OPTIMISATION OF THE ION EXCHANGE JUICE TREATMENT PLANT AT ASHTON CELLARS.

by

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of the requirements for the Degree

of

MASTER OF SCIENCE IN ENGINEERING
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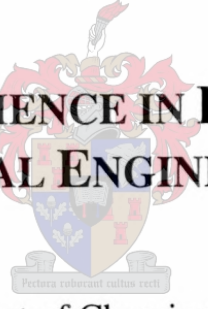

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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not previously in its entirety or in part been submitted at any university for a degree.

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SUMMARY

Recently concern has been raised regarding effluent from wine cellars, as it often does not comply with environmental legislation. It was with this in mind that the effluent problem at Ashton Cellars was addressed.

After carrying out a water audit of the plant, described in Chapter 3, it was concluded that the ion exchange plant is a significant contributor to the low pH and high conductivity of the effluent dam. Decreasing the effluent from the ion exchange plant should therefore help in improving the total effluent quality. During the water audit opportunities to improve the effluent by making small process changes in the cellar were identified.

The primary objective of this study was to provide guidelines to improve the quality and decrease the volume of the effluent from the ion-exchange plant to more environmentally acceptable levels, whilst maintaining product specifications and production rates. This was achieved by studying the operation of the plant (Chapter 4) and testing the characteristics of the current and alternative resins (Chapter 5).

Auditing of the ion exchanges plant included a detailed analysis of the regeneration and loading of the ion exchange columns. It was concluded that the operation of the plant can only be optimised once pH and/or conductivity meters, and preferably an automated control system, are installed on the plant. The results given in this thesis can be used as a guide when setting up such a control system.

Laboratory testing of the resins revealed that the cation resin currently being used on the plant has been fouled and loads at a slow rate. When the resins are replaced, the use of Purolite C150 and Purolite A103S should be considered as these resins gave the most favourable results.

Some alternative treatment methods for the processing of grape must, have been mentioned in Chapter 6.

OPSOMMING

Al meer kommer word deesdae uitgespreek oor wynkelders se afvalwater, omdat dit meerendeels nie aan die vereistes van omgewingswetgewing voldoen nie. Dit was met hierdie probleem in die oog dat die afvalwater probleem by Ashton Kelders ondersoek is.

Nadat 'n wateroudit van die fabriek, soos beskryf in Hoofstuk 3, uitgevoer is, is daar tot die slotsom gekom dat die ioonuitruilsisteem 'n groot bydra tot die lae pH en hoë konduktiwiteit van die afvaldam lewer. Indien die ioonuitruilsisteem se uitvloeisel verminder kon word, sou dit tot 'n groot mate bydrae tot 'n verbetering van die totale uitvloei kwaliteit. Gedurende die wateroudit is verskeie moontlikhede vir die verbetering van die uitvloei deur klein prosesveranderinge aan te bring, geïdentifiseer.

Hierdie studie het as hoof oogmerk die daarstelling van riglyne vir die verbetering van die kwaliteit en grote van die afvalstrome van die ioonuitruilsisteem om sodeende aan omgewingswetgewing te voldoen, maar ter selfder tyd die produk spesifikasies en tempos te handhaaf. Dit is gedoen deur die huidige bedryf van die fabriek te bestudeer (Hoofstuk 4) en die eienskappe van die huidige en alternatiewe ioonuitruilharse te toets (Hoofstuk 5).

Die oudit van die ioonuitruilsisteem het 'n gedetaileerde analiese van die hergenerasie en lading van die ioonuitruilkolomme ingesluit. Daar is tot die slotsom gekom dat die bedryf van die sisteem alleenlik geoptimiseer kon word indien pH en/of konduktiwiteitsmeters, en verkieslik 'n automatiese kontrolesisteem geinstalleer word. Die resultate van hierdie tesis kan as basis vir so 'n kontrole sisteem gebruik word.

Die laboratoriumtoetse op die harse het aan die lig gebring dat die katioonhars wat tans in gebruik is, baie vervuil is en net teen 'n lae tempo belaai kan word. Wanneer die harse vervang word, word die gebruik van Purolite C150 en Purolite A103S aangeraai, aangesien hierdie harse die beste resultate gelewer het.

Alternatiewe behandelingsmetodes van druifmos is in Hoofstuk 6 genoem.

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NOMENCLATURE

Abbreviation	Description	Units
BDL	Below Detection Levels	
BOD	Biological Oxygen Demand	mg/ℓ
COD	Chemical Oxygen Demand	mgℓ
C.O.T.	Colourless, Odourless and Tasteless juice	
DOC	Dissolved Organic Carbon	mg/ℓ
EC	Electrical Conductivity	mS/m
ICP	Inductively-Coupled Plasmaspectrometer	
SS	Suspended Solids	mg/ℓ
SAR	Sodium Absorption Ratio	
SAC	Strong Acid Cation	
t	Time	s
TDS	Total Dissolved Solids	mg/ℓ
WBA	Weak Base Anion	
Q	Volumetric flowrate	mℓ/s

CHAPTER 1

Introduction

In recent years emphasis has been placed on environmental protection. Effluent management guidelines are of increasing concern especially for wineries and distilleries. Rivers and streams are polluted daily, decreasing the quality of our country's water resources. Controlling this type of depreciation is the responsibility of every citizen.

The Department of Water Affairs and Forestry (DWAF) is concerned about the current management practices pertaining to cellar effluent. New legislation concerning the discharge of pollutant streams is to be addressed in compliance with the National Water Act (Muller, 1999). Although the local and national authorities lay down general principles concerning effluent discharged from wineries, they cannot be expected to solve technical problems associated with all types of discharge from specific cellars. This task therefore, becomes the role of specialist consultants who can evaluate and solve the problems of cellars on an individual basis.

One of the major challenges in solving any engineering problem is in determining the source, instead of simply gaining statistical information on the extent of the problem (so that the effects can be treated). This equates to the development of a fundamental understanding of the mechanism and dynamics of the total system instead of simply applying remedial measures to treat the effects. This is especially true for environmental management where the effect is often far removed from the source.

1.1 ASHTON CELLARS

Ashton Cellars is a co-operative of 92 wine farms and is situated in Ashton in the Western Cape. In addition to both red and white wines, Ashton Cellars produces a colourless, odourless and tasteless grape juice concentrate known as C.O.T.. This is used as a natural sweetener in the wine and food industries. Ashton Cellars has unique effluent problems as the effluent created during the wine making process is combined with that from the clarification and concentration of grape juice. In an average winery

the main effluent problems are the high chemical oxygen demand and the high level of suspended solids in the wastewater. At Ashton Cellars these problems also exist but they are combined with a very high salinity and conductivity and a very low pH. In order to evaluate these problems a water audit was carried out and its results are documented in Chapter 3.

The ion-exchange plant at Ashton Cellars is used for the decolourisation and demineralisation of grape juice prior to concentration. All contaminants must be removed from the juice, as they are responsible for the colour, odour and taste of the untreated juice. The effluent from the ion-exchange regeneration has been found to be a significant contributor to the total effluent stream of the cellar. The ion-exchange regenerant effluent is characterised by low pH (less than 3), high chemical oxygen demand and high conductivity and is, therefore, not suitable for direct disposal or reuse.

The presence of sodium ions, from the caustic regeneration of the anion resin, and sulphate ions, from the sulphuric acid regeneration of the cation resin, make the effluent difficult to treat using current effluent treatment methods. It is therefore, necessary to re-evaluate the current system. Currently very little treatment is being carried out at Ashton. Lime is added to the effluent from the ion exchange plant in order to increase the pH, but this is not adequate. All the effluent from the plant is collected in a dam, which is then used for the irrigation of grass fields on which cattle graze. There is evidence of the effect that this water has on the soil in these fields.

1.2 OBJECTIVES

The **primary objective** of this investigation is to provide guidelines to improve the quality and decrease the volume of the effluent from the ion-exchange plant to more environmentally acceptable levels, as described in the National Water Act (Muller, 1999), whilst maintaining product specifications and production rates.

Secondary objectives include the following:

- To complete a water audit at Ashton Cellars, to characterise the quality of water and to indicate major streams of pollution.
- The optimisation of regenerant use, chemicals and rinse water on the plant.
- To characterise the resins currently used on the plant and compare them to some alternative resins.
- To mention possible alternative methods for the production of COT. These could either replace or work in combination with the existing ion exchange plant. This part of the study is limited to a few suggestions for further research.

CHAPTER 2

Background and Literature Survey

2.1 ION EXCHANGE

2.1.1 History

While there are suggestions found in the Bible, and in writings by the ancient Greeks, that indicate that there was knowledge of desalting brackish waters, it was not until the nineteenth century that the first official studies of the phenomenon of ion exchange were documented. In 1850, Harry Thompson and John Way, two agricultural chemists in England, treated a soil sample with ammonium sulphate and then passed water through it (Dorfner, 1972). It was noted that the ammonia was retained by the soil and that calcium was leached out (gypsum was found in the eluate). They reported some observations, which have formed a foundation for the understanding of the ion exchange process:

1. The exchange of ions in soils involved the exchange of equivalent ions.
2. Some ions were more readily exchanged than others.
3. The aluminium silicates present in the soil gave it exchange characteristics.
4. The exchange of ions was different from true physical adsorption.

Since then many advances have been made to bring ion exchange to where it is today.

2.1.2 Basic Principles

Ion exchange may be defined as the reversible interchange of ions between a solid and a liquid phase in which there is no permanent change in the structure of the solid (Wheaton and Seamster, 1966). The solid is the ion exchanger and is a salt, an acid or an alkali. It is insoluble in water but is hydrated, i.e. water penetrates the resin like it would a sponge. The moisture content of an apparently dry ion exchanger can be more than 50% of its total mass. The ion exchange reactions take place in this water (Arden and De Dardel, 1986). More than 99% of the capacity of an ion exchange material is found in the interior of the bead.

Ion exchange is used in many chemical processes which can be classified in three categories:

1. Replacement: Where a valuable ion is exchanged for one of no value.
2. Separation: Where different ions can be separated out of a mixture of ions.
3. Removal: Where all the ions in a solution are removed and replaced with water. This is achieved by using both a cationic resin (in the H form) and an anionic resin (in the OH form). It is this process, also called demineralisation, which is the focus of this thesis.

2.1.3 Resin Synthesis (Arden and De Dardel, 1986)

Most ion exchange bead materials are manufactured by a suspension polymerisation process using styrene and divinylbenzene (DVB). The styrene and DVB, initially both liquid, are added to a reactor with roughly the same amount of water. A surfactant is also added. The reactor is stirred. The styrene and DVB form large globules of material. Increasing the stirring speed breaks up the globules into smaller droplet until they reach a size of about 1 millimetre. At this point the polymerisation reaction is initiated by the addition of benzoyl peroxide, which causes the styrene/DVB molecules to form the resultant small plastic beads. The divinylbenzene is a cross-linking agent that gives the beads their physical strength, and without which the styrene would be water-soluble.

A polyacrylic skeleton is produced a similar way by using an acrylate or a methylacrylate instead of styrene.

The skeleton bead needs to be chemically activated to make it perform as an ion exchange material. Active groups are attached to provide chemical functionality to the bead. Each active group has a fixed charge, which is balanced by an equivalent number of oppositely charged ions that are free to exchange with other ions.

2.1.3.1 Strong acid cation resins (SAC)

Polystyrene beads are treated with concentrated sulphuric acid (a process called sulphonation) to form permanent, negatively charged sulphonic acid groups throughout the beads.

2.1.3.2 Weak base anion resins (WBA)

Polystyrene beads are treated with chloromethyl methyl ether ($Cl\text{-}CH_2\text{-}O\text{-}CH_3$) in the absence of water and using either $AlCl_3$ or $SnCl_4$ as a catalyst. The product is chloromethyl polystyrene. The chlorine must then be replaced by an amine or ammoniac. The selection of the reaction used for this step determines the strength of the ion exchanger. The resins used in this study have tertiary amine groups, which class them as weak base anion resins. They react with strong acids in the solution but not with the neutral salts or weak acids

2.1.3.3 Macroporous resins

All the resins used in this study are classified as macroporous (also called macroreticular). At the point of polymerisation an agent, which causes pores to form, is added to the solution of monomers. This agent, an example being heptane, must be a solvent for the monomers from which the polymer precipitates.

Channels are formed within resin beads creating a synthetic porosity. These macropores form a network of channels within the resin beads. These channels are then filled with free water. The channels are large enough to allow large molecules to move freely through to the middle of the bead that then gives the ions a shorter distance (compared to gel resins) to diffuse to an active site.

2.1.4 Ion Exchange Capacity

The total number of active groups on a particular type of resin is represented by the total capacity. In this study, as it is in industry, the capacity is expressed as the number of equivalents per litre of packed resin.

The operating capacity of a resin is the fraction of the total capacity used in a certain process. This depends on the concentration and type of ion being exchanged, the flowrate, temperature, depth of the bed and the type, and concentration of the eluant. The operating capacity is a more relevant figure than the total capacity when it comes to running an ion exchange plant.

2.1.5 Selectivity of Resins

The selectivity or affinity of ion exchange resins is influenced by the properties of the bead, the ions being exchanged, and the solution in which the ions are present. Ion exchange resins generally have greater selectivities for ions with increasing valency. Among ions with the same charge, higher affinities are seen for ions with a higher atomic number.

These affinity relationships are reversed in concentrated solutions. This is what makes regeneration of exhausted resins possible.

2.2 THE COMPOSITION OF MUST (Jackson, 1994 and Boulton et al., 1996)

Once the grapes have been pressed, many components, which are distributed in varying ratios between the juice, pulp and skins, end up in the must. New components are also formed by enzymatic action during pressing. Must is therefore, composed of hundreds of components which can be divided into different classes (Table 2.1).

Table 2.1. Rough estimate of must composition on a mass percentage basis (Boulton et al., 1996)

Component Class	Percentage (%)
Water	76
Lipids and other macromolecules	0.02
Minerals	0.4
Carbohydrates	23
Acids	0.7
Phenols	0.01
Nitrogen components	0.1
Terpenoids	0.01
Other volatile components	0.01

Methods used to identify these components include gas chromatography, liquid chromatography, mass spectrometry and nuclear magnetic resonance spectroscopy.

2.2.1 Water

Must consists of about 76% water. Water is an essential component in many of the chemical reactions, which occur during grape development and must treatments.

2.2.2 Lipids and Other Macromolecules

Proteins are present in grapes and must, but are undesirable as they cause turbidity. Proteins are removed by adding bentonite to the must. During processing of grapes enzymatic proteins such as hydrolase, phenoloxidase, laccase (in *Botrytis cinerea* infected grapes), pectinase, lipoxygenase and protease are released. Each of these enzymes stimulates specific chemical reactions during wine preparation.

Vitamins are present in small amounts in must. Examples are vitamin C (ascorbic acid), vitamin B1 (thiamine), vitamin B2 (riboflavin), p-aminobenzoic acid, vitamin H (biotine) and nicotinic acid.

2.2.3 Minerals

Potassium in the most important cation and normally accounts for 50 to 70% of the total cations in must. The concentration can range from 600 mg/ℓ to over 2500 mg/ℓ in certain red grape musts (Zoecklein et al., 1995). The precipitation of potassium acid tartrate in bottled wines is a problem faced by winemakers and prevention is essential. Knowledge of the potassium and tartrate contents allows the winemaker to predict the stability of potassium acid tartrate in the wine.

Sodium is present in low concentrations, 10-172 mg/ℓ (Zoecklein et al., 1995), in must and is usually in the form of sodium chloride. Other sources include sodium sulphite, sodium metabisulphite, sodium sorbate, sodium bentonite and sodium sulphide. Sodium is not particularly important in the production of wine but does affect the production of C.O.T. by ion exchange.

Calcium concentrations in wine range from 6 to 165 mg/ℓ. Determination of calcium levels in winemaking is important as calcium tartrate and oxalate precipitation can occur after the bottling of the wine.

Other cations, which are present in must, are magnesium, zinc, copper and iron. These cations are present as oxides, carbonates, phosphates, sulphates, and chlorides. The main inorganic anions in must are nitrate and phosphate. Minerals act as cofactors for

vitamins and enzymes and are therefore important for yeast growth and the production of aromatic substances.

2.2.4 Carbohydrates

Simple sugars form polymers such as pectins, gums, starch, hemicellulose and cellulose. Because of the partial water solubility of these components, they end up in the must during pressing. This can cause problems during pressing but can be overcome by the addition of enzymes. Glucanes are produced from *Botrytis* infected grapes and can cause serious problems during the wine and juice cleaning processes.

The main sugars in must are **glucose** and **fructose** and are present in approximately equal quantities. These two sugars make up the largest percentage of the total dissolved solids in must. **Sucrose** is present in very low concentrations and is easily hydrolysed to glucose plus fructose. Other sugars that have been identified in must or grapes include arabinose, ramnose, ribose, silose, maltose, mannose and melibiose.
The level of sugar is usually measured in degrees Brix. This is defined as soluble solids per 100g of juice. Note that this includes all soluble solids in the must including pigments, acids, glycerol, sugar, etc. However, the sugar accounts for 90 to 95% of the total soluble solids, therefore degrees Brix gives a reasonable approximation of the sugar content.

Sugars combine with lactones, anthocynins, terpenes and norisoprenoids to form glycosides. Some of these compounds can contribute to the aroma of the wine and must.

2.2.5 Acids

The most important organic acids in must are tartaric acid and malic acid. Together these make up approximately 90% of the total acid content. The ratio of these two acids depends on the cultivar and environment. Small quantities of citric, isocitric, glutaric and fumaric acid are also present in must. Acids can be formed from sugars, amino acids and fatty acids. None of the organic acids have any flavour effects. The structures of the predominant acids are shown in figures 2.1, 2.2 and 2.3.

Phenolic acids are also present in must and can cause bitterness (discussed under phenols.)

Amino acids are important building bricks for various components (discussed under nitrogen containing components.)

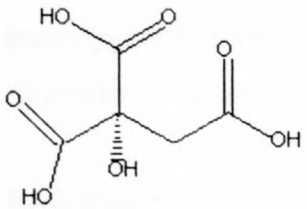

Figure 2.1 Structure of Citric acid

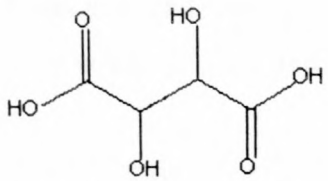

Figure 2.2 Structure of Tartaric acid

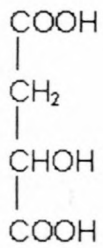

Figure 2.3. Structure of Malic Acid

2.2.6 Phenols

Phenol chemistry is a complex science and many different phenols have been identified in red grapes. Characteristics, reactivities and sensory contributions of these components vary considerably. Phenols are involved in the appearance, colour, flavour, fullness, bouquet and antimicrobic and anti-oxidising properties of red wines in particular. Phenol composition differs according to the cultivar, region, and year of harvest.

The main groups that the winemaker must take into consideration are the phenolic acids (non-flavonoids), flavonoids and tannins. Non-flavonoids are the main phenols in white wines. Flavonoids are mostly present in the skins, pips and stems. In red wine they make up about 85% of the total phenol composition, while in white wine this is

only about 20%. In white wines the phenol composition mainly consists of catechins and leucoanthocyanins, which give fullness to the wine. The most common flavonoids in grapes and wine are flavonols, catechins, anthocyanins and small amounts of leucoanthocyanins. Flavonoids are present freely and polymerised with other flavonoids, sugars, and non-flavonoids. Polymerisation of catechins and leucocyanidins yields procyanidins. While procyanidins are predominantly present as monomers in grapes, they also polymerise to form condensed tannins in wine.

Both flavonoid and non-flavonoid polymers are known as tannins. Flavonoid tannins have a prominent influence on the taste, mouth feel, and fullness of red wines. Catechins and their polymers, the procyanidins and condensed tannins are the major taste components of red wines and contribute to bitter and tart sensations.

2.2.7 Nitrogen Components

Various nitrogen-containing components are present in grapes. Examples are ammonium salts, amino acids, peptides, proteins and nucleic acid derivatives. The plant takes up nitrogen as ammonia- (NH_4^+) and nitrate- (NO_3^-) forms. This is observable in the increases in amino acids, especially proline and arginine. Nitrogen is indispensable for the feeding of yeasts and determines the progression of fermentation.

Nitrogen containing methoxypyrasines are some of the most important cultivar-typical aroma components in Sauvignon Blanc and Cabernet Sauvignon grapes and wine. These components are secondary products of amino acid catabolism. The most important pyrasine, which is usually found in the highest concentrations, is 2-methoxy-3-isobutylpyrasine, while 2-methoxy-3-isopropylpyrasine and 2-methoxy-3-secbutylpyrasine are usually found in much lower concentrations. Methoxypyrasine concentrations decrease with an increase in ripeness and exposure to sunlight of the grapes.

An important nitrogen-containing component in grapes and wine is methylanthranilate. In low concentrations it gives a pleasant berrylike aroma in wines.

2.2.8 Terpenoids

Terpenoids include nonvolatile carotenoids and sterols, as well as a large number of flavourful, 10-carbon monoterpenes and 13-carbon norisoprenoids.

More than 70 monoterpenes have been identified in grapes and are strongly related to the cultivars. Monoterpenes give prevailing pleasant aromas and come in three basic forms, namely the free volatile forms, the flavourless polyols and the non-volatile bonded glycosides. Both non-volatile forms convert easily to volatile aromas, under specific conditions. Norisoprenoids play an important role in cultivar aromas.

Monoterpenes and norisoprenoids can be considered as the most important aroma components of grapes and therefore of wine. A synergistic effect between components makes linking these components with specific cultivar aromas very difficult. During must treatments such as skin contact, monoterpenes and norisoprenoids are extracted from the skins and it is found that the concentrations increase with an increase in skin contact time and temperature.

2.2.9 Other volatile components

A small amount of aldehydes, namely hexanals, hexenals and 2,4-hexadinal are formed by enzymatic oxidation of lipids during crushing of grapes. These components are responsible for the grassy and herby bouquets of must. Most aldehydes, like acetaldehyde, are formed during fermentation.

A few ketones, like norisoprenoids, beta-damaskenone, alpha-ionone and beta-ionone, are present in grapes and therefore in must and wine. These components have low threshold values and have an important impact on aroma.

Higher alcohols and esters are byproducts of fermentation and are therefore present in wine. An exception is hexanol which gives a herby aroma in must and wine. Other higher alcohols, which are present in both must and wine, are 2-ethyl-1-hexanol, benzyl alcohol, 2-phenylethanol, 3-octanol and 1-octen-3-ol.

Lactones in wine are predominantly formed during fermentation and wood aging and the precursor sources are amino acids and organic acids, like glutamic and succinic

acid. A few lactones are present in grapes, like 2-vinyl-2-methyltetrahydrofuran-2-one and sotolone, associated with *Botrytis* infected grapes.

Volatile sulphur components are mostly present in wine and give unpleasant odours in high concentrations. These components are metabolised from sulphur sources in the grapes, e.g. proteins, peptides and amino acids.

2.2.10 Factors which influence must composition

Different climatic and viticultural factors have an effect on grape, and consequently on must compositions. Climatic factors include sunlight, temperature, and moisture retention of the soil. Some viticultural factors would be fertilization, irrigation, trimming, clone choice, production levels, etc. Extensive research has, over the years, investigated these complex effects and continues to do so, in order to optimise grape composition and grape and wine quality.

2.3 Ion Exchange of Musts (Portals Water Treatment, 1985)

In producing colourless, odourless and tasteless grape must, usually referred to as C.O.T., the ultimate aim is to be left with a solution which consists of only water and sugars. The contaminants that can be treated by ion exchange, can be divided into three main categories:

(1) Cations – normally present as potassium, sodium, magnesium and calcium ions. Several species of the organic compounds, which have cationic amine groups also fall into this category.

(2) Anions – most of the anions present are the simple organic acids i.e. tartaric, malic and citric. There are also small amounts of inorganic acid radicals such as sulphates, chlorides, carbonates, etc.

(3) Non-Ionics – these include the compounds which give rise to colour and odour. Their removal by ion exchange is a complex function based on a diffusion/adsorption mechanism and, in the case of fruit juices, is often pH dependent.

Ion exchange treatment of C.O.T. consists of a combination of cationic and anionic resins. Where a particularly high degree of purity is required, the juice can also be passed through various selective adsorbing resins.

The juice first passes through a strongly acidic cationic resin bed. Salt splitting occurs and causes a marked decrease in the pH of the juice leaving the column. Only a slight residual amount of cations is left in the product. Very little reduction of colour, odour or taste is noted.

Reaction

$R^-H^+ + M^+Ac^- \rightarrow R^-M^+ + H^+Ac^-$ [2.1]

The decationised juice is then passed through a weak anionic resin bed. An large increase in pH occurs indicating the removal of acid radicals and the presence of very small amounts of inorganic hydroxides.

Main reaction

$R^+ OH^- + H^+Ac^- \rightarrow R^+Ac^- + H^+OH^-$ [2.2]

Reaction with residual metal cations

$R^+OH^- + M^+Ac^- \rightarrow R^+Ac^- + M^+OH^-$ [2.3]

During this step most of the colour is removed to leave a clear, very pale off-white solution. After exhaustion the ion exchange beds are regenerated using dilute sulphuric acid on the cation column and caustic soda on the anion column.

If a higher degree of purity is required the liquid could be treated with a selective adsorbing resin or an activated carbon column, which can remove a particular taste-, odour- or colour-causing compound, which may be reducing the saleability of the product. A second cation column could also be added to the treatment process to remove any cations present as hydroxides.

2.3.1 Other literature

Besides the reference mentioned above, very little literature that specifically refers to the treatment of grape juice by ion exchange, could be found. KWV produces grape juice concentrate and does use ion exchange as part of the treatment process. The articles that refer to this company; (Anon., 1989) and (Reid, 1992) are written from an

economic point of view. The production of clarified grape juice concentrate is evidently highly profitable.

A related process is the softening of sugar-cane juice by ion exchange (Sun et al., 1990). In this case calcium is removed from the juice by passing it through a selective cation exchange resin. The demineralisation of diluted sugar cane syrup by ion exchange produces a heavily polluted regeneration effluent (Hanine et al., 1991). In this article the recovery of the valuable organic acid, aconitic acid, from the effluent is discussed. A similar process may be applicable to the recovery of tartrates from the effluent produced by the ion exchange of grape juice.

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CHAPTER 3

Water Audit

3.1 INTRODUCTION

Ashton Co-operative Cellars produce red and white wines, and various forms of grape juice concentrate. The effluent produced during winemaking is combined with that produced during the clarification and concentration of grape juice. A water audit was carried out in order to evaluate these effluent problems. The layout of the cellar and its wastewater streams are shown in figure 3.1. The water entering the cellar comes from a dam, which is supplied by the Brede River and a borehole.

In order to understand the sources of effluent produced during the winemaking processes, they will now be described briefly. Please note that these are generic descriptions and do not necessarily describe the exact process used at Ashton Cellars. The production of grape juice concentrate is described in chapter 4. As far as effluent production is concerned, the major difference between the production of white wine and the production of colourless, odourless and tasteless grape juice concentrate is the additional effluent produced by the ion exchange process used to demineralise and decolourise the grape juice.

3.1.1 Production of white wine

1. The white grapes are first destemmed and crushed. The juice released during crushing can be used for high quality wines. Waste is produced in the form of grape skins, pips and stems.
2. The grapes are then cooled and pressed in bag filters to release further juice. More skins and pips enter the wastewater at this point.
3. The juice may now be clarified by cold settling. This reduces the amount of suspended solids in the juice. The settled solids enter the wastewater when the settling tanks are washed.
4. Alcoholic fermentation now takes place. This is either induced by the addition of yeast culture or is left to occur naturally. Fermentation is usually conducted at 10-

16 °C. The dead yeast cells settle to the bottom of the fermentation tanks or barrels. This is termed lees and often enters the wastewater streams during washing of the tanks.

5. The wine is now cold stabilised and fined to prevent the deposition of potassium bitartrate and proteinaceous haze formation in the bottle. The fining agents and potassium bitartrate may enter the wastewater at this point.
6. The wine is filtered and bottled.

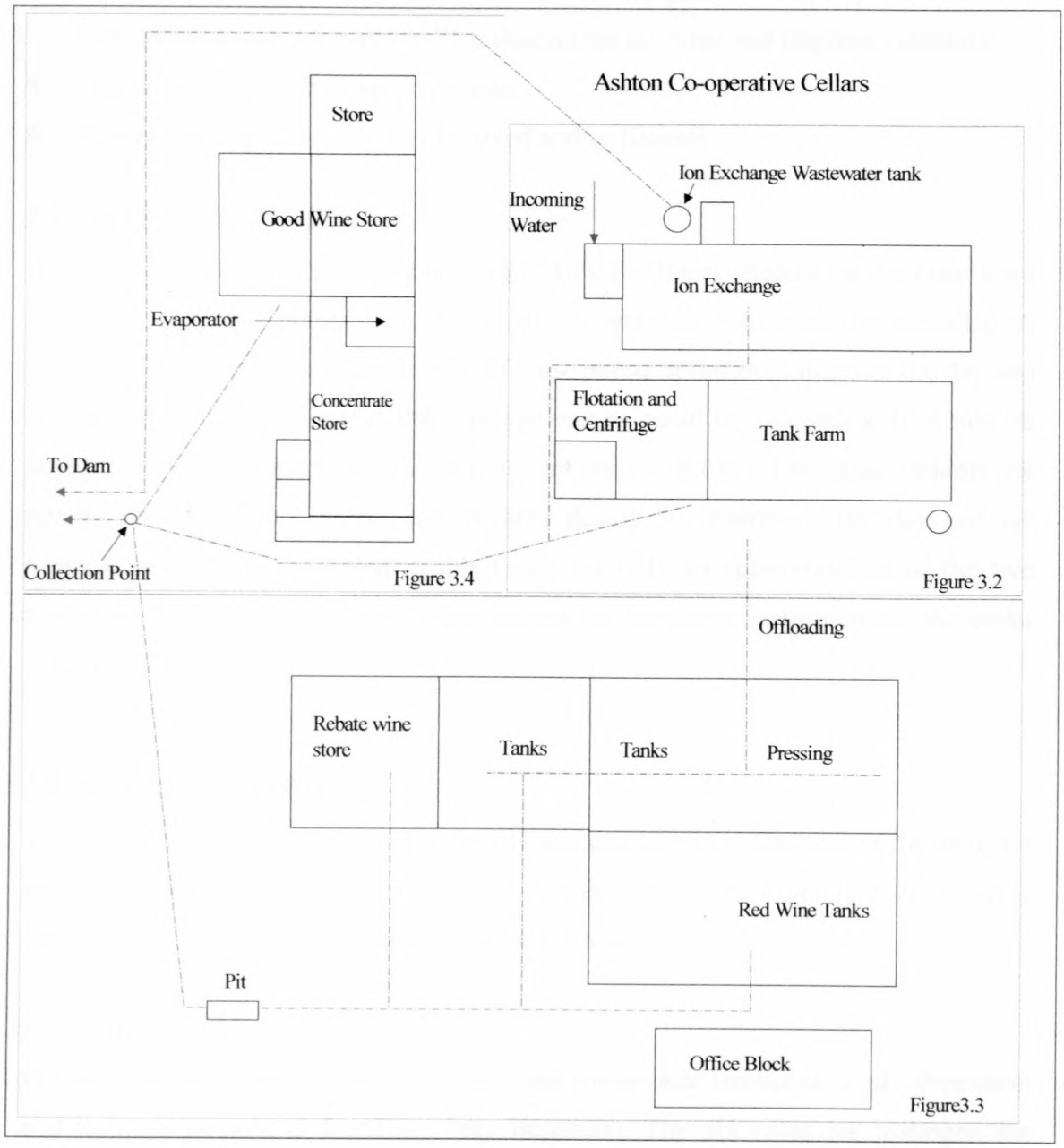


Figure 3.1 Schematic diagram of Ashton Co-operative Cellars

3.1.2 Production of Red Wine

1. The red grapes are crushed and destemmed. They are then transferred to a fermentation vessel.
2. Fermentation occurs on the skins.
3. Once sufficient colour, flavour and tannin extraction has taken place, pressing takes place. Skins may enter the wastewater from the cleaning of the presses and the fermentation tanks.
4. Fermentation continues until the wine is dry (1-2 g/ℓ reducing sugar). Malolactic fermentation also takes place. This deacidifies the wine and improves stability.
5. The wine is allowed to age in barrels.
6. Before bottling, the wine may be fined and/or filtered.

3.2 SAMPLING STRATEGY

Before analysis of the effluent could begin, all the effluent streams on the plant were identified. Sampling points were chosen so that problem areas could be identified. A number of samples were taken at each of these points at different times of the day and during different operations so that average values could be calculated. It should be noted that, because operations in the plant are carried out in a batchwise fashion, the quality of the effluent varies considerably during the course of the day and the average analysis results given in this thesis are only an approximation of the true averages. All the samples were taken during the harvesting season when the cellar was fully operational.

3.3 ANALYSIS OF SAMPLES

The samples were analysed on site for pH and conductivity. The rest of the analyses were completed at the CSIR and in the laboratories of the Chemical Engineering Department. The effluent was tested for the following:

3.3.1 pH

Practically every phase of water supply and wastewater treatment is pH dependent and its measurement is therefore, very important. The pH value (or hydrogen ion activity) indicates the intensity of the acidic or basic character of a solution.

According to the National Water Act (Muller, 1999) the pH of wastewater streams used for irrigation should lie in the region 6 to 9.

3.3.2 Conductivity

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions (their total concentration, mobility and valence) and the temperature of the sample. Solutions of inorganic compounds are usually much better conductors than solutions of organic compounds. The standards for the disposal of liquid waste by irrigation (Muller, 1999) state that the conductivity of water leaving a plant should not be more than 200 mS/m.

3.3.3 Alkalinity as $CaCO_3$ (mg/ℓ)

The alkalinity of an effluent sample is its acid-neutralising capacity. A general quality tolerance for brewery wastewater recommends an alkalinity of less than 75 mg/ℓ.

3.3.4 Hardness as $CaCO_3$ (mg/ℓ)

Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate. According to SABS Standards for drinking water (SABS, 1999) this value should be in the region 20-300 mg/ℓ.

3.3.5 Turbidity

Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the effluent sample. Suspended matter such as silt, finely divided organic and inorganic matter, soluble coloured organic compounds and other microscopic organisms causes turbidity in water.

3.3.6 Chemical Oxygen Demand (COD)

The chemical oxygen demand is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The COD should not exceed 75 mg/ℓ in effluent entering the environment. Organic matter can be present either in dissolved form or as particulate organic matter. The COD test is a useful parameter for monitoring pollution. The presence of

organic matter promotes the formation of microbiological slimes, acting as a nutrient source for bacterial growth. Such microbial slimes often contain sulphate-reducing bacteria, which are responsible for extensive damage to heat exchange and cooling systems through microbially induced corrosion (MIC). Fouling of ion-exchange resins may also occur. Products of degraded organic compounds can cause problems in steam generation systems by promoting corrosion/erosion in steam and condensate return lines.

Effluent with unacceptably high (more than 75 mg/ℓ) COD levels must be treated. Sedimentation and coagulation may remove particulate organics. The removal of dissolved organics requires more complex chemical treatment methods like ozonation and the use of ultra-violet light.

3.3.7 Dissolved Organic Carbon (DOC)

Total organic carbon is a useful expression of the total organic content of a sample. Unlike COD, it is independent of the oxidation state of the organic matter. Dissolved organic carbon is the fraction of the total organic carbon that passes through a filter of 0.45 μm pore size.

3.3.8 Total Phosphorus (TP)

Phosphorus is an element that is essential to the growth of organisms and it can be a growth-limiting nutrient for the organisms in a body of water. The addition of wastewater with a high phosphorus level to clean water can stimulate the growth of photosynthetic aquatic organisms in problematic quantities. It is therefore, important to monitor the levels of phosphorus in effluent.

3.3.9 Kjeldahl Nitrogen as N (KN)

Organic nitrogen and ammonia can be determined together and are referred to as Kjeldahl Nitrogen. Kjeldahl is the name of the analytical method used. Organic nitrogen is defined as organically bound nitrogen in the trinegative oxidation state. It includes materials such as proteins, peptides, nucleic acids, urea and synthetic organic materials. The Kjeldahl Nitrogen should fall in the region 5-70 mg/ℓ.

3.3.10 Total Oxidised Nitrogen (N)

Total oxidised nitrogen is the sum of nitrate and nitrite nitrogen. Both nitrate and nitrate can cause the illness methemoglobinemia in infants. Nitrous acid, which is formed from nitrite in acidic solution, can react with secondary amines to produce carcinogenic nitrosamines. Total oxidised nitrogen is therefore, toxicologically significant.

3.3.11 Solids

Total solids (TS) is the term applied to the material residue (both organic and inorganic) left in the vessel after evaporation and drying of a sample at a defined temperature. The SABS standards state that this value should not exceed 500 mg/ℓ in an effluent stream.

The **total dissolved solids** (TDS) is the portion of solids which passes through a filter of 2.0 μm (or smaller) nominal pore size while the **suspended solids** (SS) is the portion retained on the filter. Wastewater should not contain more than 25 mg/ℓ suspended solids.

The TDS is directly proportional to the conductivity and, in conjunction with pH, hardness and alkalinity, plays a major role in the determination of the corrosion or scaling potential of water.

Suspended solids can cause the following problems if the effluent is used for irrigation, i.e.:.

- drip irrigation systems become clogged,
- soil surface crusts will form. These may inhibit water infiltration and seedling emergence, and
- photosynthetic activity reduction.

Treatment options include the following:

- sand and screen filters that can be backwashed,
- centrifugal separators, and
- sedimentation and coagulation.

3.3.12 Sodium Absorption Ratio (SAR)

The SAR is an index of the potential of a given irrigation water to induce sodic soil conditions. Soil sodicity is usually measured by the percentage of soil's cation exchange capacity that is occupied by sodium ions. It is calculated from the concentrations of sodium, calcium and magnesium in water, and gives an indication of the level at which the exchangeable sodium percentage (ESP) of the soil will stabilise after prolonged irrigation. SAR is determined on the saturated soil extract. This value indicates the ESP of the soil. Irrigation water with high bicarbonate/carbonate concentrations gives rise to the precipitation of calcium carbonate in soil. This causes soil to become enriched with sodium, thereby increasing the SAR and ESP. This is the index for "effective " SAR calculation. Lime decreases the effective SAR. The target value for the SAR is less than 1.5.

Treatment Options

The SAR represents problems only when its value is high (above 5). The SAR of water can be reduced by either decreasing the sodium concentration or by increasing the calcium and/or magnesium concentrations. Sodium can only be removed by highly sophisticated physico-chemical separation techniques. More cost-effective, however, is the addition of calcium and magnesium salts to the irrigation water. Gypsum ($CaSO_4.2H_20$) is most generally used.

Practical Implications:

- Increase in salt has a potentially negative effect, see TDS (section 3.2.11).
- Complementary anions can have a negative effect on crop response. Thus, sulphates (not considered as a potentially toxic ion) rather than chlorides (although more soluble), are recommended.
- Ca and Mg can cause plant nutritional imbalances.
- Gypsum has limited solubility.

3.4 RESULTS

The results of the audit are summarised in figures 3.2, 3.3 and 3.4. In these figures a schematic diagram of the cellar has been divided into three sections (the divisions are shown on figure 3.1). From them the following observations can be made.

- **Incoming water:** This was found to be of satisfactory quality, i.e. all values are well below the standards set by law.

- **Ion Exchange effluent (A1):** This stream is characterised by a very low pH (less than 3) and a high salinity and conductivity. The COD level is relatively high at about 6000 mg/ℓ. A more detailed analysis of the effluent from the ion exchange plant is presented in Chapter 4.

- **Pit (A8):** This collection point contains run-off from the main cellar and has a particularly high solids content (both suspended and dissolved in the water). This effluent also has a high COD (about 8000 mg/ℓ). The pH of the stream is moderate.

- **Collection point (A7):** This stream consists of a combination of effluent streams from the rest of the cellar. It is predominantly wash water and can vary from extremely polluted (with a COD of about 150000 mg/ℓ), when the initial rinsing of a tank occurs, to almost clean water from a final rinse or where a hose is left open unnecessarily. The level of dissolved and suspended solids in this stream can be very high.

- **Dam water:** This water is highly polluted. It has a low pH, high chemical oxygen demand, high levels of suspended and dissolved solids and an unacceptably high concentration of sulphates (See Table 3.1 for a comparison of the quality of the dam water with environmental standards). The odour created by this dam is very unpleasant.

  The low pH of the dam water is mainly caused by the ion exchange water (A1). Other streams that contribute to the low pH include the flotation and centrifuge

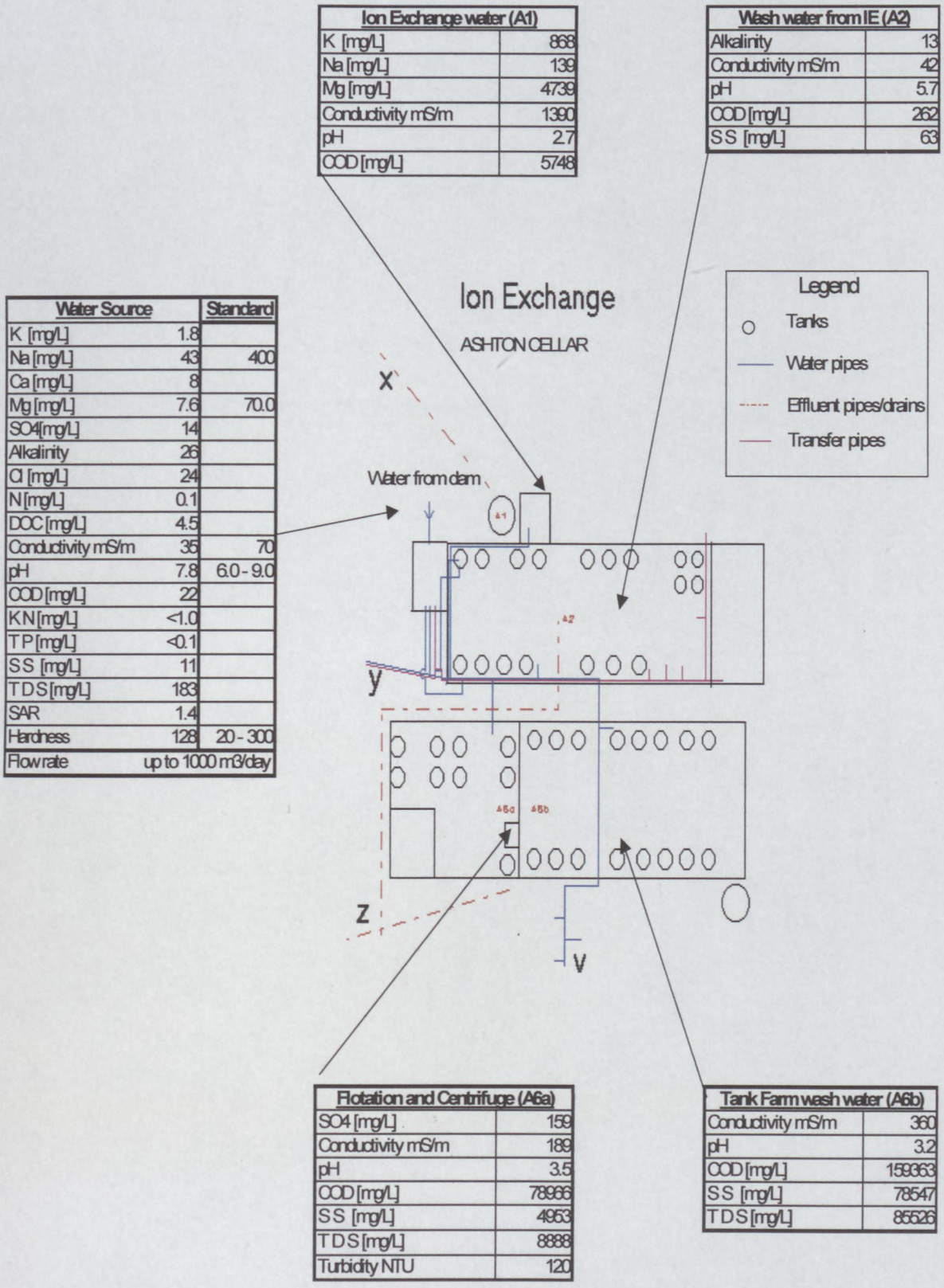


Figure 3.2 Results of water audit for the ion exchange plant and surrounding areas

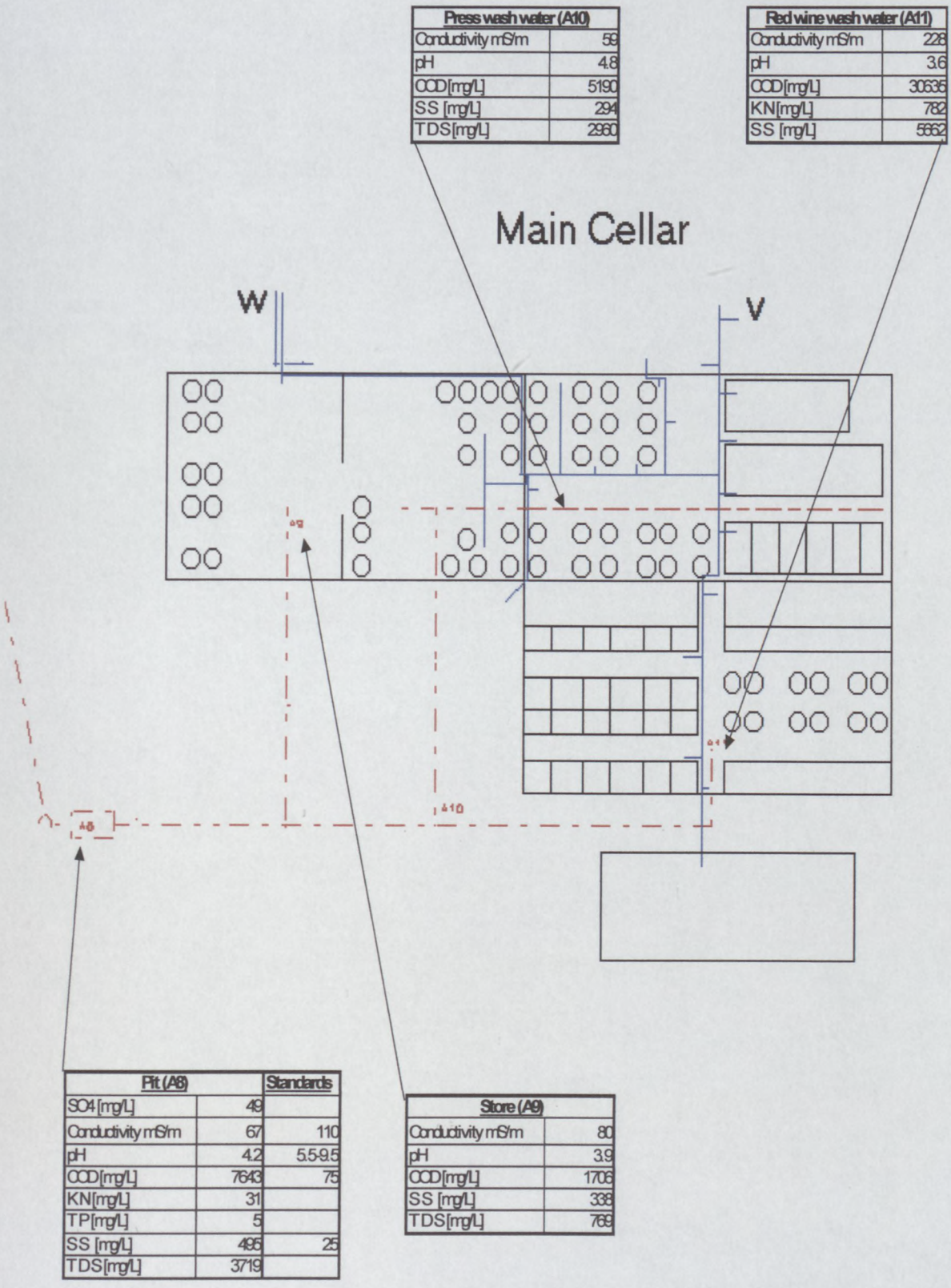
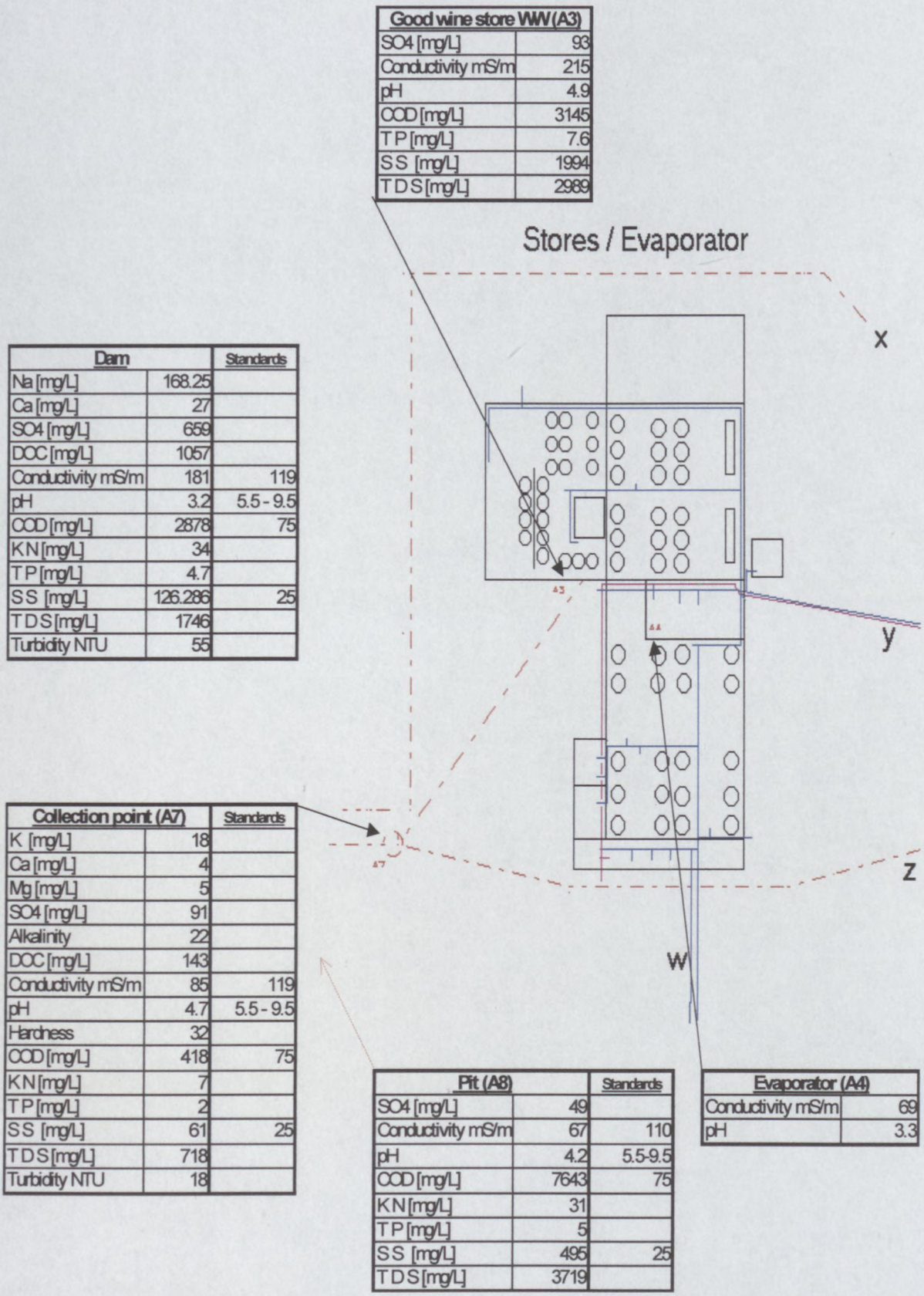


Figure 3.3: Results of water audit for the main cellar.



Good wine store WW (A3)	
SO4 [mg/L]	93
Conductivity mS/m	215
pH	4.9
COD [mg/L]	3145
TP [mg/L]	7.6
SS [mg/L]	1994
TDS [mg/L]	2989

Dam		Standards
Na [mg/L]	168.25	
Ca [mg/L]	27	
SO4 [mg/L]	659	
DOC [mg/L]	1057	
Conductivity mS/m	181	119
pH	3.2	5.5 - 9.5
COD [mg/L]	2878	75
KN [mg/L]	34	
TP [mg/L]	4.7	
SS [mg/L]	126.286	25
TDS [mg/L]	1746	
Turbidity NTU	55	

Collection point (A7)		Standards
K [mg/L]	18	
Ca [mg/L]	4	
Mg [mg/L]	5	
SO4 [mg/L]	91	
Alkalinity	22	
DOC [mg/L]	143	
Conductivity mS/m	85	119
pH	4.7	5.5 - 9.5
Hardness	32	
COD [mg/L]	418	75
KN [mg/L]	7	
TP [mg/L]	2	
SS [mg/L]	61	25
TDS [mg/L]	718	
Turbidity NTU	18	

Pit (A8)		Standards
SO4 [mg/L]	49	
Conductivity mS/m	67	110
pH	4.2	5.5-9.5
COD [mg/L]	7643	75
KN [mg/L]	31	
TP [mg/L]	5	
SS [mg/L]	495	25
TDS [mg/L]	3719	

Evaporator (A4)	
Conductivity mS/m	69
pH	3.3

Figure 3.4: Results of water audit for the evaporator and surrounding stores.

effluent (A6a), the tank farm wash water (A6b) and effluent water from the evaporator (A4).

All of the effluent streams on the plant contribute to the high COD of the dam water but particularly high levels were measured in wash water during washes of the flotation unit (A6a) and the tanks (A6b and A11).

Streams which make a significant contribution to the high level of suspended solids include the flotation and centrifuge effluent (A6a), the tank farm wash water (A6b), and the good wine store wash water (A3). Streams with high TDS include the flotation and centrifuge effluent (A6a), the tank farm wash water (A6b), the press wash water (A10) and the good wine store wash water (A3).

The ion exchange water (A1) is solely responsible for the high concentration of sulphates in the dam.

Table 3.1 Comparison of incoming and outgoing water with standards.

	Water Source	Dam	Standards	
	Raw	Effluent	SABS 241 (SABS, 1999) Drinking Water	Water Act (Muller, 1999) For irrigation
K [mg/ℓ]	1.8	-	-	-
Na [mg/ℓ]	43	168	400	-
Ca [mg/ℓ]	8	27	-	-
Mg [mg/ℓ]	7.6	-	70.0	-
Alkalinity	26	-	-	-
Conductivity [mS/m]	35	181	70	200
PH	7.8	3.2	6.0 - 9.0	6.0 – 9.0
Hardness	128	-	20 - 300	-
SO_4 [mg/ℓ]	14	659	200	-
DOC [mg/ℓ]	4.5	1057	-	-
COD [mg/ℓ]	22	2878	-	2000
K N [mg/ℓ]	<0.1	34	-	-
T P [mg/ℓ]	<0.1	4.7	-	-
S S [mg/ℓ]	11	126	-	25
T D S [mg/ℓ]	183	1746	-	-
Turbidity NTU	-	55	-	-

3.5 AUDIT 2000

The audit results presented above where for the harvesting season in 1999. Further samples where taken by the Winetech Wine Cellar Auditing project team in February 2000. A stricter sampling plan was followed i.e. samples were taken at regular intervals throughout the day.

The following results should give more representative average values for the Effluent Dam and Pit (A8).

Table 3.2 Results of water audit: February 2000

Pit (A8)	
COD [mg/ℓ]	5860
DOC [mg/ℓ]	1659
TDS [mg/ℓ]	2636
SS [mg/ℓ]	504
PH	3.3
Conductivity [mS/m]	312
SO4 [mg/ℓ]	477
Ca [ppm]	10
K [ppm]	117
Mg [ppm]	6.9
Na [ppm]	116

Dam	
COD [mg/ℓ]	7151
DOC [mg/ℓ]	2237
TDS [mg/ℓ]	3205
SS [mg/ℓ]	504
pH	4.0
Conductivity [mS/m]	102
SO_4 [mg/ℓ]	53

If these values are compared to the results from 1999 it is noted that the quality of the effluent seems to be better. This could be due to the improved sampling procedure or due to improvements made to the cellar such as the wedge wire screen added at the collection point (A7) which removes any grape skins, pips and stems from the effluent before it is pumped to the effluent dam.

3.6 SUGGESTIONS

While observing the running of the cellar it was noticed that a considerable amount of water is used unnecessarily. This does serve to dilute the effluent streams but it also means that more water is polluted. If a treatment plant is built it will be beneficial to

decrease water use as much as possible so that a smaller plant (with lower running costs) will be sufficient to treat the effluent.

Some possible methods to reduce the water use include the following:

- High-pressure nozzles with self-closing valves could be attached to hose pipes. The high velocity water stream cleans more effectively and water is not wasted by hoses left open unnecessarily.
- Closed circuit washing.
- Recycling of sealing water of vacuum filters and centrifuges.
- Methods to reduce water usage during line transfers.

It was also noted that the level of pollution in the effluent streams varies considerably. This means that relatively clean streams, which could be easily treated or even reused, are often combined with highly polluted streams. Segregation of these streams would improve effluent quality. One would, however, have to take into account the costs involved in segregating the streams and compare it to the savings achievement by lowering the volume of heavily polluted water needing extensive treatment.

Another way to improve effluent quality is to separate solids from the effluent at as early a point as possible. This keeps the level of solids in the effluent to a minimum and lowers the chemical oxygen demand. The use of screens is recommended.

In implementing any of these practises it is important that the personnel on the plant are made aware of the problems and are consulted before any changes are made. Extra training may be required.

CHAPTER 4

The Ion Exchange Plants at Ashton Cellars

The water audit described in Chapter 3 identified the ion-exchange process to be a significant contributor to the total effluent of the cellars. In this chapter the ion exchange process is looked at in more detail. Audits of the process were carried out and their results are given here. In order to give some insight into where ion exchange is used in the concentrated C.O.T. (colourless, odourless and tasteless grape juice) production process at Ashton Cellars, the whole process is described briefly below.

4.1 THE PRODUCTION OF CONCENTRATED C.O.T. AT ASHTON CELLARS

After the white grapes have been harvested they are transported to the cellar and offloaded. They are then passed through a piece of equipment, a combination destemmer and crusher, which removes the stems and breaks open the berries. The juice is drained to separate it from the broken skins and seeds. This high quality juice is used for the production of white wine. The remainder of the juice is separated with a press. This juice is used to make the C.O.T.

The following are now added to the juice:

1. **Sulphur dioxide**: This is added to inhibit oxidation reactions and as an antiseptic. The latter activity is important to inhibit indigenous yeast and bacteria. Sulphur dioxide is a slow scavenger of oxygen but shows rapid anti-oxidation activity in the inhibition of polyphenols oxidases of the must, which can cause browning. These brown pigments can become further polymerised and precipitate.

2. **Baykisol**: This is a solution of about 30% silicon dioxide in water suspension. It is the first of a series of clarifying agents added to the juice to remove proteins and polyphenols. It is negatively charged and binds with protein

molecules to increase floc sizes. It is usually used in conjunction with gelatin but must be added prior to the gelatin.

3. **Gelatin**: This is 100% animal derived gelatin composed of aminoacids, primarily glycine, proline and hydroxproline. It is colloidal in nature and primarily has a positive charge. It flocculates with tannins (polyphenols) and, once this neutralization has occurred, other turbid particles tend to agglomerate. It acts on both proteins and tannins.

4. **Bentonite**: Montmorillonite clay. It is a naturally occurring hydrated aluminosilicate of sodium, calcium, magnesium and iron. (Sometimes Kaolin clays are used as fillers in commercially available products but this lowers the surface area and efficiency of use.) Bentonite is negatively charged and attracts positively charged particles to its surface. It is a particularly effective protein remover.

These fining agents, now combined with proteins and polyphenols, are removed from the juice by dissolved air flotation.

If the juice is to be stored for later treatment by ion exchange it is sent to the vacuum evaporator to be concentrated to about 70 Brix. This is necessary as the juice can be stored for longer in its concentrated form. Later in the year when harvesting is over and there is no fresh juice available, the concentrated juice is diluted, using water filtered through a sand filter, to 22 Brix and treatment continues.

The fresh juice or diluted concentrate goes through a final clarifying step. This time bentonite, gelatin and activated carbon are added. The activated carbon is an excellent adsorbent of benzenoid compounds. It acts to remove or partially remove all classes of polyphenols and is fairly non-specific. It is used to decolourise and deodorise the juice.

These clarifying agents are allowed to settle, and then the solids are removed by sending the juice through a vacuum drum filter.

The juice is now ready to be treated by ion exchange as described in chapter 4.2.

After ion exchange, the juice is concentrated by a vacuum evaporator to give the final product; colourless, odourless and tasteless, concentrated grape juice. The above process is shown diagrammatically in figure 4.1.

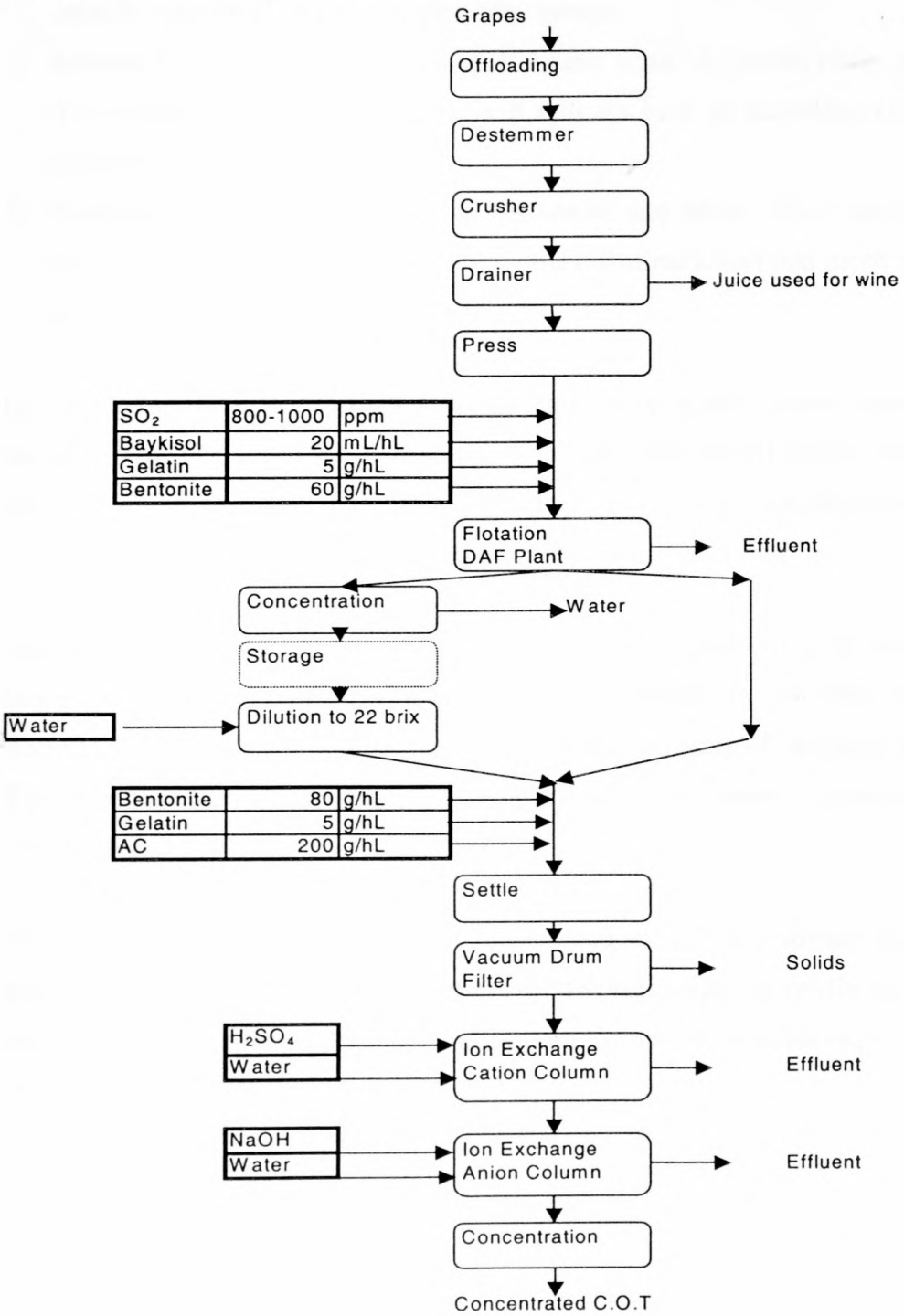


Figure 4.1 Diagram of C.O.T. production

4.2 Ion Exchange Process Description

The contaminants that must be removed from the grape juice by ion exchange fall into three categories:

1. **Cations**. Including potassium, sodium, magnesium, calcium and several species of organic compounds with cationic amine groups.
2. **Anions.** Mostly in the form of simple organic acids i.e., malic, citric, tartaric, etc. Also small amounts of inorganic acid radicals such as sulphates, chlorides and carbonates.
3. **Non-ionics**. These are responsible for colour and odour. Their removal by ion exchange is a complex function based on a diffusion/adsorption mechanism and is largely pH dependent.

In treating the juice, it is first passed through a strong acidic cationic resin bed. This removes most of the cations. During this step a reduction in pH occurs indicating salt splitting with a corresponding increase in acid value. Very little decrease in colour, taste or odour is expected at this point.

The juice is then passed through a weak anionic resin bed. Here all the negatively charged anions are removed resulting in a large increase in pH. This indicates the removal of acid radicals and the presence of small amounts of inorganic hydroxides. This step also removes non-ionics leaving the solution almost colourless, odourless and tasteless.

When the ion exchange beds are fully loaded they must be regenerated before further juice treatment can occur. **It is important to note that currently no means of monitoring the degree of loading exists, and at present is achieved by observing the colour of the product.**

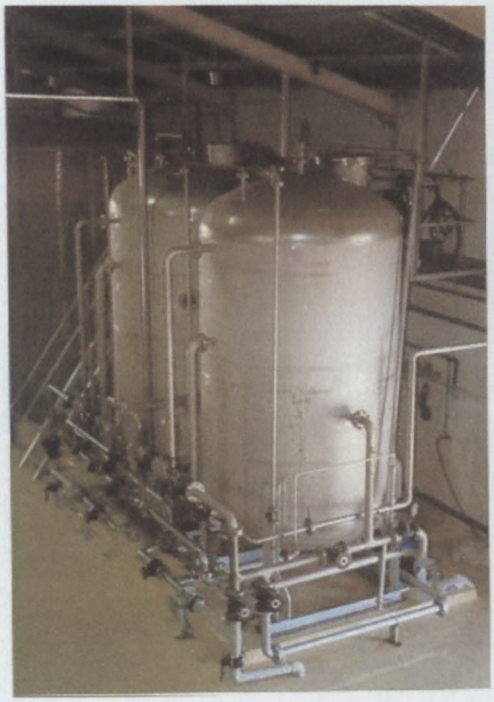


Figure 4.2a Large Ion Exchange Plant

Figure 4.2b Small/4Column Ion Exchange Plant

The plants must conform to the following specifications: (Portals Water Treatment, 1985)

1. Reduce the level of colour in the raw juice to an acceptable level. (This would be water white at 18 Brix).
2. Reduce acidity to give a pH of acceptable level (4.5 – 6).
3. Reduction of inorganic salts down to acceptable levels, usually 90% reduction down to levels below 100 ppm.

4.3 The Resins

The following are the resins, which are used at Ashton cellars. There are two ion exchange plants, shown in figure 4.2a and figure 4.2b. One consists of one cation column and one anion column (referred to as the large plant). The other one consists of two cation columns in series and two anion columns in series (referred to as the small plant). Both plants use the same amount of resin but in the small plant, the resin is divided between the two columns.

Cation Columns:	5800 litres of Amberlite 252H
Anion Columns:	1000 litres of Amberlite IRA 92
	1400 litres of Amberlite IRA 96
	1000 litres of Amberlite XE583*
	2200 litres of Amberlite IRA94S*

Note: These values came from an order form for the last batch of resin bought by the cellar. Those marked with a * are no longer available. Previously 5600 litres of Amberlite IRA 92 were used in the anion columns. Data sheets for the available resins are presented in Appendix C.

These resins should be able to treat 50 000 litres of juice and must be regenerated once every 24 hours. The plants are run for about 200 days per annum.

4.3.1 Laboratory Testing of Cation Resin

Laboratory scale testing was carried out on the cation resin (referred to as Ashton Cation to avoid confusion with new Amberlite 252H). The detail of the experimental method is described in Chapter 5, where the results are compared with new resins. The resin was taken from the plant after regeneration. Before the resin was loaded it was found that it could be regenerated further. This indicates that the regeneration cycle used on the plant is not efficient and that contaminant ions are left on the resin, lowering the capacity of the resin for the next loading cycle.

Visual examination of the resin showed a significant amount of solids in the surrounding liquid. These should have been removed from the resin during the plant's backwash cycle. In an ideal ion exchange system such solids should be removed from the juice prior to ion exchange treatment, as they foul the resin and thereby lower its capacity and decrease its life span. Before evaluating the capacity of the resin, these solids were removed.

The capacity of the cation resin was determined by loading it with sodium ions and measuring the pH of the effluent throughout the loading process. A hydrogen ion mass balance was used to calculate the specific cation capacity. The total capacity of the resin was found to be **1.86 meq/mℓ resin**. While this result is reasonable, the figure 4.3 shows that its performance is not satisfactory.

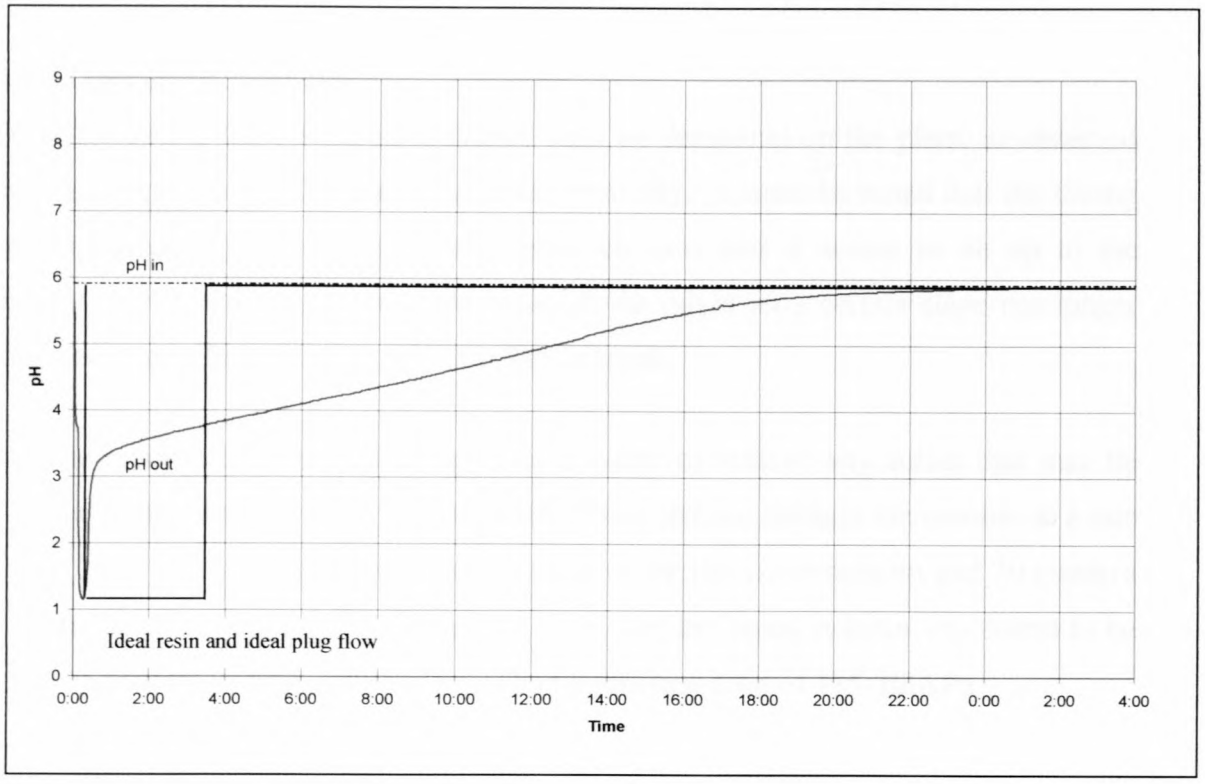


Figure 4.3 Ashton Cation Resin Capacity Experiment: pH vs. Time

The problem lies in the rate of loading. The presence of the long tail on the graph means that a large amount of the sodium solution passes through the column with only a small amount of sodium being exchanged. In practice this would mean that a large volume of product would leave the column off-spec before the column is fully loaded. Lowering of the throughput rate might also be required to ensure a better quality product. The curve of a newer, cleaner resin would approximate more closely, the curve for the theoretically perfect resin shown on the graph. New resin, of the same type used on the plant, was tested and compared with the old resin. The results are given in Chapter 5.

4.4 AUDITING OF EXISTING PLANTS

In order to evaluate the current plants and their operation, some time was spent observing and documenting the operating procedure. Samples were taken during the regeneration and loading cycles and analysed for conductivity, pH, metals, organic

acids and other factors where applicable. These samples were taken on three separate occasions and from both ion-exchange plants. The results given in this chapter are for the large ion-exchange plant unless otherwise indicated.

4.4.1 Operating Sequence

What follows is the operating sequence used by personnel on the plant, as observed during sampling runs. They run the plant manually. It must be noted that the timing of the various cycles varied greatly between runs and it seems to be up to the discretion of the plant operator. For example he might let a certain stage run longer than necessary if it coincides with his dinner break.

1. The resin is backwashed using filtered water to remove any solids that may be caught between the resin beads. Water flows upward through the column at a rate of 2.66 ℓ/s for a period of about 40 minutes for the anion column and 30 minutes for the cation column. The pressure drop over the anion column was found to be 320-340kPa and the cation column had a pressure drop of 185-200kPa.

2. Fill with regenerant. Dilute sulphuric acid (about 3%) is added to the cation column and caustic soda (about 3%) to the anion column. For the first hour, in the case of the cation column and the first half hour, for the anion ion column, the effluent is released directly into the drain. For the rest of the filling cycle the effluent is sent to a holding tank where it can be treated with lime to increase the pH before being sent to the effluent dam.

   In the cation column the cations (K, Na, Mg and Ca) are released from the resin and replaced by the hydrogen ions from the acid. This will cause an initial increase in the pH followed by a sharp drop in pH as the number of hydrogen ions entering the column exceeds the number being taken up by the resin. The effluent from this column will contain the remaining hydrogen ions, the sulphate ions from the dissociated sulphuric acid, and the cations.

   In the anion column, the introduction of caustic soda (sodium hydroxide) causes the anions on the resin to be exchanged for the hydroxyl ions. There is a slight decrease in pH (or an increase in pOH) as the number of hydroxyl ions being used

for regeneration temporarily exceeds the number being added to the column, but the pH will rise as the concentration of caustic soda in the column increases. The effluent from this column will contain the anion contaminants and sodium ions.

3. The anion column is left to stand for a while (approximately 1.5 hours), while sulphuric acid is still being fed to the cation column. At the end of this period the cation resin should be fully regenerated in the hydrogen form and the anion resin in the hydroxyl form.

4. The columns are rinsed with water to remove all the regenerant and contaminants. The anion and cation columns are rinse separately with the effluent being sent to the holding tank for the first hour and after that it is then released directly into the drain. For the last hour or so of rinsing, water flows through both columns (Shown as 'rinse together' on the graphs); the cation column followed by the anion column.

5. Loading: The resin is now ready for loading. As there is still water in the column, the water (mixed with some juice) displaced by the juice at the beginning of the loading cycle is disposed of in the drain until the product reaches 6 Brix. The juice is pumped through the columns at a rate of about 1.23 ℓ/s. The loading cycle treats about 410 hℓ in about 13 hours but this amount and time varies from one cycle to the next. The total ion exchange process, loading and regeneration takes about 20 hours.

6. Sweetening off: Filtered water is used to rinse out the juice remaining in the feed tank and is then pumped through the columns to allow the juice already in the column to move through. This takes about 3 hours. The regeneration sequence now begins again with the backwashing.

4.4.2 Results of Sampling Runs

4.4.2.1 Sampling run: 16/9/99

The first sampling run focussed on the regeneration cycle of the ion exchange plant at Ashton.

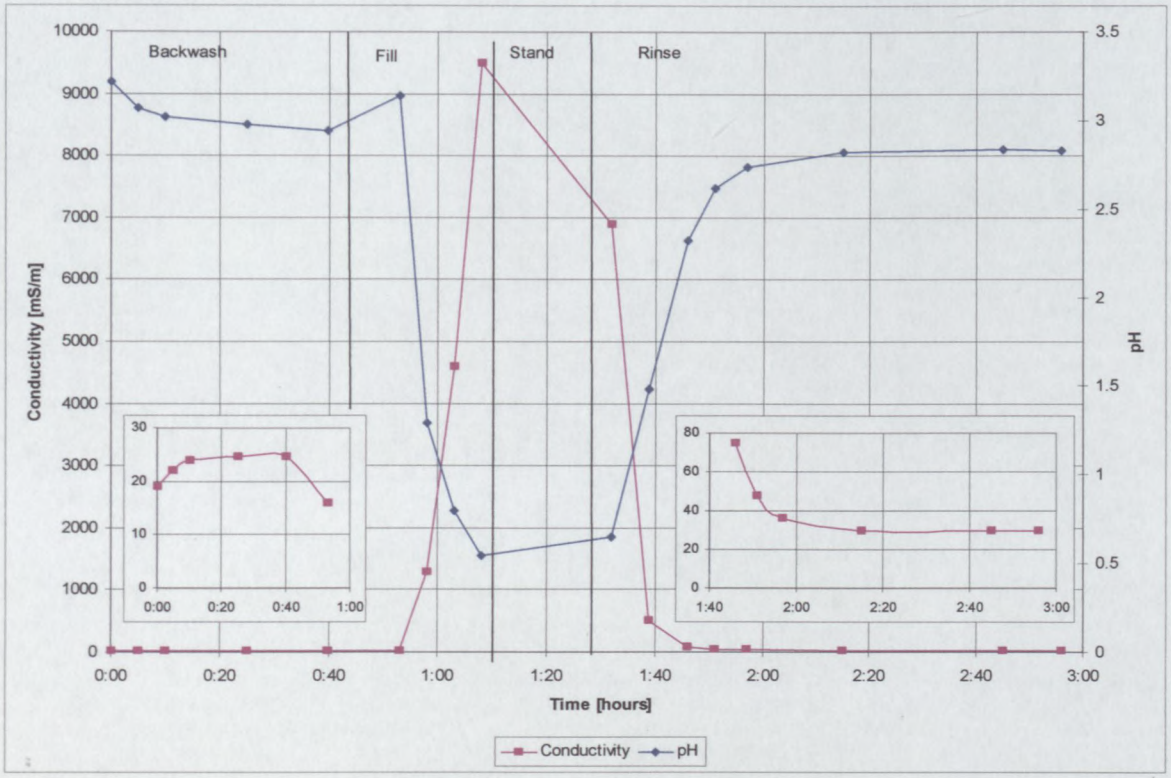


Figure 4.4: Small Ion Exchange Plant Acid Regeneration: pH and Conductivity (16/9/99)

Regeneration of the cation resin starts with a backwashing of the column. From figure 4.4 it is noted that there is only a slight drop in pH during the backwash cycle with a corresponding increase in conductivity. If the column had been fully loaded the backwash would have had little or no effect on the pH or conductivity. The drop in pH, visible here, suggests that ion exchange is continuing in the column, i.e. the cations in the water are being exchanged for hydrogen ions on the resin thereby increasing the concentration of hydrogen in the effluent.

After the backwash cycle, dilute sulphuric acid is added to the column. Approximately ten minutes after the filling has started, the pH of the effluent, which had initially increased slightly as predicted in the process description, decreases sharply (to about 0.5). The conductivity increases to about 9500 mS/m due to the

presence of a high concentration of charged particles (the metal ions and sulphates). The lag experienced at the beginning of this stage can be ascribed to the time the sulphuric acid front takes to move through the column and appear in the effluent stream. The sulphuric acid is left to stand in the column for about 20 minutes before being rinsed out.

During the rinse cycle the pH rises rapidly and levels out at a pH of about 2.8 after 35 minutes. At the same time the conductivity decreases and becomes constant at about 30 mS/m. The rinse is continued for a further 40 minutes with little change in the effluent quality. This suggests that the rinse cycle is too long and that water is being wasted.

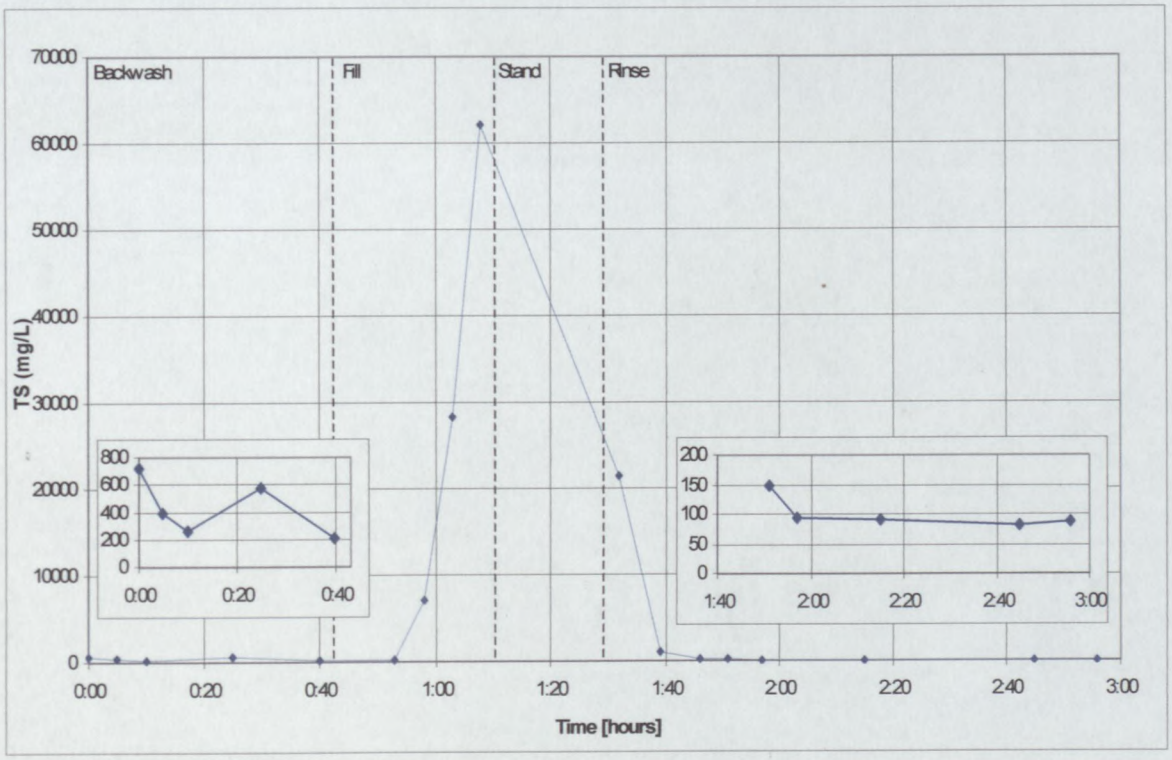


Figure 4.5: Small Ion Exchange Plant Acid Regeneration: Total Solids(16/9/99)

The main purpose of the backwash cycle is to remove suspended solids from the column (Figure 4.5). On the first magnification section of the graph, the initial rapid decrease in solids shows that the backwash is successful in lowering the level of suspended solids to a minimum within the first half-hour. This is represented more clearly in figure A4 (Appendix A: Suspended Solids during Acid Regeneration). Figure A3 (Appendix A: TDS during Acid regeneration) also shows that the backwash has very little effect on the level of dissolved solids in the effluent.

Once sulphuric acid is introduced into the column there is a ten-minute lag before the effect on the total dissolved solids in the effluent becomes evident. This is due to the time taken for the sulphuric acid to move through the column. The concentration then increases rapidly and reaches a peak of at least 62000 mg/ℓ. Although not apparent on this graph, this concentration probably levels off while the column is left to stand.

During the rinse cycle the TDS level decreases rapidly and levels off, after half an hour, at a minimum value less than 100 mg/ℓ.

The similarity between figure 4.5 and the conductivity curve shown in figure 4.4 should be noted as these two factors correspond closely.

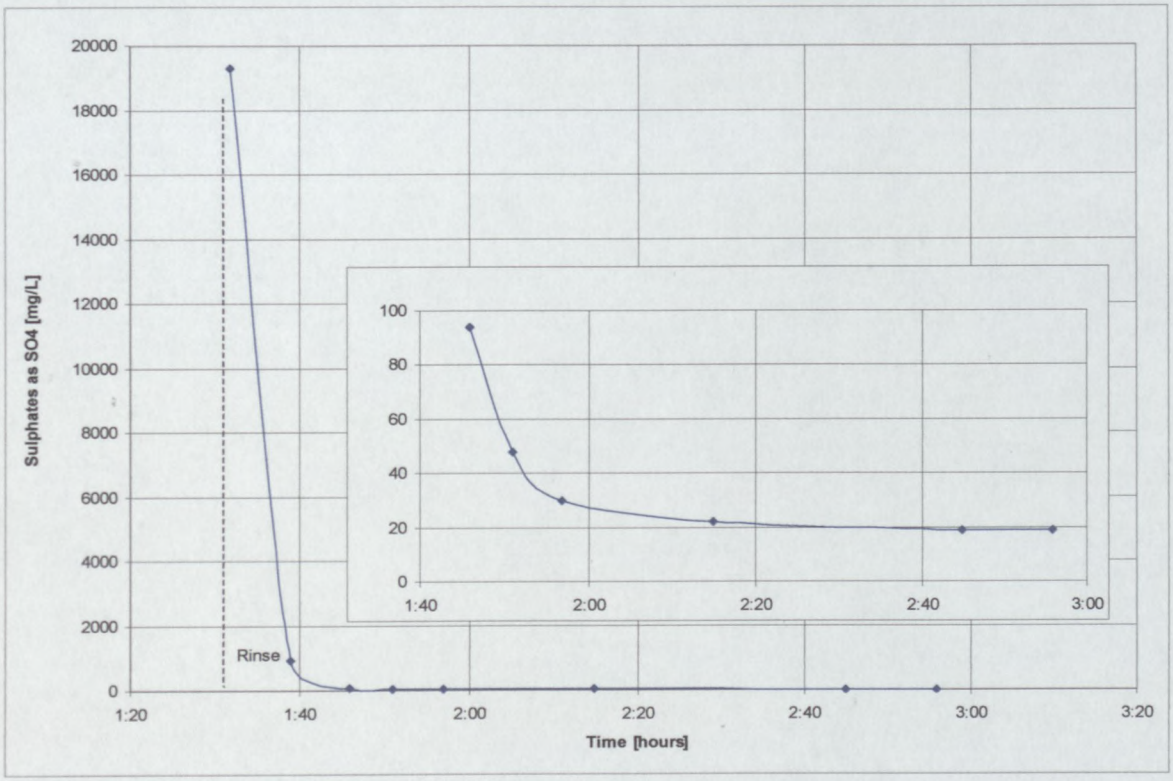


Figure 4.6: Small Ion Exchange Plant Acid Rinse: Sulphates (16/9/99)

After the resin has been standing in sulphuric acid, the effluent contains a very high concentration of sulphates, (Figure 4.6). Once the rinse starts, this concentration decreases rapidly and reaches a level lower than the SABS standard for drinking water (200 mg/ℓ) in about 15 minutes.

When this graph (Figure 4.6) is compared to the conductivity during the rinse cycle, it is found to show a very similar trend. It is therefore, appropriate to use the conductivity curve (which is easier and cheaper to determine) as an indication of the sulphate concentration in the effluent from the cation column.

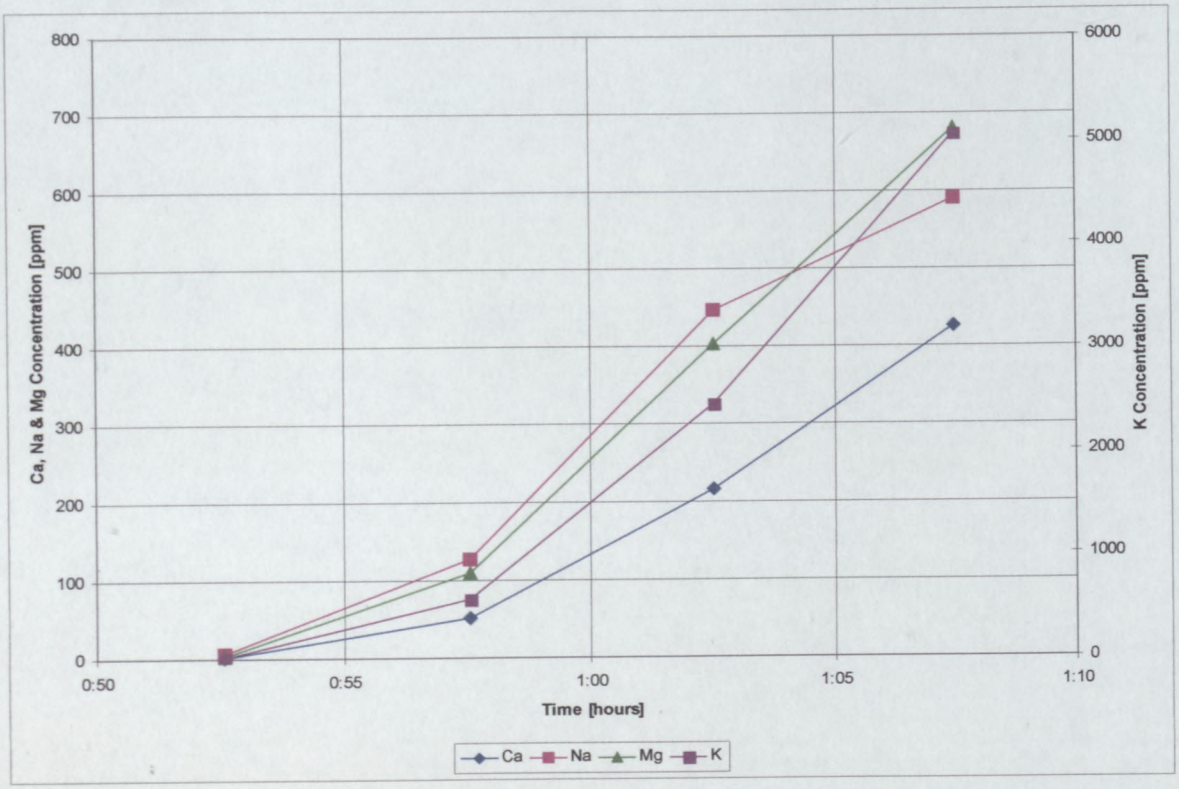


Figure 4.7: Small Ion Exchange Plant Acid Fill: Cations (16/9/99)

As the concentration of regenerant in the column increases, the cation resin releases more cations into the effluent stream. This explains the increasing trends in the figure 4.7. Analysis of the juice before treatment gave the following metal ion concentrations:

K 800ppm

Mg 40ppm

Ca 16ppm

Na 16ppm

The very high concentration of potassium ions in the juice explains why its concentration in the regeneration effluent is also very high. From this graph we can also conclude that the resin exchanges the cations for hydrogen ions in the following order of preference: Na > Mg > Ca. The concentration of sodium probably starts to become constant before any of the others, due to less sodium being present on the loaded resin.

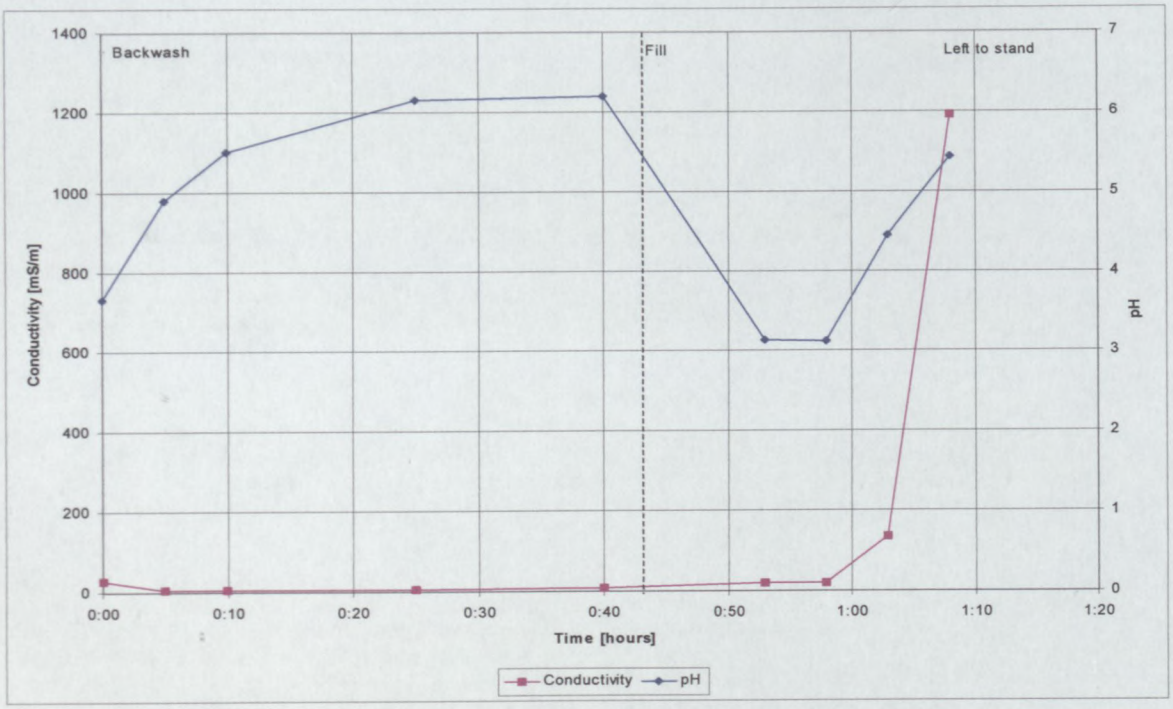


Figure 4.8: Small Ion Exchange Plant Caustic Backwash and Fill: pH and Conductivity (16/9/99)

Figure 4.8 shows the change in pH and conductivity of the effluent during the regeneration of the anion resin using caustic soda. The backwash stage has a duration of approximately 45 minutes. The pH increases steadily and becomes constant at a pH of about 6.2 after 25 minutes.

Once caustic soda is added to the column, there is a significant drop in pH. Here the regeneration of the resin has begun and the concentration of hydroxyl ions in the effluent stream is being reduced at a rate faster than they are entering the column. As the concentration of hydroxyl ions increases it eventually reaches a point at which there is an excess and the pH begins to increase. It is also at this point that the conductivity increases sharply.

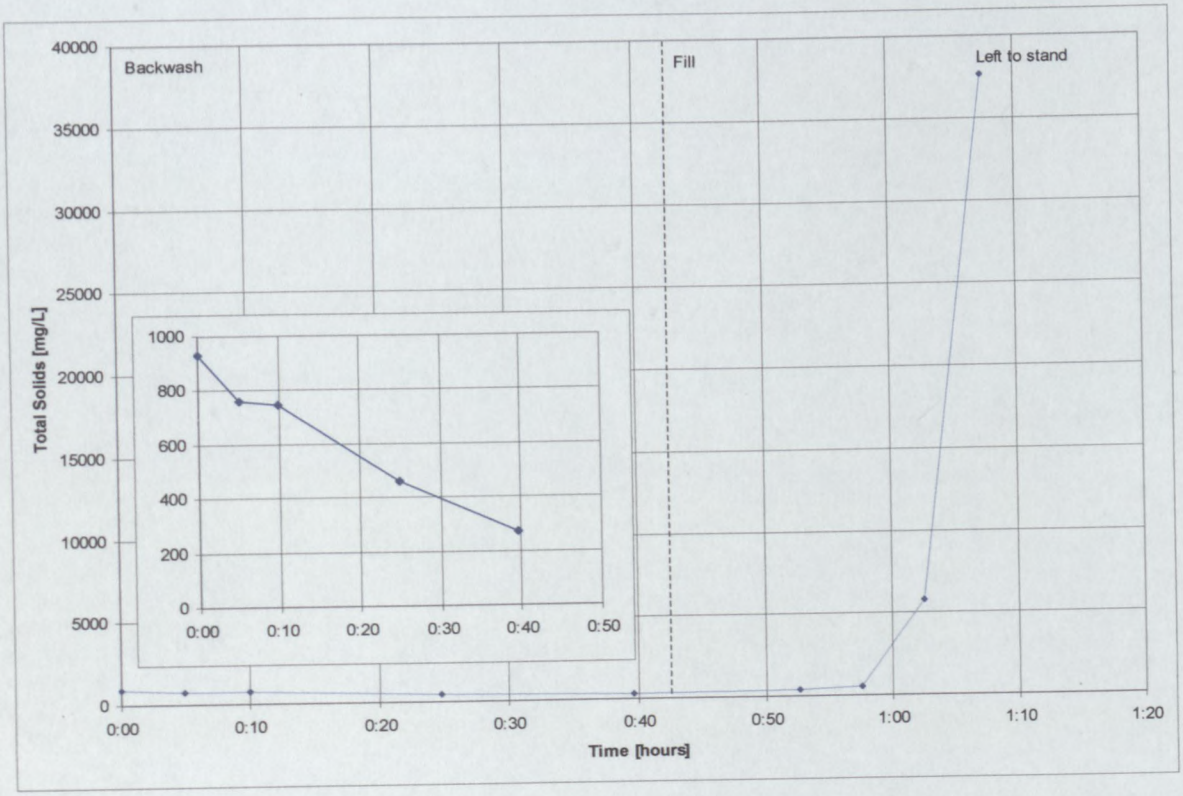


Figure 4.9: Small Ion Exchange Plant Caustic Backwash and Fill: Total Solids (16/9/99)

When compared to the backwash of the cation column, it must be noted that the decrease in suspended solids in this column is far slower. This is due to the fact that the flow rate through the column is slower. From figure A8 (Appendix A: Suspended solids during Caustic Regeneration) it is evident that a backwash time of 50 minutes allowed the suspended solids to reach a sufficiently low level (less than 25 mg/ℓ) without wasting water.

The level of total dissolved solids increases rapidly 15 minute after the caustic soda is introduced into the column. The maximum-recorded value was about 37500 mg/ℓ.

Figures 4.10 and 4.11 show results from the large ion exchange plant. In this plant the maximum recorded value for the total solids in the effluent of the anion column was about 54000 mg/ℓ.

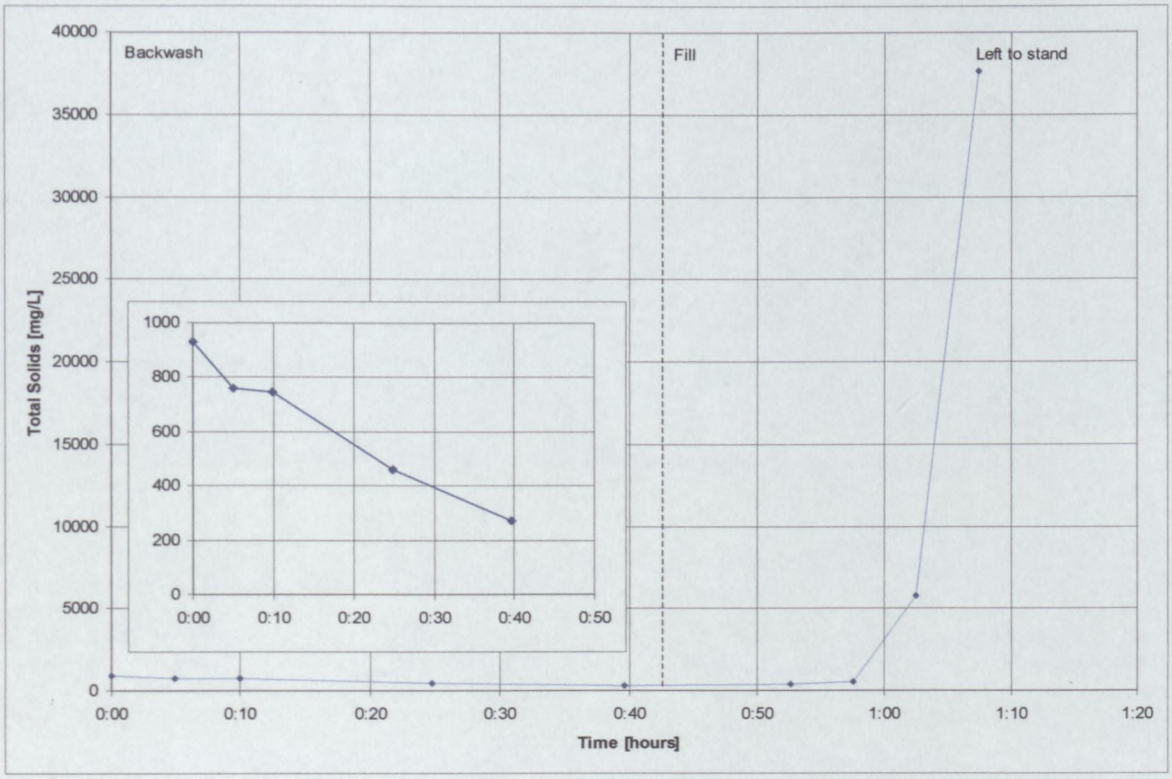


Figure 4.9: Small Ion Exchange Plant Caustic Backwash and Fill: Total Solids (16/9/99)

When compared to the backwash of the cation column, it must be noted that the decrease in suspended solids in this column is far slower. This is due to the fact that the flow rate through the column is slower. From figure A8 (Appendix A: Suspended solids during Caustic Regeneration) it is evident that a backwash time of 50 minutes allowed the suspended solids to reach a sufficiently low level (less than 25 mg/ℓ) without wasting water.

The level of total dissolved solids increases rapidly 15 minute after the caustic soda is introduced into the column. The maximum-recorded value was about 37500 mg/ℓ.

Figures 4.10 and 4.11 show results from the large ion exchange plant. In this plant the maximum recorded value for the total solids in the effluent of the anion column was about 54000 mg/ℓ.

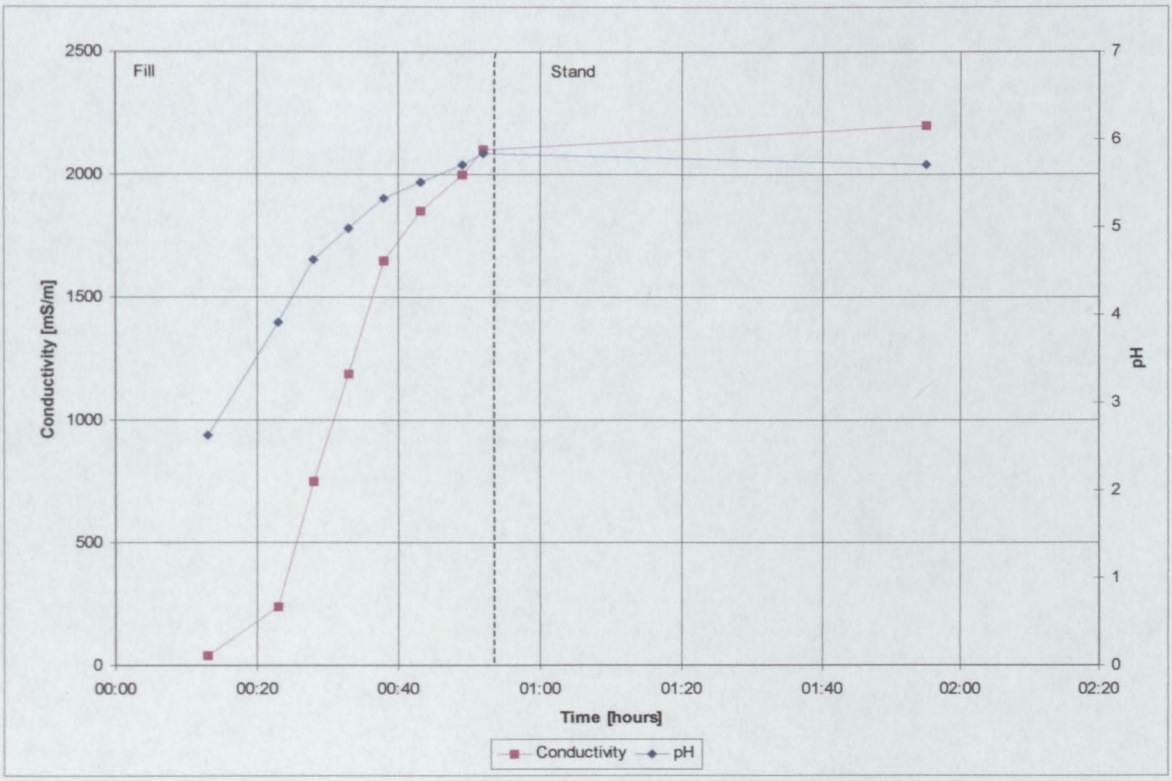


Figure 4.10: Large Ion Exchange Plant Caustic Fill And Stand: pH and Conductivity (16/9/99)

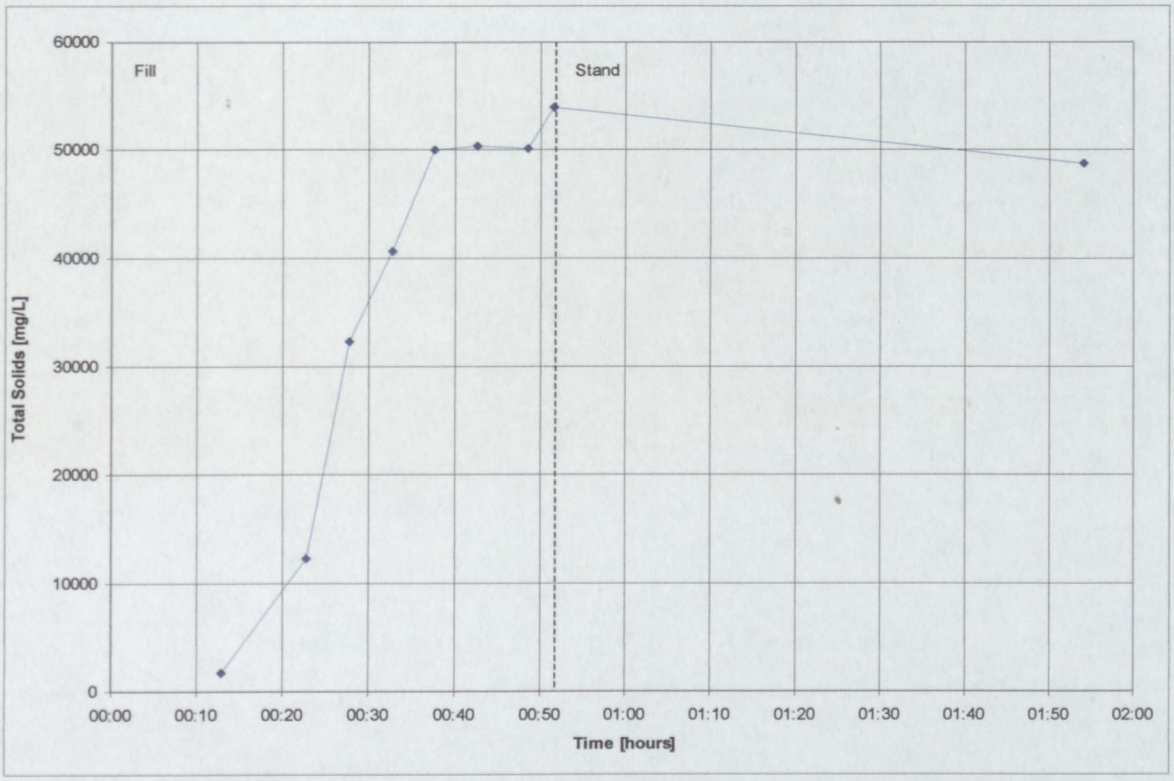


Figure. 4.11: Large Ion Exchange Plant Caustic Fill and Stand: Total Solids(16/9/99)

4.4.2.1.1 Preliminary Sampling Exercise

Included in Appendix A is a set of graphs plotted using data from a preliminary sampling exercise on the small ion exchange plant. These were taken in order to get a general idea of the trends and to determine where extra samples would be required in the subsequent sampling exercise. It should be noted that, while in most cases there is an insufficient number of data points on these graphs, some useful observations could be made from them. One which has not yet been mentioned, is the observation that COD levels in the caustic regeneration effluent are in general, a lot higher than in the acid regeneration effluent, (figures A2 and A7). For the acid rinse the COD level is found to drop to acceptable levels well before the end of the rinse cycle, (figure A2).

4.4.2.1.2 General Observations on the first sampling run (16/9/99)

There are some differences between an ideal ion exchange regeneration cycle and the cycles observed at the cellar.

- There is evidence that the loading cycle is not run to completion.
- Backwash times are the same for both the cation and anion columns even though the flow rate through the cation column is faster and the suspended solids are removed sooner than those in the anion column. Water is therefore being wasted/ contaminated unnecessarily.
- The rinse cycles are far too long, wasting both time and water.

4.4.2.2 Sampling Run 23/2/2000

In order to verify previous results and to study the loading cycle of the ion exchange plant another sampling run was carried out. On this run, samples were taken from the large ion exchange plant. As the regeneration cycle was discussed at length in the previous section, only the loading cycle and a few new observations will be discussed here.

Analyses of the incoming water, the juice entering the ion exchange columns and the regenerants were carried out. The results are given in the following tables.

Table 4.1Incoming Water

Date	23/2/00	11/10/00
pH	6.95	7.33
Conductivity [mS/m]	20	52
Na [ppm]	6.2	
K [ppm]	1.9	
Ca [ppm]	14.5	
Mg [ppm]	1.5	

Table 4.2 Diluted Concentrate (before ion exchange)

Date	23/2/00	11/10/00
pH	3.87	3.64
Conductivity [mS/m]	220	310
Na [ppm]	25.8	
K [ppm]	419	
Ca [ppm]	16.2	
Mg [ppm]	25.9	
Sulphates [mg/ℓ]	341	425
TDS [mg/ℓ]	129600	
TKN [mg/ℓ]	450	
Tartrates[mg/ℓ]		2553
Malates [mg/ℓ]		6003
Citrates [mg/ℓ]		8

Table 4.3 Caustic Soda

Date	23/2/00	11/10/00
pH	11.5	11.59
Conductivity [mS/m]	9500	6300
Na [ppm]	417	
K [ppm]	22.6	
Ca [ppm]	5.8	
Mg [ppm]	0.4	

Table 4.4 Sulphuric acid

Date	23/2/00	11/10/00
pH	0.97	1.03
Conductivity [mS/m]	5400	6000
Sulphates [mg/ℓ]	10200	10689
TDS [mg/ℓ]	11054	

These analysis results show that the quality of the incoming water varies significantly. It is interesting to note that on 23 February 2000 the concentration of calcium in the water was only slightly less that in the diluted concentrate. There is also a variation in

the composition of the diluted concentrate. This would affect the operation of the plant and should be accounted for in designing a control system. The compositions of the sulphuric acid and caustic soda seem to be relatively consistent.

4.4.2.2.1 Cation Column Results

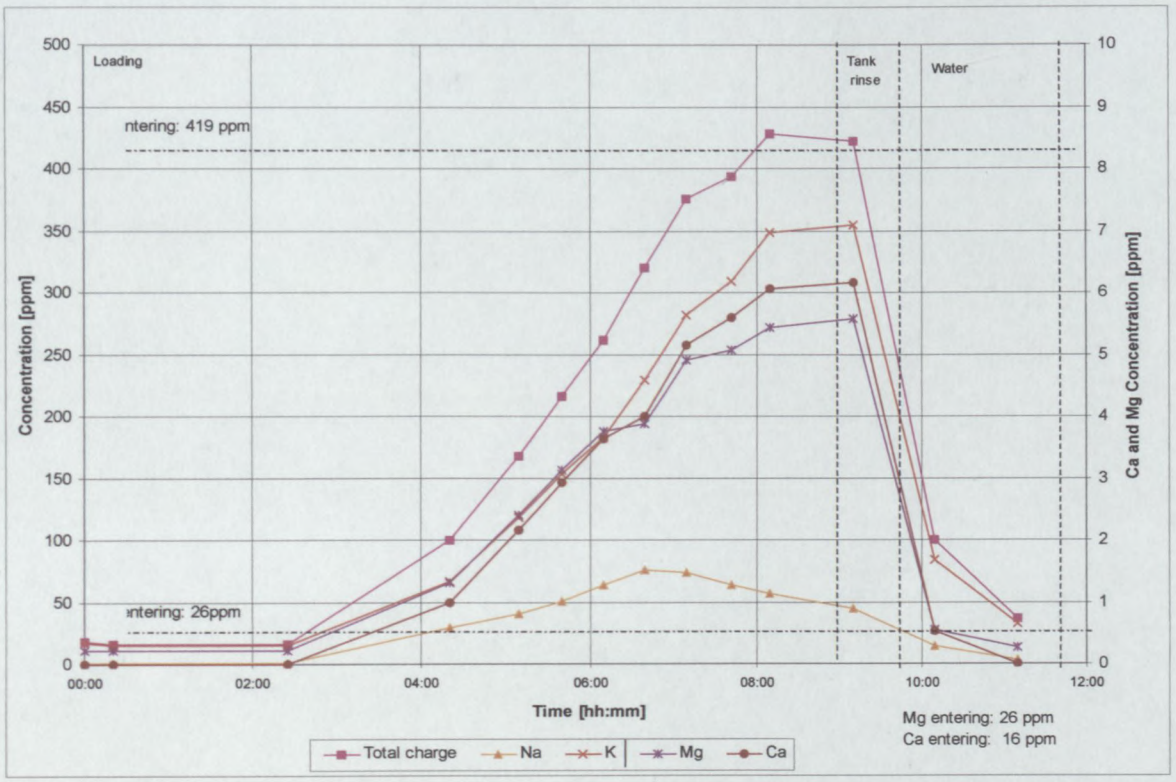


Figure 4.12 Cation Column: Concentration of metal ions during loading cycle (23/2/00)

Figure 4.12 shows that, for the first two and a half hours of loading, a maximum amount of metal ions are being removed from the juice. After that, the operating capacity of the resin decreases steadily until it approaches a minimum at just over 8 hours. Of importance is the observation that after about four and a half hours the concentration of sodium in the juice leaving the column becomes higher than that of the incoming juice. A possible explanation for this is that the resin's affinity for sodium is lower than for the other metal ions. The resin therefore, releases the sodium and takes up the other metal ions in its place.

This graph was used to calculate an estimate of the total amount of cations loaded onto the resin during this cycle. The estimate is **0.067 meq/mℓ resin**. This value is significantly lower than the resins total capacity of 1.86 meq/mℓ and it can be

concluded that the resin is not fully loaded at the end of the loading cycle. It must be noted that there are other cations, such as amino acids and proteins, present, which are not accounted for in this estimate.

The point at which loading should be stopped can be determined once definite specifications for the allowed concentrations of metal ions are given. If, for example, the maximum amount of potassium allowed in the treated juice is 20 ppm, the loading should have been stopped after two and a half hours. Because the ion concentrations cannot easily be measured during the loading cycle, it is desirable to find another indicator of the concentration of ions in the treated juice. Time is not a reliable factor, as each loading cycle will differ as far as timing is concerned. Changes in juice compositions, regeneration characteristics, operating temperatures and flowrates will all affect the timing.

Figures 4.13 and 4.14 show how the pH and conductivity of the juice change with the change in concentration of ions in the juice. They are therefore better indicators.

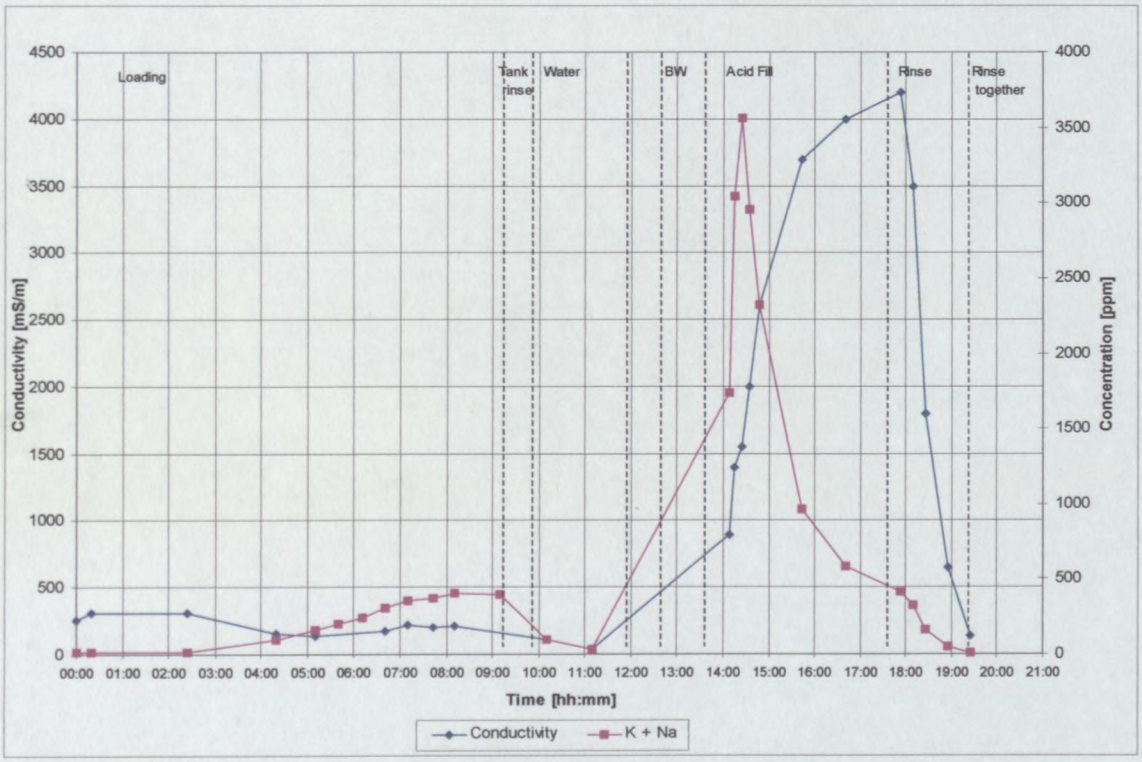


Figure 4.13: Cation column: Comparison of conductivity and metal ion concentrations (23/2/00)

Figure 4.13 shows that, as the concentration of ions in the treated juice increases, the conductivity decreases. This can be explained by the fact that the presence of free hydrogen ions has a greater influence on the conductivity than free metal ions do. As the amount of loading occurring at a given moment decreases, less free hydrogen ions are released into the juice lowering the conductivity. This also explains the increase in pH evident in figure 4.14.

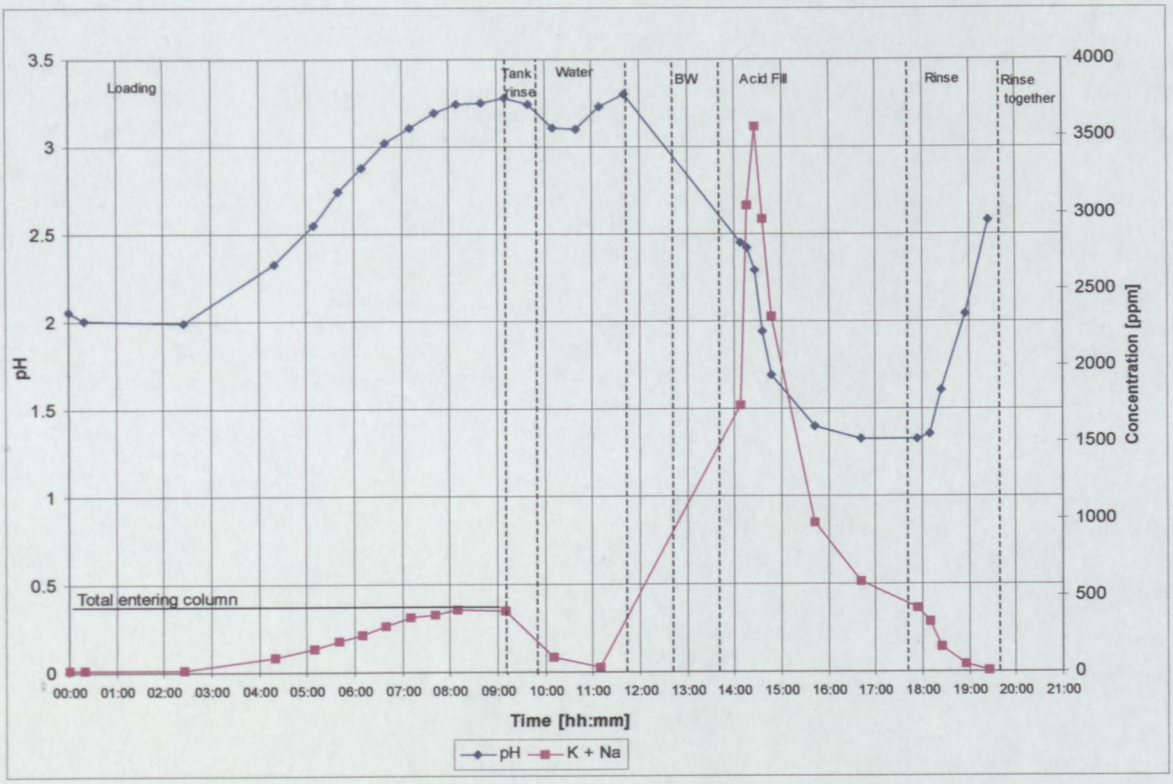


Figure 4.14: Cation Column: Comparison of pH and metal ion concentration (23/2/00)

4.4.2.2.2 Anion column results

Figures 4.15 and 4.16 compare the pH and conductivity with the metal concentration in the juice leaving the anion column. When studying the loading cycle in these two graphs, it must be kept in mind that the juice flows through the cation column before the anion column and the metal ion concentrations therefore correspond to those leaving the cation column but with a time delay.

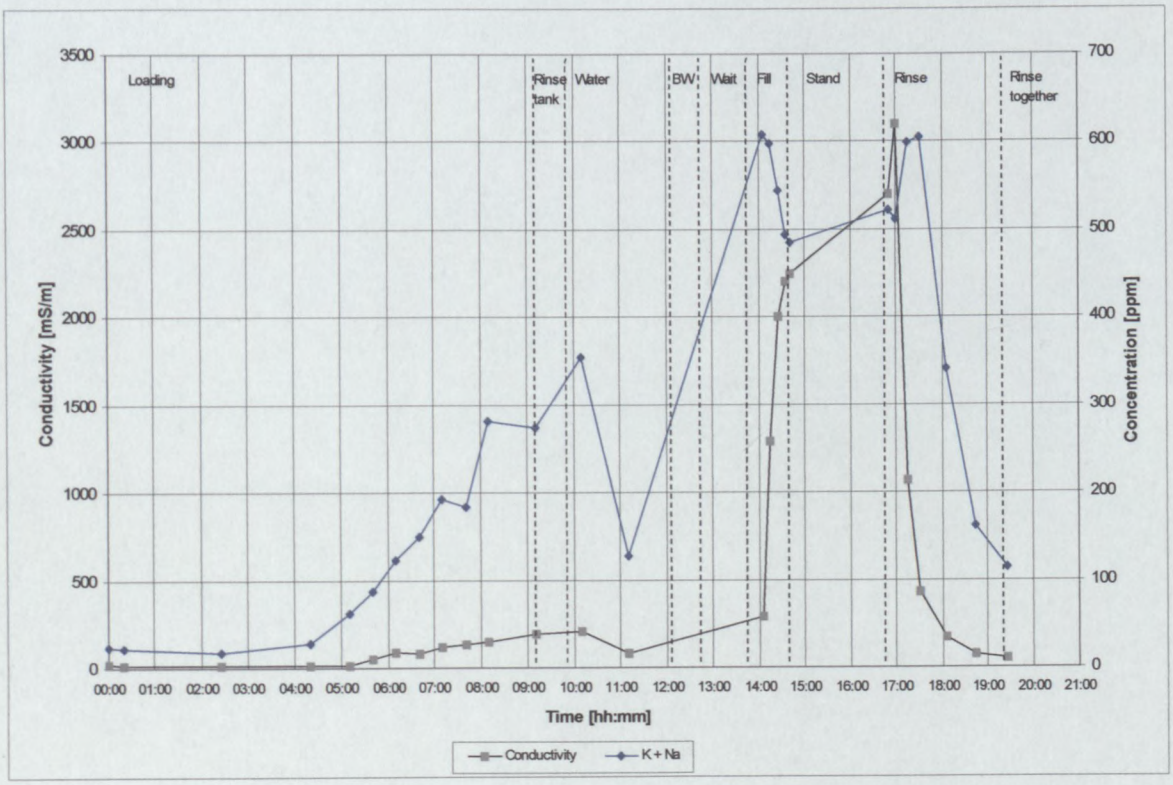


Figure 4.15: Anion Column: Comparison of conductivity and metal ion concentration (23/2/00)

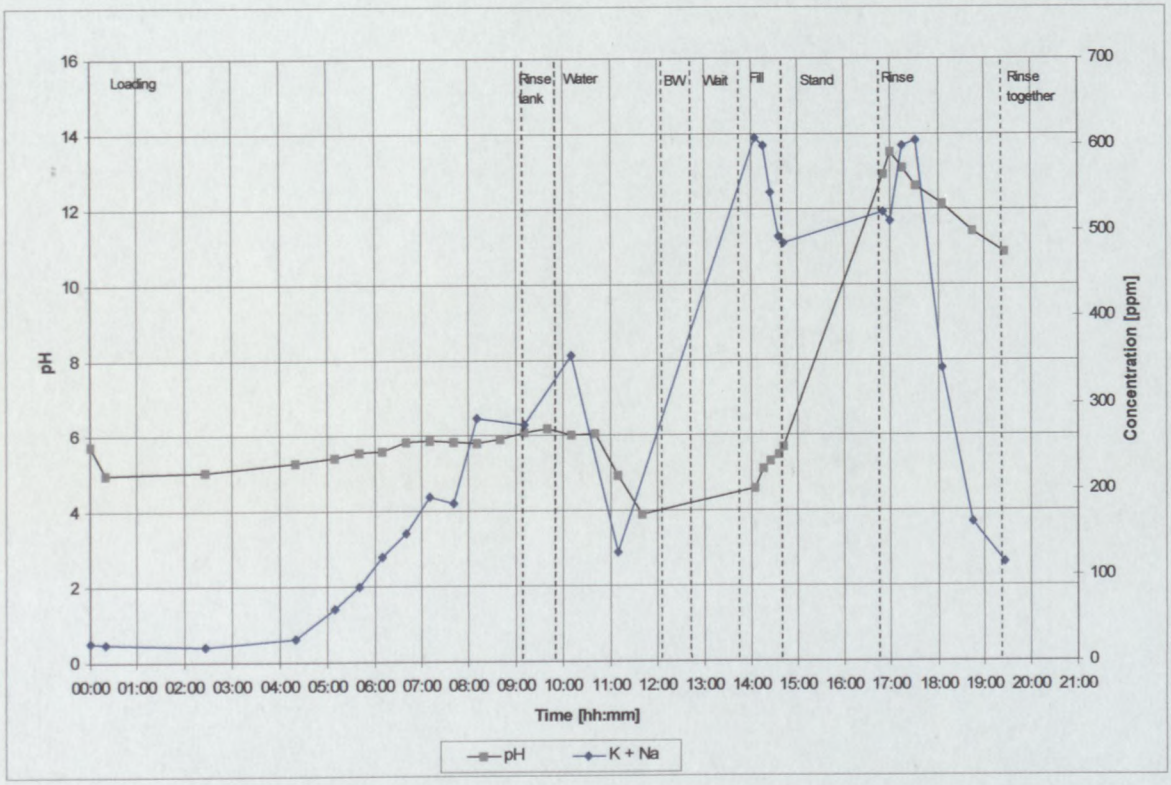


Figure 4.16: Anion Column: Comparison of pH and metal ion concentration (23/2/00)

4.4.2.3 Sampling Run: 11/10/2000

At the time of the previous sampling run (23/2/00) it was not possible to test samples from the plant for the organic acids (tartaric, malic and citric), which make up the bulk of the anions in the juice. This meant that it was not possible to discuss the anion loading cycle in any detail. A further sampling exercise was carried out once the analysis of the samples had been organised. The purpose of this sampling run was to study the organic acid concentrations in the effluent and products leaving the anion column, and to verify previous results for the both the regeneration and loading cycles.

4.4.2.3.1 Cation Column Results

In this sampling run the loading cycle was about 13 hours long; significantly longer than in the previous run (about 9 hours) and yet the results (see Figure 4.17 and compare with figure 4.12) show that the metal concentrations remained lower for longer during this run. The potassium ion concentration in the juice leaving the cation column reached a maximum of about 80 ppm after 13 hours, (in the previous run the potassium concentration reached 350 ppm). The metal concentrations show no significant increase until after 6 hours of loading and as there is no levelling out of the curves, as observed in Figure 4.12, it can be concluded that the resin does not reach a minimum operating capacity. It is not clear why this loading run appears to load significantly better than the previous one, but it must be noted that in both cases the operator would have had no idea what the operating capacity of the cation resin was at any given moment during loading.

The sharp decrease in sodium concentration while the column is being filled with H_2SO_4 and its initial increase in concentration during the loading cycle, relative to the other metal ions, confirm the observation made in section 4.4.2.2.1 that the resin has a lower affinity for the sodium ions.

As there was only a slight increase in the metal concentrations toward the end of the loading cycle, there was a similarly slight corresponding decrease in the conductivity (as shown in figure 4.18).

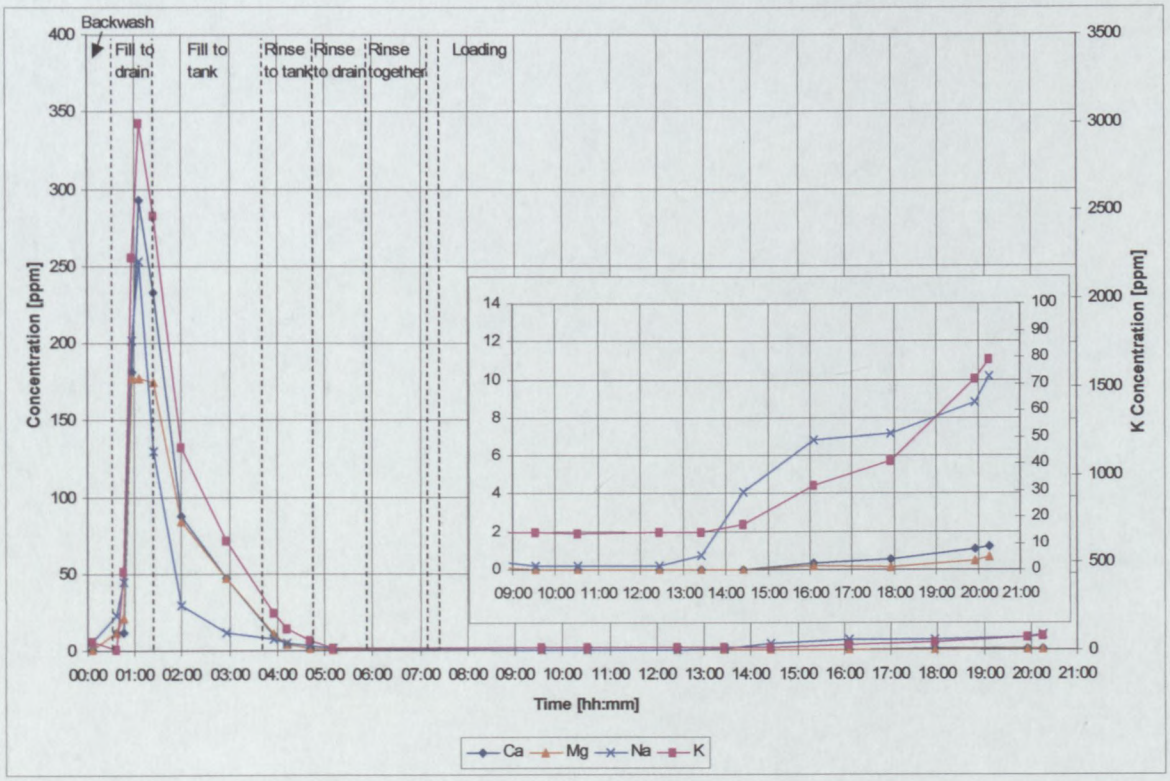


Figure 4.17 Cation Column: Metals (11/10/00)

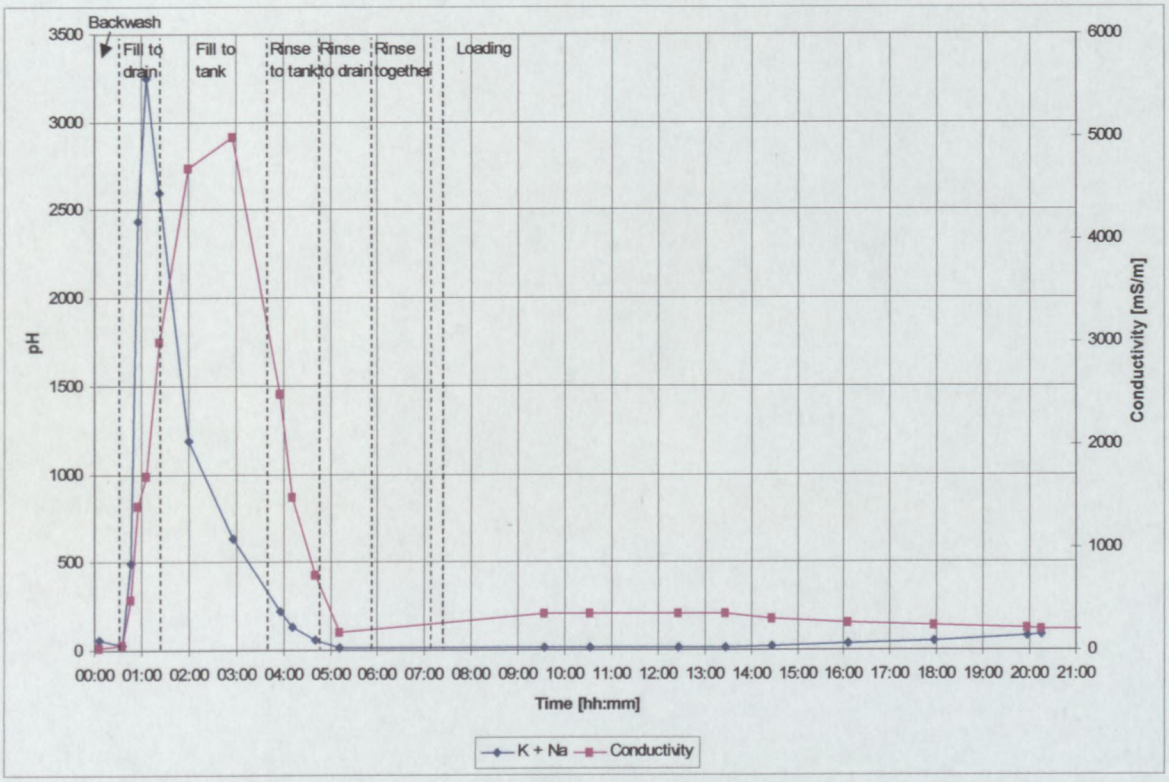


Figure 4.18: Cation Column: Metals and Conductivity (11/10/00)

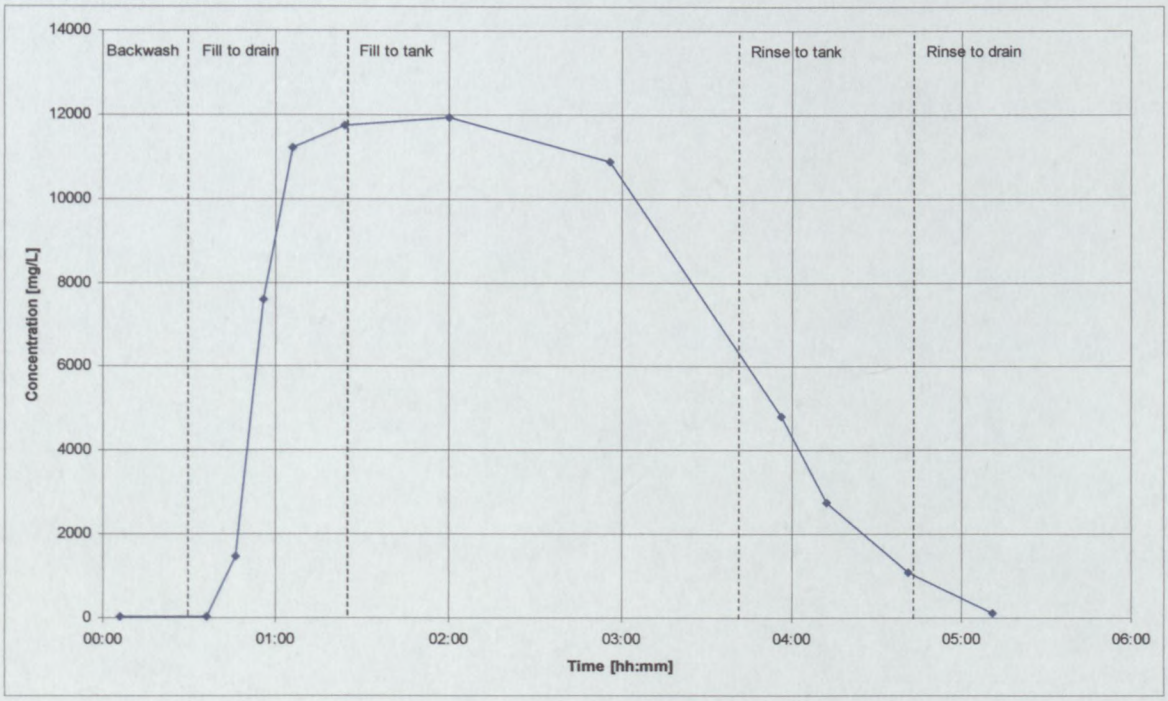


Figure 4.19: Cation Column Regeneration: Sulphates (11/10/00)

Figure 4.19 shows the sulphate concentration of the effluent from the cation column during the regeneration cycle. As sulphuric acid is added to the column there is a 10 minute delay before the sulphates appear in the effluent. The level of sulphates increases sharply and then becomes constant at about 11000 mg/ℓ when the number of sulphate ions entering and leaving the column is about the same. During the rinse cycle the level of sulphates decreases to a concentration of 115 mg/ℓ after 1.25 hours. The rest of the rinsing seems unnecessary. The conductivity during the rinse cycle corresponds with the sulphate curve and the conductivity is therefore a good indicator of the required rinsing time.

4.4.2.3.2 Anion Column Results

From Figure 4.20 it would appear, from the positions of the peaks, that the organic acids are released from the resin in the following order: malic acid, tartaric acid, citric acid.

For the entire loading cycle the levels of organics acids were below the sensitivity levels of the analysis equipment used. From this we know that the resin was working at (or close to) its maximum loading capacity for the entire cycle and the quality of

the product remained satisfactory. The resin was not fully loaded at the end of the cycle (figure 4.21).

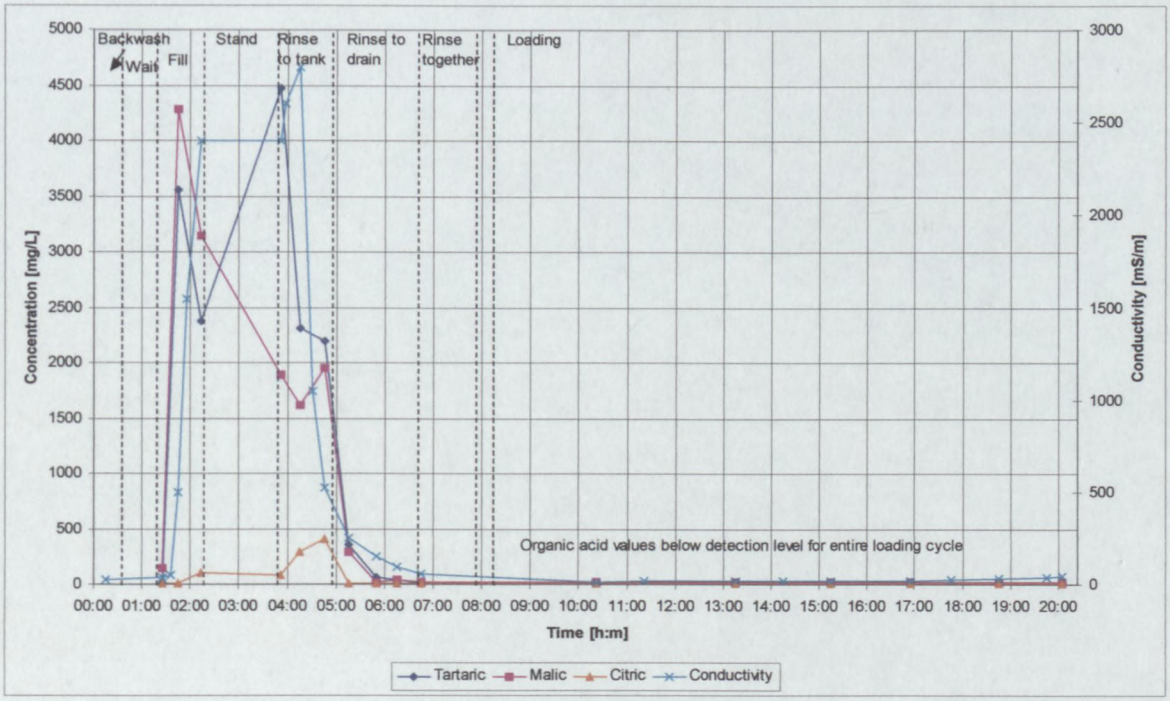


Figure 4.20: Anion Column: Organic Acids (11/10/00)

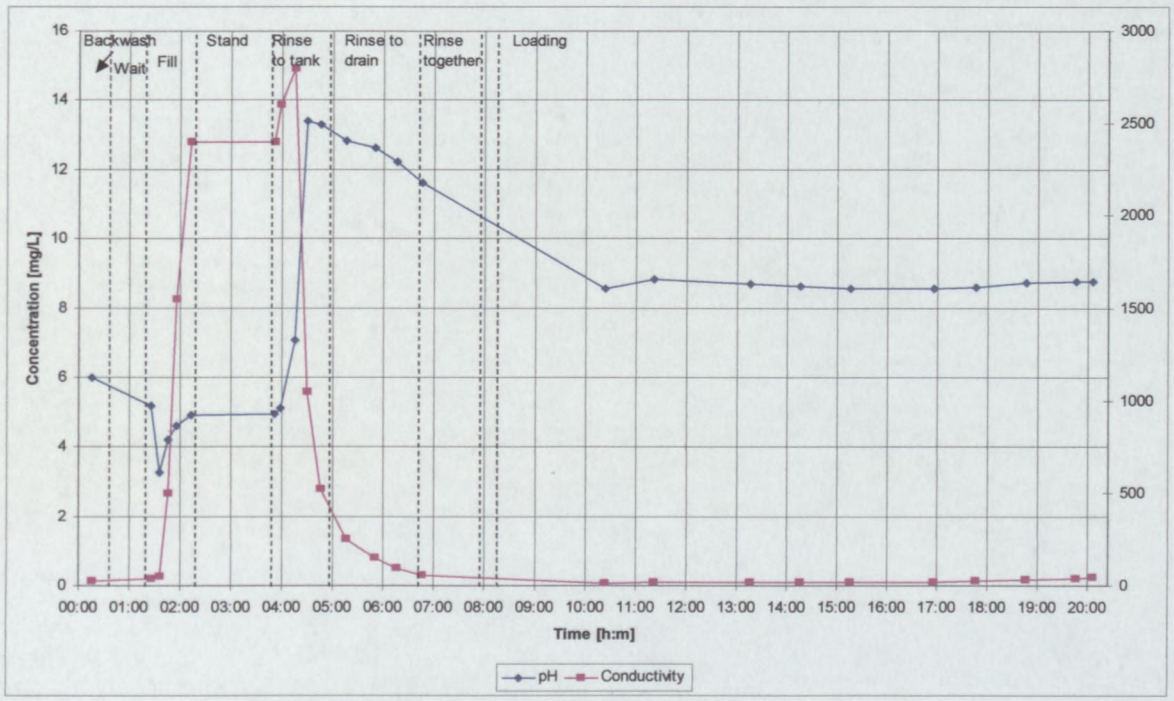


Figure 4.21: Anion Column: pH and Conductivity (11/10/00)

4.4.3.Summary

The ion exchange columns are currently being operated according to a time schedule that was developed from historical data. While this may produce satisfactory results as far as product quality is concerned, the process will never run at an optimum, i.e. using the least possible amount of regenerant and wash water while still regenerating the resin to the highest possible capacity. This is due to changes in the system on the process, for example, differing compositions of feed liquor, differing flowrates through the column and the degradation of the ion exchange resin will all affect the regeneration cycle. As the resin ages its capacity decreases and the rate of ion exchange decreases. The times used become incorrect, leading to an out of specification product and incompletely regenerated resin. An inefficient plant will also produce more wastewater than is necessary. The operators do not necessarily adhere to the time schedule (due to lunch breaks, etc.) and often leave cycles running longer than necessary.

To improve the running of the plant it is suggested that either pH or conductivity meters (or a combination of both) are used. Conductivity meters are already installed on the plant, although they are out of order, so fixing them should be the cheaper option. Conductivity meters, unlike pH meters, do not require calibration. This makes them easier to operate. The advantage of a pH meter is that its readings are easier to interpret. Both a pH and conductivity meter incorporated into an automated control system would be the ideal; especially since it would be difficult to train the operators to interpret the changes in pH and conductivity. Only once such a system is in place, can the operation of the ion exchange plants be optimised. An automated system would also eliminate the overrunning of cycles at the operators discretion.

Due to the vagueness of specifications and the fact that the pH and conductivity values marking the end of cycles, varied between runs, it was difficult for the author to decide exactly when a certain cycle should end. The results presented in this chapter can, however, be used as a guide. It is suggested that, once a monitoring or full control system is in place, samples should be taken towards the end of the rinsing and loading cycles and tested for ions. The pH and conductivity readings should also

be logged. This should be done over a few full loading and regeneration cycles. The control system should be adjusted according to these results.

The current method of filling the column with regenerant and allowing it to stand is not necessarily very efficient. It is also very difficult to use the pH or conductivity readings to determine whether regeneration is complete when this method is used. Allowing the regenerant to flow through the column until the pH of the incoming regenerant is the same as the effluent, ensures that regeneration is complete and should be considered as an alternative method.

CHAPTER 5

Resin Testing

In this chapter, the laboratory experiments carried out are documented. These were carried out in order to characterise the currently used resins, as well as some alternative resins and to possibly come up with an alternative resin process for the plants at Ashton. The experimental procedures are described and the results are given. As the procedures are similar for many of the experiments, general methods used are described separately.

5.1 EQUIPMENT

5.1.1 Resins

The resins tested include the resins currently used at Ashton Cellars, referred to as Ashton Cation (used Amberlite 252H) and Ashton Anion (the equivalent of a combination of used Amberlite IRA 92 and 96, see section 4.3) resins. They are compared with the following new and alternate resins: Amberlite 252H, Purolite C150, Amberlite IRA 92, Amberlite IRA 96 and Purolite A103S. The main characteristics of these resins are summarised in Table 5.1. The data sheets can be found in Appendix C.

5.1.2 Experimental Set-up

The resin is placed in a small glass column (about 2.5 cm diameter) with sinter glass on either end. The feed is pumped into the column using a peristaltic pump (Watson Marlow 504U). Tygon piping is used. The effluent from the column flows into a glass collecting-cup (3cm diameter, 3cm length with a rounded base). This collecting-cup is held at an angle so that the overflow drips into a container constantly. A pH electrode and temperature probe is placed in the collecting-cup so that the pH and temperature of the effluent can be monitored. The pH meter used is a Cyberscan 2000. This is connected to a computer (486V DX33) via an RS 232 port. The pH and temperature is logged using the program Cyberscan. Flowrates are measured using a measuring cylinder and stopwatch. The experimental set-up is show in figure 5.1.

Table 5.1 Resin Characteristics

Resin Type	Amberlite 252H	Purolite C150	Amberlite IRA 92	Amberlite IRA 96	Purolite A103S
Type[1]	Macroporous SAC	Macroporous SAC	Macroporous WBA	Macroreticular WBA	Macroporous WBA
Functional group	$-SO_3^-$	$-SO_3^-$	$-NR_2$: 85%	Tertiary amine	Tertiary amino
Appearance	Light grey beads	Opaque beads	Ivory-coloured beads	Opaque Spherical beads	Opaque near-white spherical beads
Ionic form	H^+	Na+	Free Base	Free Base	Free Base
Total Capacity	1.7 eq/ℓ	1.8 eq/ℓ	1.6 eq/ℓ	1.25eq/ℓ	1.6 eq/ℓ
Swelling	$Na^+ \rightarrow H^+$: 8 %	$Na^+ \rightarrow H^+$: 4 %	Free Base → Cl: 25%	Free Base → Cl: 15%	Free Base → Cl: 25%

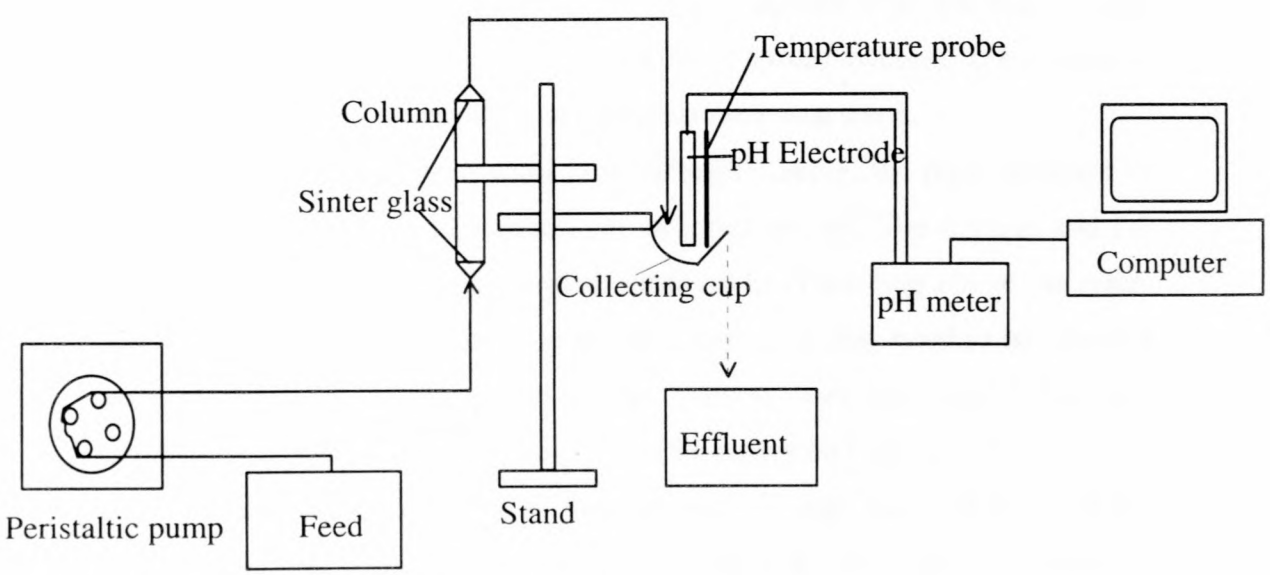


Figure 5.1 Schematic diagram of the experimental set-up (upward flow through column)

[1] SAC: Strong acid cation resin, WBA: Weak base anion resin

5.2 GENERAL EXPERIMENTAL METHODS

- The required amount of resin is measured in a 25ml measuring cylinder. The resin is poured into the cylinder together with distilled water. The cylinder is then tapped against the countertop until the resin settles and the level remains constant. More resin is added if necessary. The resin is then transferred into the column.
- Before starting any experiment, the flowrate has to be set. This is done by pumping distilled water through the system and measuring the flowrate with a measuring cylinder and stopwatch. As the pump used has to be set using a dial, it is impossible to set the flowrate to the same speed for all experiments. The flowrate is measured again during the experiment. It is this measurement that is used in all calculations (where possible the dial was not moved between experiments).
- Before every experiment the pH meter is calibrated using 3 buffer solutions (usually 4, 7 and 10). The electrode and temperature probe are then placed in the collecting cup, which is filled with water.
- Upward Flow: The experiments are started with the pipes and column full of distilled water (no bubbles). When the pipe is moved from the water to the eluant feed tank care must be taken not to introduce bubbles to the system. The experiments are timed from the moment the pump starts.
- Downward Flow: For downward flow through column, the pipes attached to the top and bottom of the column are swapped around. The column and the pipe below it, is filled with distilled water up to about 1cm above the resin. The position of the collecting cup on the retort stand may need to be adjusted so that the level of the water in the column does not drop before the experiment is started. The feed pipe must be empty and the top of the column must be detached. The eluant is then pumped through the feed pipe. At the moment the first drop of eluant reaches the end of the feed pipe, the top of the column is replaced and the timing of the experiment is started.
- Logging of pH data: The data is logged using the program Cyberscan on a computer linked to the pH meter through a RS232 port. The following settings are used.

Table 5.2 Settings used for the program Cyberscan

Baud Rate:	*9600*
Parity Bit:	*Even (2)*
Stop Bit:	*1*
Com Port:	*1*
Filename:	**.csv*

The logging process is initiated at the moment the timing of the experiment is started. The pH meter is set to send a pH reading every 60 seconds but for the first few minutes of the experiment this is not frequent enough as the pH is changing rapidly. The Print button on the pH meter must be pressed as often as required so that further readings are logged.

5.3 Resin Preparation

Before any experiments are carried out, the resins are prepared so that they are in the H^+ form, for the cation resins, or the OH^- form, for the anion resins. A 3% solution of H_2SO_4 is passed upwards through a column of cation resin until the pH of the feed into the column is equal to the pH of the effluent. The resin is then rinsed by pumping distilled water through the column. The flowrate is not measured but is just fast enough to cause fluidisation of the resin. Similarly, 3% NaOH, is used to prepare the anion resins.

Note that a column large enough to treat 800 ml resin was often used instead of the small column used in all other experiments. This was done so that large amounts could be treated at the same time, providing a stock of prepared resin for the experiments.

5.4 CAPACITY TESTS

5.4.1 Cation Resin Capacity Tests

5.4.1.1 Aim

To calculate the ion capacity of a strong acid cation resin, by measuring the pH of the effluent during a batch loading procedure. The experiment is repeated for the following resins: Ashton Cation, Amberlite 252H and Purolite C150.

5.4.1.2 Method

20 ml of resin in the H+ form is placed in a column. A 0.1 molar solution of Na_2S0_4 is pumped upwards through the column at a rate of about 10 ml/min. A computer logs the pH of the effluent from the column.

The experiment is stopped when the pH of the effluent is the same as that of the influent i.e. no more ion exchange is occurring.

5.4.1.3 Theory

Loading a strong acid resin in the H^+ form, with sodium ions results in the following reaction:

$$2\ R\text{-}SO_3^-H^+ + Na_2SO_{4(weak)} \leftrightarrow 2\ R\text{-}SO_3^-Na^+ + H_2SO_4 \qquad [5.1]$$

The hydrogen ions released from the resin settle into the applicable ionisation ratio with the anion, which accompanied the loading cation into the resin bed. e.g.

$$H^+ + SO_4^{2-} \leftrightarrow HSO_4^- \qquad [5.2]$$

A weak acid is formed.

By measuring the pH of the effluent leaving the bed it is possible to calculate the concentration of the free and complex hydrogen ions in solution.

For this experiment we know that:

$$Total[SO_4^{2-}] = [SO_4^{2-}]_{free} + [HSO_4^-] = 0.1 \qquad [5.3]$$

And that:

$$K_a = \frac{\left[H^+\right]_{Free}\left[SO_4^{-2}\right]}{\left[HSO_4^-\right]} = 0.012 \qquad [5.4]$$

Combining and rearranging [5.3] and [5.4] gives:

$$[HSO_4^-] = \frac{0.1[H^+]_{Free}}{0.012 + [H^+]_{Free}} \quad [5.5]$$

This means that:

$$Total[H^+] = [H^+]_{Free} + \frac{0.1[H^+]_{Free}}{0.012 + [H^+]_{Free}} \quad [5.6]$$

The result of the following integration should be an approximate indication of the hydrogen ions displaced during the loading, and hence the specific cation capacity of the bed. The trapezium rule for numerical integration can be used.

$$Total\ moles\ of\ hydrogen = Q * \int_{t1}^{t2} Total[H^+]dt \quad [5.7]$$

5.4.1.4 Results of Cation Resin Capacity Experiments

This experiment was repeated using three different resins. The first was Ashton Cation (used Amberlite 252H), resin taken directly from the plant at Ashton Cellars. The other two were new resins; Amberlite 252H and Purolite C150. Figure 5.2 shows the change in pH over time for each experiment. The results are given in Table 5.2.

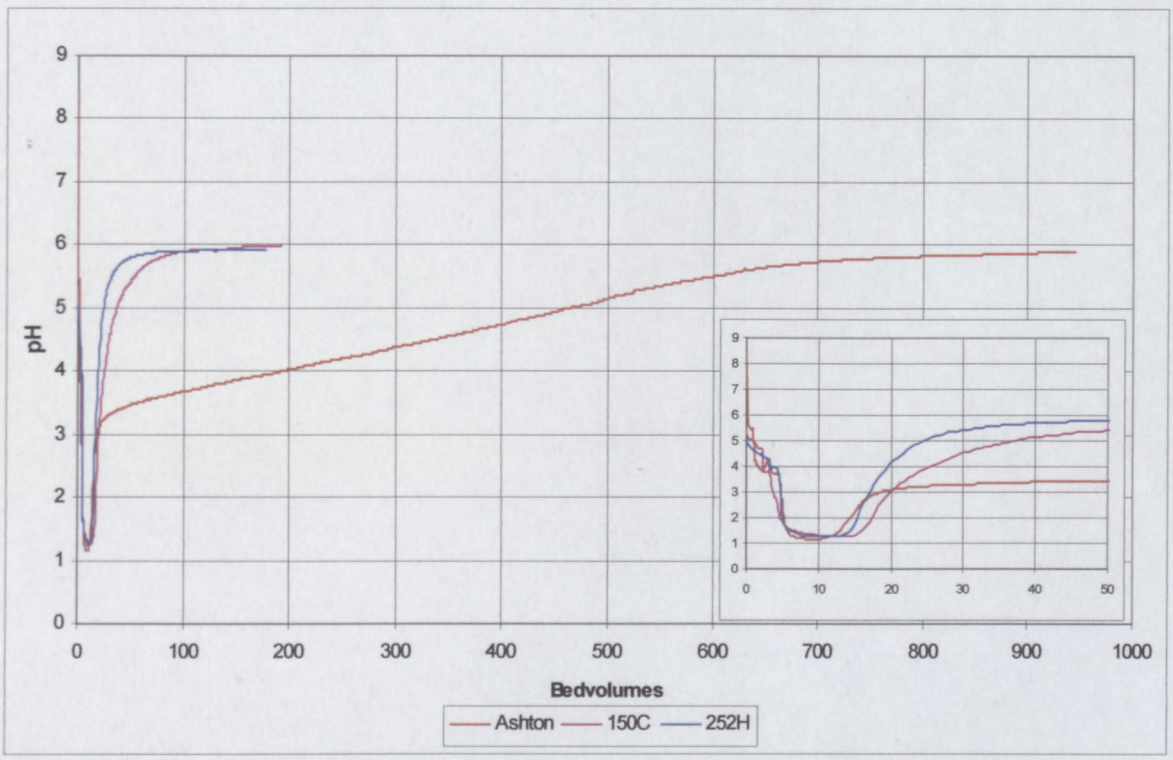


Figure 5.2 Cation Resin Capacity Tests

Table 5.3 Results of Capacity Tests for Cation Resins

Resin	Experiment ID	Capacity [equiv/ℓ]
Ashton Old Cation	TR8	1.782
Amberlite 252H	252Hcap2	1.322
	252Hcap3	1.403
	252Hcap4	1.338
Purolite 150C	C150Cap2	1.563
	C150Cap3	1.577

Comparing the two new resins, reveals that the Purolite 150C resin has a higher capacity than the Amberlite 252H. The Purolite also maintains a maximum exchange rate (at the bottom of the pH vs. time curve in figure 5.2) for a longer period of time.

These experiments show that the capacity of the resin taken from the plant at Ashton (used Amberlite 252H) appears to be higher than that of the new resin, where one would expect a used resin to show a decreasing capacity. This could be due to experimental error, as the experiment was carried out over a much longer time period than the other experiments. Slight errors in the measurement of the pH can have a large effect on the calculation of the free hydrogen ion content and the duration of the experiment will worsen this effect. Ashton Cation takes almost 5 times longer than the new resins to reach its full capacity. This indicates that it has been fouled and that the foulants seem to slow down the movement of the cations to the active sites within the resin beads.

5.4.2. Anion Resin Capacity Tests

5.4.2.1 Aim

To determine the total capacity of anion exchange resins.

5.4.2.2 Method

The method as described in the ion exchange training manual of Simon (1991) was used.

Place 15ml of resin, in the OH^- form, in a column. Pass 500 ml of 10% HCl downwards through the sample at a flowrate of about 10 mℓ/min. Rinse with distilled water until no free Cl^- ions are found in the effluent (spot check with 1% $AgNO_3$)

Place a clean 500ml volumetric flask under the collection point, then pass sufficient 10% $NaNO_3$ through the resin to fill the volumetric flask to the calibration mark. The Cl^- concentration in this solution is determined and used to calculate the total capacity of the anion resin. The following equation is used:

$$\text{Total Capacity [eq/}\ell\text{]} = \frac{C * 0.5}{V * 35.4527} \qquad [5.8]$$

Where C is the Cl^- concentration (in ppm) and V is the volume of resin (in mℓ).

5.4.2.3 Results of Anion Capacity Tests

Table 5.4 Results of Anion Capacity Experiments

Resin	Experiment ID	Cl^- Concentration	Capacity [eq/ℓ]
Ashton Anion	Anion1	1563	1.44
	Anion2	1508	1.39
IRA 92	92Cap1	602	0.57
103S	103SCap1	1250	1.18

According to these results the capacities of IRA 92 and 103S are far lower than expected. This could be due to the experimental method being employed, and it is recommended that these experiments be repeated, perhaps using a different method, for more reliable results

5.5 Loading of Resins

5.5.1 Loading of cation resins

5.5.1.1 Aim

To study the loading of grape juice onto Amberlite 252H and Purolite C150 cation resins.

5.5.1.2 Method

The method used is the same as that used for the cation capacity tests (section 5.4.1.2) except that grape juice collected from Ashton cellar (pre-ion-exchange) is used instead of Na_2SO_4.

For one of the 252H runs, samples of the effluent were taken at regular intervals and analysed for K, Ca, Na and Mg concentrations using ICP.

5.5.1.3 Results and discussion

This experiment was repeated 3/4 times for each resin but only one set of results is shown here. These results are considered to be representative.

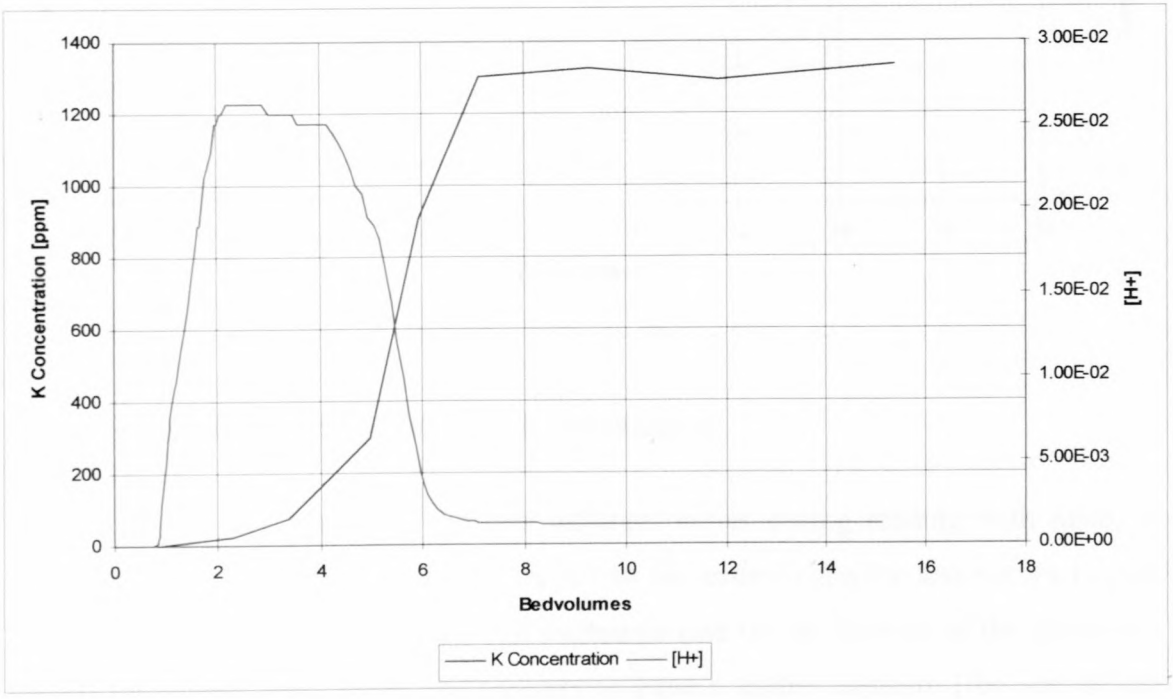


Figure 5.3 Loading of 252H with juice: Comparing hydrogen and potassium concentrations.

During these experiments it is assumed that the change in pH of the effluent is a good indication of the rate of exchange of the significant ions (in this case potassium). In this particular experiment this is tested in Figure 5.3, which shows the change in concentrations of hydrogen and potassium in the juice leaving the column over time. Both curves indicate that the resin can be considered to be fully loaded after about 7 bed volumes. However, Figure 5.4 shows that for the metals present in lower concentrations there is still ion exchange occurring after 7 bed volumes. Calcium and magnesium are still being exchanged when the experiment is terminated. The point at which the potassium concentration falls out of specification (rises above 100 ppm) at about 3.5 bed volumes cannot be estimated by looking at the hydrogen curve as there was no significant decrease at this point.

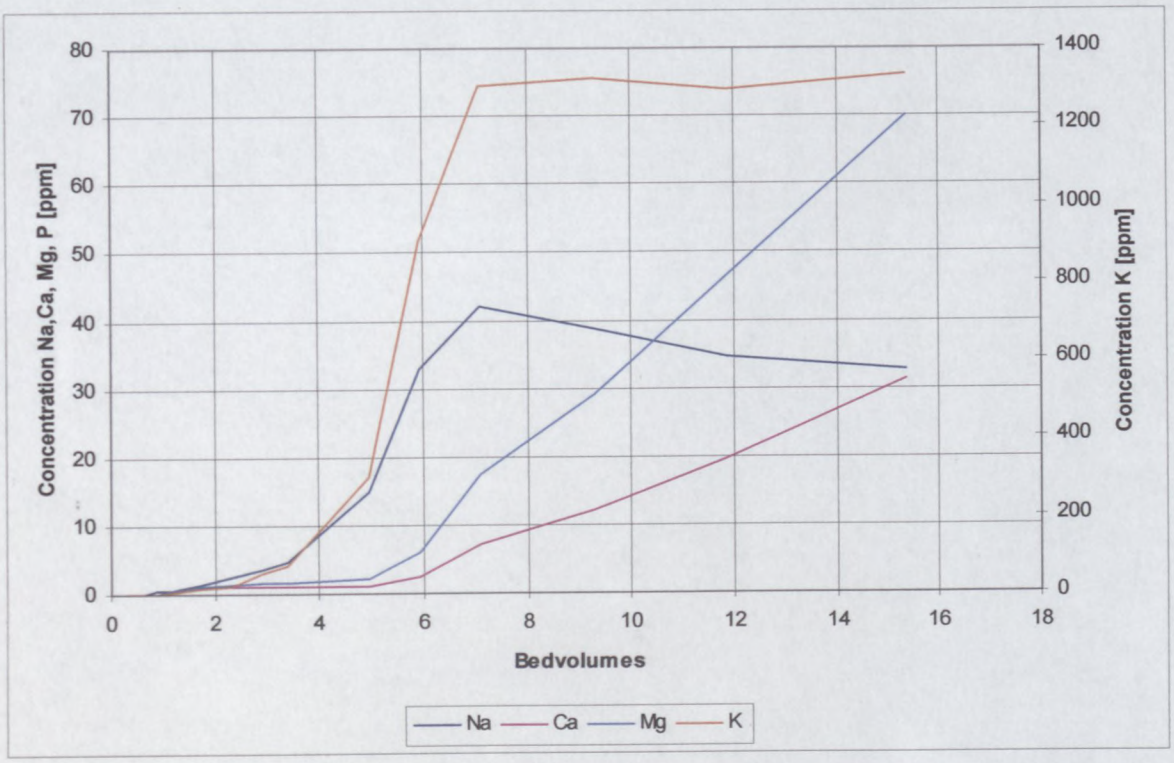


Figure 5.4: Loading of 252H with juice: Metal Concentrations

Comparing the pH curves of the two different resins during loading with juice, as shown in figure 5.5, gives a similar result to the cation capacity test curves (figure 5.2). C150 maintains a maximum ion exchange rate (at the bottom of the dip in the curve) for longer than 252H and appears to have a higher capacity (the size of the dip).

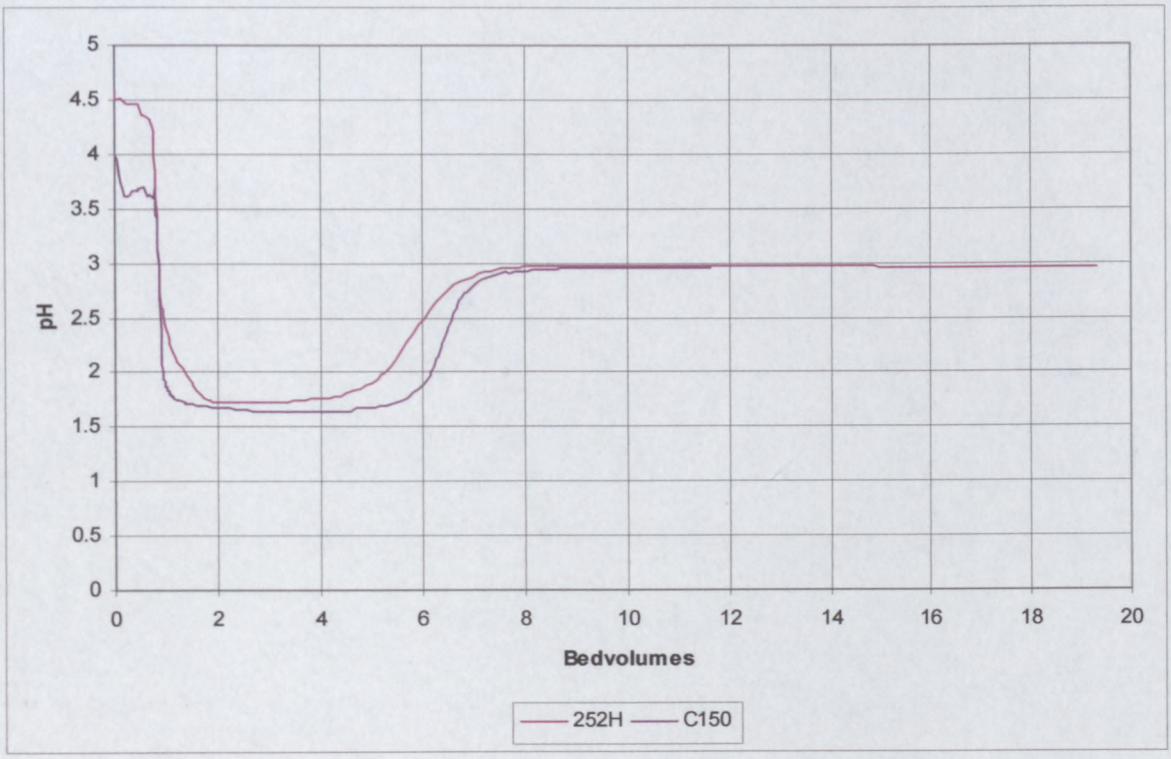


Figure 5.5 Cation resin loaded with juice: Resin Comparison

5.5.2 Loading of Anion Resins

5.5.2.1 Aim

To compare the loading (using grape juice) of Amberlite IRA 92, IRA 96 and Purolite A103S.

5.5.2.2 Method

The same method as for the loading of cation resins is followed (section 5.5.1.2). Note that the volume of the resin is measured while it is in the free base form.

5.5.2.3 Results and discussion

The results of this experiment are shown in figure 5.6. They reveal that A103S becomes fully loaded first. It is followed by IRA 96 and then IRA 92. According to their data sheets, A103S and IRA 92 are meant to have similar capacities. IRA 96 apparently has a lower capacity than the other two. The fact that A103S is "filled" first means that the rate at which it exchanges OH^- ions for organic acid ions is significantly higher than the other two resins.

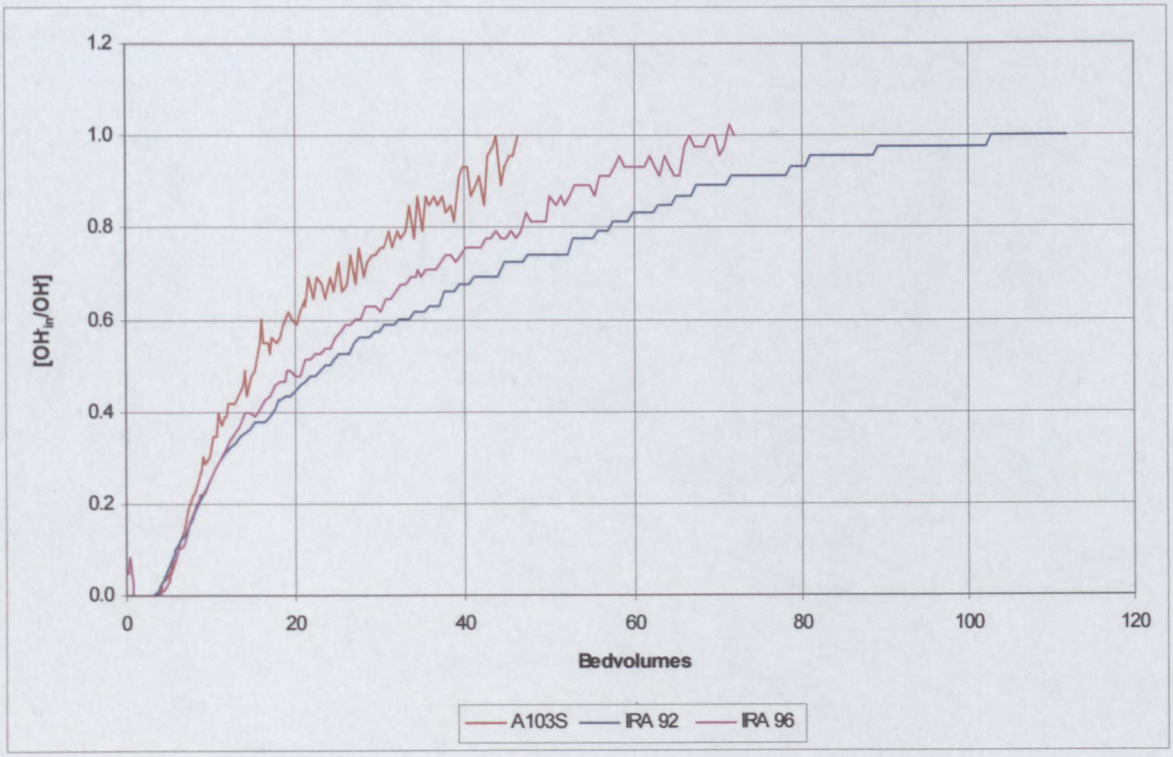


Figure 5.6 Loading with juice onto anion resins: Comparing resins

5.6 ELUTION

5.6.1 Elution of Cation Resins

5.6.1.1 Comparing Concentrations

5.6.1.1.1 Aim

To determine the effect of H_2SO_4 concentration on the metal elution rate from Amberlite 252H.

5.6.1.1.2 Method

Load at least 45ml resin with juice and then split it into 3 batches of 15ml each.

15ml of loaded 252H resin is placed in the column. 1% H_2SO_4 is pumped downwards through the column at a rate of about 11ml/min. The pH of the effluent is logged and the experiment is stopped when the pH is equal to that of the acid entering the column (check this before the experiment is started). This procedure is repeated using 3% and 5% H_2SO_4.

5.6.1.1.3 Results and Discussion

Figure 5.7 shows the results of this experiment. In this and many of the experiments to follow it was decided that the best representation of the data is a plot showing the ratio of the H^+ concentration in the effluent to the H^+ concentration of the eluant versus the bedvolumes passing through the column. This is because the pH of the eluant differs for each experiment, as does the flowrate. The elution can be considered complete when $[H^+]/[H^+in]$ equals 1.

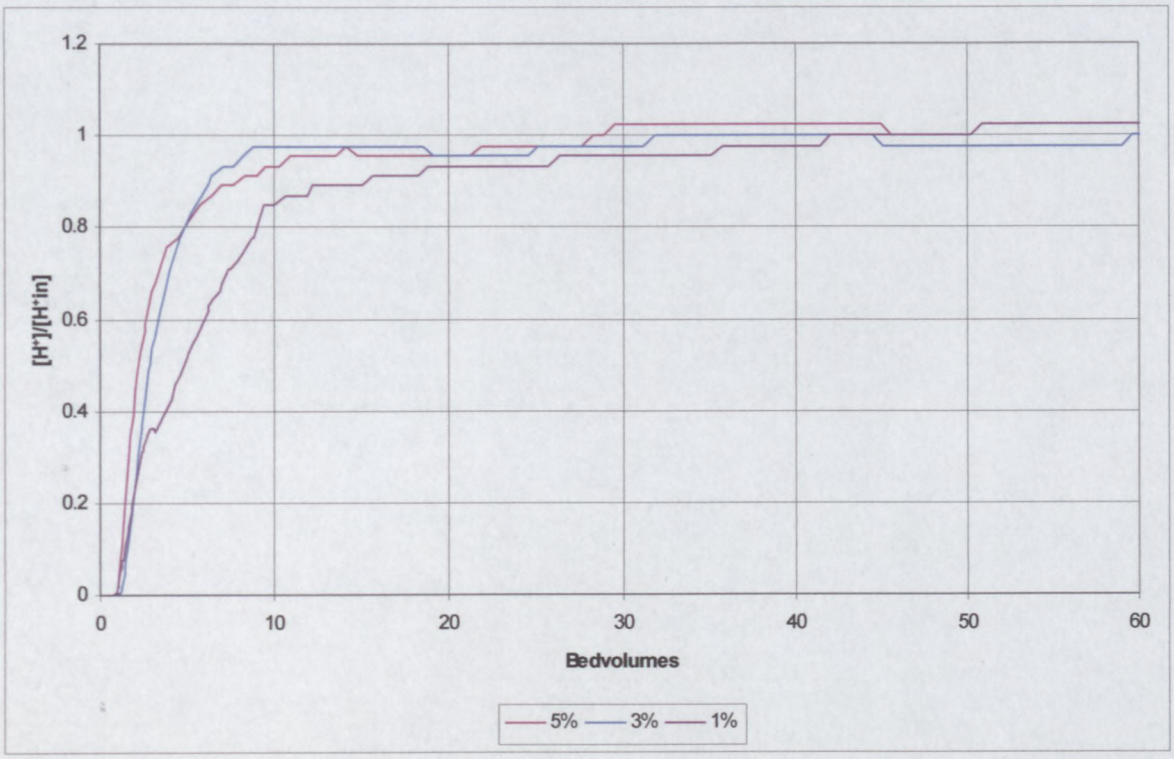


Figure 5.7 Elution of 15ml of 252H loaded with juice using H_2SO_4 at different concentrations

The results suggest that while using 1% H_2SO_4 to elute the resin is significantly slower than using a higher concentration, the difference between using 3% and 5% H_2SO_4 is insignificant. It is therefore most effective to use the 3% H_2SO_4.

5.6.1.2 Other Elutions

The above experiment was also carried out using the following resins and eluted using 3% H_2SO_4.

15ml C150 loaded with juice

15ml C150 loaded with Na

In figure 5.8 these two elutions are compared with the elution of 15ml of 252H loaded with juice. While the C150 loaded with Na appears to elute slightly slower than the other two cases, the differences are fairly insignificant.

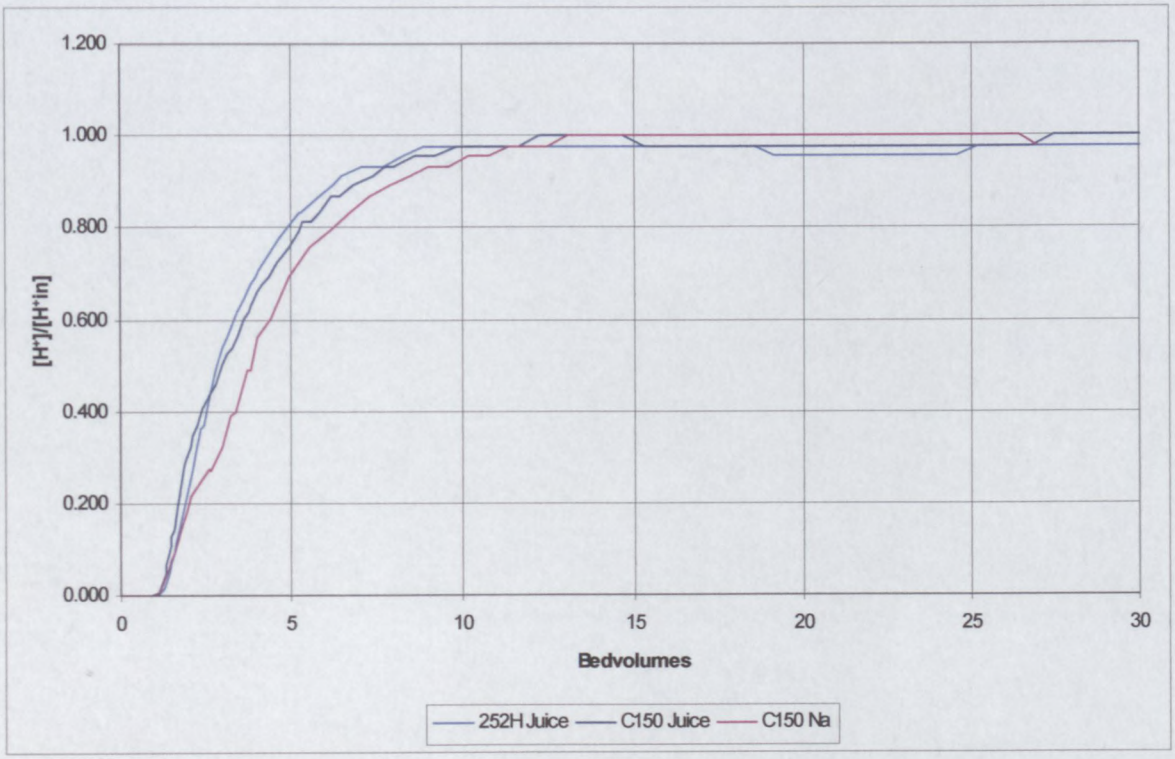


Figure 5.8: Elution of 15ml of Cation Resin loaded with either Juice or Na using 3% H_2SO_4

5.6.1.3 Metal Concentrations

While carrying out the following experiments, samples were taken at regular intervals and then tested for K, Mg, Ca and Na:

15ml 252H loaded with juice

15ml C150 loaded with juice

The results are depicted in figures 5.9 and 5.10. Note that the potassium concentrations are plotted on separate axes from the other metals. The scales of the two graphs have been made the same so that they can be compared directly. The rates of elution seem similar for each case.

The area under any of the curves is an indication of the total amount of that metal eluted from the resin. If it is assumed that all the metal ions have been eluted by the

end of these experiments, this area can be interpreted as the total amount of that metal loaded onto the resin during the loading cycle.

In light of this, it seems that the amounts of metal ions loaded onto the C150 resin were less than those loaded onto the 252H resins. This contradicts the observations made in the loading experiments where C150 appeared to have a higher capacity. One explanations could be that other cations in the juice play a more significant role than expected, or that the unseen tails of the curves in Figure 5.10 are a lot longer than those in Figure 5.9 i.e. slow elution would have continued long after the experiment was considered to be complete.

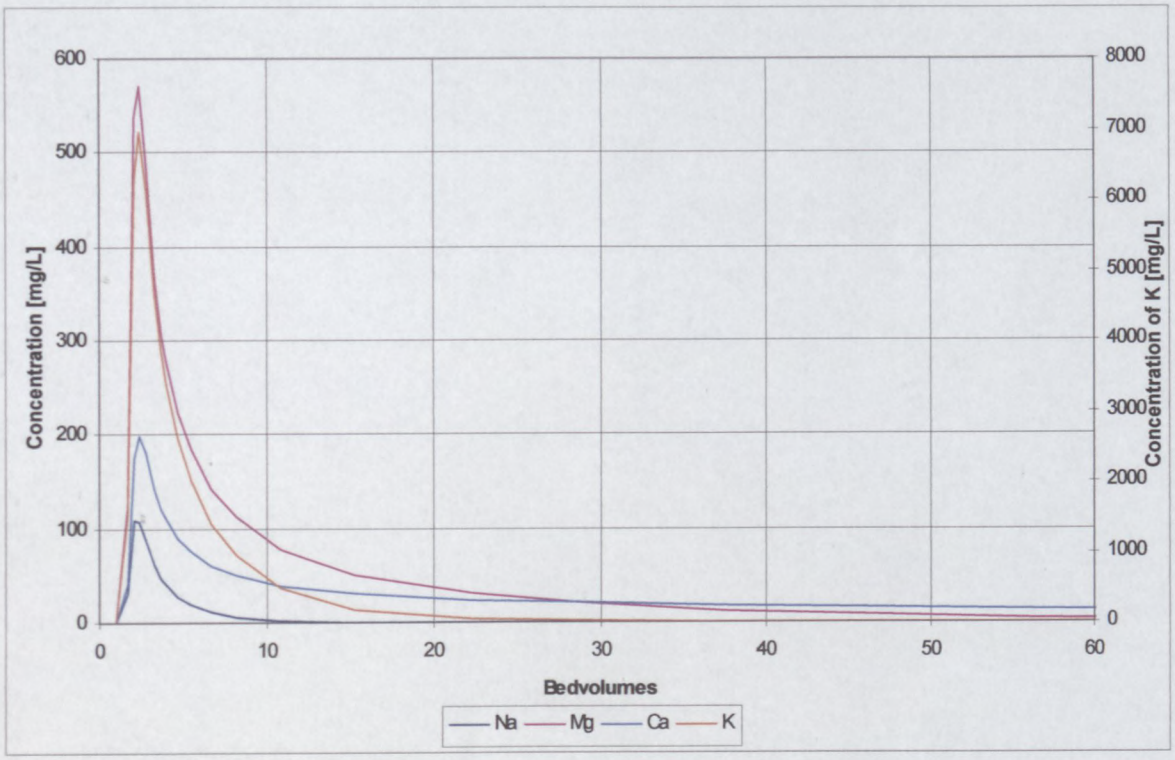


Figure 5.9 Elution of 252H loaded with juice using 3%H2SO4: Metal Concentrations

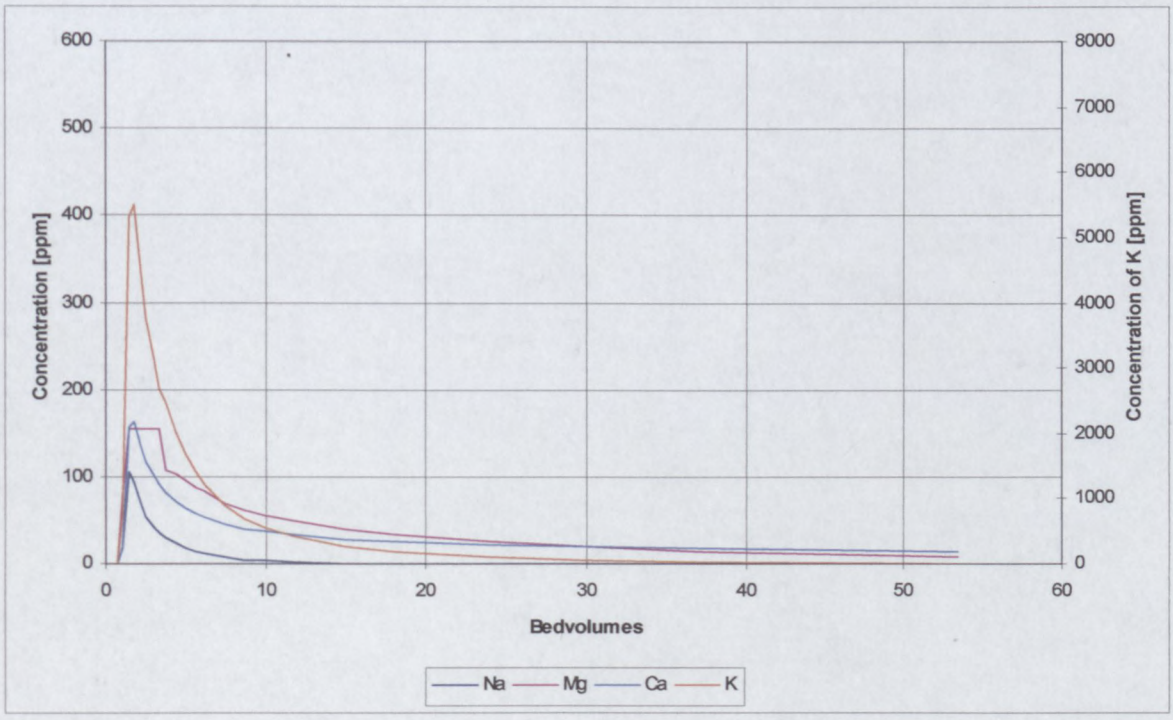


Figure 5.10 Elution of C150 loaded with juice using 3% H2SO4: Metal Concentrations

5.6.2 Elution of Anion Resins

The following elutions were carried out using the same method as used for the cation resin elutions:

1. 20 ml IRA 92 using 3% NaOH
2. 20 ml IRA 96 using 3% NaOH
3. 20 ml A103S using 3% NaOH
4. 15 ml IRA 92 using 2% NaOH
5. 15 ml IRA 92 using 4% NaOH
6. 15 ml IRA 92 using 6% NaOH

The 20 ml resin samples were measured in the free base form and the 15 ml samples were measured after the resin had been loaded with juice. Effluent samples from these experiments were taken at regular intervals and were then tested for organic acids.

5.6.2.1 Comparing Resins

The results of experiments 1-3 are compared in figures 5.11 to 5.14. The hydrogen concentration curves (figure 5.11) show very similar curves for IRA 96 and A103S. The IRA 92 resin takes longer (60 bed volumes) to become fully eluted.

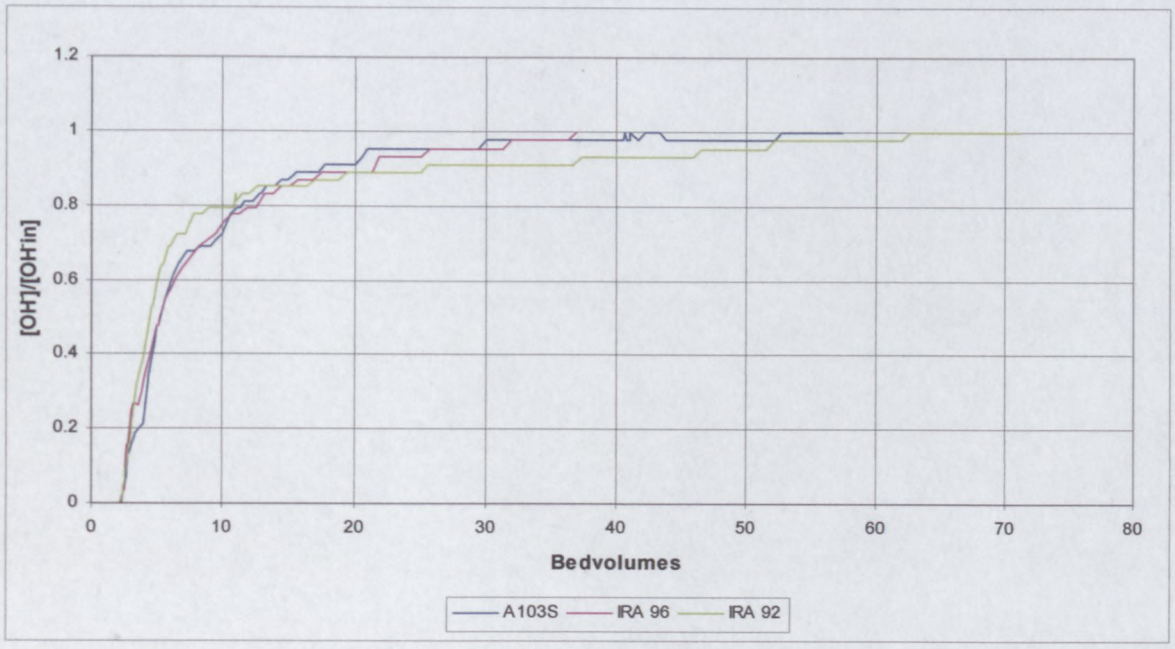


Figure 5.11 Elution of resins loaded with juice using 3% NaOH

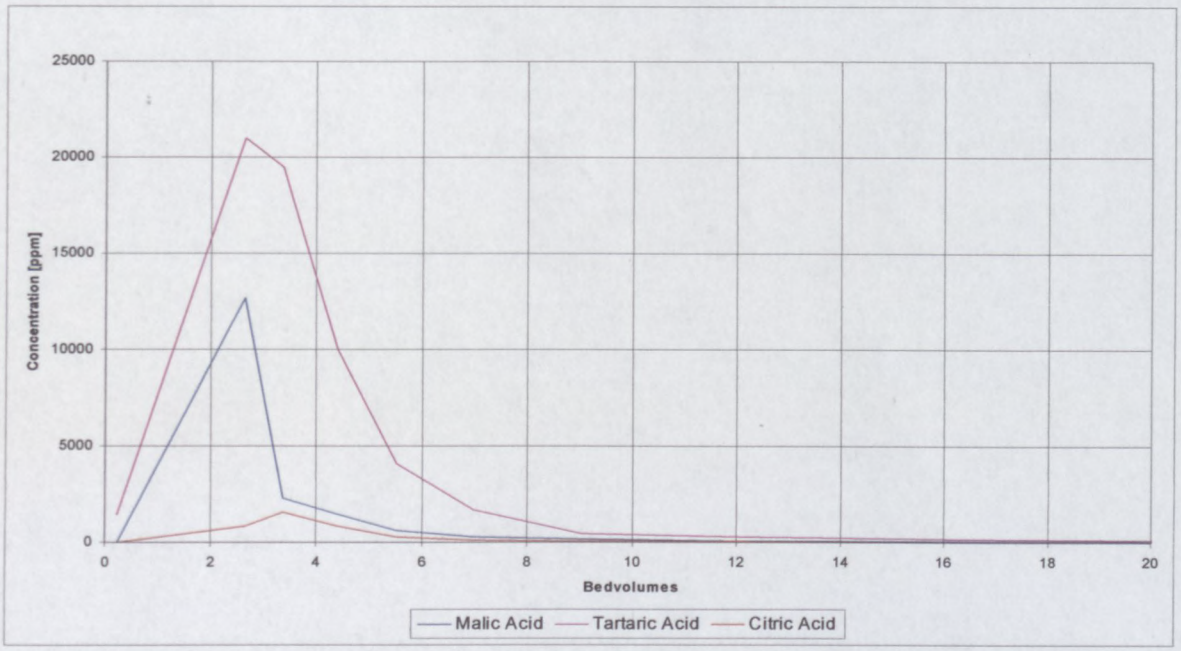


Figure 5.12 Elution of 103S

Figures 5.12 and 5.13 show the elution of the organic acid ions from the A103S and IRA 96 resins. What must be noted here is that there is a negligible amount of citric acid eluted from the IRA 96 resin. This either means that there was very little citric acid loaded onto the resin or that it is difficult to elute it from the resin. The peak of the citrate elution on figure 5.13 occurs later than that for malates and tartrates. This suggests that the A103S resin's affinity for citrate is higher than for the other two.

Comparing the elution of tartrates from all three resins clearly shows (by comparing the area under each of the graphs) that A103S released a lot more tartrates than IRA 92, which in turn released more than IRA 96.

From these results, it can be concluded that, of those tested, the best anion resin for the demineralisation of grape must is Purolite A103S, followed by Amberlite IRA 92. Amberlite IRA 96 is not recommended as it either does not remove citric acid from the grape juice or it is difficult to elute the citric acid from the resin. Neither of these situations is favourable.

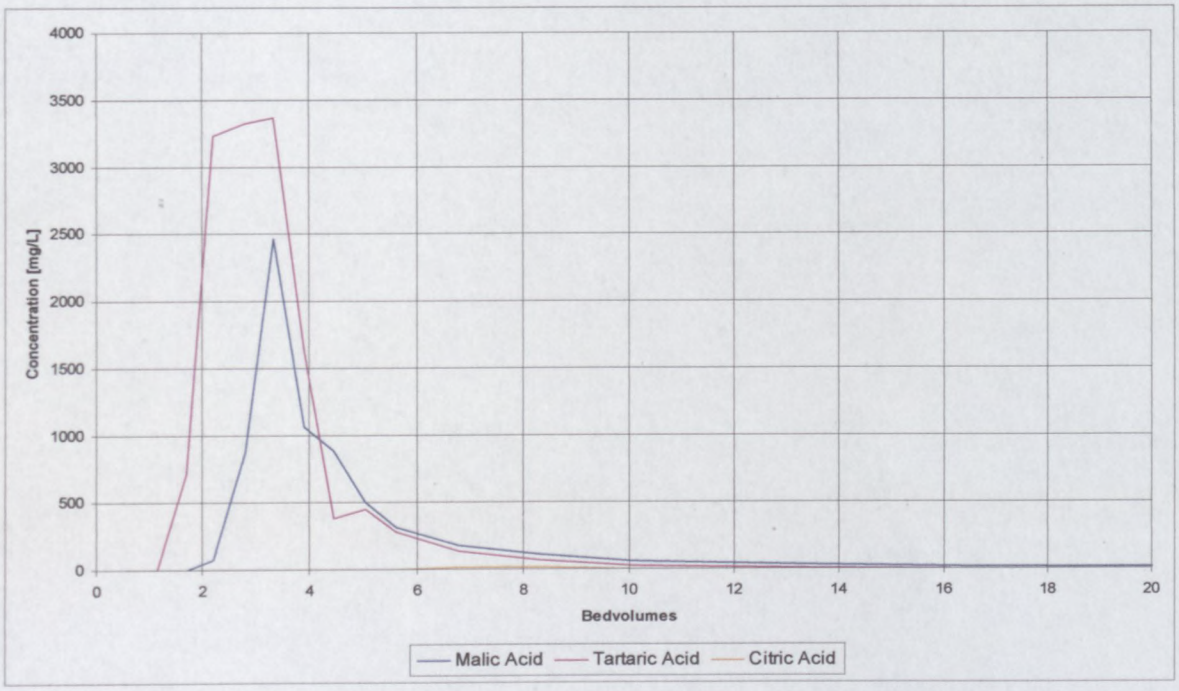


Figure 5.13 Elution of IRA 96

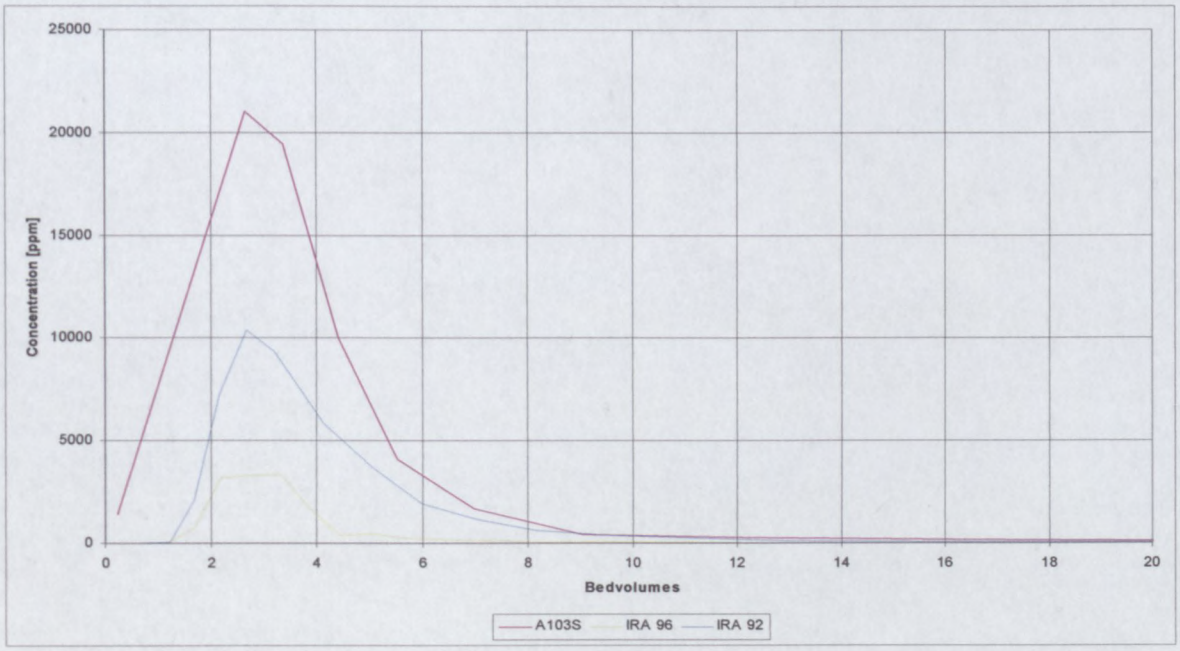


Figure 5.14 Elution of anion resins loaded with juice using 3% NaOH: Tartaric Acid Concentrations

5.6.2.2 Comparing NaOH Concentrations

From Figure 5.15 it is clear that the rate of elution is improved by increasing the NaOH concentration from 2% to 4%. Using 4% NaOH, the elution is completed in about a third of the time it takes when 2% NaOH is used. Increasing the concentration to 6% does not make a significant difference to the rate of elution.

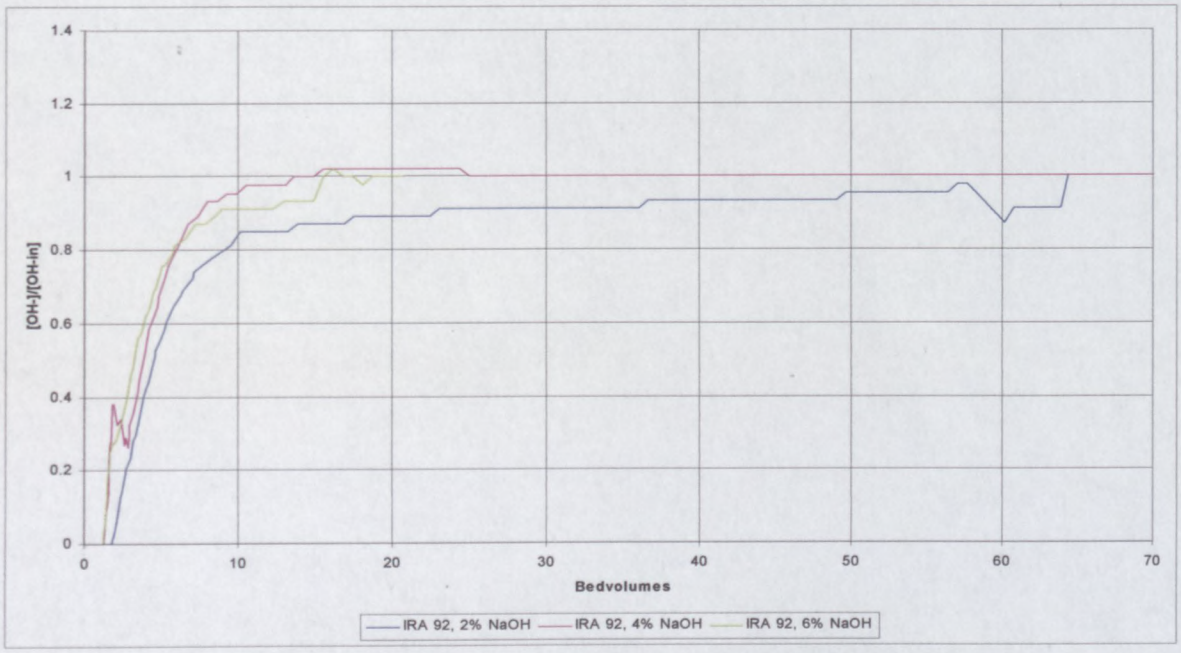


Figure 5.15 Elution of IRA 92 loaded with juice: Comparing NaOH concentrations

Figures 5.16, 5.17 and 5.18 show the effect of concentration of sodium hydroxide on the rate of elution of tartaric, malic and citric acid, respectively. For tartaric acid (figure 5.16) the effect is clear. A higher concentration causes the elution rate to reach a peak faster and the elution reaches completion faster.

For malic acid (figure 5.17) the effect is less clear as in this case the 2% NaOH elution peaks first, followed by the 6% and 4% elutions. After 5 bedvolumes more Malic acid has been eluted by the 6% NaOH followed by the 4% and then the 2%. Between 5 and 10 bevolumes all three curves are similar. It is unclear why the 6% elution has a "fat tail". This could be due to analytical inaccuracy.

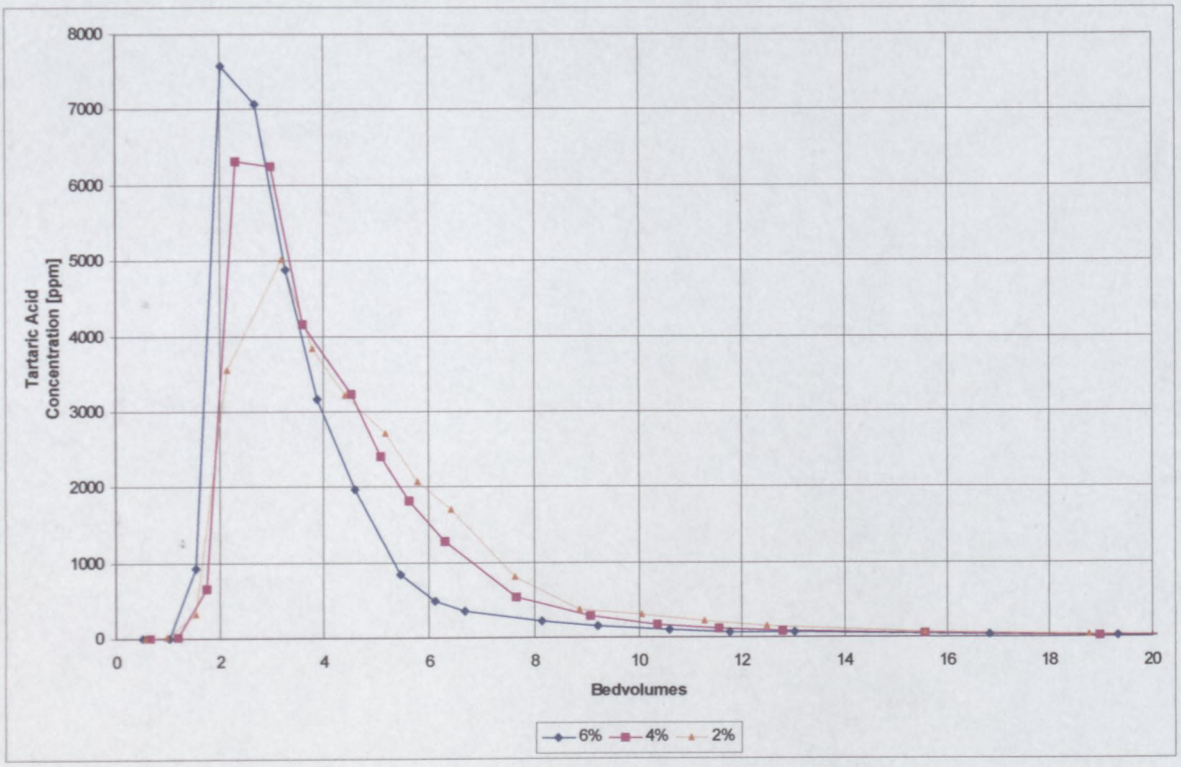


Figure 5.16 Elution of IRA 92 loaded with juice using NaOH: Tartaric Acid

Table 5.5 Amount of organic acid ions eluted off 15ml IRA 92 after approximately 93 bedvolumes

NaOH Conc.	Malates [mg]	Tartrates [mg]	Citrates [mg]	Total [mg]
2%	84	366	21	471
4%	103	369	16	488
6%	164	334	13	511

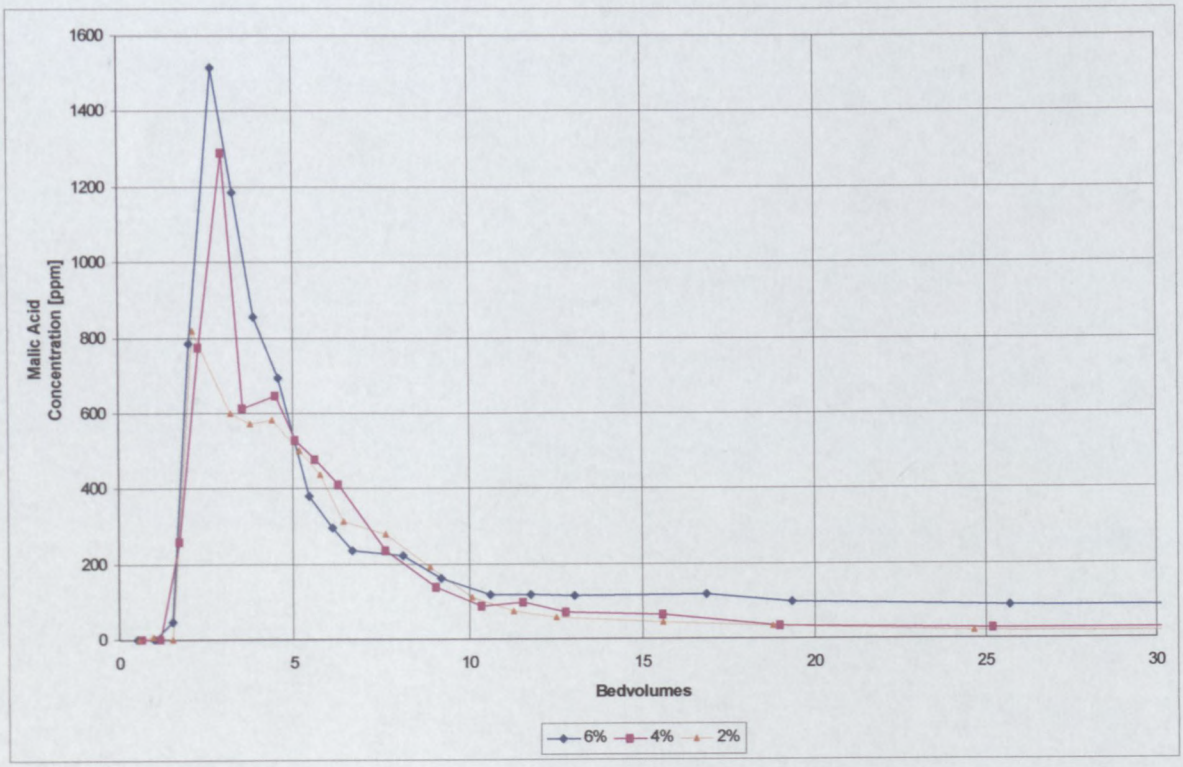


Figure 5.17: Elution of IRA 92 loaded with juice, using NaOH: Malic Acid

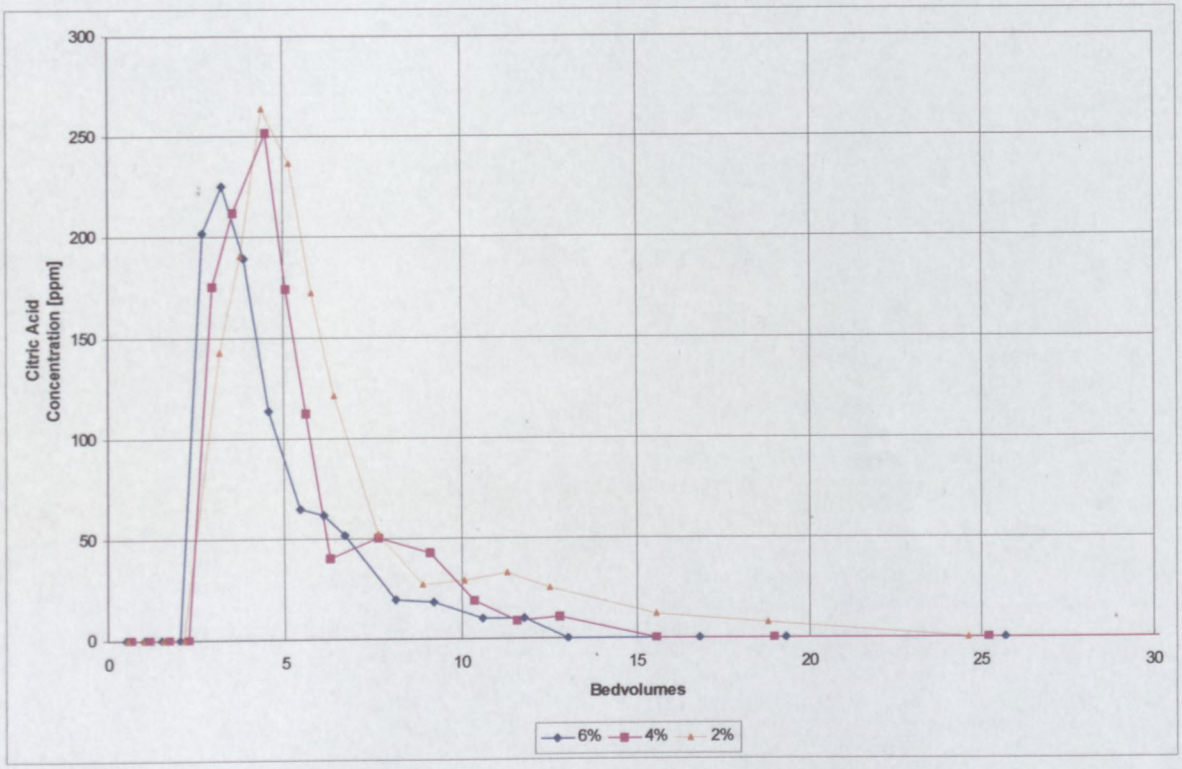


Figure 5.18: Elution of IRA 92 laoded with juice, using NaOH: Citric Acid

From Figure 5.18, it can be seen than the elution of citric acid is completed faster than the 4% and 2% (13 bedvolumes compared to 16 and 25 bedvolumes, respectively).

While the removal of colour from the juice was not specifically studied in these experiments, interesting observations were made during the elution of the anion resins which had been loaded with juice. The difference in the NaOH concentration of the eluent makes a significant difference to the rate at which colour is removed from the resin. The higher the concentration, the faster the colour is removed. This can clearly be seen in figure 5.19.

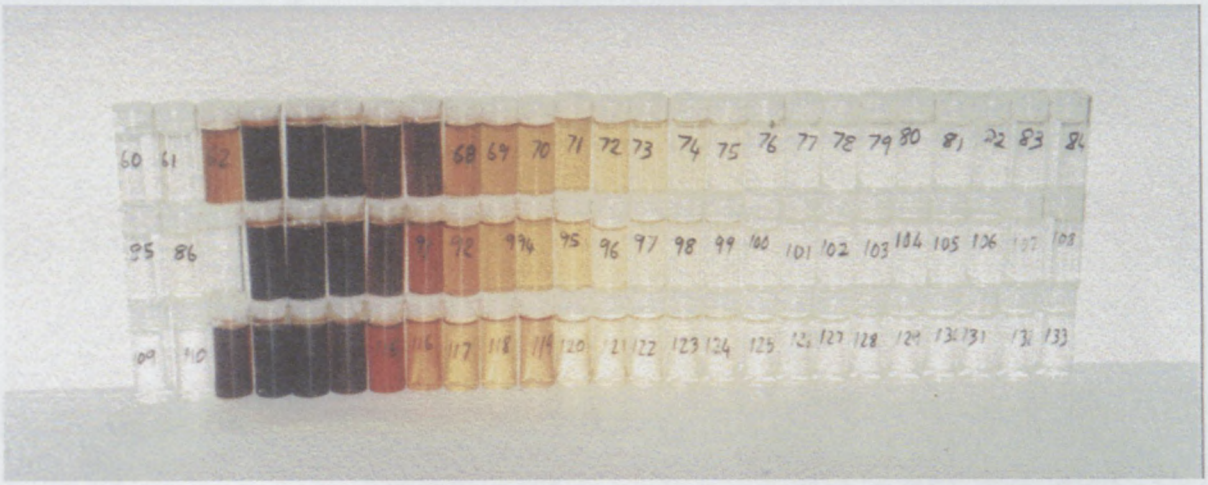


Figure 5.19 Elution of IRA 92 loaded with juice: Photo comparing NaOH concentrations

Legend:

Samples 60-84: 2% NaOH

Samples 85-108: 4% NaOH

Samples 109-133: 6% NaOH

Samples placed on top of each other were taken at approximately the same times.

Other Observations

- The colour compound in these effluent samples acts like an acid-base indicator as it changes colour from dark orange-red (at high pH) to a light yellow-orange below a pH of about 2.
- Another observation was that after elution the colour of the resin, which was originally ivory coloured, is a dark brown. This means that the resin has been fouled by a coloured compound.

5.7 SUMMARY

Testing of the used cation resin from the plant revealed that it is fouled and that loading occurs very slowly. It should be replaced to improve the efficiency of the plant. It is suggested that resin from the plant should be tested regularly to determine how fast it is aging or becoming fouled. The resin should not simply be left until the time or the number of loading and regeneration cycles stipulated by the resin sales agent has occurred as the aging process is also dependant on the process it is being used for, the regeneration, and any abuse of the resin. The loading tests for the new cation resins (Amberlite 252H and Purolite 150C), showed that Purolite C150 has a higher capacity and a more favourable loading curve. This resin should be considered when the resin on the plant is replaced. The eluant concentration should be left at 3% sulphuric acid as no significant improvement in the elution is observed at a higher concentration.

Of the anion resins tested Purolite A103S appears to be the most favourable as it loads faster than the two Amberlite resins and appears to load the most tartrate ions. Amberlite IRA 96 is not recommended for use on the plant as very little citric acid is eluted from the resin, suggesting that its affinity for citric acid is either too high (making it difficult to elute) or too low (not removing citric acid from the juice). Increasing the concentration of the eluant (sodium hydroxide) increases the rate of elution but a compromise must be made between the rate of regeneration and the cost of the eluant. The resin data sheets recommend concentrations between 2 and 4%.

CHAPTER 6

Some Alternative Separation Processes

The following processes represent some possible alternatives to the current juice stripping process. Combinations of these and the existing unit procedures, for example ion exchange, should be considered in developing an optimal plant.

6.1 FLOTATION - BUBBLE AND FOAM SEPARATIONS

The basis for separation by bubbles and foams is the difference in surface activities of various materials present in the solution or suspension of interest. Surface active materials tend to attach preferentially at the gas-liquid interface of the bubbles or foams as they rise through the column or pool of liquid. When this combination reaches the surface, the material can be removed in the relatively small amount of foam or scum formed. Non-surface-active substances may be removed by the addition of small amounts of a surface-active collector.

6.1.1 Dissolved Air Flotation

In dissolved air flotation a polluted liquid stream is pressurised to dissolve excess air, and then depressurised to release the air from solution. When the pressure is reduced, the air forms bubbles at the surface of hydrophobic 'particles' which act as nuclei, and as the bubbles rise to the water surface, the particles are drawn along with them. The particles, which accumulate at the surface as a froth or scum phase, are then skimmed off the flotation tank surface for disposal. This method is currently being used at the cellar.

6.2 MEMBRANE FILTRATION METHODS

Filtration is more commonly associated with removal of particulates from a contaminated liquid, where the particles are of a size greater than 0.5 μm. With rapid improvements in membrane technology, filtration is quickly becoming a suitable process to remove dissolved contaminants with particle sizes less than 0.5 μm.

The following table summarises some of the available membrane filtration methods.

Table 6.1: Size of Materials Retained, Driving Force, and examples of contaminants removed

Process	Size of materials retained	Driving force	Contaminants removed
Microfiltration	0.1 - 10 μm microparticles	Pressure difference (0.5 - 2 bar)	Yeasts, Bacteria, Colloids
Ultrafiltration	1 - 100 ηm macromolecules	Pressure difference (1 - 10 bar)	Viruses, organic compounds
Nanofiltration	0.5 - 5 ηm molecules	Pressure difference (10 - 70 bar)	Organic compounds, dissolved salts
Reverse Osmosis	< 1 ηm molecules	Pressure difference (10 - 100 bar)	Dissolved salts

6.2.1 Microfiltration (Cooper ,1997)

Microfiltration is a method of filtration that has two common forms: crossflow separation and dead-end filtration. In crossflow separation, a fluid stream runs parallel to a membrane. There is a pressure differential across the membrane. This causes some of the fluid to pass through the membrane, while the remainder continues across the membrane, cleaning it. Crossflow microfiltration is used in a number of applications, as either a prefiltration step or as a process to separate a fluid from a process stream

In dead-end filtration or perpendicular filtration, all of the fluid passes through the membrane, and all of the particles that cannot fit through the pores of the membrane are stopped. Dead-end microfiltration is used commonly in stopping particles in either prefiltration or final filtration before a fluid is to be used. Cartridge filters are typically composed of microfiltration material.

6.2.2 Ultrafiltration (Cooper, 1997)

Ultrafiltration is a form of filtration that uses membranes to preferentially separate different fluids or ions. It is used for removing solutes with a large molecular weight and particulate components from a solute. This would include proteins, small suspended solids and colloidal particles.

In the sugar industry ultrafiltration membrane's sharp molecular weight cut-off capabilities are used to clarify sugar streams. Colour, tannins and other undesirable organic components are preferentially rejected while sugar molecules are allowed to pass.

Ultrafiltration is probably the membrane filtration method most suited to stripping of grape juice as the nanofiltration and reverse osmosis membranes separate sugars from water.

Micro- and ultrafilters can be used for the clarification of fruit juices, replacing vacuum drum filters. Drum filters create large amounts of solid waste and fine cracks in the diatomaceous earth has been implicated as a potential carcinogen. The retentate of the micro- or ultrafilter could have the potential to be processed for the recovery of a by-product. The retentate can also be treated to recover any juice left in it.

6.2.3 Nanofiltration

Nanofiltration is a finer filtration than ultrafiltration and requires more energy to perform the separation. An example of its use is to concentrate sugar streams where traditional heat concentration processes are undesirable or inefficient. Nanofiltration membranes consistently separate sugars of a specific molecular weight and remove 60 percent of the water, concentrating raw sugar juice from 12 to 30 Brix.

6.2.4 Reverse Osmosis

Reverse osmosis, also known as hyperfiltration, is the finest filtration known. This process will allow the removal of particles as small as ions from a solution. Reverse osmosis is used to purify water and remove salts and other impurities in order to improve the colour, taste or properties of the fluid. The most common use for reverse osmosis is in purifying water. It is used to produce water that meets the most demanding specifications that are currently in place.

Reverse osmosis uses a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. Most reverse osmosis technology uses a process known as crossflow to allow the membrane to continually clean itself. As some of the fluid passes through the membrane the rest

continues downstream, sweeping the rejected species away from the membrane. The process of reverse osmosis requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving force. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases.

Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents that have a molecular weight of greater than 150-250 Dalton. The separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as organics. The larger the charge and the larger the particle, the more likely it will be rejected.

6.2.5 Solution-diffusion membranes (USDA, 2000)

Unlike filtration membranes, solution-diffusion membranes do not have pores. There is, therefore, no convective flow through the membrane. Solute molecules dissolve in the membrane phase and permeate the resin by molecular diffusion. The selectivity of such a membrane is related to the solubility and diffusivity of the solute molecules. Concentration polarization does not occur on these membranes and they therefore resist fouling.

This process is attractive for the removal of unwanted flavours in grape juice as an appropriate membrane would allow the unwanted molecules to pass through while retaining the desired components. This process has been used to debitter citrus juice.

6.3 SEDIMENTATION

Sedimentation is the partial separation or concentration of suspended solid particles from a liquid by gravity settling. Sedimentation can be divided into two functional operations namely thickening and clarification. The primary purpose of clarification is to remove a relatively small quantity of suspended solids and produce a clear effluent. Various types of clarifiers are available. Sedimentation is often used in combination with flocculation as the larger particles formed by flocculation lead to an increased sedimentation rate. It can also be used after a precipitation process, (also see 6.6)

6.4 ADSORPTION

6.4.1 Activated Carbon

Activated carbon is an amorphous form of graphite, with a random structure of graphite plates. The structure is highly porous, with a range of cracks and crevices reaching molecular dimensions. The larger openings function as transport pores through which the contaminants diffuse to the adsorption sites or pores. The removal of contaminants from a liquid occurs primarily by physical adsorption of the contaminants onto the surface of the carbon. The adsorption is due to naturally occurring attractive forces between the molecules on the carbon surfaces and those in solution. Physical adsorption is further enhanced by the lack of affinity of the contaminants for the solution.

Activated carbon is used in both granular and powder forms. The powder form is usually added to a process stream and then filtered out downstream. The granular form is most often used for water treatment, where it is typically employed in a downflow fixed bed reactor.

When used on grape juice, activated carbon adsorbs benzenoid compounds and polyphenols (with a preference for smaller phenolics). It, thereby, decolourises and deodorises the juice. It can also remove flavour if large amounts are used. Activated carbon is currently used on the plant but could possibly be used to a greater extent. The main disadvantage of activated carbon is that it cannot be reactivated on-site and therefore has to be replaced. A large amount of solid waste (activated carbon) is produced.

6.5 ELECTROPHORESIS

Electrophoresis is a separation technique that is based on the mobility of ions in an electric field. Positively charged ions migrate towards a negative electrode and negatively charged ions migrate toward a positive electrode. Ions have different migration rates depending on their total charge, size, and shape, and can therefore be separated.

6.6 PRE-TREATMENTS

6.6.1 Precipitation

If the solubility of a substance is decreased enough it will precipitate out of solution. The precipitate can then be removed from the solution by sedimentation or filtration. The solubility of a salt can often be decreased by decreasing the temperature of the solution or by pH adjustment. Addition of a counter-ion, which forms an insoluble salt with a contaminant ion, is another way to precipitate out a substance.

6.6.1.1 Cooling

It is possible to remove tartrates, calcium and potassium from grape must by cooling. When juice containing these substances is cooled to below 4°C, potassium bitartrate and calcium tartrate crystals are formed. The efficiency of this process can be improved by seeding with powdered potassium bitartrate and by effective mixing of the solution.

6.6.1.2 Precipitation using protein based fining agents

An example of this (gelatin) is described in section 4.1. Protein and protein-like fining agents have a selective affinity for wine polyphenols. Hydrogen bonding occurs between the phenolic hydroxyl groups and the carbonyl oxygen group of the peptide bond.

The selectivity of a protein fining agent is partly based on the bond strength between the agent and the phenol. It is, therefore, important to choose the fining agent that forms a strong bond with the phenols, which must be removed. There is usually a preference for larger phenols as they have more available hydroxyl groups and, therefore, more potential hydrogen bonding sites.

6.6.1.3 Precipitation using Poly-vinyl-poly-pyrrolidon (Filtrox, 1992 and Borneman, et al., 1997)

Poly-vinyl-poly-pyrrolidon (PVPP) is a synthetic cross-linked insoluble polymer resin, well known for its chemical inertness. It has the capacity to absorb large quantities of polyphenols by means of a protein-like mechanism that involves a hydrogen bond with a nitrogen group. Unlike the soluble protein fining agents, which have a preference for larger polyphenols as they can conform to the molecule and

interact with many hydroxyl groups, PVPP contacts very few reactive groups. It, therefore, finds application in the removal of smaller phenolic species such as catechins and anthocyanins. These species cause browning of wine and juice.
While the PVPP resin is far more expensive than most fining agents, unlike these other agents, it can be regenerated. It does, however, require significant plant investment. Its application to apple juice is described in the references cited.

6.6.2 Coagulation / Flocculation

Coagulants and flocculation are used to increase particle size through aggregation. The precipitation process can generate very fine particles that are held in suspension by electrostatic surface charges. These charges cause clouds of counter-ions to form around the particles, giving rise to repulsive forces that prevent aggregation and reduce the effectiveness of subsequent solid-liquid separation processes. Therefore, chemical coagulants are often added to overcome the repulsive forces of the particles. The three main types of coagulants are inorganic electrolytes (such as alum, lime, ferric chloride, and ferrous sulphate), organic polymers, and synthetic polyelectrolytes with anionic or cationic functional groups. The addition of coagulants is followed by low-sheer mixing in a flocculator to promote contact between the particles, allowing particle growth through the sedimentation phenomenon called flocculant settling. Removal of the larger particles can then be carried out by sedimentation or filtration.

6.7 SUMMARY

Of the processes described, some seem more likely to be applicable at Ashton than others:

- Dissolved air flotation, in combination with precipitation using fining agents, is already being used at the cellar.
- Activated carbon is already being used in the C.O.T. process at the cellar. It could possibly be used to a greater extent as, currently, activated carbon does not remove all the colour and odour from the grape juice.
- Ultracoolers are being installed on the plant and will be used to remove tartrates from grape juice through precipitation by cooling. The juice treated in this way will not be treated by ion exchange and will produce a tartrate-stable juice. This will be produced together with C.O.T.

- PVPP should be considered for the removal of the smaller phenolic species in the grape juice. Its applicability to fruit juice has already been proven, but the costs involved might be problematic.
- Micro- and ultrafilters could be used to replace the drum filter currently being used at the cellar.
- Solution-diffusion membranes have been proven to de-bitter citrus juice and could, therefore, possibly be used to remove flavours from grape juice.

In order to test whether any of the treatment methods described in this chapter are applicable to the C.O.T. production process at Ashton they should be researched thoroughly. The following things should be looked at:

- Laboratory experiments should be carried out to test applicability.
- The advantages and disadvantages of the processes and their constraints.
- Indicative costs
- The benefits of using any of these alternative method in terms of the environmental impact.

By doing this it should be possible to design a process, which produces a satisfactory product, at a reasonable cost and with the minimum effect on the environment.

CHAPTER 7

Conclusions and recommendations

7.1 CONCLUSIONS DRAWN FROM THE WATER AUDIT.

The effluent produced by Ashton Cellars was found to be highly polluted as expected. It is characterised by a low pH (<4), high chemical oxygen demand and high levels of suspended and dissolved solids. By examining results from the water audit it was clear that the ion exchange effluent was largely responsible for the low pH and high salinity of the effluent dam water. All the effluent streams contribute to the high chemical oxygen demand. The streams that contribute to the high level of suspended solids include wash water streams and effluent from the flotation plant.

Suggestions to reduce the amount of wastewater produced include the following:

- Water is polluted unnecessarily by leaving hoses running when they are not in use. High-pressure nozzles with self-closing valves could be attached to the hosepipes. The high velocity water stream cleans more efficiently and water is not wasted.
- Closed circuit washing, i.e. the reuse of washing water that is only slightly polluted (for example water used for the final rinse of a tank)
- Recycling of the sealing water of vacuum filters and centrifuges.

The qualities of effluent streams vary considerable and often relatively clean streams, which could easily be treated or reused, are combined with heavily polluted streams. Segregating these streams would decrease the quantity of highly polluted effluent.

Removing solids from effluent streams as early as possible would decrease the amount of solids in the effluent and its chemical oxygen demand. Wedge wire screens placed at appropriate points, for example as drain covers, could be used for this purpose.

In implementing any of these practises, it would be important to train personnel and make them aware of the effluent problems.

7.2 CONCLUSIONS DRAWN FROM THE ION EXCHANGE AUDIT

Some observations could be made from the sampling runs carried out on the ion exchange plants.

- The plants are operated according to fixed time schedules but the operators do not necessary follow the schedule strictly.
- These schedules were compiled without taking the process variables into account and are therefore not fully applicable to this plant.
- Visual observation is currently the only way for the operator to monitor the quality of the product and effluent. As it is non-ionic substances that colour the product/effluent, this is not a good indication of the ion exchange taking place.

Examining the analysis results revealed the following:

- There is evidence that the loading cycle sometimes does not run to completion. This means that the columns are being regenerated more often than necessary and are creating more effluent.
- Backwash times are the same for both the cation and anion columns even though the flow rate through the cation column is faster and the suspended solids are removed faster than those in the anion column. Water is therefore, being wasted/ contaminated unnecessarily.
- The rinse cycles are often far too long, wasting both time and water.
- Monitoring the pH and/or conductivity should allow the operator to make decisions as to when cycles should be ended. This should be particularly useful for rinsing cycles and will decrease the amount of water polluted through unnecessary rinsing.

In order to achieve optimal operation of the ion exchange plants, an automated control system, which monitors pH and conductivity, is required. If this is considered to be too expensive, the broken conductivity meters already in place on the one plant should be fixed. Once a monitoring or control system is in place, further sampling should be carried out and the system should be adjusted according to these results.

7.3 CONCLUSIONS DRAWN FROM THE RESIN TESTING

Tests, which compared cation resins, revealed the following:

- The resin used on the plant is fouled and loads slowly. This resin should be replaced, as results from the ion exchange audit revealed that the product leaving the cation column sometimes falls below specifications with reference to cations before any decrease in the efficiency of the anion column is noted.
- Purolite C150 appears to have the most favourable loading curve and has a higher capacity. This is confirmed by the loading experiments, where grape must is loaded onto the resin.
- Elution of the two different resins (Amberlite 252H and Purolite C150) revealed no significant differences.

Where the effect of the concentration of the sulphuric acid (the eluant) was tested, it was concluded that, while there is an advantage in increasing the concentration from 1% to 3%, there is no significant improvement in the elution rate when 5% sulphuric acid is used. The plant is currently using 3% sulphuric acid so it is recommended that no changes be made in this regard.

Testing of the anion resins revealed the following:

- Purolite A103S loads faster than the two Amberlite resins.
- The hydrogen concentration curves reveal that IRA 96 and A103S elute at similar rates, while IRA 92 takes longer to become fully eluted.
- The organic acid curves revealed that very little citric acid is eluted from the IRA 96 resin. This resin is, therefore, not recommended for use on the plant.
- A103S elutes (and therefore loads) the most tartrates. This resin appears to be the most favourable of the resins tested.

Results comparing the use of different concentrations of sodium hydroxide showed that the rate of elution increases significantly with each increase in concentration. It is, however, more expensive to use a higher concentration so a compromise has to be made between rate of regeneration and cost. The resin data sheets recommend concentrations of between 2 and 4%.

Although circumstances did not allow for elution testing of the anion resins using NH_4OH, this option is recommended. It eliminates the addition of sodium ions to the effluent, which, in turn, contributes significantly to the salinity of the effluent dam water.

7.4 Conclusions drawn from the survey of alternative processes

A number of alternative unit procedures for the production of C.O.T. have been identified and described briefly. These include flotation, filtration, adsorption and precipitation processes and could be used in combination with, or as alternatives in the existing process. First desktop study then laboratory testing would be required to determine the applicability of these processes to the Ashton plant. Economic and environmental evaluations should also be carried out before modifying the existing process.

7.5 Project Achievements

The following objectives were achieved in this study:

- A thorough water audit was completed at Ashton Cellars.
- Auditing the ion exchange plants gave rise to suggestions, which should lead to the optimisation of regenerant use, chemicals and rinse water on the plant.
- The resins used on the plant were characterised and compared to alternative resins.
- Alternative or additional juice treatment methods were identified and described briefly.

Following the suggestions given in this thesis, where possible, should improve the quality and reduce the quantity of effluent produced at Ashton Cellars at a cost affordable to Ashton. It could also improve the quality of the C.O.T. product and increase production.

The majority of the objectives set out in Chapter 1 have, therefore, been achieved.

This project has also contributed towards the following changes, which have been/will be implemented at the cellar.

- A wedge wire screen has been placed at the collection point (A7 on figure 3.4). This removes pits and skins from the effluent before it is pumped to the dam.
- The plant is going to be modified for anion resin regeneration using ammonia.
- Ultracoolers are being installed for juice treatment. These will cause precipitation of tartrates from the juice, leading to a tartrate stable product. This product will not be demineralised by ion exchange.
- The installation of an automated control system is being considered.

7.6 SUGGESTIONS FOR FUTURE WORK.

Allan Nesbitt and his team at the Cape Technicon have developed an automated system, which can load and regenerate a sample of resin repeatedly. This allows the degradation or fouling of the resin to be tested. They are already involved in testing resins for the production of C.O.T. If they have not done so already, it is recommended that they test Purolite C150 and Purolite A103S, as this study suggests that they might be the best resins to use at the Ashton plant. The lifespan is an important consideration when choosing a resin so this information is vital in the development of an optimal plant.

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APPENDIX A:

Sampling of Ion Exchange Plants

Sampling of Large Ion Exchange Plant 16/9/99

Time	Time from start	Description		pH	Conductivity mS/m	TS mg/L	Ca ppm	K ppm	Na ppm	Mg ppm
Anion Column										
08:17	**00:00**	Filling up column with caustic								
08:30	**00:13**	Caustic Drain	CD1	2.63	39	1790				
08:40	**00:23**		CD2	3.91	240	12315				
08:45	**00:28**		CD3	4.63	750	32290				
08:50	**00:33**		CD4	4.98	1190	40695				
08:55	**00:38**		CD5	5.33	1650	50015				
09:00	**00:43**		CD6	5.52	1850	50425				
09:06	**00:49**		CD7	5.71	2000	50195				
09:09	**00:52**	Initial	CS1	5.85	2100	53930				
10:12	**01:55**	20 min	CS2	5.71	2200	48720				
Caustic was left to stand in the column over the weekend.										
Cation Column										
08:17	**00:00**									
08:30	**00:13**		AD1	2.96	112	932	1.423	92.419	20.176	2.043
08:40	**00:23**		AD2	2.01	440	3264	11.054	556.127	114.057	18.199
08:45	**00:28**		AD3	1.94	560	4172	17.728	734.144	146.789	29.604
08:50	**00:33**		AD4	2.04	630	4668	20.684	834.941	170.621	36.434
08:55	**00:38**		AD5	2.07	660	4900	21.68	886.267	177.515	39.317
09:00	**00:43**		AD6	2.11	660	5012	24.261	946.043	182.774	41.691
09:06	**00:49**		AD7	2.09	680	4980	23.489	920.931	181.825	42.159
09:09	**00:52**		AD8	1.94	700	4900	22.822	913.423	187.427	41.364
09:30	**01:13**		AD9	2.1	700	4660	18.669	872.928	158.308	36.358
10:03	**01:46**		AD10	1.62	825	4424	12.78	730.935	87.834	22.345
A possible blockage in the pipes meant that the sulphuric acid filled the column a lot slower than usual!										
		Dam Stagnant (1/3)	D1	2.87	132					
		Dam Stagnant (other side)		2.8	132					
		Dam Entrance	D2	2.09	480					
		Water sample		6.95	12					

4 Column (Small) IX Plant 16/9/99

Time	Time from start	Notes		pH	Conductivity mS/m	TS ppm	Ca ppm	K ppm	Na ppm	Mg ppm	Sulphate ppm	TDS calc ppm
Anion Column Regeneration												
11:55	0:00:00	Start Backwash	SCBW1	3.66	28	930						
12:00	0:05:00		SCBW2	4.9	4.5	760						
12:05	0:10:00		SCBW3	5.51	4.6	748						
12:20	0:25:00		SCBW4	6.16	7	460						
12:35	0:40:00		SCBW5	6.2	7.8	270						
12:38	0:43:00	Start fill										
12:48	0:53:00		SCF1	3.13	20	368						
12:53	0:58:00		SCF2	3.12	20	520						
12:58	1:03:00		SCF3	4.44	136	5796						
13:03	1:08:00		SCF4	5.44	1190	37632						
Cation Column Regeneration												
11:55	0:00:00	Initial, Start backwash	SABW1	3.22	19	725						
12:00	0:05:00	5 min	SABW2	3.07	22	398						
12:05	0:10:00	10 min	SABW3	3.02	24	266						
12:20	0:25:00	15 min	SABW4	2.98	24.5	580						
12:35	0:40:00	35 min	SABW5	2.94	24.5	208						
12:38	0:43:00	Start fill										
12:48	0:53:00		SAF1	3.14	16	142	2.237	10.538	7.189	3.325		
12:53	0:58:00		SAF2	1.29	1300	7120	50.855	565.855	127.877	110.423		
12:58	1:03:00		SAF3	0.8	4600	28233	215.872	2448.622	446.15	403.655		
13:03	1:08:00		SAF4	0.54	9500	62020	426.311	5054.216	590.482	680.077		
13:05	1:10:00	End										
13:22	1:27:00	Start rinse										
13:27	1:32:00		SAR1	0.65	6900	21370					19318	46080
13:34	1:39:00		SAR2	1.48	500	1092					929	3552
13:41	1:46:00		SAR3	2.32	75	244					94	595
13:46	1:51:00		SAR4	2.62	48	148					48	378
13:52	1:57:00		SAR5	2.74	36	94					30	281
14:10	2:15:00		SAR6	2.82	30	90					22	239
14:40	2:45:00		SAR7	2.84	30	83					19	234
14:51	2:56:00		SAR8	2.83	30	88					19	235

Sampling of Large Ion Exchange Plant
Date: 23/2/00 Diluted Concentrate

Time	Time from start	Notes	Sample	pH	Conductivity mS/m	Na ppm	Ca ppm	K ppm	Mg ppm	SO_4 mg/L	TDS mg/L	TKN mg/L
Anion Column												
Loading												
12:50	00:00		1A	5.72	20	8.804	0.163	14.336	4.346	9	87495	14
01:10	0:20		2A	4.98	16	8.124	0.549	13.510	5.399	8	131410	
03:15	2:25		3A	5.05	13	4.080	0.791	13.529	4.127	5	143416	
05:10	4:20		4A	5.3	18	6.576	1.485	20.979	2.091	5	141475	51
06:00	5:10		5A	5.41	15	19.756	1.778	42.696	1.930	8	133067	
06:30	5:40		6A	5.55	50	27.066	1.952	60.131	1.839	12	117934	
07:00	6:10		7A	5.6	90	32.998	2.571	90.022	2.291	16	125602	230
07:30	6:40		8A	5.85	80	39.643	3.306	109.846	2.723	27	122205	
08:00	7:10		9A	5.86	120	47.758	3.915	144.755	3.373	37	130848	
08:32	7:42		10A	5.83	130	40.247	4.822	144.165	4.077	44	127590	
09:00	8:10		11A	5.81	150	60.063	4.772	221.980	4.236	58	126758	206
09:30	8:40		12A	5.92								
10:00	9:10		13A	6.07	190	41.146	5.906	233.657	5.405	69	117322	
10:30	9:40		14A	6.19								
11:00	10:10		15A	6.03	210	41.868	6.494	313.085	5.495	33	122206	
11:30	10:40		16A	6.06								
12:00	11:10		17A	4.95	84	16.803	4.161	110.103	2.501		39012	464
12:30	11:40		18A	3.92								
Backwash												
12:45	11:55	Fill up anion			320-340 kPa							
12:57	12:07	Start Backwash										
01:32	0:42	End Anion, start cation			185-200 kPa							
02:32	1:42	end cation										
Fill												
02:35	1:45	Start fill both - to drain										
02:55	2:05		F1A	4.58	290	588.93	2.267	19.110	2.352		5341	
03:05	2:15		F2A	5.11	1290	565.63	6.560	32.326	3.245		22381	
03:15	2:25		F3A	5.33	2000	517.21	5.251	26.549	2.548		35902	
03:25	2:35		F4A	5.48	2200	470.74	3.941	22.516	2.047		39018	
03:30	2:40	Cation to tank	Caustic fill end (standing)									
03:31	2:41		S1A	5.7	2250	460.14	3.714	24.977	2.391		39842	
05:40	4:50	Caustic rinse start	R1A	12.92	2700	483.23	4.420	38.680	3.074		38895	
05:50	5:00		R2A	13.52	3100	481.55	2.082	29.896	1.331		34812	
06:05	5:15		R3A	13.08	1070	588.90	0.346	10.359	0.991		8952	
06:21	5:31		R4A	12.6	430	599.12	0	5.558	0.449		5830	
06:36	5:46	Start acid rinse (to tank)										
06:39	5:49	Caustic rinse to drain										
06:55	6:05		R5A	12.12	170	337.68	0	2.958	0.255		1676	
07:35	6:45		R6A	11.41	72	159.85	0	2.209	0.365		844	
07:38	6:48	Acid to drain										
08:16	7:26	Rinse together										
08:17	7:27		R7A	10.85	52	111.88	0	2.986	0.861		597	

Cation Column 23/2/00

Time	Time from start	Sample	pH	Conductivity mS/m	Na ppm	Ca ppm	K ppm	Mg ppm	SO4 mg/L	TDS mg/L	TKN mg/L
Loading											
12:50	00:00	1C	2.06	260	0.6	0.00	17.2	0.23		145472	28
01:10	00:20	2C	2.01	310	0.5	0.00	15.4	0.23		147738	
03:15	02:25	3C	1.99	310	1.0	0.00	15.0	0.23		144002	
05:10	04:20	4C	2.33	155	29.5	0.99	66.2	1.31		143260	186
06:00	05:10	5C	2.55	140	40.4	2.17	118.4	2.39		140020	
06:30	05:40	6C	2.74		50.4	2.93	153.7	3.13		132458	
07:00	06:10	7C	2.88		63.7	3.63	182.9	3.76		134904	450
07:30	06:40	8C	3.02	175	75.3	4.01	229.3	3.89		135376	
08:00	07:10	9C	3.11	220	73.5	5.16	282.2	4.91		128484	
08:32	07:42	10C	3.19	200	63.4	5.59	309.4	5.07		123774	
09:00	08:10	11C	3.24	210	56.3	6.06	348.6	5.44		129896	620
09:30	08:40	12C	3.25								
09:45	08:55										
10:00	09:10	13C	3.28		44.7	6.16	354.3	5.57		122268	
10:30	09:40										
10:30	09:40	14C	3.24								
11:00	10:10	15C	3.11	110	14.3	0.52	83.9	0.55		31226	
11:30	10:40	16C	3.1								
12:00	11:10	17C	3.23	39	2.9	0.00	32.6	0.25		2920	394
12:30	11:40	18C	3.3								
Backwash											
12:45	11:55		320-340 kPa								
12:57	12:07										
01:32	00:42		185-200 kPa								
02:32	01:42										
Fill											
02:35	01:45	to drain									
02:58	14:08	F1C	2.45	890	306.4	95.32	1431.58	105.01	4153	7802	
03:05	14:15	F2C	2.42	1400	490.6	230.06	2553.09	203.48	7604	13752	
03:15	14:25	F3C	2.29	1550	523.3	306.09	3036.30	238.45	8854	15920	
03:25	14:35	F4C	1.94	2000	407.4	255.52	2547.05	198.78	9166	15092	
03:30	14:40	Caustic fill end (standing)									
03:37	14:47	F5C	1.69	2600	268.6	171.12	2051.50	141.78	8958	12089	
04:33	15:43	F6C	1.4	3700	56.0	63.02	913.10	55.79	8437	10480	
05:31	16:41	F7C	1.33	4000	28.0	40.20	556.77	36.02	8437	9912	
06:43	17:53	R1C	1.33	4200	32.5	33.05	382.25	28.84	7321	8280	
07:00	18:10	R2C	1.36	3500	26.8	22.17	298.78	19.49	6964	7380	
07:15	18:25	R3C	1.61	1800	14.8	6.35	145.73	6.01	3348	4500	
07:45	18:55	R4C	2.04	650	5.4	1.02	44.67	1.23	875	1010	
08:15	19:25	R5C	2.58	140	1.4	0.21	9.56	0.52	84	201	
08:16		Rinse together									

Ashton: Large Plant Diluted concentrate 410 hL treated
Date: 11/10/2000

Time	Time from start	Sample	pH	Conductivity mS/m	Na ppm	Ca ppm	K ppm	Mg ppm	SO_4 mg/L	Tartrates mg/L	Malates mg/L	Citrates mg/L
09:45	00:00	Start Backwash of anion column										
10:00	00:15	ABW1	5.99	23	11.51	8.04	19.06	4.63				
10:24	00:39	End Backwash of anion column										
11:05	01:20	Start fill - to drain										
11:10	01:25	AF1	5.2	40	11.23	3.55	42.55	3.87		14	151	8
11:20	01:35	AF2	3.28	52	23.8	10.95	11.27	10.34				
11:30	01:45	AF3	4.21	500	309.94	21.69	10.33	9.6		3561	4281	8
11:40	01:55	fill - to tank										
11:40	01:55	AF4	4.63	1550	302.4	26.22	13.13	1.58				
11:58	02:13	Start Stand										
11:58	02:13	AF5	4.91	2400	294.65	9.14	13.41	2.36		2377	3144	108
13:30	03:45	Start rinse - to tank										
13:36	03:51	AR1	4.96	2400	294.47	12.06	15.01	3.2		4470	1894	80
13:43	03:58	AR2	5.13	2600	291.48	6.03	14.9	1.61				
14:00	04:15	AR3	7.09	2800	291.44	1.05	14.28	0		2314	1620	300
14:15	04:30	AR4	13.4	1050	308.82	0.07	3.04	0				
14:30	04:45	AR5	13.31	525	310.57	0	1.16	0		2205	1955	406
14:41	04:56	Rinse - to drain										
15:00	05:15	AR6	12.84	250	134.4	0	1.25	0		358	298	8
15:35	05:50	AR7	12.64	150	87.49	0	2.45	0		67	20	8
16:00	06:15	AR8	12.24	95	64.45	0	3.97	0		40	41	8
16:30	06:45	AR9	11.62	59	43.03	0	6.84	0		14	20	8
16:30	06:45	Start rinse together										
17:37	07:52	End rinse together										
18:00	08:15	Start loading juice (Water drained from anion column until reaches 6 brix)										
20:07	10:22	AL1	8.57	14	3.58	0	11.11	6.01	3.7	14	20	8
21:06	11:21	AL2	8.82	18	3.22	0	13.25	7.07	5			
23:00	13:15	AL3	8.68	20	1.7	1.4	16.32	10.48	9	14	20	8
0:00:00	14:15	AL4	8.62	20	1.3	2.72	15.78	10.03	6.2			
01:00	15:15	AL5	8.54	20	0.98	3.86	14.72	8.25	6.6	14	20	8
02:40	16:55	AL6	8.55	21	2.88	4.9	14.14	5.34	6.8	14	20	8
03:30	17:45	AL7	8.6	26	4.48	4.77	16.7	4.41	9			
04:30	18:45	AL8	8.71	32.5	5.94	5.41	25.79	3.92	12.3	14	20	8
05:30	19:45	AL9	8.76	41	6.7	6.19	36.48	3.44	14.7			
05:50	20:05	AL10	8.77	45	7.01	6.67	43.69	3.45	16	14	20	8

Cation Column

Time	Time from start	Sample	pH	Conductivity	Ca	K	Mg	Na	SO4	TDS
				mS/m	ppm	ppm	ppm	ppm	mg/L	
10:34	00:00	Start Backwash								
10:40	00:06	CBW1	5.18	23	0.5	52.75	0.79	6.18	29	147.2
11:05	00:31	Start fill with H_2SO_4 to drain								
11:10	00:36	CF1	3.48	50	11.95	9.85	11.76	22.65	15	320
11:20	00:46	CF2	2.19	500	11.41	451.19	20.74	44.43	1482	3200
11:30	00:56	CF3	2.3	1400	181.03	2237.26	177.16	201.88	7586	8960
11:40	01:06	CF4	2.41	1700	292.64	2998.99	176.91	253.03	11228	10880
11:58	01:24	Start fill to tank								
11:58	01:24	CF5	1.39	3000	233.25	2471.78	175.04	130.04	11754	19200
12:34	02:00	CF6	1.07	4700	87.84	1162.62	84.2	29.41	11929	30080
13:30	02:56	CF7	1.05	5000	47.46	624.27	46.86	12.21	10877	32000
14:15	03:41	Start rinse to tank								
14:30	03:56	CR1	1.36	2500	10	213.68	10.79	7.43	4827	16000
14:46	04:12	CR2	1.42	1500	3.95	125.41	4.27	4.98	2758	9600
15:15	04:41	CR3	1.86	740	1.54	59.59	1.59	2.99	1086	4736
15:18	04:44	Start rinse to drain								
15:45	05:11	CR4	2.58	172	0.66	14.31	0.66	1.34	115	1100.8
16:30	05:56	**Start rinse together**								
17:37	07:03	**End rinse together**								
18:00	07:26	**Start loading juice (Water drained from anion column until reaches 6 brix)**								
20:07	09:33	CL1	1.81	350	0	14.32	0	0.23		2240
21:06	10:32	CL2	1.79	350	0	13.85	0	0.22		2240
23:00	12:26	CL3	1.9	360	0	13.92	0	0.22		2240
24:00:00	13:26	CL4	1.79	350	0	13.98	0	0.75		2240
01:00	14:26	CL5	1.84	300	0	17.26	0	4.11		1920
02:40	16:06	CL6	1.95	260	0.35	31.75	0.19	6.8		1664
03:30	17:56	CL7	2.02	240	0.54	40.9	0.13	7.17		1536
04:30	18:56	CL8	2.1	220						
05:30	19:56	CL9	2.24	200	1.08	71.54	0.5	8.81		1280
05:50	20:16	CL10	2.31	185	1.25	78.83	0.67	10.16		1184

PRELIMINARY SAMPLING RUN

Figure A1: Sulphates during Acid Regeneration

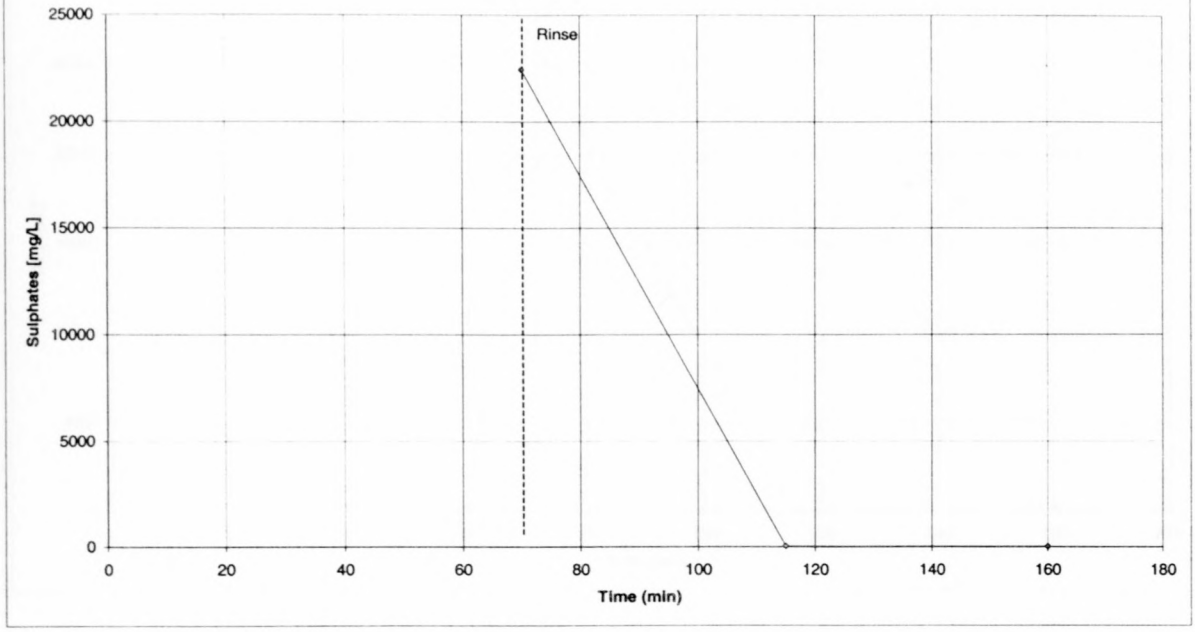


Figure A2: COD during Acid Regeneration

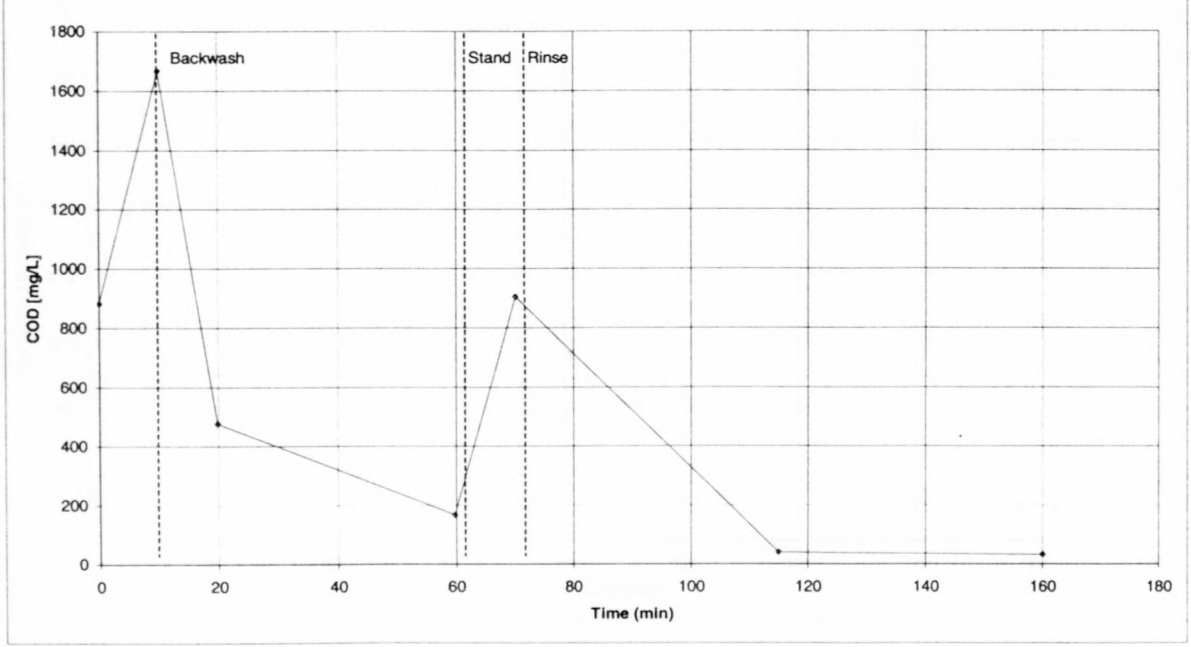


Figure A3: Total Dissolved Solids during Acid Regeneration

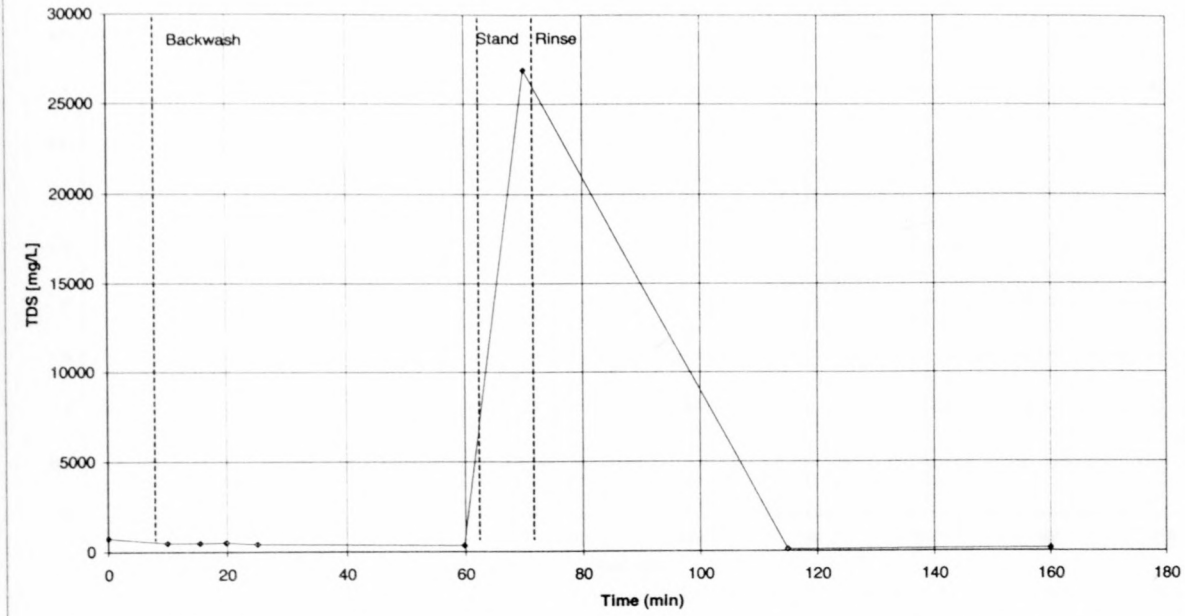


Figure A4: Suspended Solids during Acid Regeneration

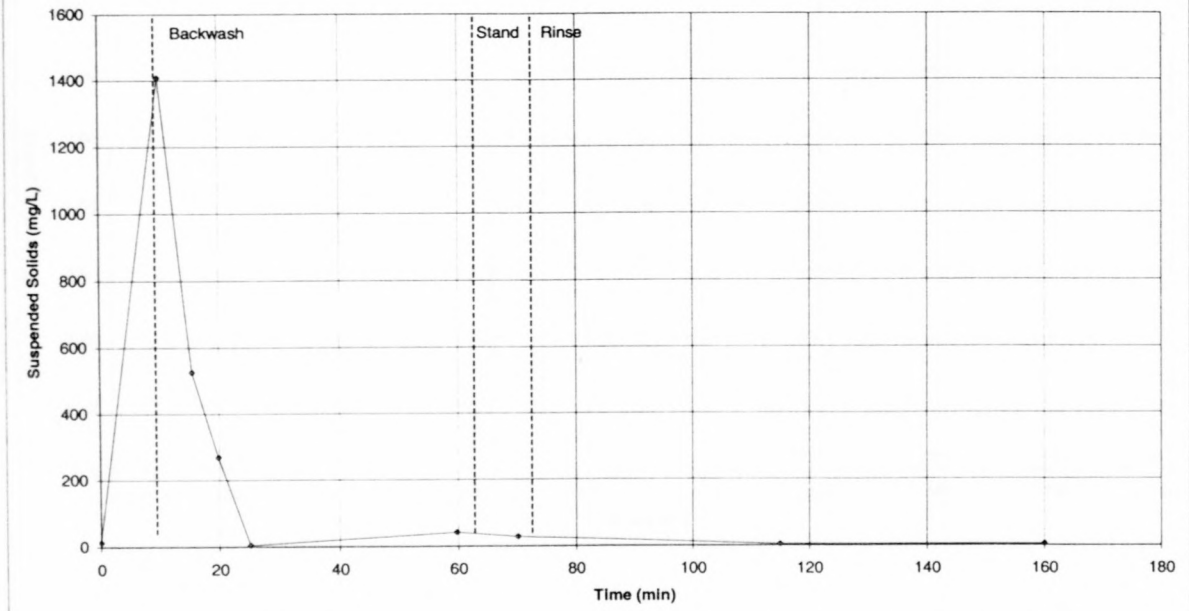


Figure A5: pH during Acid Regeneration

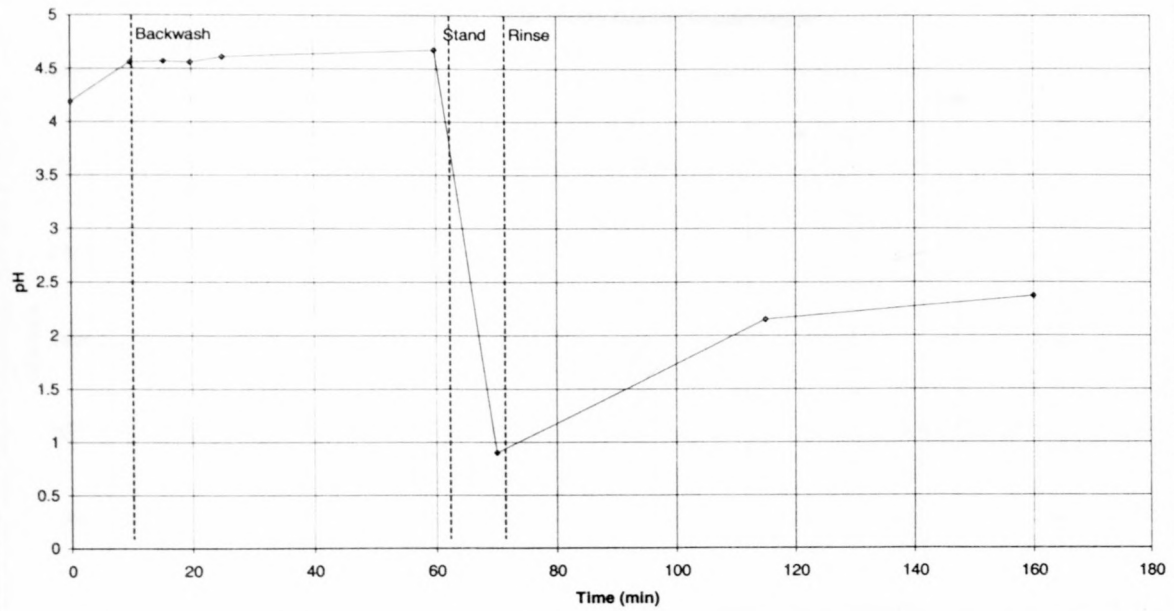


Figure A6: Conductivity during Acid Regeneration

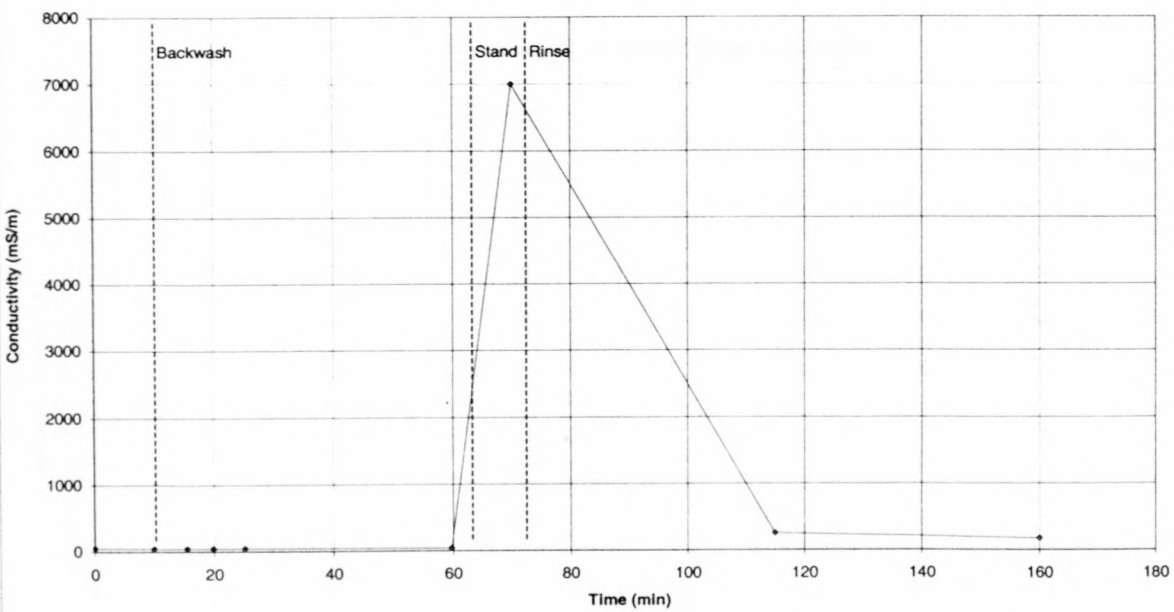


Figure A7: COD during Caustic Regeneration

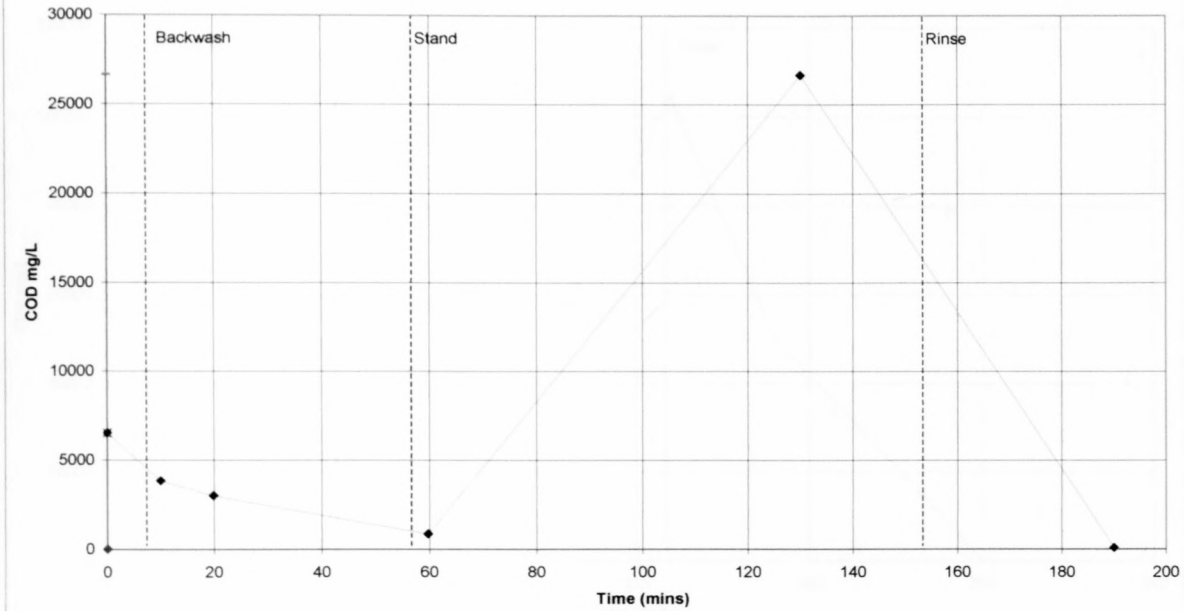


Figure A8: Suspended Solids during Caustic Regeneration

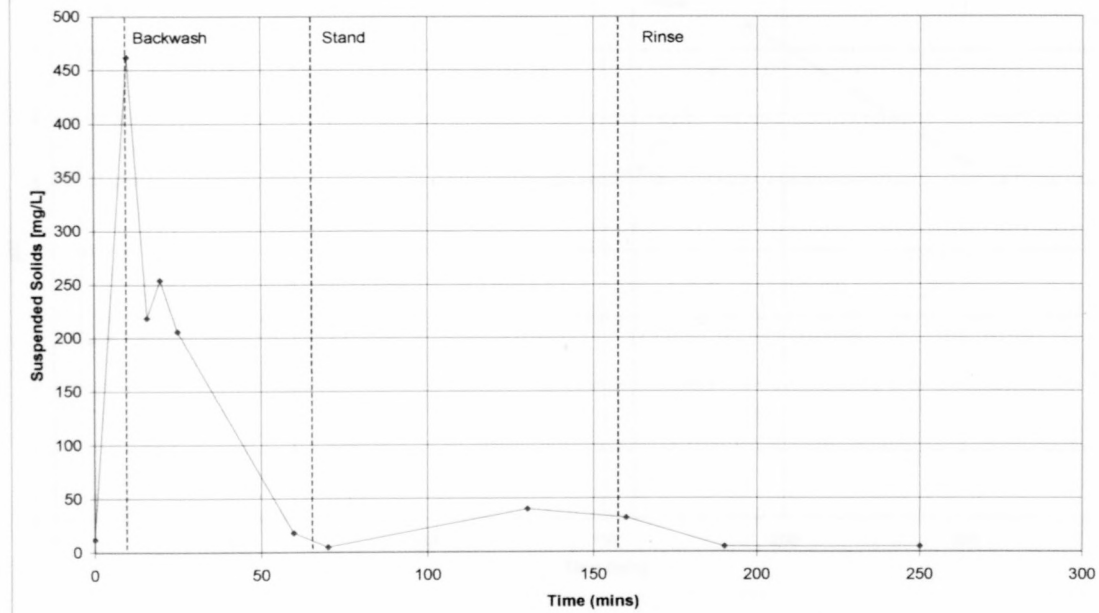


Figure A9: Total Dissolved Solids during Caustic Regeneration

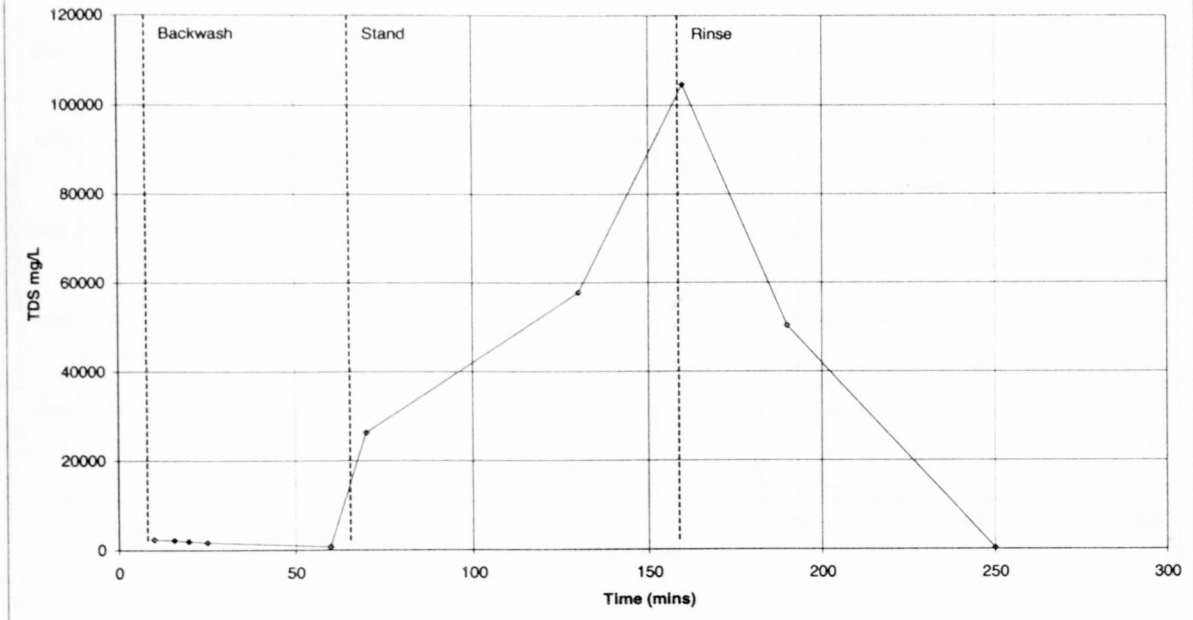


Figure A10: pH during Caustic Regeneration

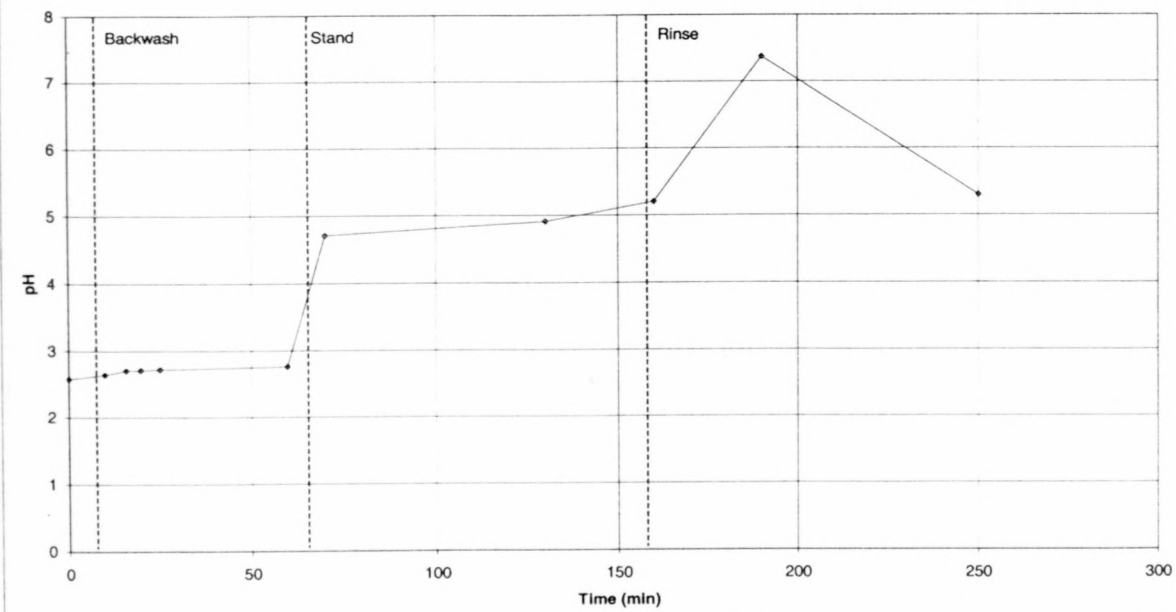
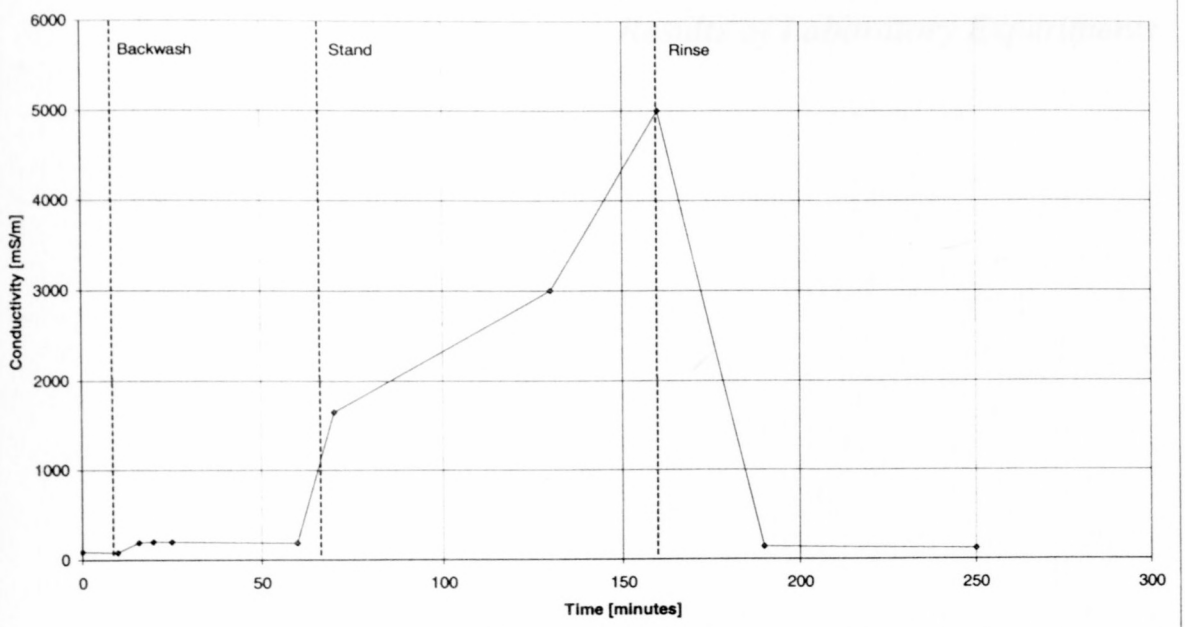


Figure A11: Conductivity during Caustic Regeneration

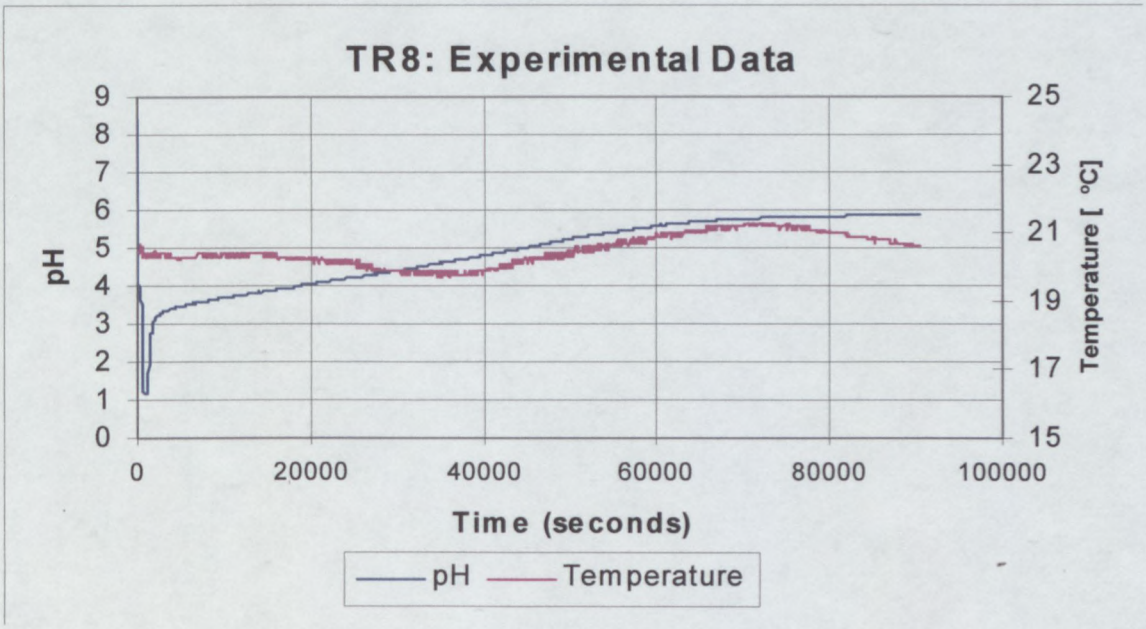


APPENDIX B:

Results of Laboratory Experiments

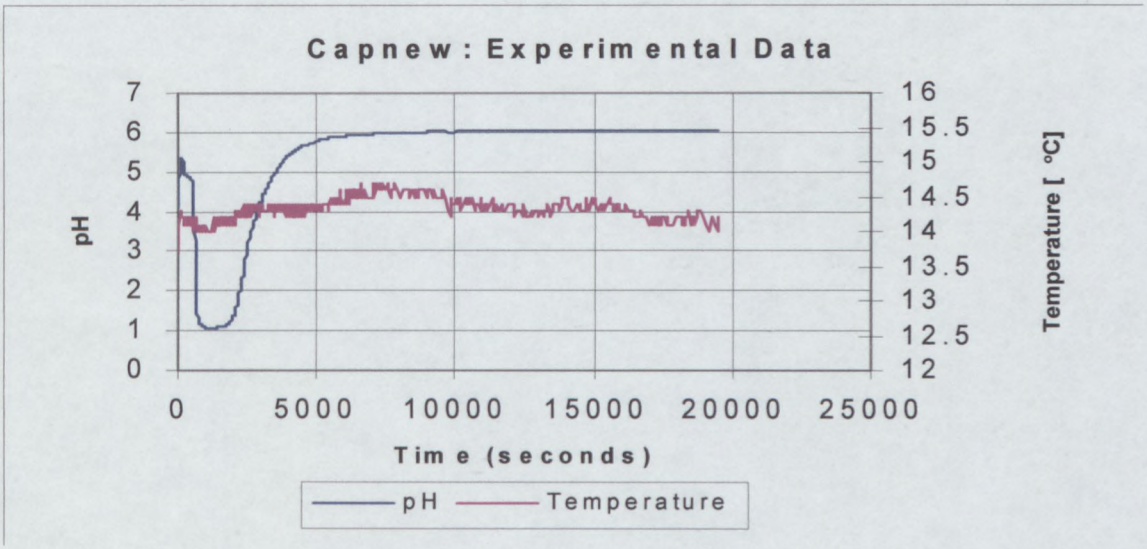
CATION CAPACITY TESTS

RunID: TR8
Date: 17-Feb-01
Resin: Ashton Cation
Volume: 20mℓ
Loaded with: Na_2SO_4
Flow: Up
Flowrate: 0.209mℓ/s
Total volume: ml
Bedvolume: 20ml
Average temp: 20.47°C
Calculated Capacity: 1.782equiv/ℓ resin

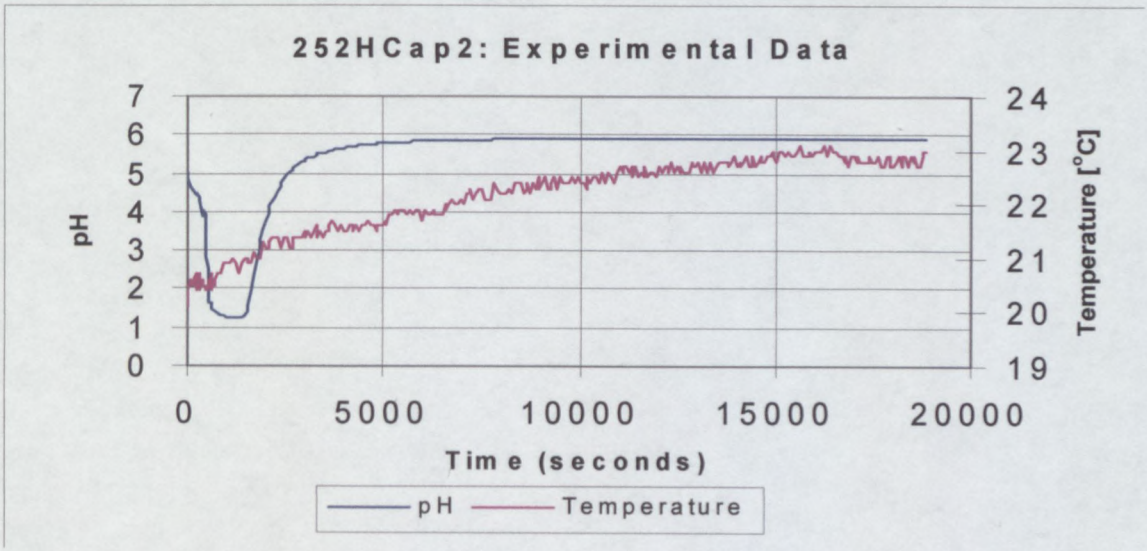


.....

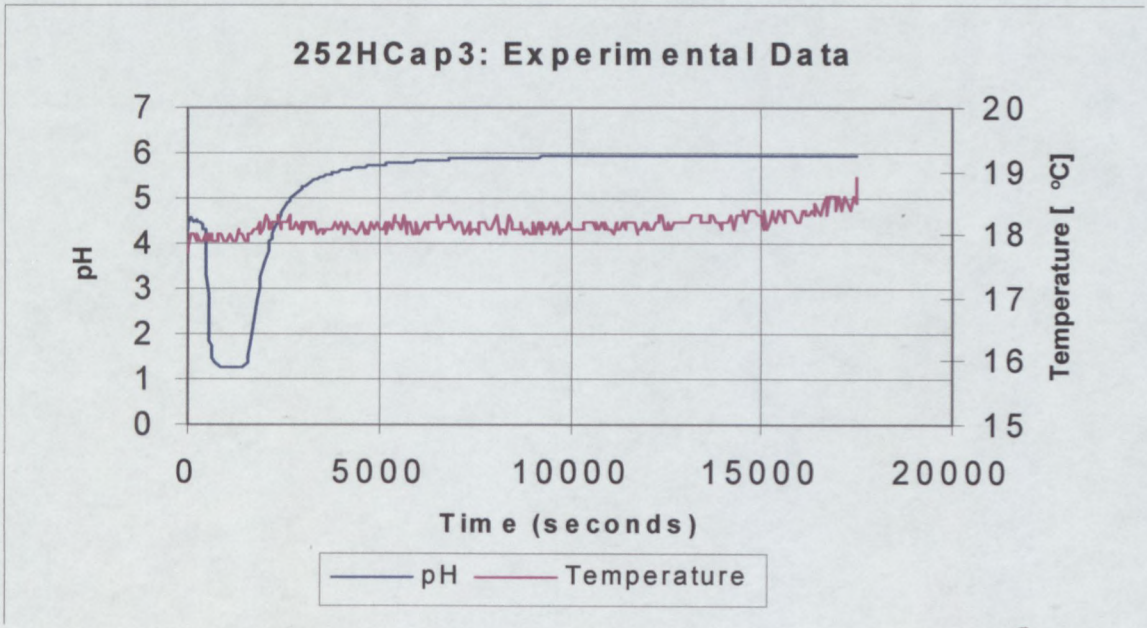
RunID: Capnew
Date: 03-Jun-00
Resin: 252H
Volume: 20ml
Loaded with: Na2SO4
Flow: Up
Flowrate: 0.186ml/s
Total volume: 3059ml
Bedvolume: 20ml
Average temp: 14.3°C
Capacity: 2.26mequiv/ml



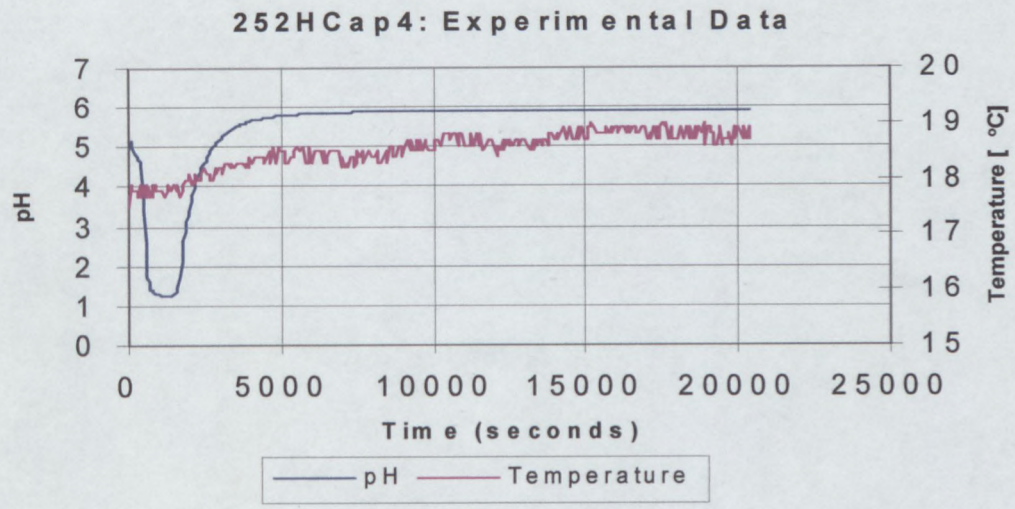
RunID: 252HCap2
Date: 27-Feb-01
Resin: 252H
Volume: 20ml
Loaded with: Na_2SO_4
Flow: Up
Flowrate: 0.189ml/s
Total volume: 3510ml
Bedvolume: 20ml
Average temp: 22.07°C
Capacity: 1.322mequiv/ml



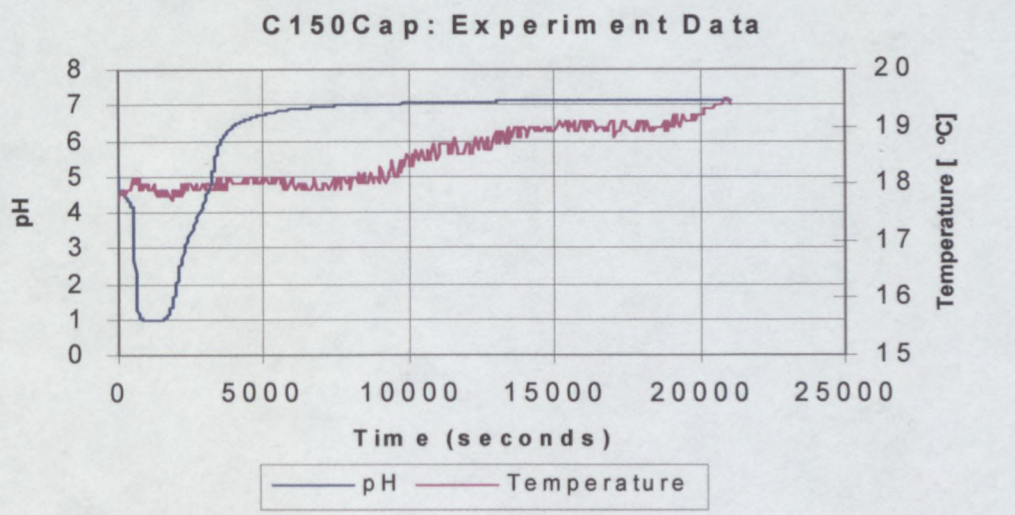
RunID: 252HCap3
Date: 06-Mar-01
Resin: 252H
Volume: 20ml
Loaded with: Na_2SO_4
Flow: Up
Flowrate: 0.190ml/s
Total volume: 3222ml
Bedvolume: 20ml
Capacity: 1.403mequiv/ml
Time: 17525sec



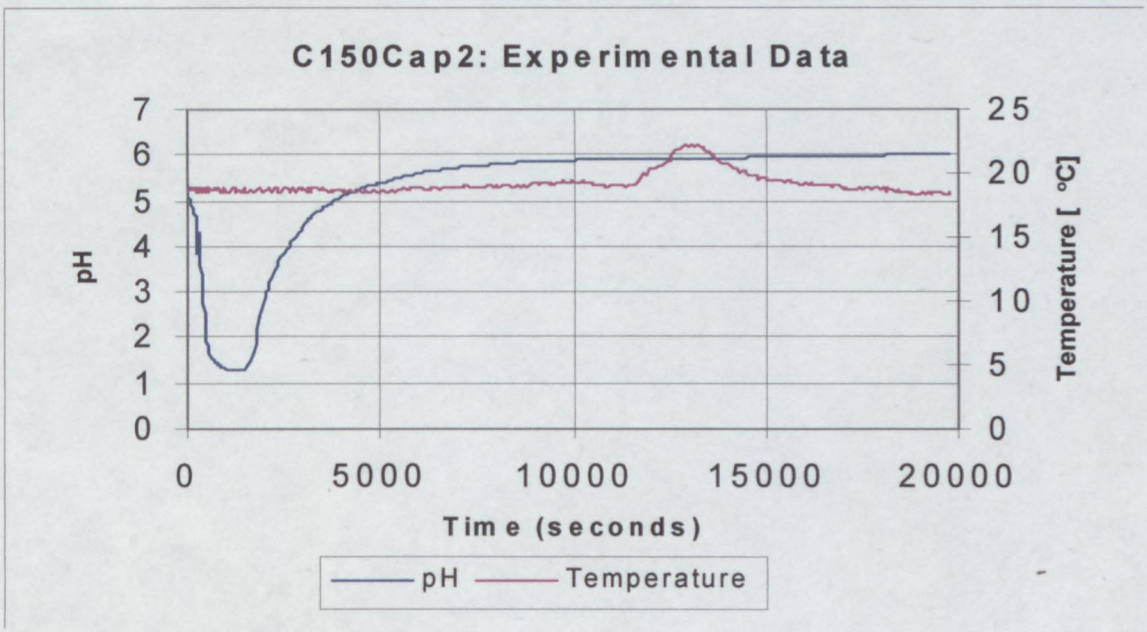
RunID: 252HCap4
Date: 07-Mar-01
Resin: 252H
Volume: 20ml
Loaded with: Na_2SO_4
Flow: Up
Flowrate: 0.186ml/s
Total volume: 4000ml
Bedvolume: 20ml
Average temp: 18.5°C
Capacity: 1.34mequiv/ml



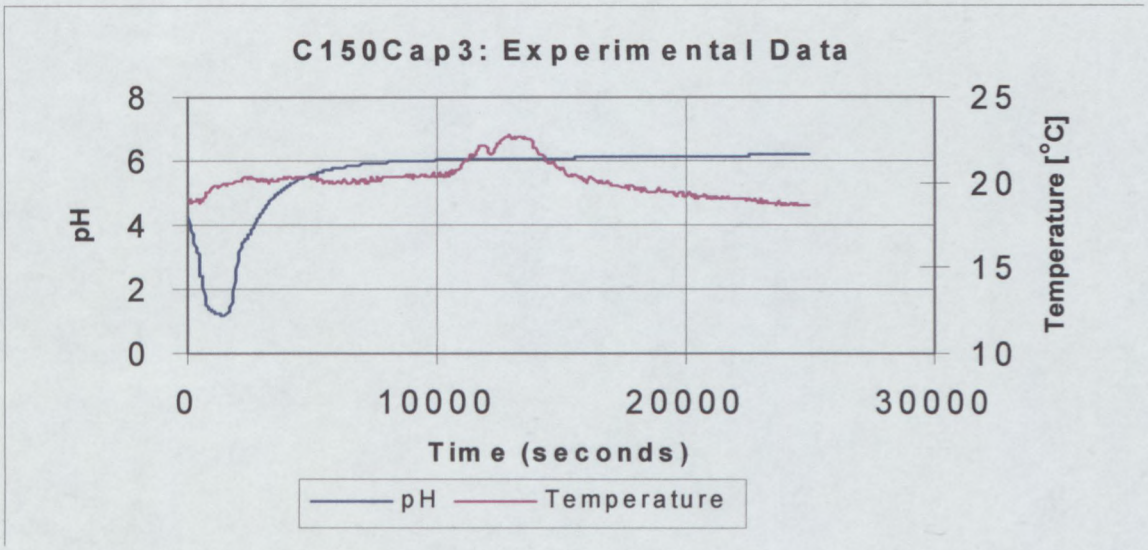
RunID: C150Cap
Date: 22-Jan-01
Resin: C150
Volume: 20ml
Loaded with: Na_2SO_4
Flow: Up
Flowrate: 0.194ml/s
Total volume: 4570ml
Bedvolume: 20ml
Average temp: 18.6°C
Capacity: 2.373mequiv/ml



RunID: C150Cap2
Date: 19-Feb-01
Resin: C150
Volume: 20ml
Loaded with: Na_2SO_4
Flow: Up
Flowrate: 0.194ml/s
Total volume: 3665ml
Bedvolume: 20ml
pH in 6.02
Average temp: 19.1°C
Capacity: 1.563mequiv/ml

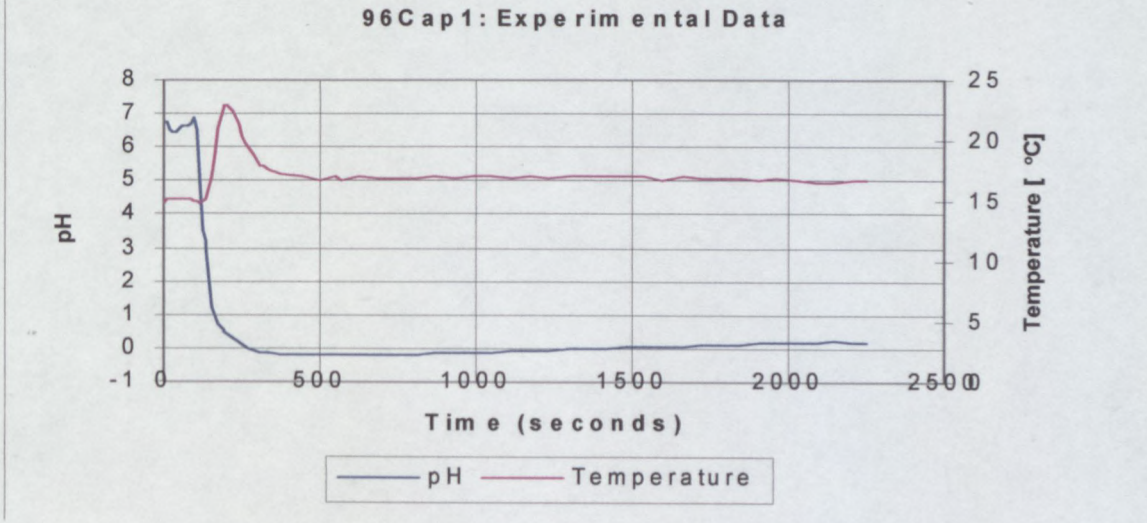


RunID: C150Cap3
Date: 23-Feb-01
Resin: C150
Volume: 20ml
Loaded with: Na_2SO_4
Flow: Up
Flowrate: 0.192ml/s
Total volume: ml
Bedvolume: 20ml
pH in 6.02
Average temp: 20.1°C
Capacity: 1.577mequiv/ml

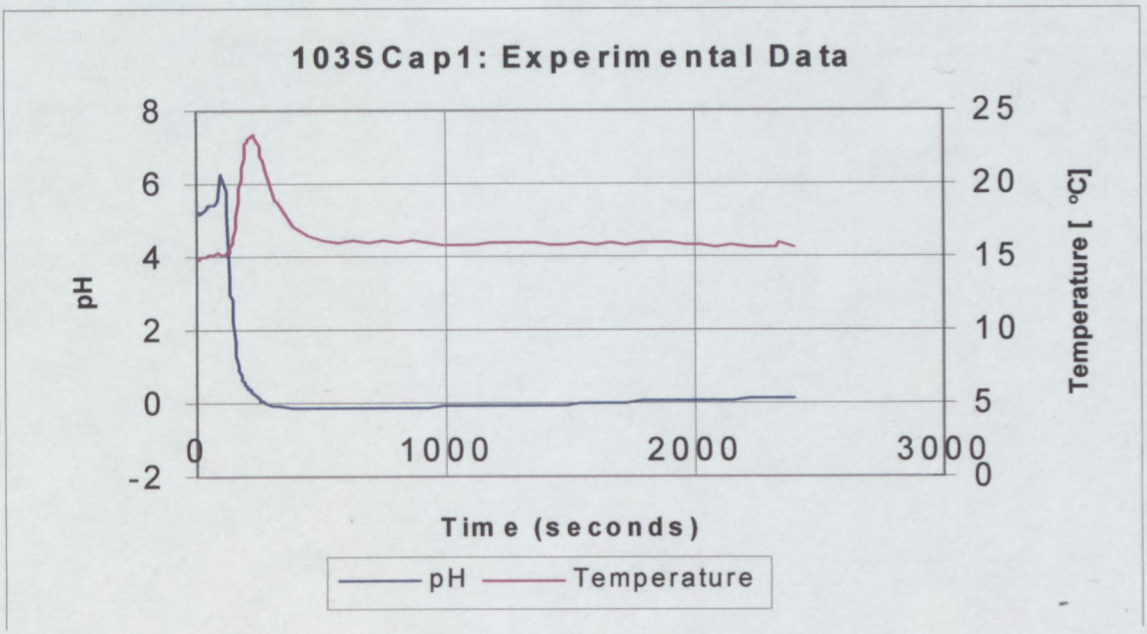


ANION CAPACITY TESTS

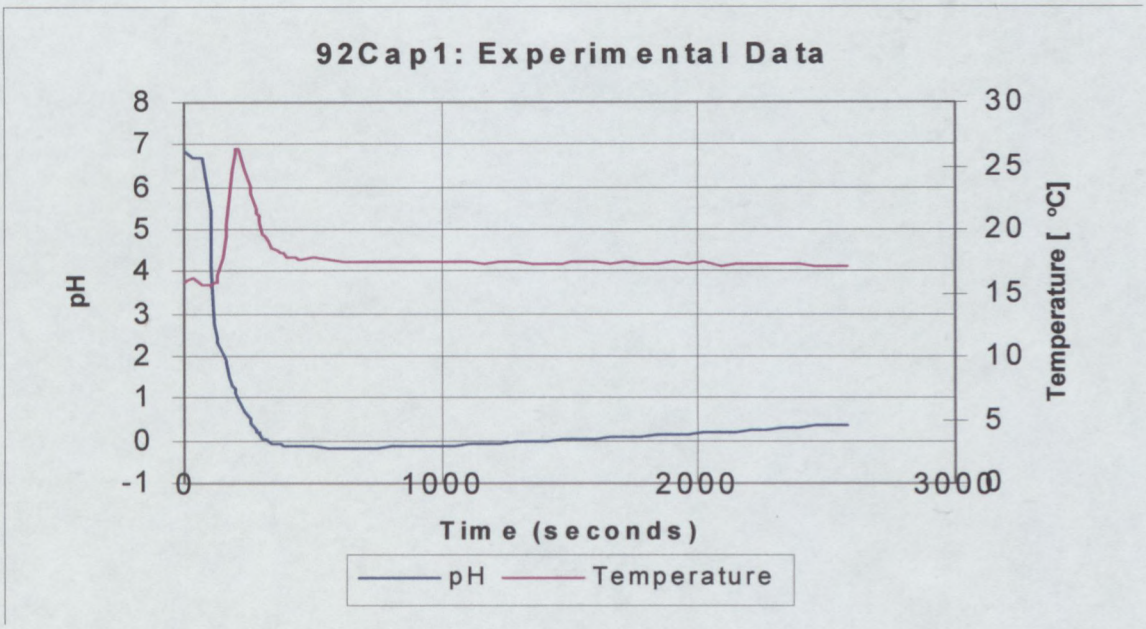
RunID:	96Cap1
Date:	10-Apr-01
Resin:	IRA 96
Volume:	15ml
Eluting with:	10% $NaNO_3$
Flow:	Down
Flow rate	10ml/min
Total volume:	500ml
Cl^- Conc	No Result ppm
Capacity	meq/ml



RunID	103Scap1
Date:	11-Apr-01
Resin:	103S
Volume:	15
Eluting with:	10% $NaNO_3$
Flow:	Down
Flow rate	10ml/min
Total volume:	500ml
Cl^- Conc	1250ppm
Capacity	1.18meq/ml

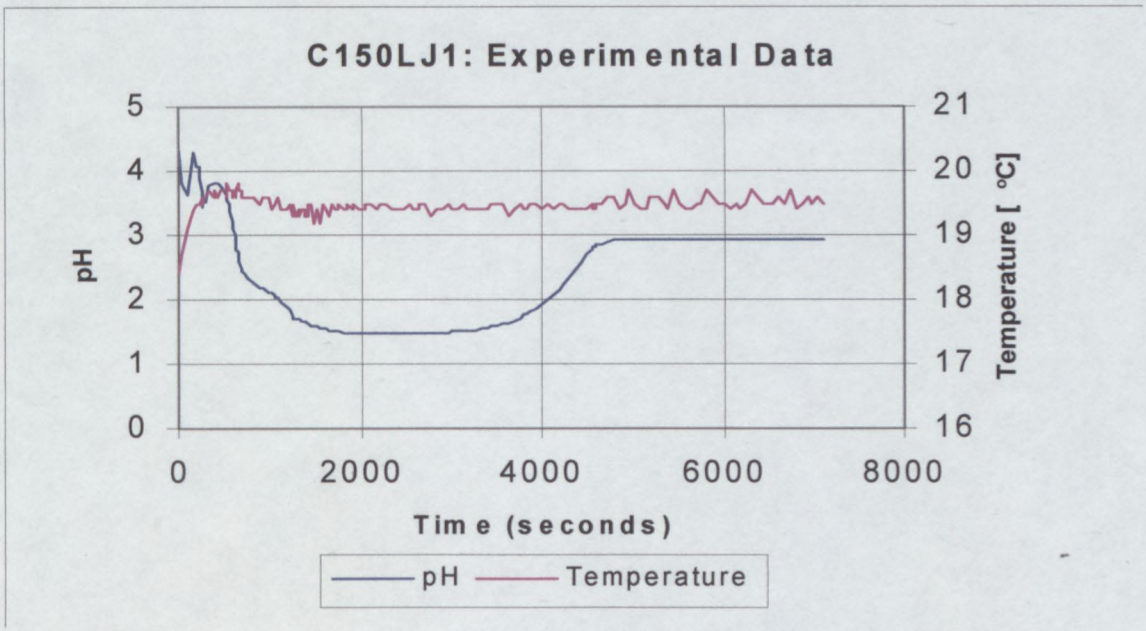


RunID:	92Cap1
Date:	09-Apr-01
Resin:	IRA 92
Volume:	15ml
Eluting with:	10% $NaNO_3$
Flow:	Down
Flow rate	10ml/min
Total volume:	496ml
Cl^- Conc	602ppm
Capacity	0.57meq/ml

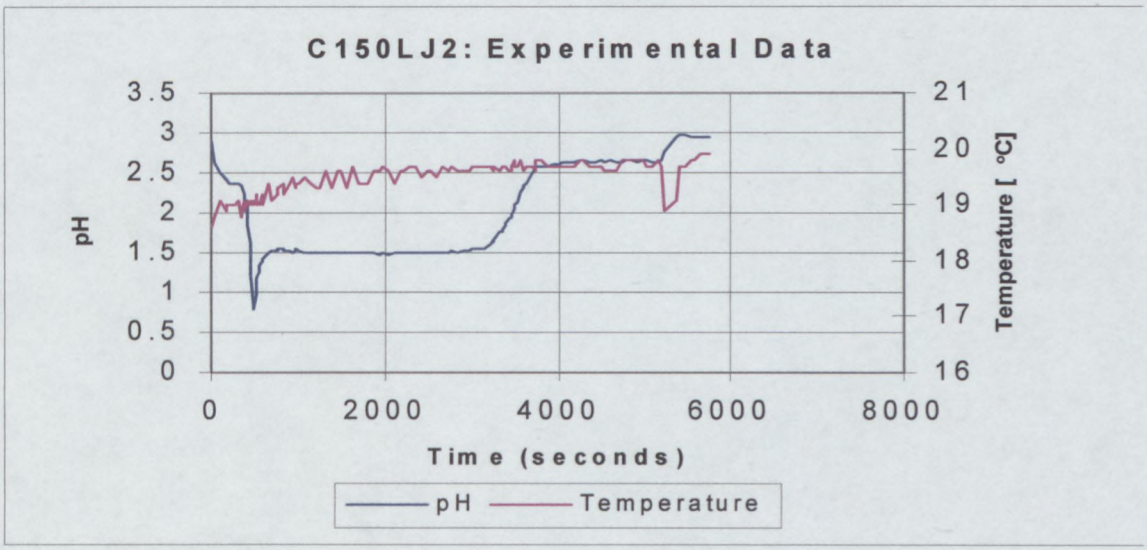

92Cap1: Experimental Data
pH
Temperature [°C]
Time (seconds)
pH
Temperature
8
7
6
5
4
3
2
1
0
-1
30
25
20
15
10
5
0
0
1000
2000
3000

CATION LOADING

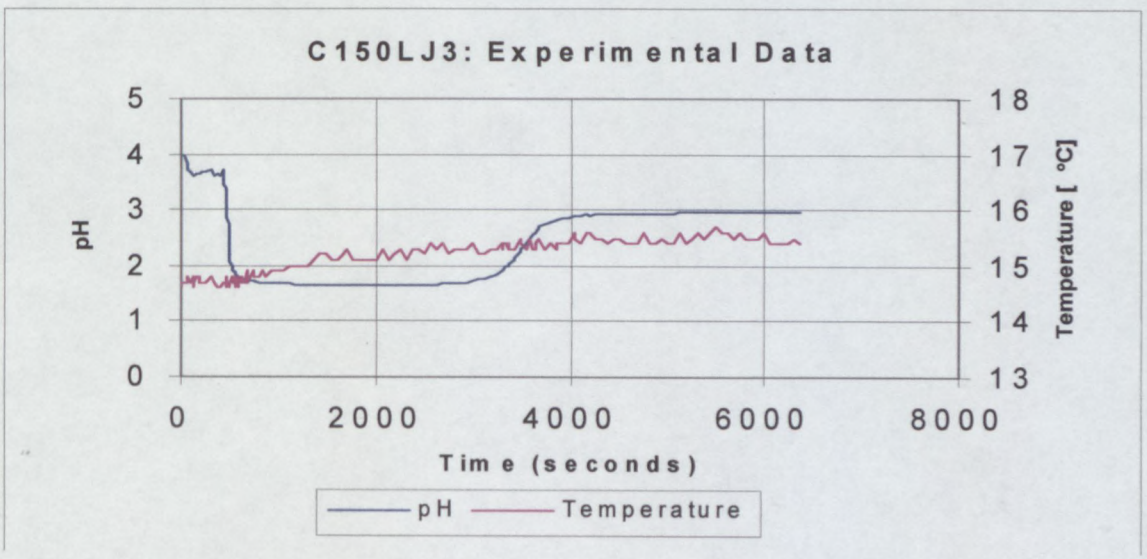
RunID: C150lj1
Date: 26-Jan-01
Resin: C150
Volume: 20 ml
Loading with: Juice (batch3)
Flow: Up
Flow rate 0.16 ml/s
Total volume: 1270
Bed volume: 108 ml
pH in 2.94



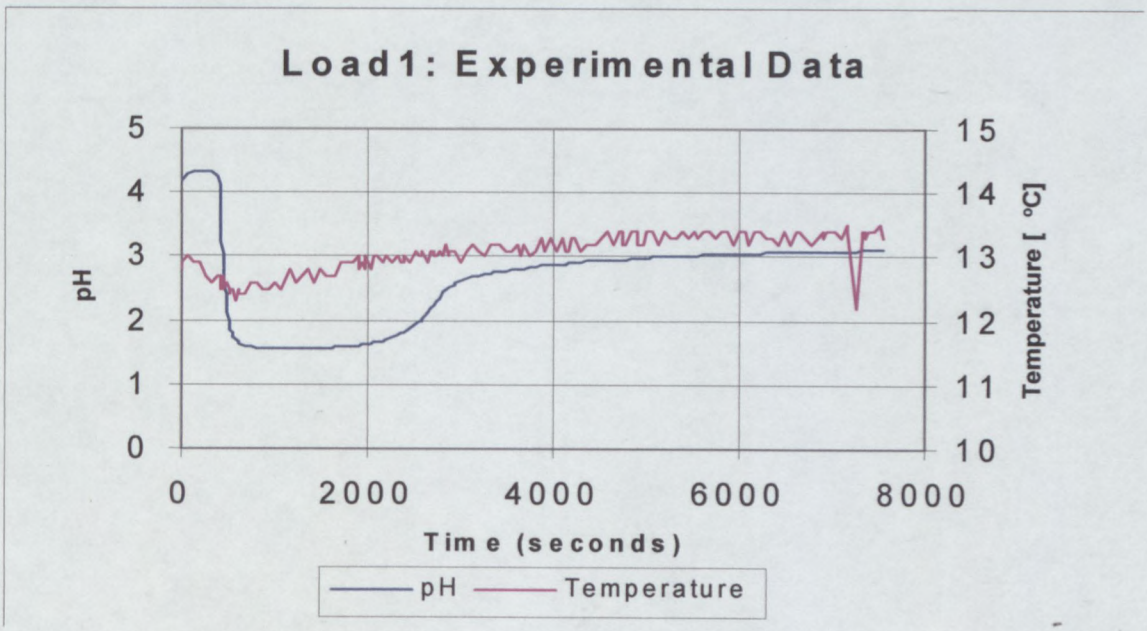
RunID: C150lj2
Date: 08-Feb-01
Resin: C150
Volume: 20ml
Loading with: Juice (batch3)
Flow: Up
Flow rate 0.17ml/s
Total volume: 1000
Bed volume: 108ml
pH in 2.92



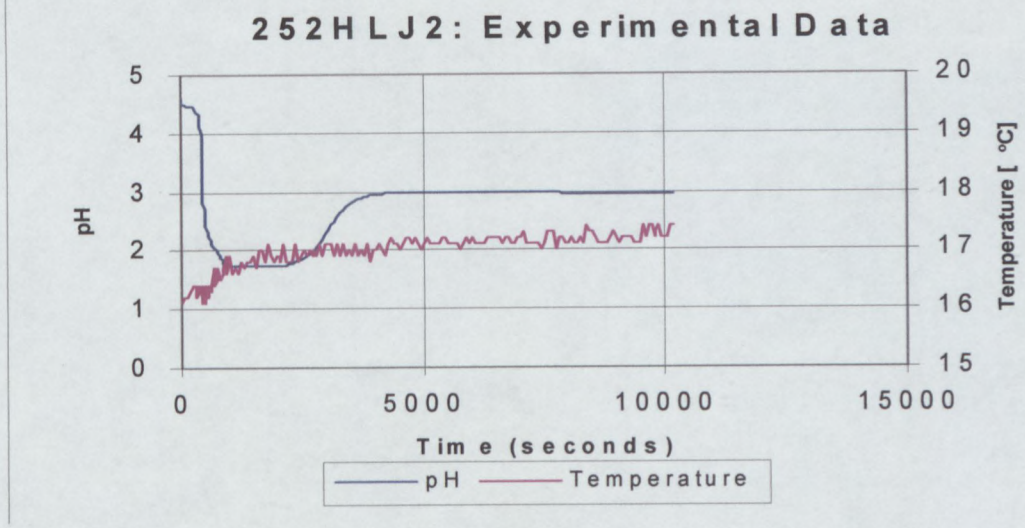
RunID: C150lj3
Date: 16-Apr-01
Resin: C150
Volume: 20ml
Loading with: Juice (batch3)
Flow: Up
Flow rate 0.1975ml/s
Total volume: 1265ml
Bed volume: 108
pH in 2.96



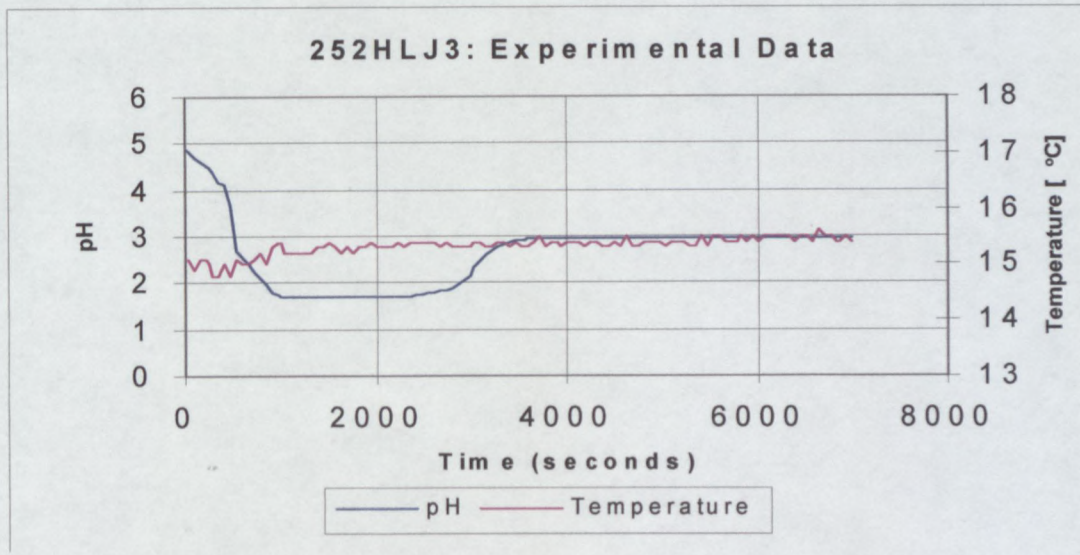
RunID: Load1
Date: 27-Oct-00
Resin: 252H
Volume: 20ml
Loading with: Juice (batch3)
Flow: Up
Flow rate 0.1825ml/s
Total volume: 1435
Bed volume: 108ml
pH in 3.11



RunID: 252Hlj2
Date: 08-Mar-01
Resin: 252H
Volume: 20ml
Loading with: Juice (batch3)
Flow: Up
Flow rate 0.205ml/s
Total volume: 2054ml
Bed volume: 108ml

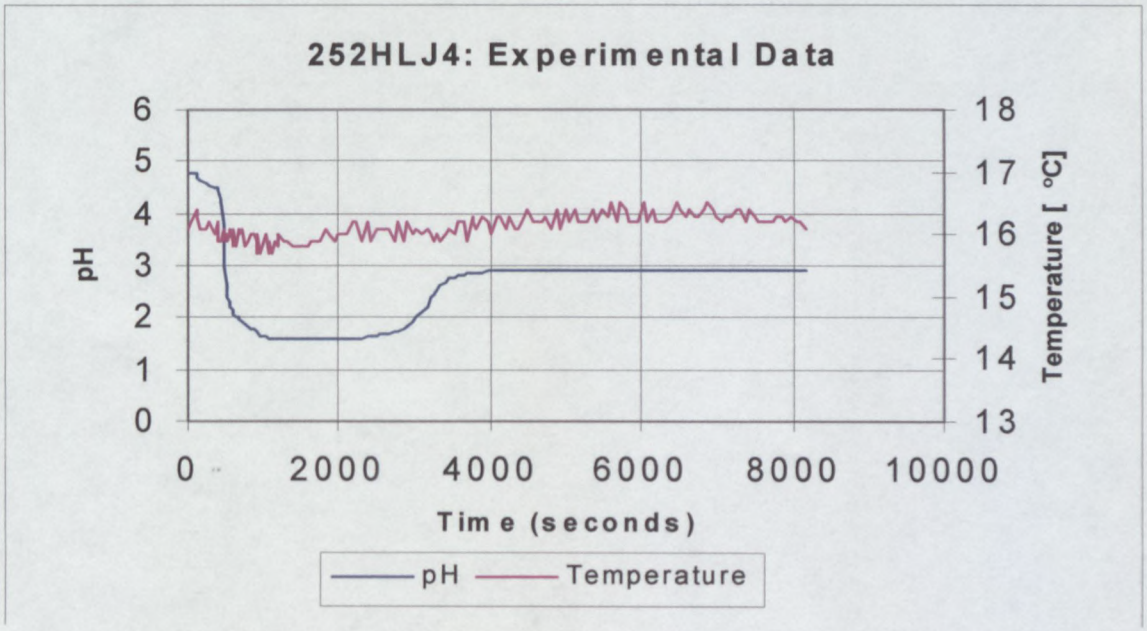


RunID: 252Hlj3
Date: 12-Mar-01
Resin: 252H
Volume: 20ml
Loading with: Juice (batch3)
Flow: Up
Flow rate 0.206ml/s
Total volume: 1440ml
Bed volume: 108ml
pH in 2.97



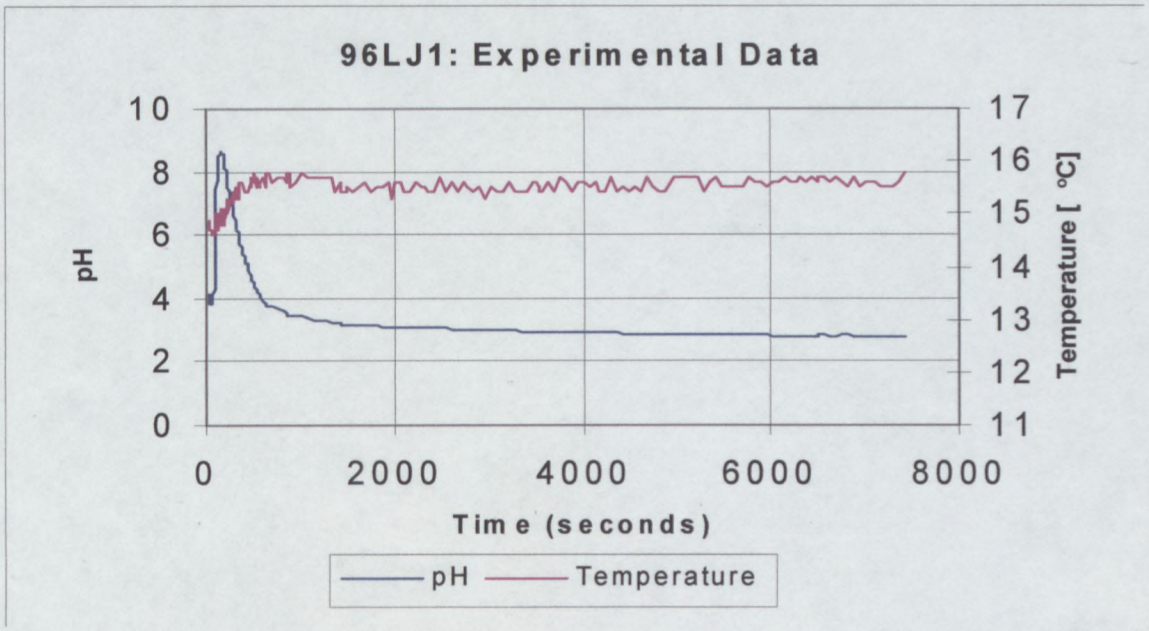
RunID:	252Hlj4
Date:	13-Mar-01
Resin:	252H
Volume:	20
Loading with:	Juice (batch3)
Flow:	Up
Flow rate	0.200
Total volume:	1485
Bed volume:	108
pH in	2.92

SampleID	Time	Bedvolumes	Na	Ca	K	Mg	P
	[sec]		[ppm]	[ppm]	[ppm]	[ppm]	[ppm]
MD1	155	0.29	0	0.02	0.18	0.01	0
MD2	352	0.65	0	0.03	0.18	0.02	0.11
MD3	488	0.90	0.43	0.11	0.67	0.03	0.96
MD4	627	1.16	0.54	0.6	3.03	0.63	98.53
MD5	920	1.70	1.31	0.96	14.67	1.24	121.15
MD6	1250	2.31	2.38	0.99	21.25	1.36	127.66
MD7	1568	2.90	3.57	1.03	52.32	1.56	127.81
MD8	1830	3.39	4.75	1.03	74.4	1.53	129.99
MD9	2678	4.96	14.83	1.09	299.97	2.23	134.97
MD10	3200	5.93	32.9	2.57	907.08	5.99	134.97
MD11	3830	7.09	41.94	7.31	1301.37	17.57	134.35
MD12	5013	9.28	38.71	12.05	1323.66	29.09	134.59
MD13	6398	11.85	34.65	19.56	1293.12	46.41	136.05
MD14	8295	15.36	32.63	31.39	1333.02	70.09	137.38



ANION LOADING

RunID: 96lj1
Date: 14-Apr-01
Resin IRA 96
Volume: 20 ml
Loading with: Juice (batch3)
Flow: down
Flowrate: 0.20
Total volume: 1520 ml
Bed volume: 21 ml



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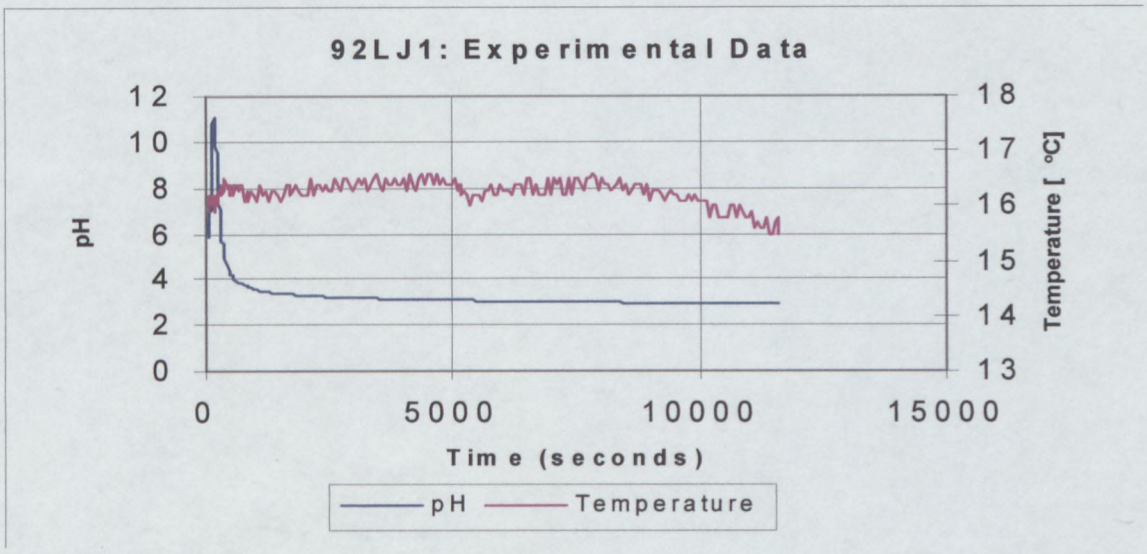
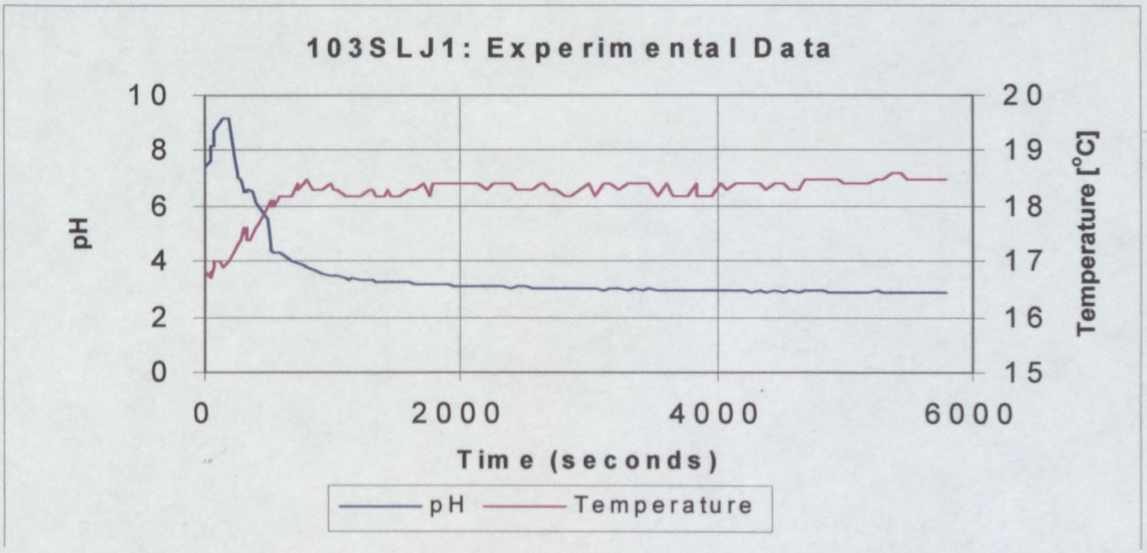
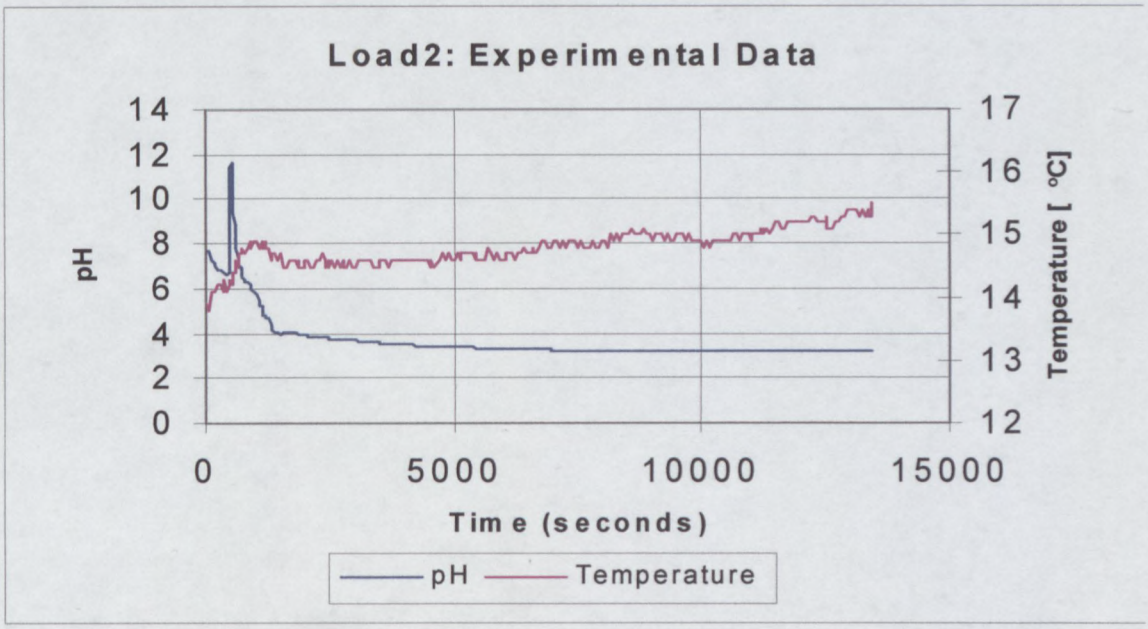
RunID: 92lj1
Date: 05-Apr-01
Resin IRA 92
Volume: 20ml
Loading with: Juice (batch3)
Flow: down
Flowrate: 0.202ml/s
Total volume: 2260ml
Bed volume: 21ml



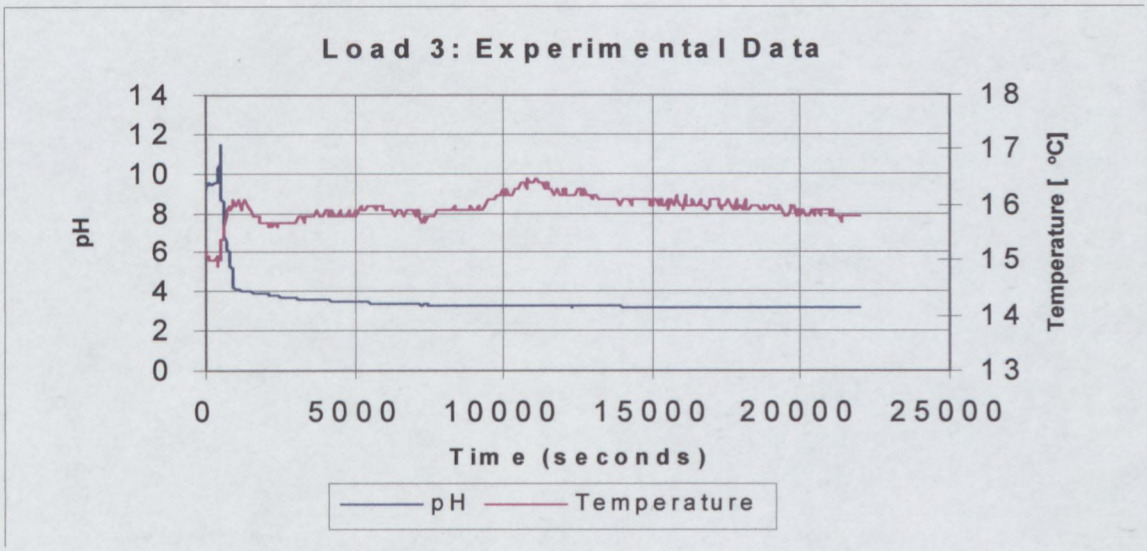
RunID: 103slj1
Date: 31-Jan-01
Resin: A103S
Volume: 20ml
Loading with: Juice (batch3)
Flow: down
Flow rate 0.169ml/s
Total volume: 1090
Bed volume: 21
pH in 2.84



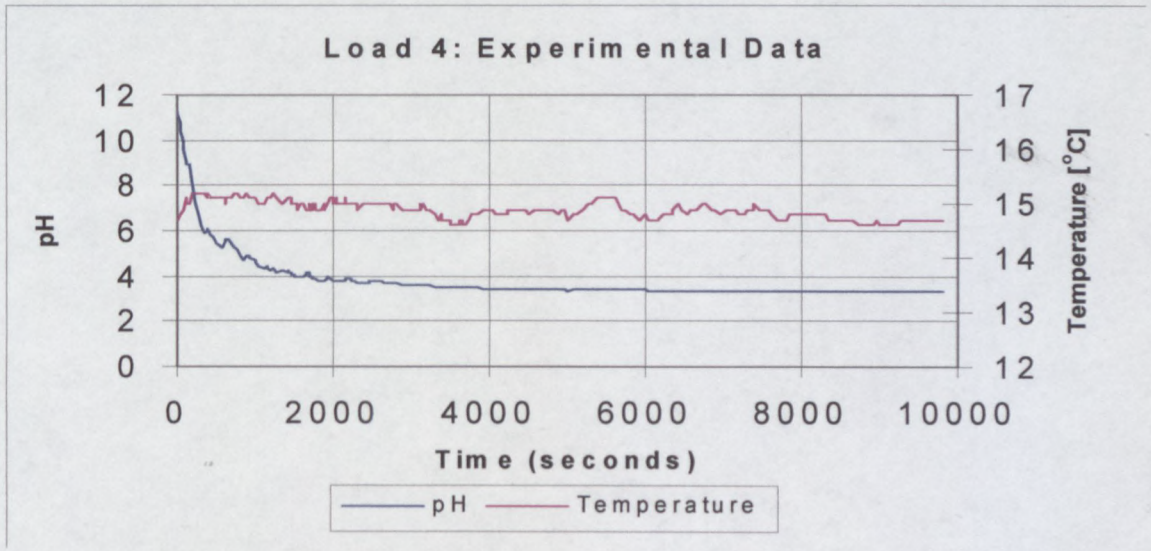
RunID:	Load2
Date:	01-Nov-00
Resin:	IRA 96
Volume:	20ml
Loading with:	Juice (batch3)
Flow:	up
Flow rate	0.1825ml/s
Total volume:	2135ml
Bed volume:	21
pH in	3.16



RunID:	Load3
Date:	02-Nov-00
Resin:	IRA 92
Volume:	20
Loading with:	Juice (batch3)
Flow:	up
Flow rate	0.1825ml/s
Total volume:	3840ml
Bed volume:	21ml
pH in	3.2



RunID: Load4
Date: 04-Nov-00
Resin: IRA 96
Volume: 20ml
Loading with: Juice (batch3)
Flow: down
Flow rate 0.1825ml/s
Total volume: 1925ml
Bed volume: 21
pH in 3.27

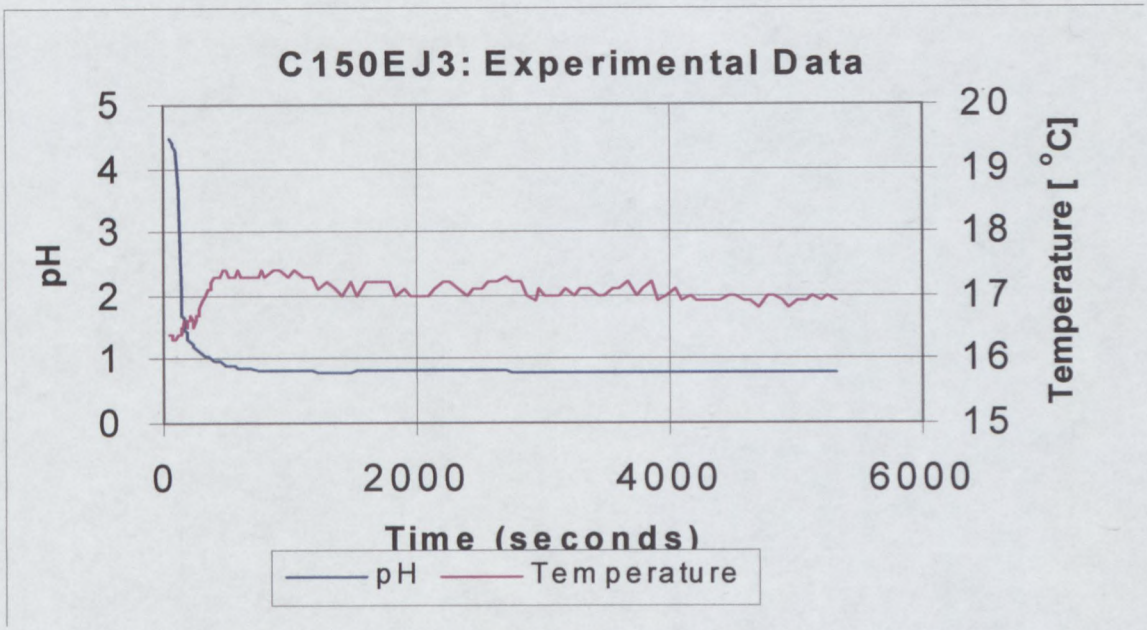


CATION ELUTIONS

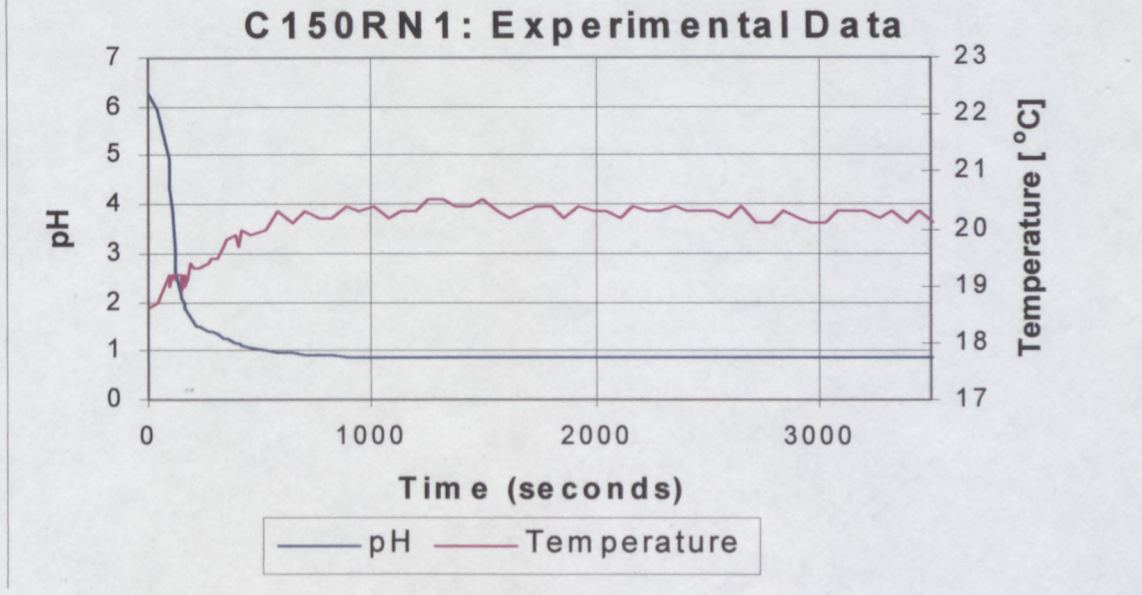
RunID: C150ej3
Date: 17-Apr-01
Resin: C150
Volume: 15 ml
Loaded with: Juice
Eluent: 3% H_2SO_4
Flow: down
Flowrate: 0.199167 ml/s
Total volume: 1095 ml
Bedvolume: 20 ml
pH in 0.79

ICP Results

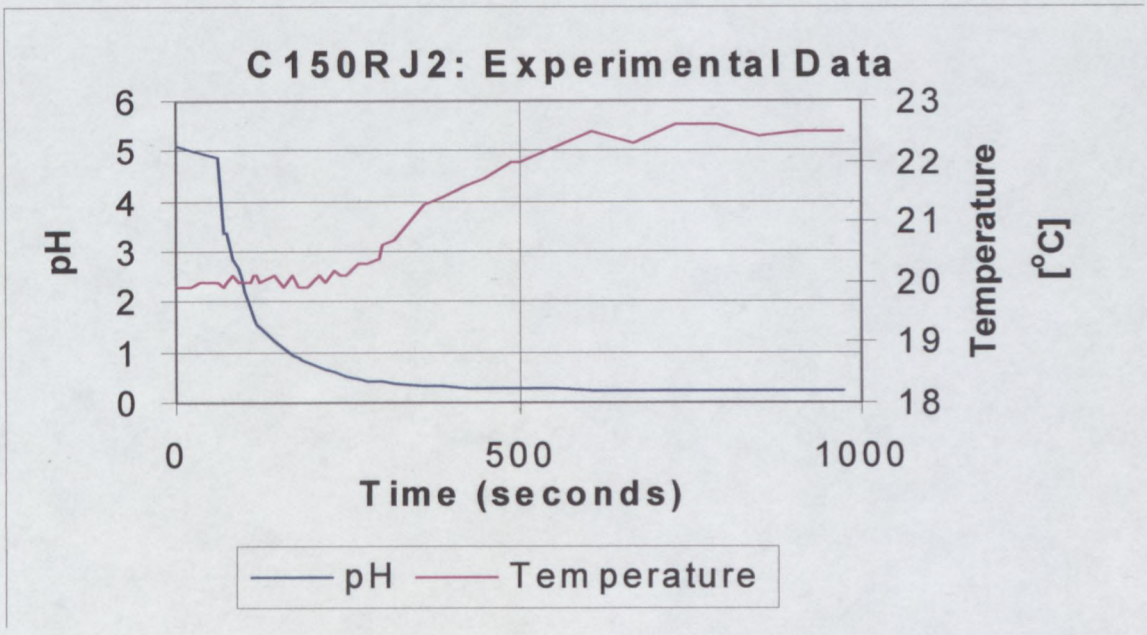
Time		Bedvolume	Na	Mg	K	Ca
hh:mm:ss	sec		mg/L	mg/L	mg/L	mg/L
0:00:33	33	0.33	0	0	1.16	0
0:01:09	69	0.69	0	0	0.77	0
0:01:49	109	1.09	18.18	77.34	754.71	19.75
00:02:26	146	1.45	106.2	154.69	5318.9	158.37
00:03:03	183	1.82	94.62	154.69	5498.2	162.78
00:03:40	220	2.19	69.2	154.81	4481	136.43
00:04:16	256	2.55	54.24	154.97	3766.4	117
00:05:02	302	3.01	41.62	155.05	3134.5	101.05
00:05:41	341	3.40	34.92	155.09	2692.1	91.94
00:06:22	382	3.80	30.3	107.93	2462.3	82.03
00:07:21	441	4.39	23.16	104.49	2029.8	72.37
00:08:26	506	5.04	17.17	95.93	1664.5	64.22
00:09:25	565	5.63	14.06	88.33	1418.9	58.5
00:10:18	618	6.15	11.73	82.73	1225.5	54.44
00:12:26	746	7.43	7.33	70.61	900.59	46.11
00:14:35	875	8.71	4.68	61.92	679	40.49
00:16:33	993	9.89	3.24	56.1	547.73	37.15
00:19:32	1172	11.67	1.89	49.28	414.82	33.04
00:24:58	1498	14.92	0.7	40.49	267.85	28.5
00:30:14	1814	18.06	0.2	34.21	182.87	25.25
00:39:59	2399	23.89	0	25.64	96.7	21.56
00:50:17	3017	30.04	0	19.94	53.85	19.35
01:02:10	3730	37.14	0	14.92	27.47	17.51
01:29:24	5364	53.42	0	7.84	6.23	14.69
01:30:00	5400	53.78	2.94	35.01	298.8	26



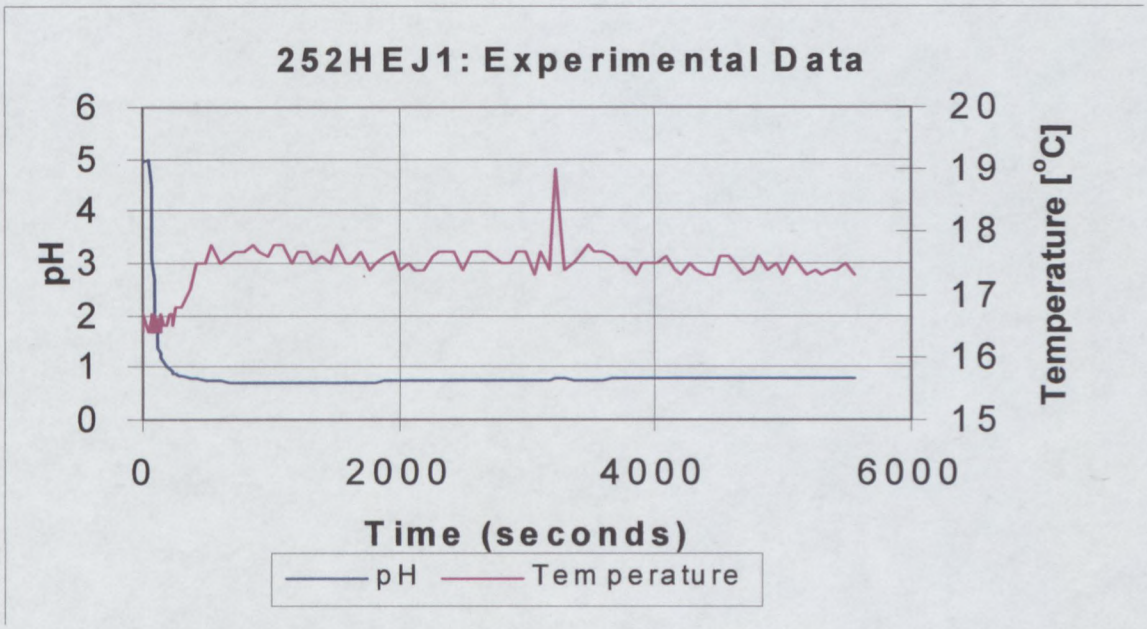
RunID: C150RN1
Date: 21-Feb-01
Resin: C150
Volume: 15ml
Loaded with: Na
Eluent: 3%H_2SO_4
Flow: down
Flowrate: 0.19ml/s
Total volume: 1810ml
Bedvolume: 20ml
pH in 0.79



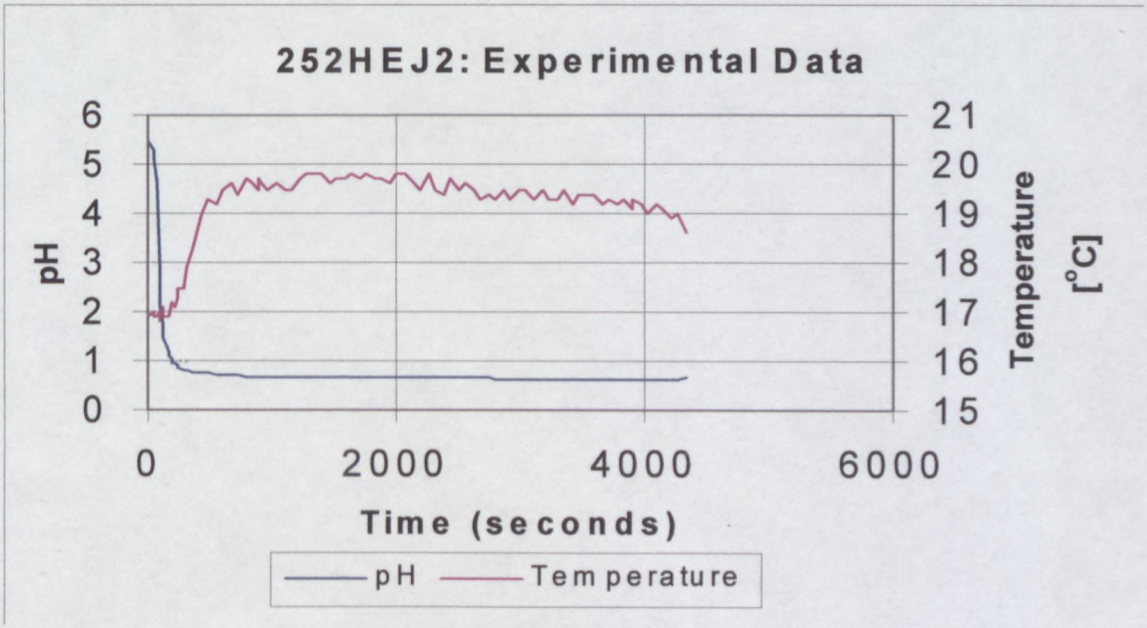
RunID: C150RJ2
Date: 14-Feb-01
Resin: C150
Volume: 15ml
Loaded with: Juice (batch 3)
Eluent: 3%H_2SO_4
Flow: down
Flowrate: 0.187ml/s
Total volume: 1030ml
Bedvolume: 20ml
pH in 0.79



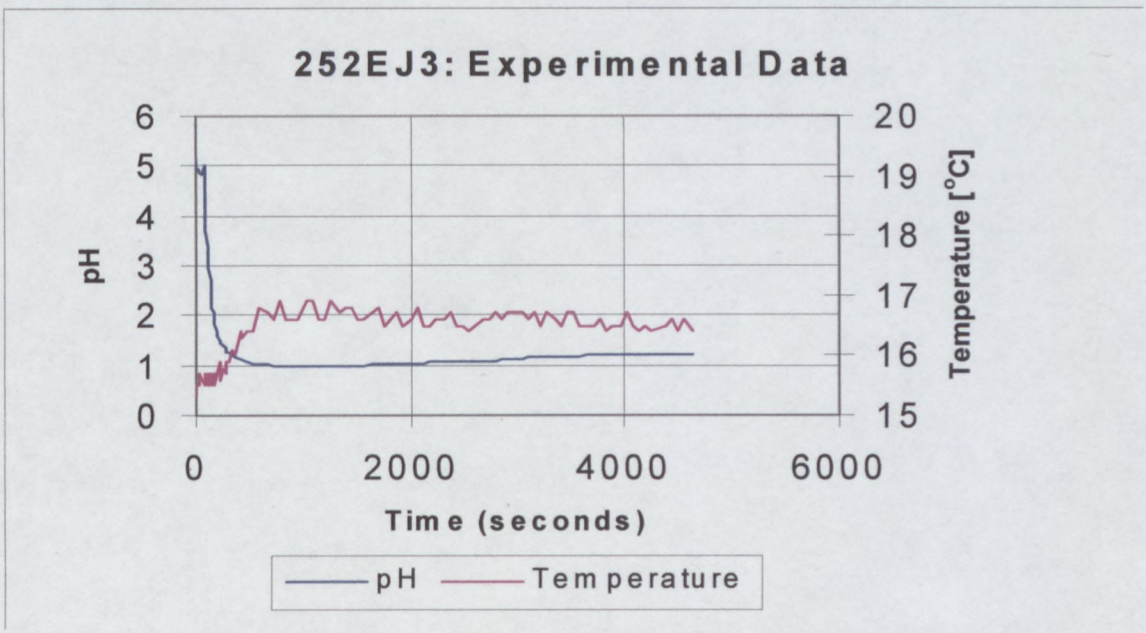
RunID: 252Hej1
Date: 15-Mar-01
Resin: 252H
Volume: 15ml
Eluent: 3%H_2SO_4
Flow: down
Flowrate: 0.218627ml/s
Total volume: 1090ml
Bedvolume: 20ml



RunID: 252Hej2
Date: 16-Mar-01
Resin: 252H
Volume: 15ml
Eluent: 5%H_2SO_4
Flow: down
Flowrate: 0.211ml/s
Total volume: 880ml
Bedvolume: 20ml

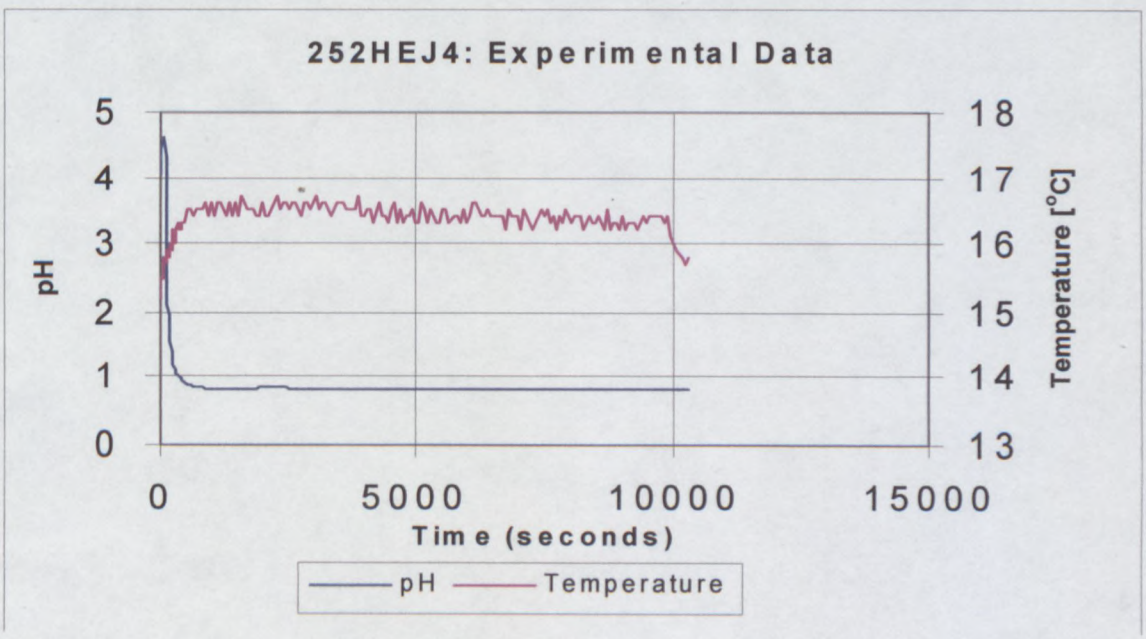


RunID: 252Hej3
Date: 18-Mar-01
Resin: 252H
Volume: 15ml
Eluent: 1%H_2SO_4
Flow: down
Flowrate: 0.204ml/s
Total volume: 955ml
Bedvolume: 20ml



RunID: 252Hej4
Date: 29-Mar-01
Resin: 252H
Volume: 15ml
Eluent: 3%H_2SO_4
Flow: down
Flowrate: 0.198148ml/s
Total volume: 1921.1ml
Bedvolume: 20ml

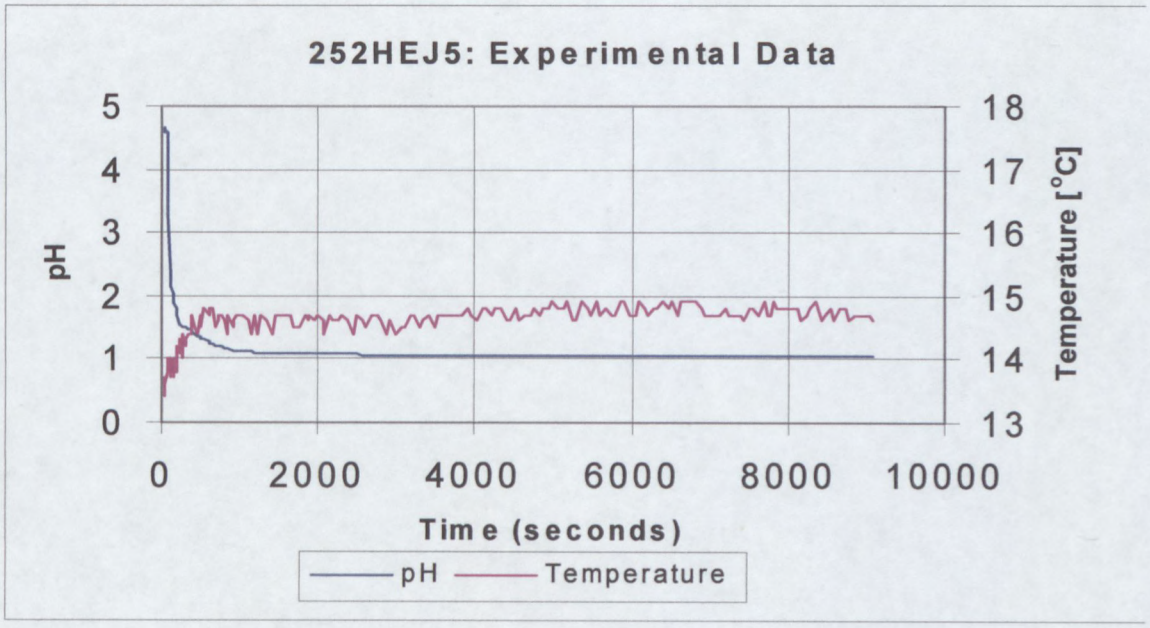
ICP Results							
Time		Bedvolume	Na	Mg	K	Ca	P
hh:mm:ss	sec		mg/L	mg/L	mg/L	mg/L	mg/L
0:01:40	100	0.991	0.113	0.072	2.662	0.392	0.52
0:02:48	168	1.664	31.994	122.828	1506.213	41.491	0.08
0:03:28	208	2.061	110.061	537.812	6271.942	174.7	0
0:04:05	245	2.427	107.743	570.395	6956.583	199.144	0
0:04:49	289	2.863	88.147	490.282	6152.369	180.608	0
0:05:34	334	3.309	61.446	369.904	4668.671	142.229	0
0:06:11	371	3.676	46.598	308.296	3866.544	120.766	0
0:06:47	407	4.032	40.334	278.778	3403.493	110.287	0
0:07:58	478	4.736	28.159	224.665	2623.529	88.856	0
0:09:17	557	5.518	20.237	184.76	2035.432	75.458	0
0:11:17	677	6.707	11.923	142.163	1413.936	60.857	0
12:13:48	828	8.203	6.626	112.674	969.487	51.518	0.06
0:06:19	1099	10.888	2.227	77.857	490.151	39.268	0
25:44:00	1544	15.297	0.504	51.136	190.819	30.207	0
37:27:00	2247	22.262	0.172	31.086	50.312	24.289	0
0:47:40	2860	28.335	0.103	21.344	15.682	21.478	0
1:03:00	3780	37.450	0.161	11.953	2.47	18.313	0
1:35:09	5709	56.561	0.125	3.505	0.248	13.272	0
2:50:00	10200	101.056	0.11	0.271	0.84	6.734	0
rest			1.49	21.13	138.76	19.22	



RunID: 252Hej5
Date: 03-Apr-01
Resin: 252H
Volume: 15ml
Eluent: 1% H_2SO_4
Flow: down
Flowrate: 0.2061ml/s
Total volume: ml
Bedvolume: 20ml

ICP Results

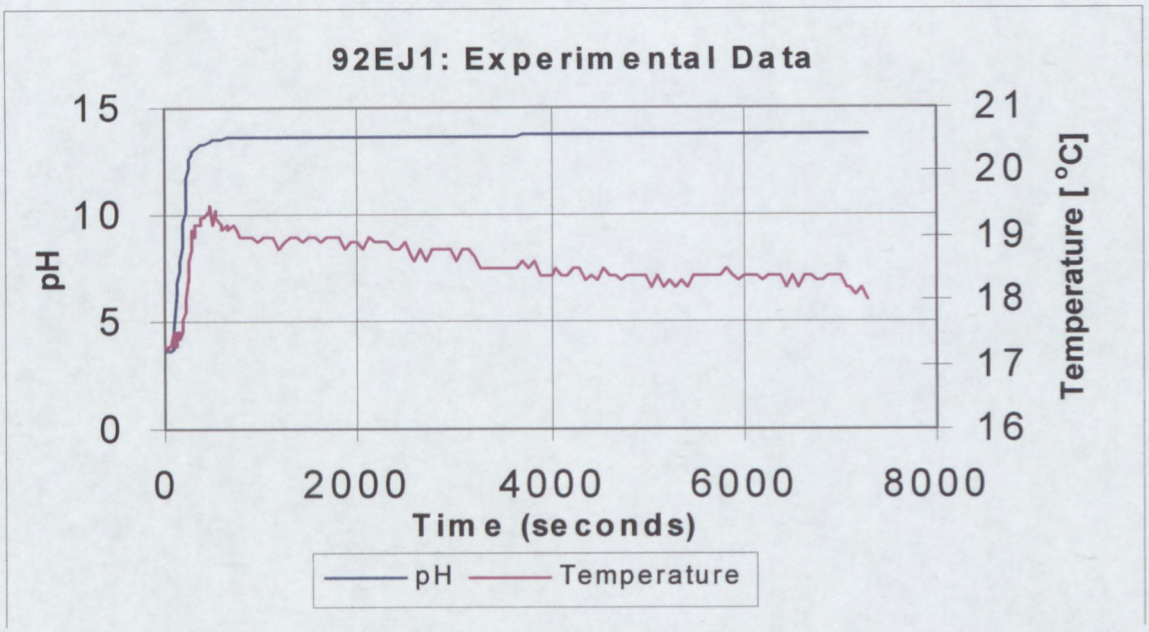
Time		Bedvolume	Na	Mg	K	Ca
hh:mm:ss	sec		mg/L	mg/L	mg/L	mg/L
0:00:44	44	0.453	0.29	0	2.71	0.05
0:01:34	94	0.968	0.12	0	7.24	0.03
0:02:19	139	1.432	24.52	50.79	1054.5	14.81
0:02:56	176	1.813	74.47	149.54	3495.8	54.66
0:03:36	216	2.225	81.82	154.92	4143.7	63.85
0:04:12	252	2.596	70.8	150.12	3899.2	57.65
0:04:48	288	2.967	59.73	137.73	3517.7	51.05
0:05:38	338	3.482	49.13	122.81	3059.9	44.17
0:06:22	382	3.936	41.69	110.58	2677.8	38.77
0:07:36	456	4.698	30.94	94.22	2160.4	31.82
0:08:14	494	5.090	27.59	87.87	1962.5	29.21
0:08:54	534	5.502	23.69	81.44	1773.5	26.81
0:10:17	617	6.357	18.15	71.07	1457.2	22.88
0:12:12	732	7.542	15.3	66.76	1290.7	21.07
0:14:50	890	9.170	8.32	51.2	887.78	15.88
0:19:06	1146	11.807	4.23	41.56	611.03	12.77
0:25:44	1544	15.908	1.6	32.5	383.58	10.18
0:34:40	2080	21.430	0.48	26.09	223.84	8.34
0:45:05	2705	27.870	0.12	21.41	126.73	7.14
0:55:36	3336	34.371	0	18.7	75.4	6.44
1:15:38	4538	46.755	0	15.2	27.63	5.78
1:54:33	6873	70.813	0	10.62	3.75	3.75
2:31:38	9098	93.737	0	7.3	0.8	4.78
02:32:00	9120	93.964				


252HEJ5: Experimental Data
pH
Temperature [°C]
5
4
3
2
1
0
18
17
16
15
14
13
0
2000
4000
6000
8000
10000
Time (seconds)
pH
Temperature

ANION ELUTIONS

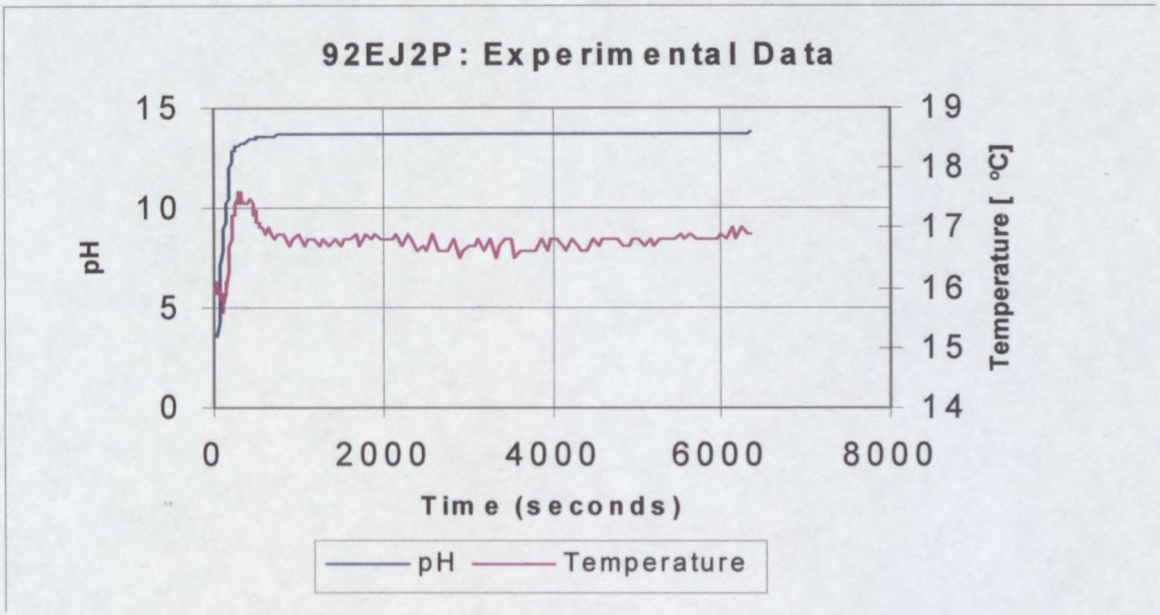
RunID: 92ej1
Date: 07-Apr-01
Resin: IRA 92
Volume: 20ml
Eluent: 3%NaOH
Flow: down
Flowrate: 0.202ml/s
Total volume: 1935ml
Bedvolume: 20ml

HPLC Results		Time	Bedvolumes	Malic Acid	Tartaric acid	Citric Acid
	00:00	Sec		mg/l	mg/l	mg/l
16	00:00:58	58	0.586	BDL	9.592	BDL
17	00:02:02	122	1.232	BDL	29.173	BDL
18	00:02:47	167	1.686	BDL	2116.59	BDL
19	00:03:36	216	2.181	2062.59	7253.31	167.662
20	00:04:26	266	2.686	929.23	10386.74	752.194
21	00:05:19	319	3.221	1302.96	9312.6	815.13
22	00:06:50	410	4.140	924.75	5854.78	642.15
23	00:08:20	500	5.049	599.55	3748.91	394.56
24	00:09:53	593	5.988	322.66	1964.265	164.52
25	00:11:39	699	7.059	210.35	1142.04	60.06
26	00:13:28	808	8.159	240.9	633.94	47.53
27	00:15:52	952	9.613	115.56	348.77	0
28	00:21:18	1278	12.905	78.77	100.71	0
29	00:26:08	1568	15.834	83.94	45.06	0
30	00:38:43	2323	23.458	19.343	28.858	BDL
31	00:49:30	2970	29.991	17.806	20.661	BDL
32	00:59:06	3546	35.808	13.537	17.761	BDL
34	01:15:22	4522	45.663	12.83	16.02	BDL
35	01:34:50	5690	57.458	8.74	11.85	BDL
36	02:00:00	7200	72.706	12.53	11.77	BDL
37	02:35:08	9308	93.993	7.92	BDL	BDL
end 137				35.74	143.63	18.744



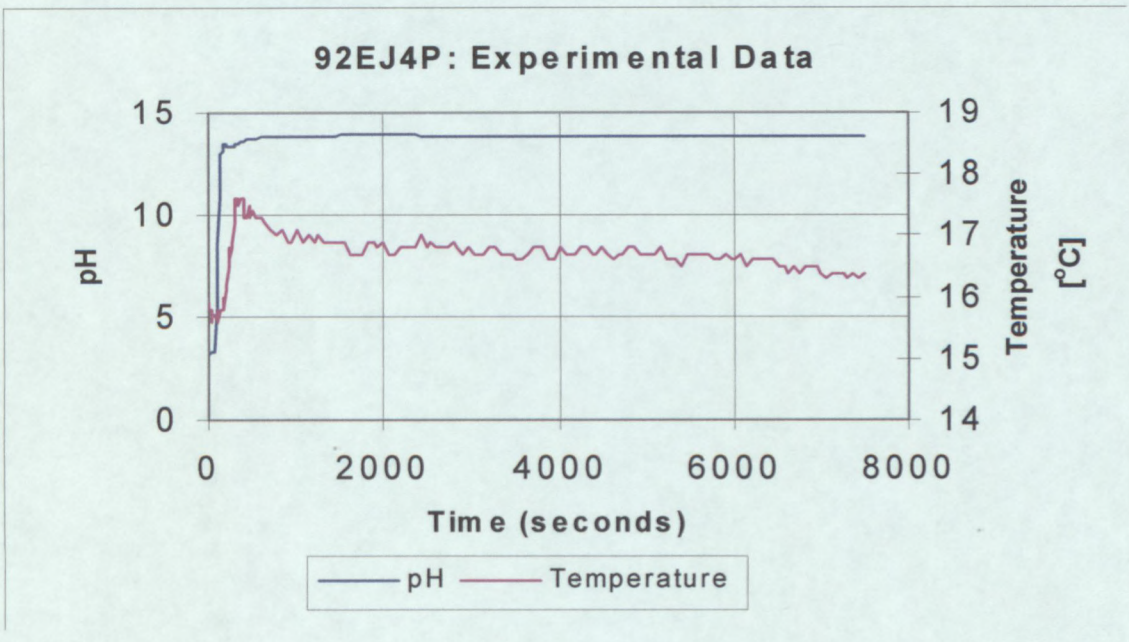
RunID: 92ej2p
Date: 19-Apr-01
Resin: IRA 92
Volume: 20ml
Eluent: 2%NaOH
Flow: down
Flowrate: 0.202ml/s
Total volume: 1885ml
Bedvolume: 20ml

HPLC results	Time	Time	Bedvolumes	Malic Acid	Tartaric acid	Citric Acid
Sample No	00:00:00	Sec		mg/l	mg/l	mg/l
60	00:00:56	56	0.567	BDL	BDL	BDL
61	00:01:38	98	0.992	6.79	9.847	BDL
62	00:02:33	153	1.548	BDL	313.30	BDL
63	00:03:32	212	2.145	819.61	3550.89	BDL
64	00:04:21	261	2.641	238.43	4569.13	BDL
65	00:05:17	317	3.208	599.13	5012.81	142.78
66	00:06:13	373	3.774	570.95	3848.12	190.77
67	00:07:16	436	4.412	583.99	3211.90	263.95
68	00:08:32	512	5.181	503.02	2706.94	237.02
69	00:09:32	572	5.788	437.17	2064.92	172.47
70	00:10:35	635	6.426	312.27	1708.38	121.03
71	00:12:35	755	7.640	279.95	802.51	52.41
72	00:14:37	877	8.874	191.88	374.36	27.261
73	00:16:35	995	10.068	110.70	297.30	29.156
74	00:18:34	1114	11.273	73.56	215.81	32.984
75	00:20:34	1234	12.487	56.15	145.70	24.956
76	00:25:38	1538	15.563	44.27	65.15	11.755
77	00:30:55	1855	18.771	34.87	35.66	7.447
78	00:40:34	2434	24.630	19.72	13.55	BDL
79	00:50:36	3036	30.721	16.31	7.79	BDL
80	01:00:33	3633	36.763	14.97	6.15	BDL
81	01:15:50	4550	46.042	12.35	4.30	BDL
82	01:30:59	5459	55.240	9.17	2.67	BDL
83	02:00:53	7253	73.393	6.36	2.17	BDL
84	02:30:58	9058	91.658	5.43	1.48	BDL
end rest 136	02:31:03			36.66	95.27	12.88



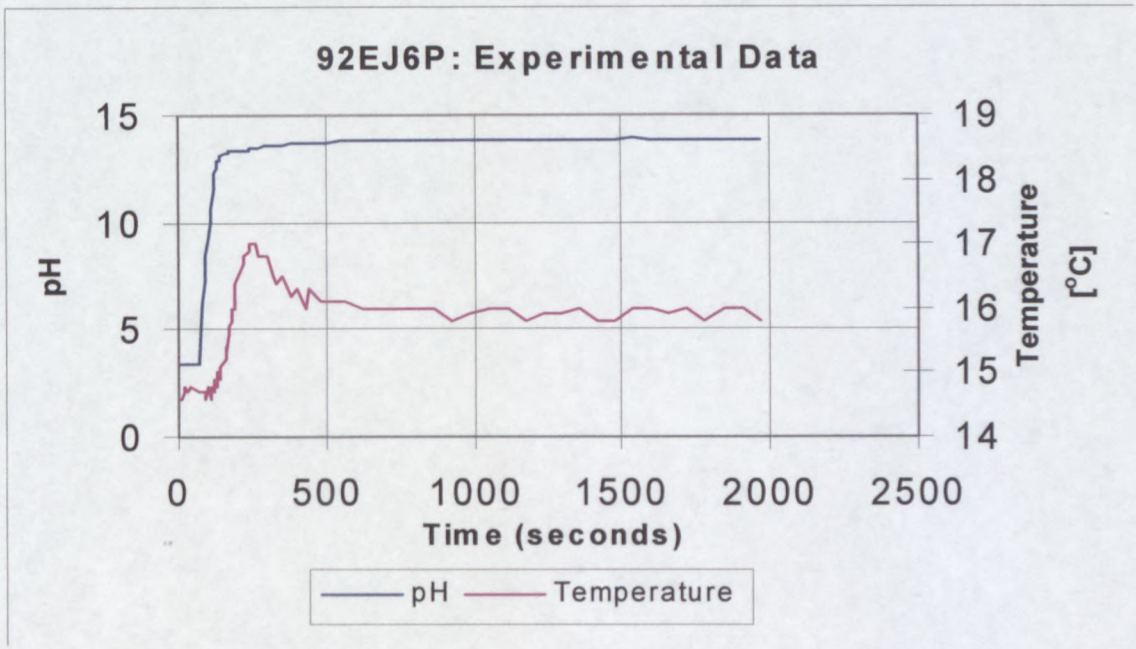
RunID: 92ej4p
Date: 19-Apr-01
Resin: IRA 92
Volume: 20ml
Eluent: 4%NaOH
Flow: down
Flowrate: 0.207ml/s
Total volume: 1895ml
Bedvolume: 20ml

HPLC Results		Time	Bedvolumes	Malic Acid	Tartaric acid	Citric Acid
Sample No.		Sec		mg/l	mg/l	mg/l
85	00:01:04	64	0.661	BDL	BDL	BDL
86	00:01:55	115	1.188	BDL	9.06	BDL
87	00:02:49	169	1.746	257.75	653.11	BDL
88	00:03:43	223	2.304	774.80	6322.69	BDL
89	00:04:48	288	2.976	1289.05	6244.45	175.79
90	00:05:47	347	3.586	614.52	4154.48	212.11
91	00:07:18	438	4.526	646.37	3233.01	252.22
92	00:08:12	492	5.084	528.05	2412.35	174.58
93	00:09:05	545	5.632	476.75	1820.83	112.19
94	00:10:09	609	6.293	412.31	1287.10	40.173
95	00:12:20	740	7.647	236.09	545.05	50.362
96	00:14:39	879	9.083	139.24	282.94	42.748
97	00:16:43	1003	10.364	86.16	169.40	18.644
98	00:18:39	1119	11.563	96.86	113.03	8.926
99	00:20:38	1238	12.793	71.09	81.54	10.836
100	00:25:06	1506	15.562	63.76	46.30	BDL
101	00:30:36	1836	18.972	34.46	24.69	BDL
102	00:40:39	2439	25.203	26.41	15.60	BDL
103	00:50:32	3032	31.331	27.98	13.41	BDL
104	01:01:16	3676	37.985	21.64	10.85	BDL
105	01:15:26	4526	46.769	21.56	10.80	BDL
106	01:30:58	5458	56.399	16.21	9.74	BDL
107	02:01:24	7284	75.268	8.79	BDL	BDL
108	02:29:57	8997	92.969	10.33	BDL	BDL
end rest 135	02:31			38.65	96.03	16.95



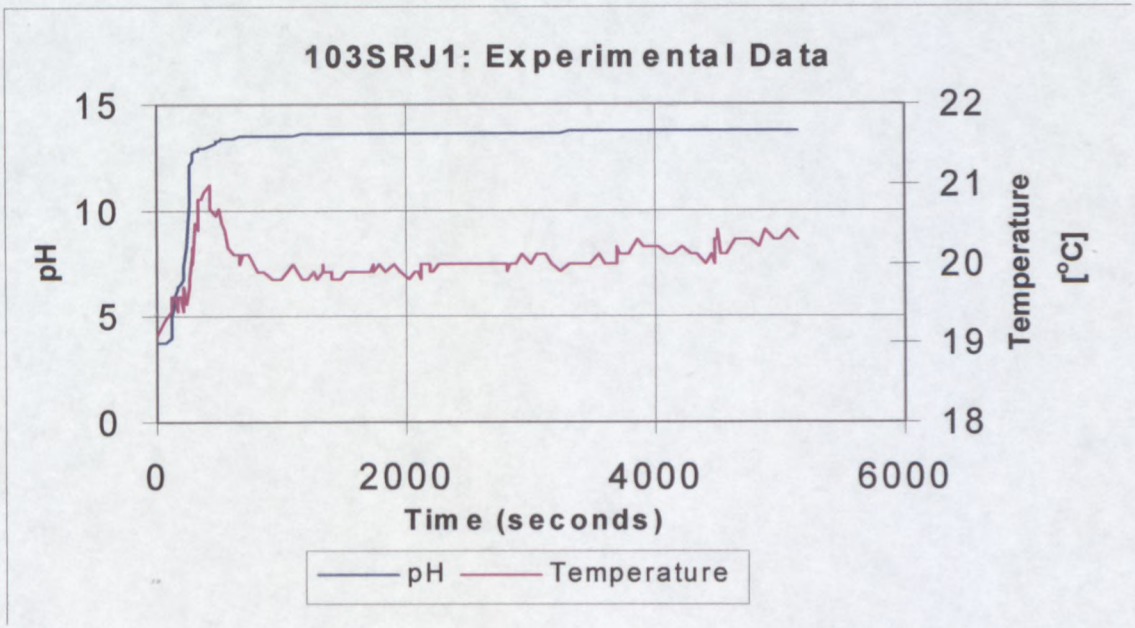
RunID: 92ej6p
Date: 20-Apr-01
Resin: IRA 92
Volume: 20ml
Eluent: 6%NaOH
Flow: down
Flowrate: 0.211ml/s
Total volume: 1890ml
Bedvolume: 20ml
pH in 13.67

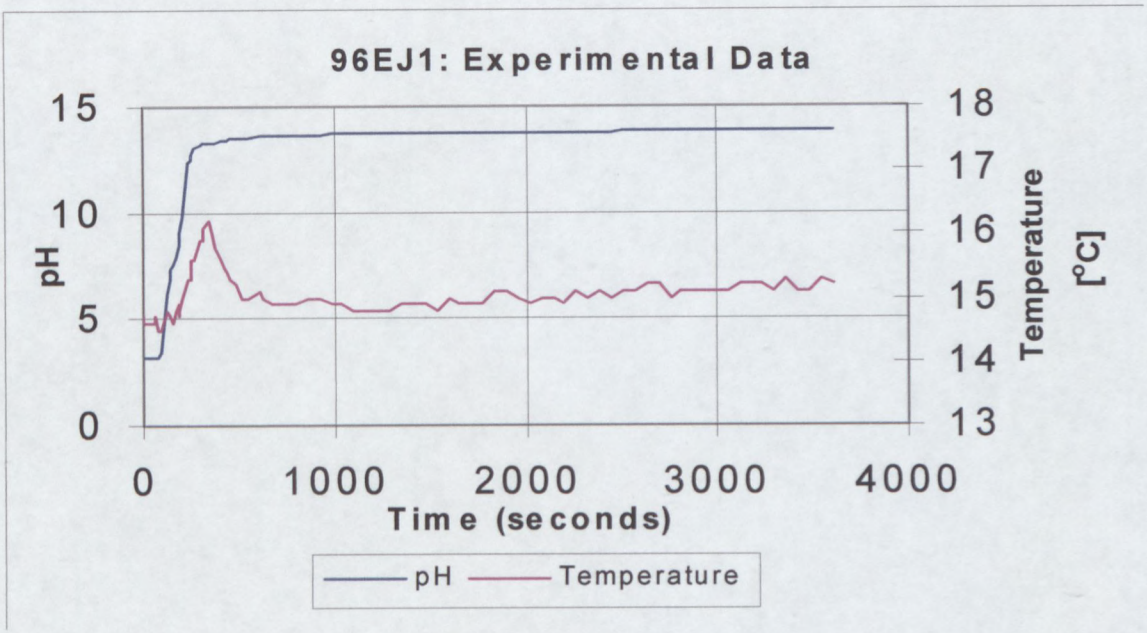
HPLC Results		Time	Bedvolumes	Malic Acid	Tartaric acid	Citric Acid
Sample No.		Sec		mg/l	mg/l	mg/l
109	00:00:49	49	0.516	BDL	BDL	BDL
110	00:01:38	98	1.032	BDL	BDL	BDL
111	00:02:26	146	1.537	48.32	925.45	BDL
112	00:03:13	193	2.032	784.78	7575.28	BDL
113	00:04:16	256	2.695	1516.85	7068.23	201.83
114	00:05:11	311	3.274	1186.47	4879.97	225.53
115	00:06:08	368	3.874	854.42	3171.93	189.62
116	00:07:17	437	4.600	694.78	1962.17	113.514
117	00:08:38	518	5.453	381.20	847.62	64.915
118	00:09:41	581	6.116	296.61	485.11	62.048
119	00:10:35	635	6.684	237.38	352.33	51.9
120	00:12:53	773	8.137	221.93	224.32	19.35
121	00:14:35	875	9.211	162.88	156.53	18.108
122	00:16:47	1007	10.600	118.30	105.53	10.35
123	00:18:38	1118	11.768	117.64	72.25	10.223
124	00:20:38	1238	13.032	115.73	60.01	BDL
125	00:26:38	1598	16.821	117.01	26.13	BDL
126	00:30:35	1835	19.316	97.54	16.45	BDL
127	00:40:40	2440	25.684	87.33	7.41	BDL
128	00:50:38	3038	31.979	NO SAMPLE AVAILABLE		
129	01:00:35	3635	38.263	85.81	2.29	BDL
130	01:15:39	4539	47.779	73.85	1.16	BDL
131	01:30:33	5433	57.189	75.24	0.73	BDL
132	02:04:18	7458	78.505	NO SAMPLE AVAILABLE		
133	02:30:44	9044	95.200	69.19	0.30	BDL
end rest 134	02:31:05			76.68	66.32	10.99



RunID: 103Srj1
Date: 7-Feb-01
Resin: A103S
Volume: 20ml
Eluent: 3%NaOH
Flow: down
Flowrate: 0.182ml/s
Total volume: 1980ml
Bedvolume: 20ml
pH in 13.7

HPLC Results		Time	Bedvolumes	Malic Acid	Tartaric acid	Citric Acid
Sample No	16:35:12	Sec		mg/ℓ	mg/ℓ	mg/ℓ
1	16:35:37	25	0.227	1.1	1439.614	9.247
2	16:40:05	293	2.661	12706	21018	815.16
3	16:41:23	371	3.370	2284.76	19479	1554.86
4	16:43:17	485	4.405	1479.15	10018.28	869.17
5	16:45:20	608	5.523	627.15	4097.4	306.45
6	16:48	768	6.976	298.93	1661.47	102.61
7	16:51:47	995	9.038	142.124	447.959	37.565
8	16:57:39	1347	12.235	69.193	277.065	30.305
9	17:05	1788	16.241	47.493	176.951	20.613
10	17:11:32	2180	19.802	44.928	108.865	9.344
12	17:36:21	3669	33.327	27.329	51.794	7.617
13	17:50:03	4491	40.793	20.869	31.141	7.421
14	18:21:28	6376	57.915	19.125	13.784	7.107
15	18:48:14	7982	72.503	9.486	11.364	BDL




96EJ1: Experimental Data
15
10
5
0
pH
18
17
16
15
14
13
Temperature [°C]
0
1000
2000
3000
4000
Time (seconds)
pH
Temperature

RunID: 96ej1
Date: 15-Apr-01
Resin: IRA 96
Volume: 20ml
Eluent: 3%NaOH
Flow: down
Flowrate: 0.205ml/s
Total volume: 1715ml
Bedvolume: 20ml
pH in 13.8

HPLC Results		Time	Bedvolumes	Malic Acid	Tartaric acid	Citric Acid
Sample No.		Sec		mg/l	mg/l	mg/l
38	00:00:54	54	0.553	BDL	BDL	BDL
39	00:01:53	113	1.156	BDL	BDL	BDL
40	00:02:46	166	1.698	BDL	716.11	BDL
41	00:03:35	215	2.200	72.86	3230.94	BDL
42	00:04:34	274	2.803	874.61	3327.29	BDL
43	00:05:26	326	3.335	2471.63	3372.10	BDL
44	00:06:21	381	3.898	1065.47	1632.56	BDL
45	00:07:16	436	4.461	886.38	379.20	BDL
46	00:08:13	493	5.044	500.86	449.72	BDL
47	00:09:09	549	5.617	318.01	284.86	BDL
48	00:11:03	663	6.783	179.21	138.571	18.991
49	00:13:33	813	8.318	110.462	67.80	18.788
50	00:16:24	984	10.068	55.88	28.60	BDL
51	00:21:33	1293	13.229	32.25	6.53	BDL
52	00:26:50	1610	16.473	21.21	3.09	BDL
53	00:39:20	2360	24.146	12.38	1.17	BDL
54	00:49:27	2967	30.357	11.20	1.40	BDL
55	00:59:47	3587	36.700	BDL	BDL	BDL
56	01:15:52	4552	46.574	BDL	BDL	BDL
57	01:31:18	5478	56.048	BDL	BDL	BDL
58	02:00:35	7235	74.025	1.16	9.96	BDL
59	02:16:46	8206	83.960	1.09	9.67	BDL
138	end			23.26	43.29	BDL

APPENDIX C:

Resin Data Sheets

AMBERLITE 252 H

Industrial Grade Strong Acid Cation Exchange Resin

AMBERLITE 252 H is a macroporous cation exchange resin based on sulphonated crosslinked polystyrene. It has a moderate degree of crosslinking resulting in good regeneration efficiency. It is very resistant to osmotic shock and to mechanical attrition. AMBERLITE 252 H is suited for use in a variety of demanding applications, such as condensate polishing or treatment of oxidising solutions. AMBERLITE 252 H has a reduced amount of fines, allowing it to be used at high flow rate or in conventional reverse flow regenerated units.

PROPERTIES

Matrix	Styrene divinylbenzene copolymer
Functional groups	$-SO_3^-$
Physical form	Light grey beads
Ionic form as shipped	H^+
Total exchange capacity	≥ 1.7 eq/L (H^+ form)
Moisture holding capacity	47 to 54 % (Na^+ form)
Specific gravity	1.24 to 1.28 (Na^+ form)
Bulk density	720 to 790 g/L (H^+ form)
Particle size	
Effective size	≥ 450 µm
Mean diameter	600 - 800 µm
Uniformity coefficient	≤ 1.6
Maximum reversible swelling	$Na^+ \rightarrow H^+$: 8 %

ISO 9002

Test methods available upon request

SUGGESTED OPERATING CONDITIONS

Minimum bed depth	700 mm	
Service flow rate	5 to 170 BV*/h (5 to 120 m/h)	
Regenerants	HCl	H_2SO_4
Flow rate (BV/h)	4 to 6	4 to 12
Concentration (%)	4 to 10	1 to 5
Level (g/L)	45 to 150	50 to 200
Minimum contact time	30 minutes	
Slow rinse	2 BV at regeneration flow rate	
Fast rinse	2 to 4 BV at service flow rate	

** 1 BV (Bed Volume) = 1 m^3 solution per m^3 resin*

PDS 0523 A - July 95

HYDRAULIC CHARACTERISTICS

AMBERLITE 252 H gives a pressure drop of about 12 kPa/m bed depth per 10 m/h at 15°C.
A backwash flow rate of 19 m/h gives a bed expansion of about 65 % at 15°C in water.
Pressure drop data are valid at the start of the service run with a clear water and a correctly classified bed.

LIMITS OF USE

AMBERLITE 252 H is suitable for industrial uses. For all other specific applications such as pharmaceutical, food processing or potable water applications, it is recommended that all potential users seek advice from Rohm and Haas in order to determine the best resin choice and optimum operating conditions.

CAUTION

Ion exchange resins and polymeric adsorbents, as produced, contain by-products resulting from the manufacturing process. The user must determine the extent to which organic by-products must be removed for any particular use and establish techniques to assure that the appropriate level of purity is achieved for that use. The user must ensure compliance with all prudent safety standards and regulatory requirements governing the application. Except where specifically otherwise stated, Rohm and Haas Company does not recommend its ion exchange resins or polymeric adsorbents, as supplied, as being suitable or appropriately pure for any particular use. Consult your Rohm and Haas technical representative for further information. Acidic and basic regenerant solutions are corrosive and should be handled in a manner that will prevent eye and skin contact. Nitric acid and other strong oxidising agents can cause explosive type reactions when mixed with Ion Exchange resins. Proper design of process equipment to prevent rapid buildup of pressure is necessary if use of an oxidising agent such as nitric acid is contemplated. Before using strong oxidising agents in contact with Ion Exchange Resins, consult sources knowledgeable in the handling of these materials.

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PUROLITE

C-150

Macroporous Strong Acid Cation-Exchange Resin
(FOR THE TREATMENT OF WATER)

Technical Data

PRODUCT DESCRIPTION

Purolite C-150 is a macroporous poly(styrene sulphonate) cation-exchange resin with excellent resistance to both osmotic and thermal shock. Its special sponge-like structure permits higher rates of diffusion of most cations including those of heavy metals and amines and also positively charged organics of higher molecular weight, and facilitates their removal on regeneration. These properties of physical robustness, good regenerability, and fast kinetics of exchange make it ideal for a range of applications. In such cases, it is the general rule that a specially graded particle size is required. Please refer to the **Purolite Summary Brochure** for further details of various grades available.

Purolite C-150 of specially tailored particle sizes find applications in mixed beds, for make-up and condensate polishing, for hydrometallurgy, for sugar treatment, and demineralisation of numerous organic solutions to name but a few. With the macroporous **Purolite C-150**, continuous softening of sugar solutions by the Asahi process is feasible. Here, no gel resin is normally recommended because of the extra osmotic and mechanical stresses imposed by the external regeneration of the resin and its subsequent return to service.

CHEMICAL STABILITY

Purolite C-150 is insoluble in acids, alkalies, and all common solvents. However, exposure to significant amounts of free chlorine or other strong oxidising agents over long periods of time will eventually break down the crosslinking. This will tend to increase the moisture content of the resin, decreasing its mechanical strength, and should be avoided.

Typical Chemical and Physical Characteristics

Polymer Structure	**Macroporous polystyrene crosslinked with divinylbenzene**
Appearance	**Spherical beads**
Functional Group	**Sulphonic acid**
Ionic Form - as shipped	**Sodium - Na^+**
Total Capacity (Na^+ Form) min	**1.8 eq/l min**
Moisture Retention (Na^+ Form)	**48-53%**
Bead Size Range (microns)	**+1200 <5 %, -300 <1%**
Screen Size Range (U.S. Standard Screen)	**16-50 mesh**
Reversible Swelling ($Na^+ \rightarrow H^+$)	**5%**
Specific Gravity (Na^+ Form)	**1.25**
Shipping Weight	**785-825 kg/m^3 (49-51.5 lb/ft^3)**
Temperature Limit (H^+ Form)	**120°C (250°F)**
(Na^+ Form)	**140°C (285°F)**
pH Limits	**None**

PRODUCT DATA SHEET

AMBERLITE IRA92

Industrial Grade Weak Base Anion Exchanger

AMBERLITE IRA92 is a high capacity polystyrenic macroporous, weak base anion exchanger. This resin is highly efficient for the uptake of strong acids (e.g. HCl, H_2SO_4) when following a strong acid cation exchanger in the H form. Its structure ensures excellent adsorption and desorption of organic matter. It has an outstanding mechanical and osmotic stability, making it suitable for the treatment of solution with high ionic concentrations.

PROPERTIES

Matrix	Macroporous polystyrene
Functional groups	$-NR_2$: 85 %
Physical form	Ivory-coloured beads
Ionic form as shipped	Free Base (FB)
Total exchange capacity	≥ 1.60 eq/L (FB form)
Moisture holding capacity	40 to 48 % (FB form)
Bulk density	620 to 690 g/L (FB form)
Specific gravity	1.035 to 1.065 (FB form)
Particle size	
Effective size	≥ 450 µm
Mean diameter	600 to 800 µm
Uniformity coefficient	≤ 1.8
Maximum reversible swelling	FB → Cl^- : 25 %
Chemical resistance	Insoluble in dilute solutions of acids or bases and common solvents

ISO 9002

SUGGESTED OPERATING CONDITIONS • *1 BV (Bed Volume)= 1 m^3 solution per m^3 resin*

Operating temperature limit	90°C (FB form)		
Service flow rate	5 to 30 BV*/h		
Regenerants	NaOH	NH_3	Na_2CO_3
Level (g/L)	40 to 80	40 to 80	60 to 130
Concentration (%)	2 to 6	2 to 3	5 to 8
Flow rate (BV/h)	2 to 8	2 to 8	2 to 8
Minimum contact time	30 minutes		
Slow rinse	2 BV at regeneration flow rate		
Fast rinse	4 to 8 BV at service flow rate		

PDS 0516 A - Sep. 95

APPLICATIONS

The high total capacity of AMBERLITE IRA92 makes it particularly suitable for the removal of strong anions from solutions with relatively high dissolved solids ; its regeneration efficiency is close to the theoretical output. A high operating capacity is obtained from AMBERLITE IRA92 under conditions where a high TDS water is treated at a moderate specific flow rate. The combined adsorption efficiency and physical stability of AMBERLITE IRA92 make it the product of choice for demineralisation of sugar juices.
On account of its outstanding characteristics AMBERLITE IRA92 is used in the following special applications :

- De-acidification of formol,
- Purification of alcaloids,
- Demineralisation of gelatine, lactose, glucose,
- Recovery of chromates from cooling circuits,
- Recycling of rinse water in electroplating workshop.

FOOD PROCESSING

Rohm and Haas manufactures special resins for food processing and drinking water applications. As governmental regulations vary from country to country, it is recommended that potential users contact their Duolite representative to assess the best choice of resin and optimum operating conditions.

Rohm and Haas/Ion Exchange Resins - 75579 Paris Cedex 12 - Tel. (33-1) 40 02 50 00 - Fax : 43 45 28 19

PRODUCT DATA SHEET

AMBERLITE IRA96

Industrial Grade Weak Base Anion Exchanger

AMBERLITE IRA96 is a macroreticular weak base anion exchange resin. Its very stable structure and limited reversible swelling make it very resistant to osmotic shock. The high degree of porosity of this resin provides efficient adsorption of large organic molecules and their desorption during regeneration, thus allowing excellent protection against organic fouling. AMBERLITE IRA96 is intended primarily for the removal of strong acids from water following a strongly acidic cation exchange resin, and it provides excellent protection against organic fouling for the strong base anion exchange resin placed downstream in a deionization plant.

PROPERTIES

Matrix	Styrene divinylbenzene copolymer
Functional groups	Tertiary amine
Physical form	Opaque spherical beads
Ionic form as shipped	Free base (FB)
Total exchange capacity	≥ 1.25 eq/L (FB form)
Moisture holding capacity	57 to 63 % (FB form)
Specific gravity	1.040 to 1.060 (FB form)
Bulk density	610 to 680 g/L (FB form)
Particle size	
Effective size	≥ 430 µm
Mean diameter	550 to 750 µm
Uniformity coefficient	≤ 1.8
Maximum reversible swelling	FB → Cl^- : 15 %

ISO 9002

Test methods available upon request

SUGGESTED OPERATING CONDITIONS

Maximum operating temperature	100°C		
Minimum bed depth	700 mm		
Service flow rate	5 to 40 BV*/h		
Regenerant	NaOH	NH_4OH	Na_2CO_3
Flow rate (BV/h)	2 to 8	2 to 8	2 to 8
Concentration (%)	2 to 4	2 to 4	4 to 8
Level	120 % of ionic load		
Minimum contact time	30 minutes		
Slow rinse	2 BV at regeneration flow rate		
Fast rinse	4 to 8 BV at service flow rate		

* *1 BV (Bed Volume) = 1 m^3 solution per m^3 resin*

PIS 0211 A - Oct. 95

PERFORMANCE

The Engineering data sheet EDS 0255 A provides information to calculate the operating capacity of AMBERLITE IRA96 used in water treatment.

LIMITS OF USE

AMBERLITE IRA96 is suitable for industrial uses. For all other specific applications such as pharmaceutical, food processing or potable water applications, it is recommended that all potential users seek advice from Rohm and Haas in order to determine the best resin choice and optimum operating conditions.

HYDRAULIC CHARACTERISTICS

Figure 1 shows the bed expansion of AMBERLITE IRA96 as a function of backwash flow rate and water temperature.

Figure 2 shows the pressure drop data for AMBERLITE IRA96 as a function of service flow rate and water temperature. Pressure drop data are valid at the start of the service run with a clear water and a correctly classified bed.

These data are valid for water treatment and have to be corrected according to the solution to be treated.

Figure 1

BED EXPANSION

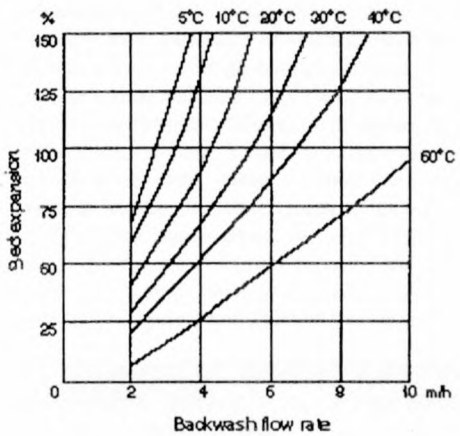
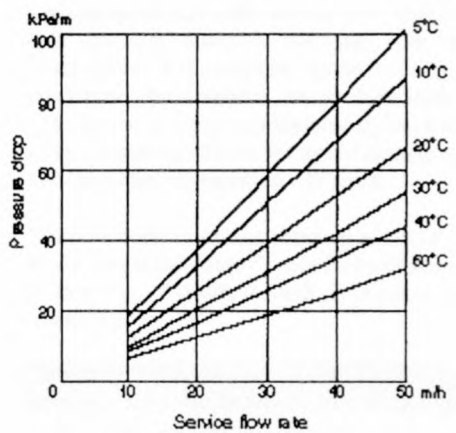


Figure 2

PRESSURE DROP



CAUTION

Ion exchange resins and polymeric adsorbents, as produced, contain by-products resulting from the manufacturing process. The user must determine the extent to which organic by-products must be removed for any particular use and establish techniques to assure that the appropriate level of purity is achieved for that use. The user must ensure compliance with all prudent safety standards and regulatory requirements governing the application. Except where specifically otherwise stated, Rohm and Haas Company does not recommend its ion exchange resins or polymeric adsorbents, as supplied, as being suitable or appropriately pure for any particular use. Consult your Rohm and Haas technical representative for further information. Acidic and basic regenerant solutions are corrosive and should be handled in a manner that will prevent eye and skin contact. Nitric acid and other strong oxidising agents can cause explosive type reactions when mixed with Ion Exchange resins. Proper design of process equipment to prevent rapid buildup of pressure is necessary if use of an oxidising agent such as nitric acid is contemplated. Before using strong oxidising agents in contact with Ion Exchange Resins, consult sources knowledgeable in the handling of these materials.

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PUROLITE®
ION EXCHANGE RESINS

A-103S

Macroporous Weak Base Anion Exchange Resin

(For the demineralization of sugar solutions)

Technical Data

PRODUCT DESCRIPTION

Purolite A-103S is a macroporous poly (vinylbenzyl) tertiary amine exchanger of moderate porosity, specially developed for use in the demineralization of juices from the beet, cane and liquid sugar industries. Its (relatively high) basicity permits adsorption of organic acids of pKa values up to about 5, and its macroporous structure results in excellent resistance to both osmotic shock and organic fouling. As a result, many of the high molecular weight color bodies present are also removed, (in beet sugar juices, the reduction in color may be 80% or more), and these color bodies can readily be eluted during the regeneration. This can be carried out with low amounts of caustic soda, ammonia, or soda ash to give high operating capacities. The resin, with its macroporous styrene-divinylbenzene matrix, not only possesses good rinse characteristics, but its high total exchange capacity ensures high ash-removal figures (often >75% of total), with significant savings in running cost thanks to its excellent regeneration efficiency.

Where both the ionic concentration and color are particularly high in the influent juice, the more porous version of this resin, **Purolite A-100S**, is recommended as an alternative.

Typical Physical & Chemical Characteristics	
Polymer Matrix Structure	Macroporous Styrene-divinylbenzene
Physical Form and Appearance	Opaque near-white spherical beads
Whole Bead Count	95% min.
Functional Groups	Tertiary amino
Ionic Form, as shipped	Free base
Shipping Weight (approx.)	650 g/l (41 lb/ft³)
Screen Size Range: - U.S. Standard Screen	16 - 40 mesh, wet
Particle Size Range	+1.2 mm <2%, -0.42 mm <2%
Moisture Retention, FB form, Cl⁻ form,	40 - 45% 48 - 55%
Reversible Swelling FB → Cl⁻	25% max.
Specific Gravity, moist FB Form moist Cl⁻ Form	1.04 1.06
Total Exchange Capacity, Cl⁻ form, wet, volumetric dry, weight	 1.6 meq/ml min. 4.1 meq/g min.
Strong Base %	12 - 20
Operating Temperature, Cl⁻ Form	100°C (212°F) max.
pH Range, Stability	0 - 14
pH Range, Operating	0 - 8

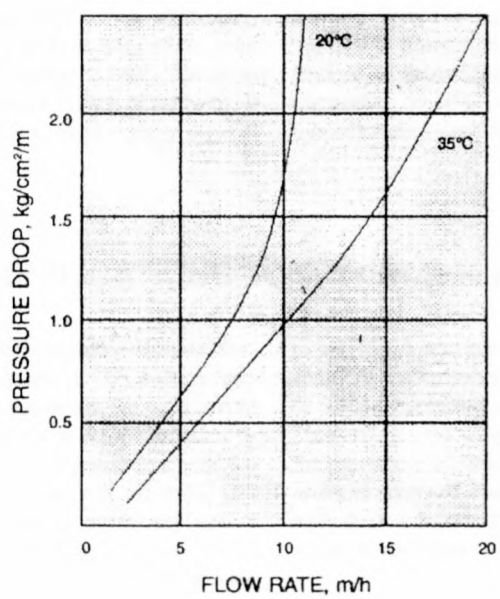
HYDRAULIC CHARACTERISTICS

The pressure drop (headloss) across a properly classified bed of ion-exchange resin depends on the particle size distribution, bed depth, and void volume of the exchanger, and on the flowrate and viscosity (and hence on the temperature) of the influent solution. Anything affecting any of these parameters, for example the presence of particulate matter filtered out by the bed, abnormal compaction of the resin bed, or the incomplete classification of the resin spheres will have an adverse effect, and result in an increased headloss.

Pressure drop figures obtained on thin sugar juice, at 12°Brix and temperatures of 20°C, (68°F), and 35°C, (95°F), correspond to those for 5°C and 20°C respectively in water itself, and are given in the graph below for **Purolite A-103S**.

During upflow backwash, the resin bed should be expanded in volume by 50%, in order to free it from any particulate matter in the influent solution, to clear the bed of bubbles and voids, and to reclassify the resin particles as much as possible, ensuring minimum resistance to flow. Since both viscosities and densities of the influent in special applications systems will vary quite widely, backwash expansion figures are not given here, but for dilute aqueous solutions the expansion as a function of flowrate is essentially similar to that of **Purolite A-103S** on backwash after rinse with demineralized water.

PRESSURE DROP IN 12°BRIX THIN JUICE



Conversion of Units	
1 m/h (cubic meters per square meter per hour)	= 0.341 gpm/ft² = 0.409 U.S. gpm/ft²
1 kg/cm²/m (kilograms per square cm per meter of bed)	= 4.33 psi/ft = 1.03 atmos/m = 10 ft H_2O/ft

CHEMICAL STABILITY

Purolite A-103S is insoluble in acids, alkalies, and all common solvents. Most salt forms and the free base are stable at elevated temperatures, and may be used in continuous service at temperatures up to about 90°C (ca. 195°F) without significant change occurring. However, exposure to free chlorine, and certain oxidizing agents such as peroxides may lead to loss in exchange capacity as the result of ongoing chemical reaction, and should therefore be avoided.

APPLICATIONS TO SUCROSE

The principal sources of sucrose are sugar cane and sugar beet, which are crushed or shredded respectively before extraction with hot water to obtain the impure sugar juice. The first purification step on this juice is the removal of both soluble and colloidal impurities by the addition of lime, followed by precipitation of the calcium as calcium carbonate by carbonation with CO_2. After filtration, and cooling to minimize sucrose breakdown catalyzed by H^+ ions from the cation exchanger, the thin juice at a concentration of 10 - 15°Brix may be demineralized using a strong-acid cation exchanger, **Purolite C100S**, followed by a weak-base anion resin such as **Purolite A-103S** or **Purolite A-100S**. The elimination of the residual Ca^{++} ions and much of the residual color results in increased yields of higher purity sugar at the crystallization stage. With liquid sugar solutions, where no additional purification on crystallization can take place, effective demineralization and decolorization are essential for high-purity products.

Regeneration of a **Purolite A-103S** (or **A-100S**) unit is normally carried out with 2% caustic soda at about 4 bed volumes (b.v.) per hour, after a 1.5 b.v. "sweetening off" and backwashing. Following a rinse with water, and "sweetening on" with a further 1.5 b.v. of the thin decationized juice, the unit is ready to recommence service. The run is monitored by conductivity and color, and a lifetime of approximately 1000 cycles may be expected (depending on the characteristics of the juice being treated) before performance is seriously affected.

APPLICATIONS TO OTHER SUGARS

Purolite A-103S may also be used in the demineralization of high-solids glucose liquors, or HFCS (high fructose corn syrups), where a strongbase anion resin cannot be used in the OH^- form because of color formation by the so-called Maillard reaction. Regeneration with 5% soda ash, or better 2.5% ammonia, will minimize OH^- formation on the small amount of quaternary groups which may be present. Ammonia is preferred because of its lower cost, ease of recovery, and the lower rinse requirements accompanying its use. Since the influent solutions are, in general, relatively high viscosity liquids (a 50°Brix solution at about 30°C has a viscosity of about 10 cp.), the temperatures used are higher than with the thin juices to obtain suitable flow rates. The macroporous structure of **Purolite A-103S** is designed to resist both the osmotic and thermal shocks arising from this mode of operation.

OTHER APPLICATIONS

Deionization of sorbitol solutions is carried out in essentially the same way as for solutions of sugar. The efficient removal of formic acid from quite concentrated solutions of formaldehyde at temperatures up to 60 - 65°C can be achieved, provided that multivalent cations of iron and other transition metals are absent. Operating capacities of 45 - 50g HCOOH per l of resin (2.8 - 3.0 lb./ft³) have been recorded, depending on the influent temperature, concentration, and the regeneration level of the exchanger.