.32	54.89	1.21	54.09	1.95	46.62	1.01	18.37	6.19
3	4.86	1.79	63.37	2.25	54.48	1.18	53.44	1.95	46.41	1.02	21.38	6.09
3.5	4.86	1.80	62.43	2.26	54.20	3.62	53.65	1.93	46.75	1.02	24.22	6.00
4	4.86	1.80	62.64	2.18	53.11	3.29	53.33	1.94	46.64	1.03	24.91	6.00
4.125	4.86	1.79	62.13	2.24	53.98	3.02	53.91	1.98	47.20	1.33	25.59	6.46
4.25	4.86	1.78	61.60	2.20	53.36	2.57	53.53	1.94	47.26	1.88	26.94	6.46
4.625	4.86	1.78	61.62	2.18	52.77	2.46	53.72	1.96	47.04	2.04	27.59	6.46
4.75	4.86	1.78	60.83	2.18	52.78	2.44	54.70	1.97	47.45	2.12	28.19	6.98
5	4.86	1.79	60.81	2.18	52.37	2.39	54.50	1.98	47.53	2.06	29.33	6.98
5.5	4.86	1.77	61.26	2.24	53.61	2.39	55.48	2.03	49.03	2.15	31.33	7.20
6	4.86	1.78	59.59	2.17	52.38	2.32	54.25	1.99	47.81	2.11	35.38	7.44
6.5	4.86	1.77	59.28	2.14	51.68	2.27	53.76	2.00	48.35	2.04	37.36	7.32
7	4.86	1.77	59.31	2.20	53.15	2.34	55.59	2.04	49.38	2.17	38.96	7.21
7.5	4.86	1.77	59.02	2.19	52.61	2.32	55.11	2.00	48.55	2.14	40.51	7.07
8	4.86	1.77	58.10	2.18	52.46	2.32	53.97	2.02	49.17	2.14	42.06	6.93

Table C.33: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 9 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	rolyte (g	/L)	Cumulative	Q	
(h)	7 (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	4.85	1.88	59.22	2.07	48.34	1.05	58.40	2.08	48.60	1.06	0	6.69
0.125	4.86	1.86	65.67	2.19	53.01	1.11	51.82	1.82	43.39	0.92	1.42	6.69
0.25	4.86	1.86	66.39	2.25	53.02	1.14	51.92	1.85	43.00	0.93	2.88	6.67
0.5	4.86	1.86	66.73	2.32	53.27	1.17	52.65	1.87	43.42	0.95	5.72	6.67
0.625	4.86	1.85	67.00	2.28	53.79	1.16	51.62	1.79	42.68	0.9	7.29	6.67
0.75	4.86	1.84	68.00	2.32	54.28	1.17	50.26	1.76	42.12	0.89	9.02	6.65
7	4.86	1.83	67.39	2.26	53.76	1.15	51.35	1.78	42.24	0.91	9.02	6.65
1	4.86	1.82	66.92	2.26	54.10	1.15	52.81	1.87	43.20	0.95	15.04	6.94
1.5	4.86	1.81	64.37	2.17	52.36	1.11	52.02	1.82	42.33	0.92	21.43	7.28
2	4.86	1.80	62.81	2.23	51.22	1.13	54.79	1.92	45.13	0.96	25.65	7.92
2.5	4.86	1.80	61.92	2.10	50.76	1.06	55.86	1.96	46.14	1.00	29.12	8.66
3	4.86	1.80	60.92	2.13	50.21	1.07	54.81	1.90	45.54	0.96	32.68	8.49
3.5	6.68	1.92	59.03	2.10	49.01	1.05	54.67	1.95	45.76	0.98	35.66	8.32
4	6.68	1.93	59.25	2.14	49.29	1.08	54.45	1.96	45.78	0.99	36.37	8.32
4.125	6.68	1.93	59.15	2.10	49.54	1.06	53.76	1.96	45.19	0.99	37.09	8.41
4.25	6.68	1.93	59.30	2.10	49.63	1.06	55.59	2.00	46.79	1.01	38.24	8.41
4.625	6.68	1.93	59.79	2.13	49.82	1.07	55.47	2.00	47.09	1.01	38.81	8.41
4.75	6.68	1.93	59.75	2.13	50.00	1.07	54.91	1.98	46.47	1.01	39.41	8.51
5	6.68	1.93	58.55	2.04	49.15	1.04	54.58	1.97	46.40	0.99	40.61	8.51
5.5	6.68	1.93	58.05	2.08	49.31	1.05	56.38	2.06	47.92	1.03	42.04	8.51
6	6.68	1.93	57.71	2.10	49.46	1.06	53.83	1.93	46.49	0.98	44.01	8.51
6.5	6.68	1.93	57.37	2.10	49.41	1.06	53.91	2.02	46.86	1.02	45.92	8.05
7	6.68	1.93	56.30	2.05	49.35	1.03	52.84	1.98	46.52	1.00	47.92	7.67
7.5	6.68	1.93	56.47	2.03	49.47	1.03	54.78	2.09	48.60	1.04	49.11	7.46
8	6.68	1.93	55.79	2.13	49.65	1.06	51.79	1.95	46.44	0.99	50.86	7.23

Table C.34: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 10 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	/ (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	6.68	2.07	51.78	4.01	73.09	3.24	51.43	3.99	72.59	3.21	0	5.75
0.125	6.68	2.09	54.39	4.14	75.60	3.35	45.61	3.62	65.54	2.90	1.58	5.75
0.25	6.68	2.08	55.63	4.21	76.85	3.37	42.55	3.39	61.42	2.72	3.79	5.60
0.5	6.68	2.07	54.19	4.04	74.93	3.26	46.11	3.60	65.91	2.89	6.77	5.60
0.625	6.68	2.07	54.60	4.19	75.99	3.37	41.86	3.59	59.97	2.89	8.71	5.60
0.75	6.68	2.06	55.87	4.33	77.82	3.47	45.61	3.61	65.44	2.90	10.53	5.44
7	6.68	2.06	54.17	4.18	76.16	3.35	44.11	3.44	63.30	2.77	14.29	5.44
1	6.68	2.05	51.16	3.96	71.94	3.18	46.41	3.72	67.03	2.98	18.57	6.12
1.5	6.68	2.03	50.95	3.93	72.14	3.15	47.37	3.70	67.92	2.97	21.61	6.91
2	6.68	2.02	51.57	4.07	73.64	3.27	46.26	3.70	66.90	2.97	25.27	6.81
2.5	6.68	2.02	51.55	4.09	74.38	3.3	47.31	3.84	69.51	3.08	28.53	6.72
3	6.68	2.01	49.89	3.99	72.39	3.19	44.05	3.57	64.78	2.85	32.90	6.72
3.5	6.68	2.01	45.69	4.04	73.47	3.24	40.37	3.56	64.57	2.67	38.29	6.72
4	6.68	2.02	42.56	4.10	74.39	3.31	37.07	3.59	65.17	2.79	39.66	6.72
4.125	6.68	2.03	41.04	4.14	75.16	3.34	41.09	3.62	65.67	2.91	40.82	6.51
4.25	6.68	2.03	40.02	4.00	73.72	3.22	39.41	3.65	66.66	2.93	42.77	6.51
4.625	6.68	2.03	39.90	3.95	72.99	3.18	38.72	3.67	66.42	2.96	43.65	6.51
4.75	6.68	2.03	40.12	4.00	73.38	3.24	38.36	3.64	66.35	2.93	44.51	6.30
5	6.68	2.03	40.12	3.99	73.23	3.23	37.49	3.67	66.67	2.95	46.10	6.30
5.5	6.68	2.02	40.13	3.99	73.11	3.22	37.50	3.71	68.03	3.00	48.84	6.35
6	6.68	2.02	40.22	3.99	73.14	3.22	37.32	3.75	68.41	3.02	51.36	6.41
6.5	6.68	2.03	38.75	3.92	71.06	3.16	37.09	3.70	68.59	2.98	53.49	6.64
7	6.68	2.03	37.73	3.74	69.13	3.01	36.77	3.79	68.97	3.05	55.01	6.87
7.5	6.68	2.03	38.58	3.98	72.41	3.21	37.01	3.74	67.89	3.01	56.85	6.87
8	6.68	2.04	38.36	4.03	72.74	3.25	36.15	3.84	69.61	3.08	58.56	6.87

Table C.35: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 11 in Table A.8.

Time (h) / (A)		Adva	nce ele	ctrolyte (	g/L)	Spe	nt elect	r <b>olyte (</b> g	/L)	Cumulative	Q	
(h)	7 (A)	0(v)	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	<i>х</i> Со	<i>m</i> Cu (g)	(L/h)
0	6.67	2.14	53.74	4.12	76.44	3.32	53.23	4.08	75.72	3.29	0	4.71
0.125	6.67	2.01	49.66	3.82	69.88	3.07	58.75	4.70	84.81	3.78	0	4.71
0.25	6.67	1.98	54.80	4.29	78.16	3.47	50.47	4.02	73.22	3.22	1.26	5.13
0.5	6.67	1.87	51.81	4.04	74.23	3.24	54.00	4.34	79.32	3.50	1.26	5.13
0.625	6.67	1.95	54.45	4.31	78.62	3.49	48.59	3.95	70.67	3.17	2.96	5.13
0.75	6.67	1.95	55.19	4.38	79.85	3.51	48.86	4.05	71.33	3.25	4.40	5.57
7	6.67	1.94	55.41	4.56	79.41	3.65	48.31	4.00	70.95	3.21	4.41	5.57
1	6.67	1.92	54.96	4.42	79.81	3.55	46.56	3.85	68.79	3.09	11.54	6.22
1.5	6.67	1.90	55.04	4.51	81.06	3.62	47.68	3.98	71.31	3.19	17.42	7.04
2	6.67	1.89	54.01	4.31	79.66	3.45	49.00	4.03	71.55	3.23	22.02	7.01
2.5	6.67	1.89	53.72	4.49	80.66	3.59	46.70	3.98	71.36	3.20	22.02	6.99
3	6.67	1.89	52.50	4.34	80.26	3.48	46.88	4.01	71.23	3.22	27.22	7.53
3.5	6.67	1.89	50.78	2.55	79.09	3.53	46.84	3.88	72.36	3.21	32.02	8.17
4	6.67	1.91	50.75	2.28	78.79	3.45	46.42	3.57	72.71	3.25	33.08	8.17
4.125	6.67	1.92	50.06	2.34	78.56	3.44	45.87	3.28	71.58	3.16	34.11	7.43
4.25	6.67	1.91	50.27	2.57	78.77	3.44	45.42	3.03	71.82	3.24	35.99	7.43
4.625	6.67	1.91	50.50	2.70	79.22	3.51	46.60	3.00	73.20	3.29	36.84	7.43
4.75	6.67	1.90	50.53	2.71	79.30	3.48	45.87	2.80	71.37	3.15	37.72	6.82
5	6.67	1.90	49.72	2.73	77.50	3.43	45.40	2.73	71.50	3.18	39.37	6.82
5.5	6.67	1.89	49.48	2.74	77.08	3.37	45.99	2.68	72.38	3.21	42.15	7.50
6	6.67	1.88	48.78	2.75	76.41	3.36	44.91	2.61	71.25	3.16	45.42	8.25
6.5	6.67	1.89	48.87	2.96	77.27	3.39	44.11	2.59	71.41	3.14	48.68	6.90
7	6.67	1.89	48.71	2.81	77.04	3.43	43.04	2.60	70.42	3.16	51.91	5.77
7.5	6.67	1.90	48.05	2.81	77.79	3.48	42.04	2.53	69.40	3.08	55.34	5.57
8	6.67	1.90	47.90	2.82	77.88	3.43	40.94	2.51	68.64	3.06	59.02	5.39

Table C.36: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 12 in Table A.8.

Time (h)	/ (A)	<i>U</i> (V)	Advance electrolyte (g/L)				Spe	nt elect	Cumulative	Q		
			<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	6.69	2.10	47.40	3.97	72.07	3.18	47.55	3.98	72.3	3.19	0	4.34
0.125	6.69	2.16	48.64	4.10	74.1	3.28	45.71	3.90	70.52	3.13	0.72	4.34
0.25	6.69	2.14	49.33	4.17	74.92	3.36	45.82	3.99	71.71	3.21	1.49	5.14
0.5	6.69	2.11	49.18	4.12	74.66	3.30	46.88	4.01	72.42	3.21	2.73	5.14
0.625	6.69	2.10	50.36	4.21	76.45	3.37	44.92	3.85	69.73	3.09	3.98	5.14
0.75	6.69	2.09	51.07	4.37	78.10	3.47	40.98	3.53	63.86	2.83	7.04	6.20
7	6.69	2.07	51.27	4.39	78.76	3.51	44.41	3.87	69.62	3.10	8.45	6.20
1	6.69	2.05	49.83	4.26	76.86	3.42	45.41	3.93	71.25	3.15	8.45	6.14
1.5	6.69	2.03	49.29	4.24	76.87	3.41	48.79	4.26	77.04	3.41	8.45	6.07
2	6.69	2.03	48.22	4.21	75.98	3.38	47.18	4.24	75.82	3.40	8.45	6.59
2.5	6.69	2.02	48.97	4.36	78.05	3.49	48.39	4.36	78.04	3.48	8.45	7.14
3	6.69	2.02	49.57	4.33	79.51	3.46	48.98	4.31	79.33	3.44	8.45	6.91
3.5	6.69	2.02	50.83	4.70	73.37	3.75	44.10	3.97	71.85	3.18	14.39	6.70
4	6.69	2.02	51.68	4.32	64.84	3.46	45.5	4.05	69.11	3.24	15.57	6.70
4.125	6.69	2.02	54.60	4.58	67.55	3.65	48.22	4.36	70.59	3.46	16.52	6.54
4.25	6.69	2.02	54.88	4.65	65.15	3.71	47.82	4.25	66.25	3.38	19.04	6.54
4.625	6.69	2.01	52.62	4.42	62.37	3.53	47.12	4.20	63.78	3.35	20.30	6.54
4.75	6.69	2.01	55.31	4.72	66.14	3.75	48.89	4.23	64.86	3.38	21.49	6.36
5	6.69	2.01	53.99	4.53	64.89	3.61	48.75	4.26	63.81	3.39	23.91	6.36
5.5	6.69	2.00	53.07	4.52	65.70	3.62	48.95	4.25	63.07	3.39	28.12	6.22
6	6.69	2.00	55.47	4.81	69.88	3.83	50.04	4.30	64.04	3.44	32.84	6.11
6.5	6.69	2.00	53.18	4.73	68.22	3.77	49.25	4.35	63.75	3.46	38.27	6.14
7	6.69	2.00	52.76	4.57	67.00	3.64	47.25	4.21	61.94	3.36	43.84	6.17
7.5	6.69	2.00	55.64	4.77	71.42	3.82	46.11	4.23	61.25	3.38	51.98	6.14
8	6.69	2.00	49.53	4.43	64.62	3.54	47.47	3.96	62.89	3.17	57.99	6.11

Table C.37: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 13 in Table A.8.

Time (h)	/ (A)	<i>ม</i> (v)	Advance electrolyte (g/L)			Spe	nt elect	r <b>olyte (</b> g	Cumulative	Q		
			<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хCo	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	6.66	2.11	45.01	4.06	71.44	3.18	44.71	4.03	73.53	3.16	0	5.14
0.125	6.66	2.21	45.29	4.12	74.34	3.22	42.88	4.09	70.86	3.20	0.51	5.14
0.25	6.66	2.19	45.32	4.08	72.17	3.18	44.68	4.16	73.66	3.25	0.51	5.35
0.5	6.66	2.14	48.29	4.41	77.48	3.45	40.56	3.78	66.41	2.95	2.91	5.35
0.625	6.66	2.12	48.35	4.43	77.69	3.45	40.90	3.88	67.23	3.02	4.12	5.35
0.75	6.66	2.11	46.60	4.25	78.00	3.32	41.12	3.88	67.59	3.03	5.25	5.57
7	6.66	2.08	46.87	4.29	75.53	3.35	42.75	4.02	70.35	3.15	6.50	5.57
1	6.66	2.06	47.25	4.54	77.37	3.49	40.77	3.89	67.62	3.03	6.50	5.55
1.5	6.66	2.04	47.63	4.53	78.60	3.54	38.22	3.74	65.48	2.92	12.31	5.53
2	6.66	2.03	47.20	4.52	78.71	3.53	38.97	3.74	65.90	2.92	17.70	5.49
2.5	6.66	2.03	46.54	4.52	78.66	3.52	39.65	3.89	67.56	3.02	22.76	5.47
3	6.66	2.03	45.75	4.54	78.10	3.54	38.04	3.78	65.78	2.94	28.13	5.55
3.5	6.66	2.02	43.26	4.38	76.41	2.23	38.15	3.85	67.04	2.91	32.55	5.62
4	6.66	2.03	42.91	4.34	76.30	1.93	38.04	3.79	66.72	2.66	33.58	5.62
4.125	6.66	2.04	43.20	4.41	76.71	1.95	38.43	3.89	68.00	2.64	34.54	5.94
4.25	6.66	2.03	41.98	4.23	74.86	1.95	37.06	3.84	66.76	2.40	36.41	5.94
4.625	6.66	2.03	41.29	4.20	73.61	1.97	37.10	3.81	66.67	2.28	37.28	5.94
4.75	6.66	2.03	42.12	4.30	75.06	2.03	37.20	3.92	67.43	2.27	38.12	6.27
5	6.66	2.02	41.05	4.22	73.61	2.04	36.18	3.77	66.07	2.11	39.91	6.27
5.5	6.66	2.02	41.11	4.24	74.28	2.14	35.54	3.76	65.90	1.97	43.59	5.96
6	6.66	2.01	40.80	4.20	74.12	2.14	36.17	3.87	66.85	2.02	46.89	5.65
6.5	6.66	2.01	40.45	3.93	73.87	2.02	35.54	3.70	66.25	1.91	50.26	6.07
7	6.66	2.01	40.17	4.26	73.75	2.19	35.34	3.84	66.21	1.97	53.83	6.50
7.5	6.66	2.01	39.14	4.10	72.25	2.10	34.16	3.72	65.11	1.90	57.70	6.54
8	6.66	2.01	37.99	4.12	71.94	2.11	34.44	3.76	66.05	1.91	61.16	6.59

Table C.38: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 14 in Table A.8.

Time (h)	/ (A)	<i>ม</i> (v)	Advance electrolyte (g/L)				Spe	nt elect	Cumulative	Q		
			<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>x</i> Cu	<i>x</i> Fe	<i>x</i> Ni	хСо	<i>m</i> Cu (g)	(L/h)
0	6.67	2.08	49.67	4.05	73.79	3.27	49.84	4.07	74.04	3.28	0	5.75
0.125	6.67	2.11	51.23	4.17	75.58	3.35	47.35	3.71	69.63	3.01	0.56	5.75
0.25	6.66	2.09	50.93	3.93	72.39	3.15	44.81	3.61	66.82	2.91	1.28	5.63
0.5	6.66	2.12	50.85	3.98	69.49	3.06	49.38	3.97	72.74	3.20	1.28	5.63
0.625	6.66	2.11	50.65	4.02	69.01	2.99	49.54	3.96	72.36	3.18	1.28	5.63
0.75	6.66	2.12	53.63	3.92	71.64	3.15	49.70	4.00	73.14	3.22	1.28	5.50
7	6.66	2.11	55.31	4.17	75.62	3.35	48.58	3.81	70.47	3.06	2.32	5.50
1	6.66	2.12	55.61	4.15	76.77	3.35	47.75	3.72	68.33	2.99	6.23	6.08
1.5	6.66	2.12	55.64	4.19	76.62	3.38	49.38	3.89	70.53	3.12	9.24	6.65
2	6.66	2.11	55.82	4.24	77.37	3.39	47.19	3.75	67.23	2.97	14.04	6.94
2.5	6.66	2.11	54.90	4.17	75.72	3.34	47.22	3.69	67.02	2.95	18.64	7.26
3	6.66	2.09	53.39	4.15	75.32	3.31	49.84	3.84	70.48	3.08	21.36	6.97
3.5	4.84	1.92	53.22	4.08	74.44	3.27	51.22	4.04	72.70	3.23	22.64	6.70
4	4.84	1.93	53.58	4.06	74.33	3.25	49.83	3.84	70.44	3.08	23.04	6.70
4.125	4.84	1.94	54.02	4.07	74.19	3.26	49.67	3.80	70.14	3.04	23.48	6.96
4.25	4.84	1.93	54.38	4.13	75.14	3.30	49.57	3.78	69.84	3.02	24.63	6.96
4.625	4.84	1.94	53.74	4.10	74.76	3.28	46.35	3.66	65.65	2.95	25.38	6.96
4.75	4.84	1.97	55.14	4.12	75.15	3.31	43.83	3.46	67.30	2.99	26.30	7.24
5	4.84	1.96	54.83	4.14	75.78	3.31	48.53	3.74	68.32	3.00	28.06	7.24
5.5	4.84	1.96	55.03	4.15	75.67	3.32	50.22	3.95	71.05	3.18	30.78	7.19
6	4.84	1.96	54.61	4.12	75.09	3.30	50.49	3.85	70.48	3.07	33.27	7.14
6.5	4.84	1.96	54.49	4.14	75.11	3.31	50.16	3.85	70.13	3.09	35.71	7.03
7	4.84	1.96	54.72	4.15	75.35	3.33	45.99	3.52	64.06	2.82	39.66	6.92
7.5	4.84	1.96	55.80	4.24	76.77	3.40	47.53	3.67	66.55	2.93	43.84	6.66
8	4.84	1.96	56.28	4.29	77.36	3.42	42.47	3.30	59.52	2.63	49.90	6.42

Table C.39: Validated dynamic electrowinning data for the bench-scale electrowinning experiment corresponding to Run 15 in Table A.8.



Figure C.6: Comparison between raw and validated cumulative mass copper plated for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure C.6 (continued)



Figure C.6 (continued)



Figure C.7: Comparison between raw and validated copper plating rate for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure C.7 (continued)



Figure C.7 (continued)



Figure C.8: Comparison between raw and validated advance and spent electrolyte cobalt concentrations for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure C.8 (continued)



Figure C.8 (continued)



Figure C.9: Comparison between raw and validated advance and spent electrolyte copper concentrations for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure C.9 (continued)



Figure C.9 (continued)



Figure C.10: Comparison between raw and validated advance and spent electrolyte iron concentrations for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure C.10 (continued)



Figure C.10 (continued)



Figure C.11: Comparison between raw and validated advance and spent electrolyte nickel concentrations for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure C.11 (continued)


Figure C.11 (continued)



Figure C.12: Comparison between raw and validated flow rate for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure C.12 (continued)



Figure C.12 (continued)

### C.2 SAMPLE CALCULATIONS

#### C.2.1 Bench-Scale Electrowinning Experiments Uncertainty

### Copper plating rate uncertainty

The selected experimental design for the bench-scale electrowinning experiments resulted in three sets of five experiments conducted at similar base conditions (Table A.8). The conditions at the first four hours, before the respective disturbances were induced, were, therefore, identical for each set (containing five experiments). Consequently, the uncertainty associated with the calculated copper plating rates could be quantified. Upper and lower uncertainty limits were determined as the final reconciled copper plating rate at the respective sampling times,  $\pm$  one standard deviation. The average standard deviation for the sampling times for which repeats were available (up to four hours into the eight hour runs) were used for the remainder of the sampling times in the respective runs.

It was elected to quantify the uncertainty associated with the final reconciled copper plating rate instead of the measured advance and spent electrolyte copper concentrations, and subsequently propagating the error to the copper plating rate. This method was used as an attempt to account for deviations inserted via the preprocessing and reconciliation of data.

The standard deviation was first calculated, at each individual sampling time up to t = 3.5 h, for the copper plating rates that formed part of a set (Equation C.1). The standard deviation for the remaining sampling times was taken as the average of the calculated standard deviations for t = 0 h to t = 3.5 h. Following, lower and upper uncertainty limits were calculated (Equation C.2 and Equation C.3, respectively). Table C.40 gives an example of the calculated standard deviations for the copper plating rates, for the five experiments forming the first set.

$$s_{P_{Cu_t}} = \sqrt{\frac{\sum_{i=1}^{5} (P_{Cu_{t,r}})}{4}}$$
 [C.1]

$$L_{\text{upper}} = P_{\text{Cu}_{t,r}} + s_{P_{\text{Cu}_t}}$$
 [ C.2 ]

$$L_{\text{lower}} = P_{\text{Cu}_{t,r}} - s_{P_{\text{Cu}_t}}$$
 [C.3]

where s is the sample standard deviation,  $P_{Cu}$  is the copper plating rate (g/s), t is the time (h), r is the experiment number, and L is the uncertainty limit.

Time (h)			aDC:: (a/a)			
Time (n)	Run 1	Run 2	Run 3	Run 4	Run 5	sPCu (g/s)
0	1.85 × 10 <sup>-8</sup>	1.97 × 10 <sup>-7</sup>	1.98 × 10 <sup>-7</sup>	1.98 × 10 <sup>-7</sup>	1.78 × 10 <sup>-8</sup>	9.82 × 10 <sup>-8</sup>
0.125	5.78 × 10 <sup>-5</sup>	$4.44 \times 10^{-7}$	1.72 × 10 <sup>-3</sup>	3.60 × 10 <sup>-5</sup>	1.96 × 10 <sup>-7</sup>	$7.58 \times 10^{-4}$
0.25	4.45 × 10 <sup>-7</sup>	3.66 × 10 <sup>−8</sup>	6.94 × 10 <sup>-4</sup>	3.16 × 10 <sup>-4</sup>	$2.08 \times 10^{-4}$	2.86 × 10 <sup>-4</sup>
0.5	3.65 × 10 <sup>-4</sup>	7.30 × 10 <sup>-4</sup>	9.97 × 10⁻⁴	2.10 × 10 <sup>-3</sup>	7.68 × 10 <sup>-4</sup>	6.58 × 10 <sup>-4</sup>
0.625	5.62 × 10 <sup>-4</sup>	1.69 × 10 <sup>-3</sup>	8.11 × 10 <sup>-4</sup>	1.75 × 10⁻³	$6.49 \times 10^{-4}$	$5.81 \times 10^{-4}$
0.75	$4.90 \times 10^{-4}$	8.82 × 10 <sup>-4</sup>	9.75 × 10 <sup>-4</sup>	1.43 × 10 <sup>-3</sup>	3.67 × 10 <sup>-4</sup>	$4.21 \times 10^{-4}$
1	3.17 × 10 <sup>-4</sup>	1.38 × 10 <sup>-3</sup>	1.83 × 10 <sup>-3</sup>	6.96 × 10 <sup>-4</sup>	7.82 × 10 <sup>-4</sup>	$6.00 \times 10^{-4}$
1.5	7.55 × 10 <sup>-4</sup>	7.33 × 10 <sup>-4</sup>	2.54 × 10 <sup>-3</sup>	1.79 × 10 <sup>-3</sup>	8.56 × 10 <sup>−8</sup>	1.00 × 10 <sup>-3</sup>
2	$9.48 \times 10^{-4}$	1.52 × 10 <sup>-3</sup>	1.74 × 10 <sup>-3</sup>	1.51 × 10 <sup>-3</sup>	1.97 × 10 <sup>-7</sup>	$7.04 \times 10^{-4}$
2.5	1.24 × 10 <sup>-3</sup>	$2.02 \times 10^{-2}$	$1.60 \times 10^{-3}$	1.52 × 10 <sup>-3</sup>	8.61 × 10 <sup>-8</sup>	$7.67 \times 10^{-4}$
3	8.77 × 10 <sup>-4</sup>	1.31 × 10 <sup>-2</sup>	$1.64 \times 10^{-3}$	1.69 × 10 <sup>-3</sup>	$4.44 \times 10^{-7}$	$6.98 \times 10^{-4}$
3.5	7.09 × 10 <sup>-4</sup>	1.90 × 10 <sup>-3</sup>	1.63 × 10 <sup>-3</sup>	1.68 × 10 <sup>-3</sup>	$6.72 \times 10^{-4}$	5.81 × 10 <sup>-4</sup>
Average						$5.88 \times 10^{-4}$

Table C.40: Calculated standard deviations of the copper plating rate for the bench-scale electrowinning experiments corresponding to Run 1 to Run 5 in Table A.8.

#### SEC uncertainty

The quantified error in the copper plating rate was propagated through to the calculation of the SEC, but not the current efficiency. It was not possible to propagate the error to the current efficiency as it was calculated using the cumulative mass copper plated, and not the instantaneous copper plating rate, as was the SEC. Equation C.4, which is a manipulated form of Equation 2.25, was used to calculate the SEC. The previously calculated standard deviations for the copper plating rates were propagated to the SEC using Equation C.5. The upper and lower uncertainty limits were calculated as above (Equation C.2 and Equation C.3, respectively). Table C.41 gives an example of the calculated standard deviations for the SEC, for the five experiments forming the first set.

$$SEC = \frac{IU}{P_{Cu_{t,r}}}$$
[C.4]

$$s_{\text{SEC}_{t,r}} = \text{SEC}_{t,r} \sqrt{\left(\frac{s_I}{I}\right)^2 + \left(\frac{s_U}{U}\right)^2 + \left(\frac{s_{P_{\text{Cu}_t}}}{P_{\text{Cu}_t}}\right)^2} \qquad [C.5]$$

where  $s_I$  and  $s_{II}$  were taken as 0.

Time		SEC (I	«Wh/t)				sSEC (	kWh/t)		
(h)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 1	Run 2	Run 3	Run 4	Run 5
0	1.17 × 10 <sup>8</sup>	1.07 × 10 <sup>7</sup>	1.10 × 10 <sup>7</sup>	1.21 × 10 <sup>7</sup>	1.20 × 10 <sup>8</sup>	6.21 × 10 <sup>8</sup>	5.34 × 10 <sup>6</sup>	5.45 × 10 <sup>6</sup>	6.00 × 10 <sup>6</sup>	6.64 × 10 <sup>8</sup>
0.125	3.73 × 104	4.70 × 10 <sup>6</sup>	1248	6.22 × 10 <sup>4</sup>	1.09 × 10 <sup>7</sup>	4.90 × 10⁵	8.02 × 10 <sup>9</sup>	551	1.31 × 10 <sup>6</sup>	4.21 × 10 <sup>10</sup>
0.25	4.84 × 10 <sup>6</sup>	5.70 × 10 <sup>7</sup>	3073	7008	1.03 × 104	3.11 × 10 <sup>9</sup>	4.46 × 10 <sup>11</sup>	1268	6347	1.42 × 104
0.5	5910	2841	2127	1039	2775	1.66 × 104	2563	1404	326	2377
0.625	3813	1219	2599	1238	3266	3940	418	1861	411	2921
0.75	4398	2323	2163	1511	5781	3778	1108	934	446	6638
1	6735	1490	1144	3061	2710	1.28 × 104	650	375	2638	2079
1.5	2808	2781	820	1175	2.46 × 10 <sup>7</sup>	3723	3802	323	655	2.87 × 10 <sup>11</sup>
2	2225	1333	1197	1395	1.07 × 10 <sup>7</sup>	1652	617	483	650	3.82 × 10 <sup>10</sup>
2.5	1712	1001	1301	1386	2.43 × 10 <sup>7</sup>	1061	380	623	699	2.16 × 10 <sup>11</sup>
3	2418	1546	1270	1244	4.75 × 10 <sup>6</sup>	1926	824	540	513	7.47 × 10 <sup>9</sup>
3.5	2992	1069	1278	1247	3136	2454	328	455	431	2711

Table C.41: Calculated standard deviations of the SEC for the bench-scale electrowinning experiments corresponding to Run 1 to Run 5 in Table A.8.

# APPENDIX D MODEL RESULTS

Appendix D provides additional information pertaining to the model-predicted results for the four datasets used in this project. The actual values, model-predicted values, and applicable model error terms are given for the steady-state experimental dataset (Section D.1), steady-state industrial dataset (Section D.2), dynamic experimental datasets (Section D.3), and dynamic industrial dataset (Section D.4). A summary of the statistical analysis for the various regression models is also included (Section D.5).

## D.1 STEADY-STATE EXPERIMENTAL MODEL PREDICTIONS

Table D.1: Comparison between actual and model-predicted potential and spent electrolyte copper concentration for the steady-state experimental data generated by Tucker (2019).

Dura		Potential (V)		Spent electrolyte Cu concentration (g/L)			
Kun	Actual	Predicted	Error (%)	Actual	Predicted	Error (%)	
1	2.0	2.1	3.8	50.3	51.4	2.1	
2	2.1	2.1	1.0	53.7	52.4	2.4	
3	2.1	2.1	1.6	49.4	50.3	1.8	
4	2.1	2.1	2.2	29.6	28.6	3.4	
5	1.9	1.9	2.3	50.8	50.6	0.4	
6	2.0	2.1	6.6	50.7	53.7	5.9	
7	1.9	1.8	2.9	31.9	34.4	8.0	
8	2.0	2.1	2.0	31.0	33.6	8.5	
9	1.9	1.9	1.6	48.2	53.7	11.4	
10	2.1	2.1	1.3	29.8	28.9	3.0	
11	1.9	1.9	2.1	52.3	53.9	3.0	
12	2.1	2.1	1.2	31.2	30.0	3.8	
13	1.9	1.9	1.4	52.0	53.1	2.1	
14	1.9	1.8	2.8	27.1	31.0	14.4	
15	1.9	1.9	2.8	33.7	34.5	2.4	
16	1.9	1.8	2.8	33.9	35.2	3.8	
17	2.0	2.1	3.6	50.1	51.0	1.8	
18	2.1	2.1	1.2	41.2	50.7	23.0	
19	2.1	2.1	0.4	31.2	31.6	1.3	

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Run		Potential (V)		Spent electrolyte Cu concentration (g/L)			
Kun	Actual	Predicted	Error (%)	Actual	Predicted	Error (%)	
20	1.9	1.9	2.1	40.7	50.2	23.3	
21	2.0	2.1	3.2	29.7	31.7	6.7	
22	1.9	1.9	2.3	51.4	49.1	4.5	
23	2.0	2.0	1.5	31.2	33.3	6.8	
24	1.9	1.9	2.1	32.4	30.7	5.1	

Table D.2: Comparison between actual and model-predicted KPIs for the steady-state experimental data generated by Tucker (2019).

	Curi	Current efficiency (%)			SEC (kWh/t)		Cu plating rate (g/s/m <sup>2</sup> )		
Run	Actual	Predicted	MAPE (%)	Actual	Predicted	MAPE (%)	Actual	Predicted	MAPE (%)
1	90.7	92.5	2.1	1860.9	1888.9	1.5	0.0965	0.0988	2.3
2	91.0	98.0	7.8	1947.3	1787.2	8.2	0.0968	0.1043	7.8
3	91.3	92.5	1.4	1903.7	1904.1	0	0.0970	0.0985	1.6
4	90.3	92.6	2.5	1961.4	1868.1	4.8	0.0961	0.0987	2.7
5	87.7	89.1	1.6	1827.9	1751.1	4.2	0.0634	0.0647	2.0
6	97.2	98.2	1.1	1736.2	1829.2	5.4	0.1088	0.1100	1.1
7	86.9	89.0	2.5	1845.3	1742.0	5.6	0.0627	0.0645	2.9
8	96.1	98.1	2.1	1773.2	1769.9	0.2	0.1023	0.1046	2.2
9	87.6	89.0	1.6	1829.0	1764.7	3.5	0.0632	0.0644	2.0
10	89.9	92.6	3.0	1970.9	1884.5	4.4	0.0956	0.0987	3.2
11	94.3	97.1	3.0	1699.0	1612.9	5.1	0.0678	0.0699	3.1
12	95.1	98.1	3.1	1818.3	1783.2	1.9	0.1012	0.1044	3.2
13	94.4	97.2	2.9	1697.8	1625.3	4.3	0.0683	0.0703	3.0
14	95.0	97.1	2.2	1686.9	1603.2	5.0	0.0685	0.0701	2.3
15	85.9	88.6	3.2	1875.8	1760.2	6.2	0.0620	0.0643	3.6
16	94.9	96.9	2.1	1688.9	1606.1	4.9	0.0667	0.0681	2.2
17	97.8	99.5	1.8	1725.8	1755.3	1.7	0.1030	0.1049	1.8
18	97.8	99.9	2.1	1784.8	1769.7	0.8	0.1042	0.1064	2.1
19	99.0	100.0	0.9	1771.7	1762.6	0.5	0.1109	0.1119	0.9
20	97.9	100.0	2.1	1637.1	1568.5	4.2	0.0706	0.0721	2.1
21	98.3	99.5	1.3	1725.7	1758.9	1.9	0.1044	0.1057	1.3

	Current efficiency (%)			SEC (kWh/t)			Cu plating rate (g/s/m <sup>2</sup> )		
Run	Actual	Predicted	MAPE (%)	Actual	Predicted	MAPE (%)	Actual	Predicted	MAPE (%)
22	98.5	99.3	0.8	1626.8	1576.4	3.1	0.0692	0.0698	0.8
23	99.1	99.7	0.7	1703.1	1666.2	2.2	0.0898	0.0904	0.7
24	97.4	99.3	1.9	1645.0	1580.3	3.9	0.0704	0.0717	1.9

## D.2 STEADY-STATE INDUSTRIAL MODEL PREDICTIONS

Table D.3: Comparison between actual and model-predicted potential and spent electrolyte copper concentration for the ten steady-state industrial validation runs.

Run		Potential (V)		Spent electrolyte Cu concentration (g/L)			
Kun	Actual	Predicted	Error (%)	Actual	Predicted	Error (%)	
16	1.5	1.4	8.4	19.7	20.3	3.1	
18	1.6	1.5	6.2	18.5	19.0	2.7	
26	1.6	1.9	14.3	27.5	29.0	5.2	
32	1.6	1.7	3.0	23	24.2	5.4	
40	1.6	2.0	20.3	28.1	29.1	3.5	
50	1.6	1.9	18.8	31.8	33.0	3.6	
61	1.6	1.9	19.4	23.3	23.9	2.6	
74	1.6	2.0	27.6	30.4	31.2	2.5	
91	1.6	1.9	13.9	21.1	21.5	2.0	
93	1.6	1.5	7.4	18.2	19.0	4.6	

Table D.4: Comparison between actual and model-predicted KPIs for the ten steady-state industrial validation runs.

	Current efficiency (%)			SEC (kWh/t)			Cu plating rate (g/s/m <sup>2</sup> )		
Run	Actual	Predicted	MAPE (%)	Actual	Predicted	MAPE (%)	Actual	Predicted	MAPE (%)
16	86.2	89.5	3.9	1299.2	1317.2	1.4	0.0103	0.0107	3.9
18	89.7	90.9	1.4	1308.6	1383.8	5.7	0.0137	0.0139	1.4
26	95.1	90.3	5.0	1284.4	1757.1	36.8	0.0303	0.0288	4.9
32	94.1	88.8	5.7	1299.1	1612.6	24.1	0.0225	0.0212	5.6
40	94.5	94.0	0.5	1269.4	1750.0	37.9	0.0338	0.0337	0.5
50	92.9	95.3	2.6	1250.6	1658.1	32.6	0.0296	0.0303	2.6
61	94.6	96.1	1.7	1277.8	1710.1	33.8	0.0338	0.0344	1.7
74	93.8	96.7	3.1	1251.4	1771.2	41.5	0.0373	0.0385	3.1
91	94.2	96.5	2.5	1285.6	1628.2	26.6	0.0300	0.0307	2.5
93	88.7	92.6	4.4	1302.5	1323.9	1.6	0.0123	0.0129	4.4

## D.3 DYNAMIC EXPERIMENTAL MODEL PREDICTIONS

## **D.3.1** Screening Experiments

Table D.5: Comparison between actual and model-predicted KPIs, generated at input conditions specified in Table A.6, for the screening experiments. The grey shading highlights the validation runs. Start-up period included.

Dura	Current e	efficiency	SE	EC	Cu plating rate		
Kun	nRMSE (%)	MAPE (%)	nRMSE (%)	MAPE (%)	nRMSE (%)	MAPE (%)	
1	3.8	3.7	17.2	17.2	20.2	3.4	
2	11.8	11.3	50.9	50.4	20.2	9.8	
3	7.5	7.5	35.8	36.3	20.4	7.2	
4	8.6	8.5	46.1	46.3	20.6	8.3	
5	0.6	0.4	27.3	27.4	20.6	0.2	
6	0.8	0.8	31.3	31.4	20.6	0.7	
7	5.7	5.6	15.4	13.2	20	4.9	
8	8.3	8.1	45.1	46.2	20.2	7.5	
9	53.9	270.6	219.3	44.3	53.7	272.4	
10	81.7	59.4	81.8	24.3	72.2	60.1	
11	27.3	24.8	79.6	46.2	31.9	28.2	
12	66.4	16.9	59.5	68.8	63.7	16.7	
13	51.7	62.9	64.4	33.9	57.6	64.7	
14	18.6	17.4	16.3	13.6	30	15.7	
15	44.1	1562.1	337.2	26.7	44.7	1564.4	
16	342.7	1676.8	352.6	57.1	343.1	1468.9	
17	11.3	7.8	21.8	21.3	30.3	19.3	
18	64.4	587.3	320	27.5	75.1	598.9	
19	38.6	14.7	29.2	26.5	41.6	23.8	
20	56	212.5	269.2	18.5	51.4	216.7	
21	86.9	292.6	186.1	32.6	90.8	308.2	
22	44.7	28.3	64.5	70.6	44.4	28.5	
23	120.5	34.4	25.9	16.9	95.2	43.4	
24	22.7	23.7	25.9	17.3	30.7	25.9	



Figure D.1: Comparison between actual and model-predicted copper plating rate for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure D.1 (continued)



Figure D.1 (continued)



Figure D.1 (continued)



Figure D.2: Comparison between actual and model-predicted current efficiency for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure D.2 (continued)



Figure D.2 (continued)



Figure D.2 (continued)



Figure D.3: Comparison between actual and model-predicted SEC for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure D.3 (continued)



Figure D.3 (continued)



Figure D.3 (continued)



Figure D.4: Comparison between actual and model-predicted potential for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure D.4 (continued)



Figure D.4 (continued)



Figure D.4 (continued)



Figure D.5: Comparison between actual and model-predicted spent electrolyte copper concentrations for Run 1 (a) to Run 24 (x). The run numbers correspond the experimental design in Table A.6.



Figure D.5 (continued)



Figure D.5 (continued)



Figure D.5 (continued)

# D.3.2 Bench-Scale Electrowinning Experiments

Table D.6: Comparison between actual and model-predicted KPIs, generated at input conditions specified in Table A.8, for the bench-scale electrowinning experiments. The grey shading highlights the validation runs. Start-up period included.

Dum	Current	efficiency	SI	EC	Cu plating rate		
Kun	nRMSE (%)	MAPE (%)	nRMSE (%)	MAPE (%)	nRMSE (%)	MAPE (%)	
1	97.6	383.4	487.4	56.2	73.2	—	
2	54.3	35406.2	360	40.7	59	—	
3	26.3	16.1	37.4	31.7	44.2	—	
4	36.6	185	255.6	26.1	44.2	—	
5	149.1	28303.4	229.9	59.3	72.5	_	
6	42.6	109357.2	247.3	31.8	54.5	_	
7	44.2	310765.7	238.5	51.6	64	_	
8	28.5	20.7	30	25.1	35	_	
9	44.4	67.7	490	38.9	53.7	_	
10	51.1	38.1	499	73.9	71.8	_	
11	46.4	34.9	53.6	56.4	56.2	—	
12	36.5	32985.2	275	55.1	59.5	_	
13	47.6	42.8	344.5	76.4	76.2	_	
14	30.4	26.6	497.4	40	45.1	_	
15	45.8	45.8	304.9	47	69.1	—	



Figure D.6: Comparison between actual and model-predicted copper plating rate for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure D.6 (continued)



Figure D.6 (continued)


Figure D.7: Comparison between actual and model-predicted current efficiency for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.







Figure D.7 (continued)



Figure D.8: Comparison between actual and model-predicted SEC for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure D.8 (continued)



Figure D.8 (continued)



Figure D.9: Comparison between actual and model-predicted potential for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure D.9 (continued)



Figure D.9 (continued)



Figure D.10: Comparison between actual and model-predicted spent electrolyte copper concentrations for Run 1 (a) to Run 15 (o). The run numbers correspond the experimental design in Table A.8.



Figure D.10 (continued)



Figure D.10 (continued)

## D.4 DYNAMIC INDUSTRIAL MODEL PREDICTIONS

#### D.4.1 Additional Model Results

Table D.7: MAPE and nRMSE values for the prediction of KPIs and intermediary variables for one cell of the industrial case-study tankhouse, for the model with (w) and without (w/o) the online parameter-fitting approach implemented.

Indiantan	trai	ning	Сус	le a	Сус	le b	Сус	le c	Сус	le d	Сус	le e
Indicator	w	w/o										
MAPE (%)												
Current efficiency	5.5	4.8	14.9	21.8	6.4	21.1	6.1	26.2	5.8	22.7	6.5	24.7
Cu plating rate	_	_	_	_	_	_	_	_	_	_	_	_
SEC	55.1	56.5	47.2	56.2	23.3	42.2	18.1	43.6	21.4	40.4	21.9	40.2
Potential	3.5	5.4	4.8	9.7	2.4	6.3	1.7	6.6	2.1	5.8	2.8	5.9
Spent <i>x</i> Cu	8.1	8.0	6.3	6.6	4.5	5.9	4.8	7.4	5.1	6.9	5.2	7.4
nRMSE (%)												
Current efficiency	5.9	5.5	16.6	20.2	10.0	23.0	7.7	26.7	7.0	23.3	8.6	25.3
Cu plating rate	39.2	38.3	45.5	44.5	25.8	28.6	23.8	31.0	24.9	31.1	26.3	31.1
SEC	252	251	225	224	30.7	38.9	48.2	55.0	49.5	53.3	42.5	45.4
Potential	5.2	6.8	6.9	11.4	3.2	6.9	2.3	7.3	3.0	6.5	4.2	6.8
Spent <i>x</i> Cu	9.5	9.3	7.6	8.0	5.7	7.2	6.3	8.5	6.2	8.3	7.1	8.4



Figure D.11: Comparison between actual and model-predicted copper plating rate for the three 14-day training cycles for the dynamic industrial data.



Figure D.12: Comparison between actual and model-predicted current efficiency for the three 14-day training cycles for the dynamic industrial data.



Figure D.13: Comparison between actual and model-predicted SEC for the three 14-day training cycles for the dynamic industrial data.



Figure D.14: Comparison between actual and model-predicted potential for the three 14-day training cycles for the dynamic industrial data.



Figure D.15: Comparison between actual and model-predicted spent electrolyte copper concentrations for the three 14day training cycles for the dynamic industrial data.

#### D.4.2 Parameters

Figure D.16 shows the response of the model parameters refitted using the online parameter-fitting approach, for the five dynamic industrial validation cycles.



Figure D.16: Response of the parameters refitted during online parameter-fitting for one cell of the industrial electrowinning tankhouse over five 14-day validation cycles (Cycle a to Cycle e).

The refitted mass-transfer coefficient for iron reduction (Figure D.16 (a)) remained relatively constant for Cycle a, Cycle c, and Cycle d, as expected for the system. As previously discussed in Chapter 4, losses due to reasons other than the reduction of iron are expected to dominate for the case-study tankhouse. The fitted parameter for Cycle b and Cycle e, however, showed notable variation over the investigated time-period.

The nickel concentrations for Cycle b varied significantly compared to that for the remainder of the cycles. The electrolyte nickel concentration is known to affect the electrolyte viscosity and, therefore, mass-transfer conditions. For Cycle b the nickel concentration reached a maximum of approximately 65 g/L, with variations as large as 30 g/L, within the investigated time-period. The nickel concentrations for the other cycles reached a maximum of approximately 45 g/L, with variations limited to approximately 20 g/L, within the respective time-periods.

For Cycle e, a significant increase in the fitted parameter was observed (t = 130 h to t = 200 h). During this time-period the actual current was consistently at the upper limit of the current observed for the tankhouse (12 000 A). Simultaneously, the actual copper plating rate varied significantly (Figure 9.28 (e)). Per the developed online parameter-fitting approach it is sensical for the iron reduction reaction to be varied to account for the dynamics observed in the copper plating rate. This, however, contradicts the assumption that iron reduction is not expected to contribute significantly to the current losses for the case-study tankhouse. It is possible that the increased oxygen evolution associated with the water oxidation reaction at the higher applied current densities improved the mass-transfer conditions for the mass-transfer-limited iron reduction reaction. The current density, however, also reached 12 000 A periodically during other cycles without a significant effect on the fitted mass-transfer coefficients. Regardless, the observed behaviour for Cycle e does correspond with the actual tankhouse data available (specifically the copper plating rate), for the relevant time-period, as shown by the acceptable model fidelity. The availability of more comprehensive, good-quality data (for example, dynamic iron concentrations), would be required to further elucidate the fitted parameter behaviour.

The mean current loss over the entire time-period, for all five investigated validation cycles, is 28.8% (Figure D.16 (b)). Keeping in consideration that the contribution of iron reduction to current losses is expected to be minimal (due to the low concentrations), this corresponds well with the average current efficiency of 75% reported by the case-study tankhouse. Figure D.16 (b) does, however, show a spike in the fitted current loss parameter at approximately t = 12 h, for Cycle a. This corresponds with the observed decrease in copper plating rate (Figure 9.28 (a)). In the previous horizon (used to refit for the parameters), the actual copper plating rate is shown to be consistently close to 0 (Figure 9.28 (a)). The observed spike in the fitted current loss parameter highlights a limitation associated with the developed model; as with all data-driven models, the quality of data available significantly influences simulation success.

The fitted Butler–Volmer equation parameters for water oxidation are reported in Figure D.16 (c) and Figure D.16 (d), for the charge-transfer coefficient and exchange current density, respectively. The charge-transfer coefficient for water oxidation was consistently at the maximum of the allowable range (Equation 8.4) for Cycle b to Cycle e. The parameter sensitivity analyses showed that the gradient for the water oxidation current density, plotted as a function of the overpotential, was steeper for a lower charge-transfer coefficient (Figure 7.4). At the maximum allowable value for the charge-transfer coefficient, the associated current density would, therefore, be less sensitive to a change in overpotential, enabling more accurate model predictions.

A notable exception is observed for Cycle a, between t = 14 h and t = 42 h, where the charge-transfer coefficient decreases to a minimum of 0.6. During this time-period the online parameter-fitting approach is attempting to correct for the overprediction of the potential (Figure 9.30 (a)). By decreasing

the charge-transfer coefficient the approach is able to decrease the overpotential for water oxidation (thereby correcting for the potential), but still maintain the current density associated with the reaction at an acceptable value. Overall, the fitted value remained well within the allowable range specified in Equation 8.4.

The exchange current density has previously been reported to be a function of the reactant and product concentrations, temperature, and the electrolyte–electrode interface, amongst other system-specific factors (Chapter 7). The fitted exchange current density varied between approximately 0.8 A/m<sup>2</sup> and 2 A/m<sup>2</sup> over the entire time-period, for Cycle b to Cycle e (Figure D.16 (d)). The parameters fitted for Cycle a were, again, a notable exception, reaching a minimum of approximately 0.01 A/m<sup>2</sup> and a maximum of approximately 11 A/m<sup>2</sup>. Nevertheless, the fitted values remained within the allowable range (Equation 8.4). If the variability in the fitted exchange current density is undesired for a specific system, the range specified in the applicable system model (Equation 8.4) can be adapted accordingly.

Figure D.17 shows a graphical representation of the correlation matrix for the model parameters refitted using the online parameter-fitting approach, for the combined five dynamic industrial validation cycles. Spearman's rank correlation coefficient was used to measure the correlation between the parameters, as the refitted parameters were not normally distributed. Figure D.17 supports that the parameters are weakly correlated.



Figure D.17: Graphical representation of the correlation matrix consisting of the Spearman's rank correlation coefficients for the online parameters refitted for one cell of the industrial electrowinning tankhouse, over the combined five 14-day validation cycles.

## D.5 SUMMARY OF STATISTICAL ANALYSIS

# D.5.1 Limiting-Current Density Models

Table D.8: Summary of the *p*-values calculated during regression of the limiting-current density models, with a 95% confidence level.

Taura	<i>p</i> -value			
Term	Model A	Model B		
Constant	< 0.001	< 0.001		
хСи	< 0.001	< 0.001		
xH <sub>2</sub> SO <sub>4</sub>	0.712	0.955		
xNi	< 0.001	< 0.001		
<i>x</i> Fe	0.015	0.029		
хСо	0.758	0.139		
1/7	< 0.001	0.732		
$\omega^{1/2}$	< 0.001	< 0.001		
<i>x</i> Cu · <i>x</i> Fe	_	0.004		
<i>x</i> Ni · <i>x</i> Fe	_	< 0.001		
<i>x</i> Ni · <i>x</i> Co	_	0.019		
<i>x</i> Fe · <i>x</i> Co	_	0.002		
<i>x</i> Fe · 1/ <i>T</i>	—	0.005		

# D.5.2 Online Parameter-Fitting Surrogate Models

Table D.9: Summary of the *p*-values calculated during regression of the surrogate system models, with a 95% confidence level.

Tarra	<i>p</i> -value			
Term	Model <i>P</i> Cu	Model Potential		
Constant	0.372	0.178		
хCu	-	0.001		
<i>x</i> H₂SO₄	-	0.024		
хNi	-	< 0.001		
хFе	0.583	0.001		
хСо	-	0.002		
1	< 0.001	< 0.001		
$m_{ m Fe^{3+}}$	< 0.001	< 0.001		
$\alpha_{\rm H_2O}$	-	0.056		
i <sub>0,H2</sub> 0	-	0.01		
<i>x</i> Ni · xCo	-	0.005		
$\alpha_{\mathrm{H_2O}} \cdot i_{0,\mathrm{H_2O}}$	-	< 0.001		
$m_{ m Fe^{3+}}\cdot$ xFe	< 0.001	_		
$(m_{\rm Fe^{3+}})^2$	< 0.001	-		
<i>x</i> Fe <sup>2</sup>	0.001	-		
$\left( lpha_{\mathrm{H_2O}}  ight)^2$	_	0.091		
$\left( lpha_{\mathrm{H_2O}} \right)^3$	_	0.051		

# APPENDIX E MODEL SUMMARY

Appendix E provides a summary of the model variables, parameters, and constants (Section E.1). A summary of the model assumptions and equations are also provided (Section E.2), alongside a list of the hardcoded limits and warnings (Section E.3). In-depth discussion of the information summarised in this appendix was previously presented in the various thesis chapters. Specifically, in Chapter 2 (Literature review), Chapter 3 (Property Correlations), and Chapter 4 (Model Development). Chapter 4 further presented the approach for solving the set of equations summarised in this appendix.

## E.1 MODEL VARIABLES, PARAMETERS, AND CONSTANTS

Symbol	Description	Unit
$x_{i,\mathrm{in}}$	concentration of species i in advance electrolyte	g/L
A	electrode area	m²
$Q_{ m in}$	flow rate of advance electrolyte	L/s
U <sub>h</sub>	hardware loss	V
d	interelectrode distance	m
N	number of cathodes	dimensionless
Т	temperature	°C or K
$I_{\mathrm{T}}$	total current	А
V	volume of cell	L

Table E.1: Summary of the model input variables.

Symbol	Description	Unit	
A <sub>i</sub>	A parameter in the Debye-Hückel model	dimensionless	
$\gamma_i$	activity coefficient of species i	dimensionless	
$a_i$	activity of species i	dimensionless	
I <sub>a</sub>	anodic current	А	
B <sub>i</sub>	B parameter in the Debye-Hückel model	dimensionless	
I <sub>c</sub>	cathodic current	А	
$x_{i,\text{out}}$	concentration of species i in spent electrolyte	g/L	
к	conductivity	S/m	
P <sub>Cu</sub>	copper plating rate	g/s	
i	current density	A/m <sup>2</sup>	
β	current efficiency	fraction	
$I_{\rm L}$	current loss	А	
IB	current through each individual main branch	А	
Ii	current used in reaction of species i	А	
$ ho_{\mathrm{H_2}o}$	density of water	g/L	
$\epsilon_{r,i}$	dielectric constant of species i	dimensionless	
$ ho_{ m electrolyte}$	electrolyte density	g/L	
R <sub>s</sub>	electrolyte resistance	Ω	
$Q_{\rm out}$	flow rate of spent electrolyte	L/s	
IS	ionic strength	mol/m <sup>3</sup>	
m <sub>i</sub>	mass	g or kg	
$C_i$	molar concentration of species i	mol/m <sup>3</sup>	
Wi	rate of generation	g/s	
Ei	reduction potential of species i	V	
S	scale-up factor	dimensionless	
SEC	specific energy consumption	kWh/t	
t	time	s or h	
UT	total potential	V	
$U_{\rm L}$	voltage loss term	V	

Table E.2: Summary of the model intermediate and output variables.

Symbol	Description	Unit	Initial Value
$\alpha_{Cu}$	charge-transfer coefficient for copper reduction	dimensionless	0.5
$\alpha_{\rm H_2O}$	charge-transfer coefficient for water oxidation	dimensionless	0.7
$L_I$	current loss parameter	fraction	0.2
$\eta_{\mathrm{Cu}}$	estimated overpotential for copper reduction	V	-0.5*
$\eta_{ m H_2O}$	estimated overpotential for water oxidation	V	0.5
i <sub>0,Cu</sub>	exchange current density for copper reduction	A/m²	15
i <sub>0,H2</sub> 0	exchange current density for water oxidation	A/m²	10
$m_{\rm Fe^{2+}}$	mass-transfer coefficient for iron oxidation	m/s or cm/s	1 × 10⁻² m/s
$m_{\mathrm{Fe}^{3+}}$	mass-transfer coefficient for iron reduction	m/s or cm/s	1 × 10 <sup>-7</sup> m/s

Table E.3: Summary of the model parameters.

\*The negative overpotential arises from the positive current density associated with the reduction reaction.

Table E.4: Summary of the model constants.

Symbol	Description	Unit	Value
Zi	charge of species i	dimensionless	_
F	Faraday's constant	C per equivalent mol	96 485
R	gas constant	J/(mol K)	8.314
M <sub>i</sub>	molecular mass of species i	g/mol	_
n <sub>i</sub>	number of electrons	dimensionless	_
$e_0$	permittivity of the vacuum	F/m	8.85 × 10 <sup>-12</sup>
C <sup>0</sup>	reference concentration	mol/L or mol/m <sup>3</sup>	1
r <sub>i</sub>	radius of species i	m	_
$E_i^0$	standard reduction potential	v	_
s <sub>i</sub>	stoichiometric coefficient	dimensionless	_

#### E.2 MODEL EQUATIONS

#### E.2.1 Cathodic Current Calculations

Assuming the copper reduction reaction is reaction-rate-limited, the current density was calculated using Equation E.1 (Butler–Volmer equation). The corresponding current was calculated using Equation E.2.

$$i_{\rm Cu} = i_{0,\rm Cu} \left[ \exp\left(\frac{-\alpha_{\rm Cu} n_{\rm Cu} F}{R T} \eta_{\rm Cu}\right) - \exp\left(\frac{(1-\alpha_{\rm Cu}) n_{\rm Cu} F}{R T} \eta_{\rm Cu}\right) \right]$$
[E.1]

$$I_{\rm Cu} = (i_{\rm Cu}) \left(\frac{1}{2}A\right)$$
 [E.2]

Assuming the iron reduction reaction is mass-transfer-limited, the current density was calculated using Equation E.3. The surface concentration of the species was taken as zero, due to the assumed mass-transfer-limited nature of the reaction. The corresponding current was calculated using Equation E.4.

$$i_{\rm Fe^{3+}} = n_{\rm Fe^{3+}} F m_{\rm Fe^{3+}} (C_{\rm Fe^{3+}, bulk} - C_{\rm Fe^{3+}, surface})$$
 [E.3]

$$I_{\rm Fe^{3+}} = (i_{\rm Fe^{3+}}) \left(\frac{1}{2}A\right)$$
 [E.4]

The cathodic current was calculated using Equation E.5.

$$I_c = (i_{\rm Cu} + i_{\rm Fe^{3+}}) \left(\frac{1}{2}A\right)$$
 [E.5]

#### E.2.2 Anodic Current Calculations

Assuming the water oxidation reaction is reaction-rate-limited, the current density was calculated using Equation E.6 (Butler–Volmer equation). The corresponding current was calculated using Equation E.7.

$$i_{\rm H_2O} = i_{0,\rm H_2O} \left[ \exp\left(\frac{-\alpha_{\rm H_2O} \, n_{\rm H_2O} \, F}{R \, T} \, \eta_{\rm H_2O}\right) - \exp\left(\frac{(1-\alpha_{\rm H_2O}) \, n_{\rm H_2O} \, F}{R \, T} \, \eta_{\rm H_2O}\right) \right] \qquad [E.6]$$

$$I_{\rm H_2O} = (i_{\rm H_2O}) \left(\frac{1}{2}A\right)$$
 [E.7]

Assuming the iron oxidation reaction is mass-transfer-limited, the current density was calculated using Equation E.8. The surface concentration of the species was taken as zero, due to the assumed mass-transfer-limited nature of the reaction. The corresponding current was calculated using Equation E.9.

$$i_{\rm Fe^{2+}} = n_{\rm Fe^{2+}} F m_{\rm Fe^{2+}} \left( C_{\rm Fe^{2+}, bulk} - C_{\rm Fe^{2+}, surface} \right)$$
[E.8]

$$I_{\rm Fe^{2+}} = (i_{\rm Fe^{2+}}) \left(\frac{1}{2}A\right)$$
 [E.9]

The anodic current was calculated using Equation E.10.

$$I_a = (i_{\rm H_2O} + i_{\rm Fe^{2+}}) \left(\frac{1}{2}A\right)$$
 [E.10]

### E.2.3 Scale-Up Calculations

The scale-up factor was defined using Equation E.11.

$$S = 2 N \qquad [E.11]$$

The current loss parameter was calculated using Equation E.12, and the current loss using Equation E.13.

$$L_I = 1 - \bar{\beta} \qquad [E.12]$$

$$I_{\rm L} = I_{\rm T} L_I \qquad [E.13]$$

The scaled-up total current was calculated using Equation E.14 and E.15, and the scaled-up current for each species using Equation E.16 to E.19.

$$I_{\rm B} = I_c = I_a \qquad [E.14]$$

$$I_{\rm T} = I_{\rm B} S + I_{\rm L}$$
 [E.15]

$$I_{\mathrm{T,Cu}} = I_{\mathrm{Cu}} S \qquad [E.16]$$

$$I_{\rm T,Fe^{3+}} = I_{\rm Fe^{3+}} S$$
 [E.17]

$$I_{\rm T,H_2O} = I_{\rm H_2O} S$$
 [E.18]

$$I_{\rm T,Fe^{2+}} = I_{\rm Fe^{2+}} S$$
 [E.19]

## E.2.4 Concentration Calculations

The rate of generation for each species was calculated using Equations E.20 to E.26 (variations of Faraday's law). It was assumed that no nickel or cobalt was generated or consumed.

$$P_{\rm Cu} = \frac{s_{\rm Cu} \, M_{\rm Cu} \, I_{\rm T,Cu}}{n_{\rm Cu} \, F}$$
 [ E.20 ]

$$w_{\rm H_2O} = \frac{s_{\rm H_2O} M_{\rm H_2O} I_{\rm T,H_2O}}{n_{\rm H_2O} F}$$
[E.21]

$$w_{\rm Fe^{3+}} = \frac{s_{\rm Fe^{2+}} M_{\rm Fe} I_{\rm T, Fe^{2+}}}{n_{\rm Fe^{2+}} F} - \frac{s_{\rm Fe^{3+}} M_{\rm Fe} I_{\rm T, Fe^{3+}}}{n_{\rm Fe^{3+}} F}$$
[E.22]

$$w_{\rm Fe^{2+}} = \frac{s_{\rm Fe^{3+}} M_{\rm Fe} I_{\rm T, Fe^{3+}}}{n_{\rm Fe^{3+}} F} - \frac{s_{\rm Fe^{2+}} M_{\rm Fe} I_{\rm T, Fe^{2+}}}{n_{\rm Fe^{2+}} F}$$
[E.23]

$$w_{\rm H_2SO_4} = \frac{w_{\rm H_2O}}{M_{\rm H_2O}} M_{\rm H_2SO_4}$$
 [E.24]

$$w_{\rm Ni} = 0$$
 [E.25]

$$w_{\rm Co} = 0$$
 [E.26]

The spent electrolyte copper concentration, sulfuric acid concentration, density, and flow rate was calculated by solving the system of differential-algebraic equations (DAEs). The system consists of the overall conservation of mass equation (Equation E.27), the copper conservation equation (Equation E.28), the sulfuric acid conservation equation (Equation E.29), and the density correlation (Equation E.30, refer to Chapter 3 for coefficients).

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{V\mathrm{d}(\rho_{\mathrm{electrolyte,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}\rho_{\mathrm{electrolyte,in}} - Q_{\mathrm{out}}\rho_{\mathrm{electrolyte,out}} - P_{\mathrm{Cu}} \qquad [E.27]$$

$$\frac{\mathrm{d}m_{\mathrm{Cu}}}{\mathrm{d}t} = \frac{\mathrm{d}(Vx_{\mathrm{Cu,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Cu,in}} - Q_{\mathrm{out}}x_{\mathrm{Cu,out}} - P_{\mathrm{Cu}} \qquad [E.28]$$

$$\frac{\mathrm{d}m_{\mathrm{H}_{2}\mathrm{SO}_{4}}}{\mathrm{d}t} = \frac{\mathrm{d}(Vx_{\mathrm{H}_{2}\mathrm{SO}_{4},\mathrm{out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{H}_{2}\mathrm{SO}_{4},\mathrm{in}} - Q_{\mathrm{out}}x_{\mathrm{H}_{2}\mathrm{SO}_{4},\mathrm{out}} + w_{\mathrm{H}_{2}\mathrm{SO}_{4}} \qquad [E.29]$$

$$\rho_{\text{electrolyte,in}} = a_1 + a_2 x \text{Cu} + a_3 x \text{H}_2 \text{SO}_4 + a_4 x \text{Ni} + a_5 x \text{Fe} + a_6 x \text{Co} + a_7 x \text{As} + a_8 T$$
[E.30]

The remainder of the spent electrolyte component concentrations were calculated by solving the ordinary differential equations (ODEs). The ODEs consist of the water conservation equation (Equation E.31), ferric iron conservation equation (Equation E.32), ferrous iron conservation equation (Equation E.33), nickel conservation equation (Equation E.34), and the cobalt conservation equation (Equation E.35).

$$\frac{\mathrm{d}m_{\rm H_2O}}{\mathrm{d}t} = \frac{\mathrm{d}(V\rho_{\rm H_2O,out})}{\mathrm{d}t} = Q_{\rm in}\rho_{\rm H_2O,in} - Q_{\rm out}\rho_{\rm H_2O,out} + w_{\rm H_2O} \qquad [E.31]$$

$$\frac{\mathrm{d}m_{\mathrm{Fe}^{3+}}}{\mathrm{d}t} = \frac{\mathrm{d}(vx_{\mathrm{Fe}^{3+},\mathrm{out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Fe}^{3+},\mathrm{in}} - Q_{\mathrm{out}}x_{\mathrm{Fe}^{3+},\mathrm{out}} + w_{\mathrm{Fe}^{3+}} \qquad [E.32]$$

$$\frac{dm_{\rm Fe^{2+}}}{dt} = \frac{d(Vx_{\rm Fe^{2+},out})}{dt} = Q_{\rm in}x_{\rm Fe^{2+},in} - Q_{\rm out}x_{\rm Fe^{2+},out} + w_{\rm Fe^{2+}}$$
[E.33]

$$\frac{\mathrm{d}m_{\mathrm{Ni}}}{\mathrm{d}t} = \frac{\mathrm{d}(Vx_{\mathrm{Ni,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Ni,in}} - Q_{\mathrm{out}}x_{\mathrm{Ni,out}} + w_{\mathrm{Ni}} \qquad [E.34]$$

$$\frac{\mathrm{d}m_{\mathrm{Co}}}{\mathrm{d}t} = \frac{\mathrm{d}(vx_{\mathrm{Co,out}})}{\mathrm{d}t} = Q_{\mathrm{in}}x_{\mathrm{Co,in}} - Q_{\mathrm{out}}x_{\mathrm{Co,out}} + w_{\mathrm{Co}} \qquad [E.35]$$

#### E.2.5 Potential Calculations

The ionic strength of the solution was calculated using Equation E.36.

$$IS = 0.5 \left( z_{Cu^{2+}}^2 C_{Cu^{2+}} + z_{H^+}^2 C_{H^+} + z_{HSO_4^-}^2 C_{HSO_4^-} + z_{Fe^{2+}}^2 C_{Fe^{2+}} + z_{Fe^{3+}}^2 C_{Fe^{3+}} \right) [E.36]$$

The dielectric constant was calculated using Equation E.37 (Werner et al. (2018) correlation).

$$\epsilon_{r,Cu^{2+}} = 127.9614 + 0.01378 \, IS + 5.6111 \times 10^{10} \, r_{Cu^{2+}} + 2.5422 |z_{Cu^{2+}}| \qquad [E.37]$$

The activity coefficient was calculated using Equation E.38 and E.39 (Samson et al. (1999) model).

$$A_{\rm Cu^{2+}} = \frac{\sqrt{2} F^2 e_0}{8 \pi \left(\epsilon_0 \epsilon_{r,\rm Cu^{2+}} R T\right)^{\frac{3}{2}}} \quad \text{and} \quad B_{\rm Cu^{2+}} = \sqrt{\frac{2 F^2}{\epsilon_0 \epsilon_{r,\rm Cu^{2+}} R T}} \qquad [E.38]$$

$$\ln(\gamma_{\rm Cu^{2+}}) = -\frac{A \, z_{\rm Cu^{2+}}^2 \sqrt{IS}}{1+B \, r_{\rm Cu^{2+}} \sqrt{IS}} + \frac{(0.2 - (4.17 \times 10^{-1}) \, IS) A \, z_{\rm Cu^{2+}}^2 \, IS}{\sqrt{1000}}$$
[E.39]

The activity for the copper in solution was calculated using Equation E.40. The activity for the plated copper is 1, as it is a solid (Equation E.41).

$$a_{Cu^{2+}} = \gamma_{Cu^{2+}} \left(\frac{c_{Cu^{2+}}}{c^0}\right)$$
 [E.40]

$$a_{\rm Cu} = 1$$
 [E.41]

The reduction potential under non-standard conditions was calculated using Equation E.42 (Nernst equation).

$$E_{\rm Cu} = E_{\rm Cu}^0 + \frac{RT}{nF} \ln\left(\frac{a_{\rm Cu}^{2+}}{a_{\rm Cu}}\right)$$
[E.42]

The dielectric constant was calculated using Equation E.43 (Werner et al. (2018) correlation).

$$\epsilon_{r,\mathrm{H}^+} = 127.9614 + 0.01378 \, IS + 5.6111 \times 10^{10} \, r_{\mathrm{H}^+} + 2.5422 |z_{\mathrm{H}^+}| \qquad [E.43]$$

The activity coefficient was calculated using Equation E.44 and E.45 (Samson et al. (1999) model).

$$A_{\rm H^+} = \frac{\sqrt{2} F^2 e_0}{8 \pi \left(\epsilon_0 \epsilon_{r,\rm H^+} R T\right)^{\frac{3}{2}}} \quad \text{and} \quad B_{\rm H^+} = \sqrt{\frac{2 F^2}{\epsilon_0 \epsilon_{r,\rm H^+} R T}} \qquad [E.44]$$

$$\ln(\gamma_{\rm H^+}) = -\frac{A \, z_{\rm H^+}^2 \sqrt{IS}}{1+B \, r_{\rm H^+} \, \sqrt{IS}} + \frac{(0.2 - (4.17 \times 10^{-15}) \, IS) A \, z_{\rm H^+}^2 \, IS}{\sqrt{1000}}$$
[E.45]

The activity was calculated using Equation E.46 and Equation E.47.

$$a_{\rm H^+} = \gamma_{\rm H^+} \left(\frac{c_{\rm H^+}}{c^0}\right)$$
 [E.46]

$$a_{\rm H_2O} = 1$$
 [E.47]

The reduction potential under non-standard conditions was calculated using Equation E.48 (Nernst equation).

$$E_{\rm H_2O} = E_{\rm H_2O}^0 + \frac{RT}{nF} \ln\left(\frac{a_{\rm H^+}}{a_{\rm H_2O}}\right)$$
[E.48]

The electrolyte conductivity was calculated using the conductivity correlation (Equation E.49, refer to Chapter 3 for coefficients).

 $\kappa = a_1 + a_2 x \text{Cu, out} + a_3 x \text{H}_2 \text{SO}_4, \text{out} + a_4 x \text{Ni, out} + a_5 x \text{Fe, out} + a_6 x \text{Co, out} + a_7 x \text{As, out} + a_8 T + a_n \text{ (combined effect term)}$ [E.49]

The electrolyte resistance was calculated using Equation E.50.

$$R_s = \frac{d}{\kappa A} \qquad [E.50]$$

The voltage loss term was calculated using Equation E.51.

$$U_{\rm L} = R_{\rm s} I_c + U_{\rm h} \qquad [E.51]$$

The total potential was calculated using Equation E.52.

$$U_{\rm T} = |E_{\rm Cu} + E_{\rm H_2O}| + \eta_{\rm H_2O} + \eta_{\rm Cu} + U_{\rm L}$$
 [E.52]

## E.2.6 Key Performance Indicator Calculations

The cumulative mass copper plated was calculated using Equation E.53.

$$m_{\rm Cu,cumul} = \sum_{t=0}^{t} P_{\rm Cu} \qquad [E.53]$$

The theoretical copper plating rate was calculated using Equation E.54 (Faraday's law).

$$P_{\text{Cu,theoretical}} = \frac{s_{\text{Cu}} M_{\text{Cu}} I_{\text{T}}}{n_{\text{Cu}} F} \qquad [\text{ E.54 ]}$$

The theoretical cumulative mass copper plated was calculated using Equation E.55.

$$m_{\text{Cu,theoretical,cumul}} = \sum_{t=0}^{t} P_{\text{Cu,theoretical}}$$
 [E.55]

The current efficiency was calculated using Equation E.56.

$$\beta = \frac{m_{\text{Cu,cumul}}}{m_{\text{Cu,theoretical,cumul}}} \quad [E.56]$$

The specific energy consumption was calculated using Equation E.57.

$$SEC = \frac{I_T U_T t}{m_{Cu}}$$
 [E.57]

## E.3 HARDCODED MODEL LIMITS AND WARNINGS

Table E.5: List of conditions for hardcoded model limits and warnings, corresponding message type, and message description.

Message Condition	Туре	Description
xCu < 0	Error	Copper concentration decreased to below 0.
xFe2 < 0	Error	Ferrous iron concentration decreased to below 0.
xFe3 < 0	Error	Ferric iron concentration decreased to below 0.
xNi < 0	Error	Nickel concentration decreased to below 0.
xCo < 0	Error	Cobalt concentration decreased to below 0.
Qin < 0	Error	Flow rate in decreased to below 0.
Qout < 0	Error	Flow rate out decreased to below 0.
((sum(variableLengthNotScalars)/ length(variableLengthNotScalars)) ~ = variableLengthNotScalars(1,1))	Error	Input manipulated variables are required to be equal length vectors, if not constant.
limitingCurrentDensityPercentCu > 10	Warning	Operating at more than 10% of limiting current density for copper reduction.
iterationCounterConcentration = = 6000	Warning	Maximum number of iterations is reached in concentration loop.
iterationCounterCurrentCathode = = 3000	Warning	Maximum number of iterations is reached in cathodic current loop.
iterationCounterCurrentAnode = = 3000	Warning	Maximum number of iterations is reached in cathodic current loop.

# **APPENDIX F**

# PUBLICATIONS BASED ON DISSERTATION

Appendix F provides additional information pertaining to the publications, based on sections of this dissertation, that have been submitted to refereed conference proceedings and journals.

## F.1 CONFERENCE PROCEEDINGS

The following refereed full-length papers based on this work have been submitted for publication in conference proceedings.

- Grobbelaar, S., Dorfling, C., Tadie, M., 2023. Evaluating the value of including physicochemical property correlations on the prediction capability of a dynamic electrowinning model, in: Proceedings of Copper Cobalt Africa. The Southern African Institute of Mining and Metallurgy, Johannesburg. pp. 333–343.
- Grobbelaar, S., Dorfling, C., Tadie, M., 2023. Evaluating the use of a dynamic model to predict direct copper electrowinning tankhouse performance, in: Proceedings of 9<sup>th</sup> Hydrometallurgy Conference. Society for Mining, Metallurgy, and Exploration, Englewood. [Manuscript accepted for publication].

## F.2 JOURNAL ARTICLES

The following full-length papers based on this work have been submitted for publication in refereed journals.

- Grobbelaar, S., Dorfling, C., Tadie, M., 2023. Development of a dynamic semi-empirical model for simulation of the copper electrowinning process. [Manuscript under consideration].
- Grobbelaar, S., Dorfling, C., Tadie, M., 2023. Parameter estimation for modelling copper electrowinning using moving horizon estimation. [Manuscript submitted to industry partner for approval].