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Ion Exchange Demineralisation for Recycling of Flowing Rinse Wastewater Within Printed Circuit Board Manufacturing

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ION EXCHANGE DEMINERALISATION FOR RECYCLING OF FLOWING RINSE WASTEWATER WITHIN PRINTED CIRCUIT BOARD MANUFACTURING

By

Fraser Kent

M. A. Sc. Thesis

Submitted to the Faculty of Graduate and Postgraduate Studies

Under the Supervision of Dr. R. M. Narbaitz

In partial fulfillment of the requirements for the degree of M. A. Sc. in Environmental Engineering

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ABSTRACT

In the last fifty years the electronics industry experienced substantial growth. During this period of growth technologies for manufacturing printed circuit boards, the heart of most electronics, have evolved continually. These improvements include many environmentally conscious innovations within the manufacturing process. Flowing rinse systems are an essential part of the manufacturing process. These flowing rinse baths utilize a very large amount of water. Environmental benefits and economic gain can sometimes be achieved through recycling the flowing rinse effluent for reuse.

Ion exchange is a conventional water treatment technology that is well suited to the application of recycling flowing rinse water from circuit manufacturing processes. This is due to the dilute nature of the solutions as well as the high proportion of ionic constituents that must be removed. Specifically, ion exchange demineralisation holds the capacity to treat flowing rinse water to a high purity allowing optimal rinsing efficiency and continual reuse of the same water.

Experiments were undertaken, using a variety of ion exchange demineralisation set-ups and materials to prove that this technology will work for a specific application at an Ottawa circuit board manufacturer. A series of experimental runs were performed leading to the conclusion that ion exchange demineralisation is effective for the recycling of this manufacturer's flowing rinse wastewater.

The Serfilco MBD-10 mixed bed resin showed the best performance although, being a mixed bed resin, it is not readily regenerated leading to a high operating cost of approximately \$8.65/m^3 of water treated. It is expected that a two-bed system with the same type of resins (strong acid and strong base) would have the capability of treating the same water to an acceptable level at a much lower cost and this type of set-up is recommended for future work. It was demonstrated that chelating strong acid resins such as the ones used in some of the experiments are not effective for demineralisation.

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Most of all, I would like to thank my family: David, Kathleen, Graham, Allison and Louise for their continual support that has helped me through the challenges that I have faced.

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LIST OF ABBREVIATIONS

AA - Atomic Absorption Spectrometer

BV - Bed Volume

D - Degasifier

DOC - Dissolved Organic Carbon

DVB - Divinylbenzene

EDTA - Ethylenediaminetetraacetic acid

FMI - Filran Microcircuits Incoporated

GAC - Granular Activated Carbon

ICP - Inductively Coupled Plasma

IX - Ion Exchange

MB - Mixed Bed

ND - Not Detected

NOM - Natural Organic Matter

PCB - Printed Circuit Board

PTH - Plated Through Holes

PVC - Polyvinylchloride

SAR - Strong Acid Resin

SBR - Strong Base Resin

TOC - Total Organic Carbon

U.S. EPA - United States Environmental Protection Agency

WAR - Weak Acid Resin

WBR - Weak Base Resin

CHAPTER 1 – INTRODUCTION

The growth in technology within the past fifty years has been astounding. This is especially true within the high-technology sector with the development of electronic devices such as radios, telephones, televisions and more recently cellular telephones and personal computers. This growth has not been without its associated environmental challenges that are faced through the manufacturing of these devices, their deployment in society, as well as their ultimate disposal.

One common element to many of the electronic devices used today is their fundamental building block: the printed circuit board. Printed circuit boards are found in the majority of modern-day electronic devices, especially computers and telecommunications devices. They are composed of a non-conductive board that supports an intricate network of conductive circuitry, consisting of copper and other metals. During the manufacturing of printed circuit boards a substantial amount of water is used for rinsing. The water that is used in most rinsing applications is demineralised to improve the effectiveness of rinsing. By treating and recycling the flowing rinse wastewater, the same water can be used repeatedly, and the cost of buying water from a community treatment plant can be greatly reduced.

Ion exchange is a water treatment technology that is well suited for recycling of flowing rinse water. By using an ion exchange demineralization system, virtually all ions can be removed from the rinse wastewater so that it may be reused. As long as the cost of treating a unit volume of this wastewater is less expensive than the corresponding cost per unit volume of demineralising municipal drinking water, recycling flowing rinse wastewater is economically feasible.

1.1 – Objective

The goal of this thesis is to determine whether ion exchange demineralization is an appropriate technology for recycling the flowing rinse wastewater generated by Filtran Microcircuits Inc., a printed circuit board manufacturer in Ottawa, Canada. Thus, this document includes a literature review that outlines both how this type of wastewater is created within printed circuit board manufacturing and the fundamental concepts involved in the ion exchange demineralization processes. It then presents a description of investigations that were undertaken to prove that an ion exchange demineralization system is appropriate for this application.

CHAPTER 2 – BACKGROUND

Printed circuit boards are made of non-conductive panels that have a pattern of conductive circuitry attached to them. The circuitry is usually made of copper and is sometimes covered with an additional surface coating. An example of a printed circuit board is shown in Figure 2.1. Boards can range in size from less than one square centimetre to hundreds of times larger, and can have a single layer or be composed of many layers that connect through holes in the panels. As manufacturers of circuit boards continue production, new innovative designs and manufacturing techniques are constantly being introduced, however the basics of the manufacturing process are outlined in the following section.

2.1 – Printed Circuit Board Manufacturing

Manufacture of printed circuit boards is a fairly complex operation. The manufacturing process begins with a simple copper-clad laminated panel. It consists of a substrate, which is a non-conductive material that is laminated to a very thin layer of copper foil. These copper foil layers can be applied to one or both sides of a substrate depending on the specifics of the desired product. Printed circuit boards come in three general types: single-sided, double-sided and multi-layered. A cross-section of a typical double-sided copper-clad panel is shown in Figure 2.2.

In many of the processes used, these panels are immersed in a solution within a container or bath. These solutions are used to perform various tasks such as cleaning, etching, plating and rinsing of the boards. Cleaning is a preparation step that allows good contact between the solution and the board to enhance subsequent processes.

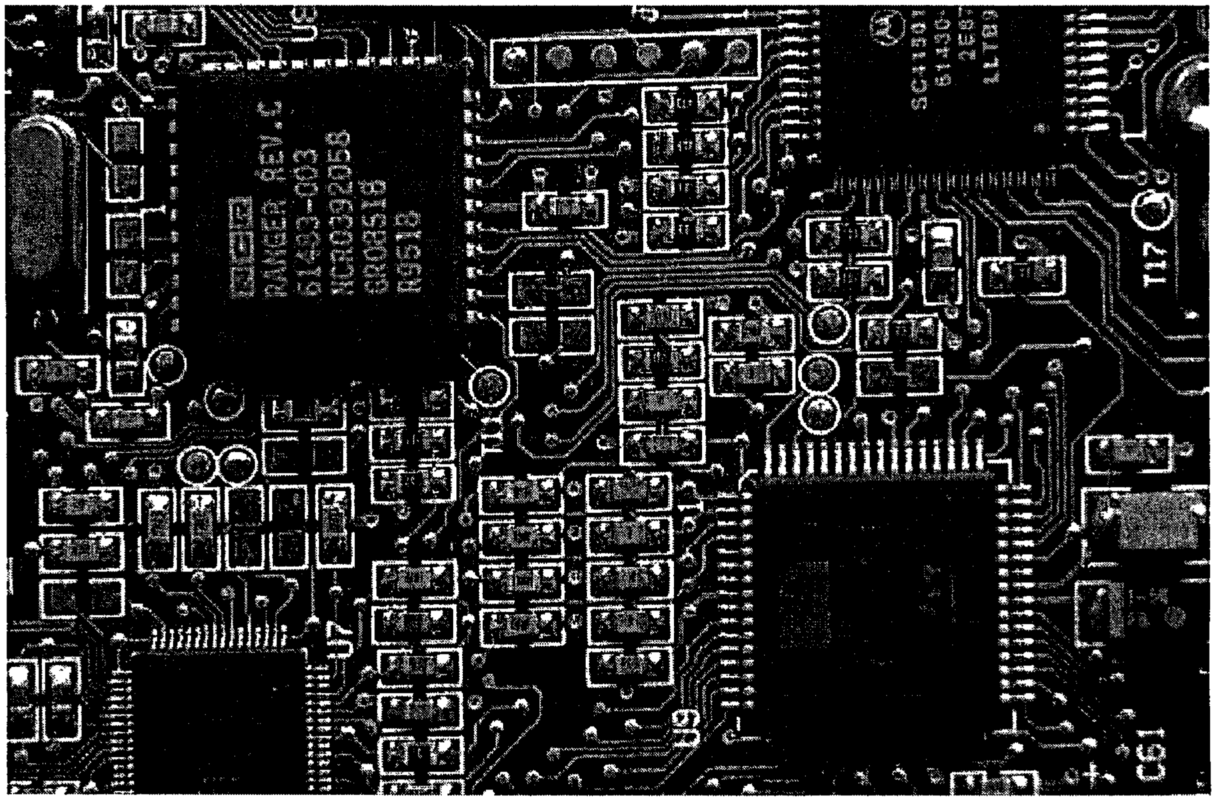

Figure 2.1- An Example of a Printed Circuit Board

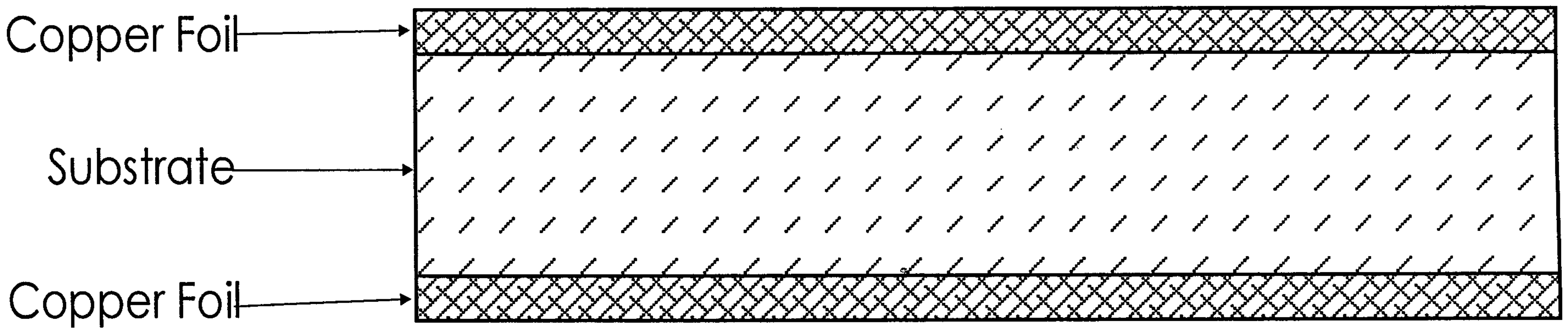

Figure 2.2 - Cross-Section of a Double-Sided Copper Clad Panel

Etching is a chemical process where a solution is used to remove copper, tin, lead or spent resist material (a polymeric film) from a board. By covering up certain portions of a circuit board, selective etching can be achieved. This type of selective process is very commonly used in the manufacturing process. Plating is the mechanism, whether electrically or chemically driven, that is used to deposit metals on printed circuit boards. These metals can also be deposited selectively, as in etching, by covering some portions of the board with resistant material (Kent, 2000).

Once the specific design of a circuit board is complete, tiny holes are drilled in the appropriate places using a computerized drilling machine. Holes through printed circuits, commonly referred to as vias, are needed to connect circuitry from one layer to another and for subsequent mounting of hardware. Many of the processes used to create circuitry, involve electrolytic plating as the mechanism of metals deposition. Before this can occur, a conductive seed layer must exist to act as a cathode upon which metals can be deposited. Unfortunately, the inside surfaces of the vias are not conductive as illustrated in Figure 2.3.

The vias must be given a conductive seed layer of copper to allow subsequent electroplating for completion of the circuitry to the given specifications. Making these holes conductive is typically done through a process referred to as plating through holes (PTH). It is also called electroless plating because electricity is not directly used. Instead, copper is chemically reduced to provide a preliminary conductive layer of sufficient thickness to accommodate electroplating. The electroless operation provides a copper layer of 0.5-2.5 micrometers in thickness.

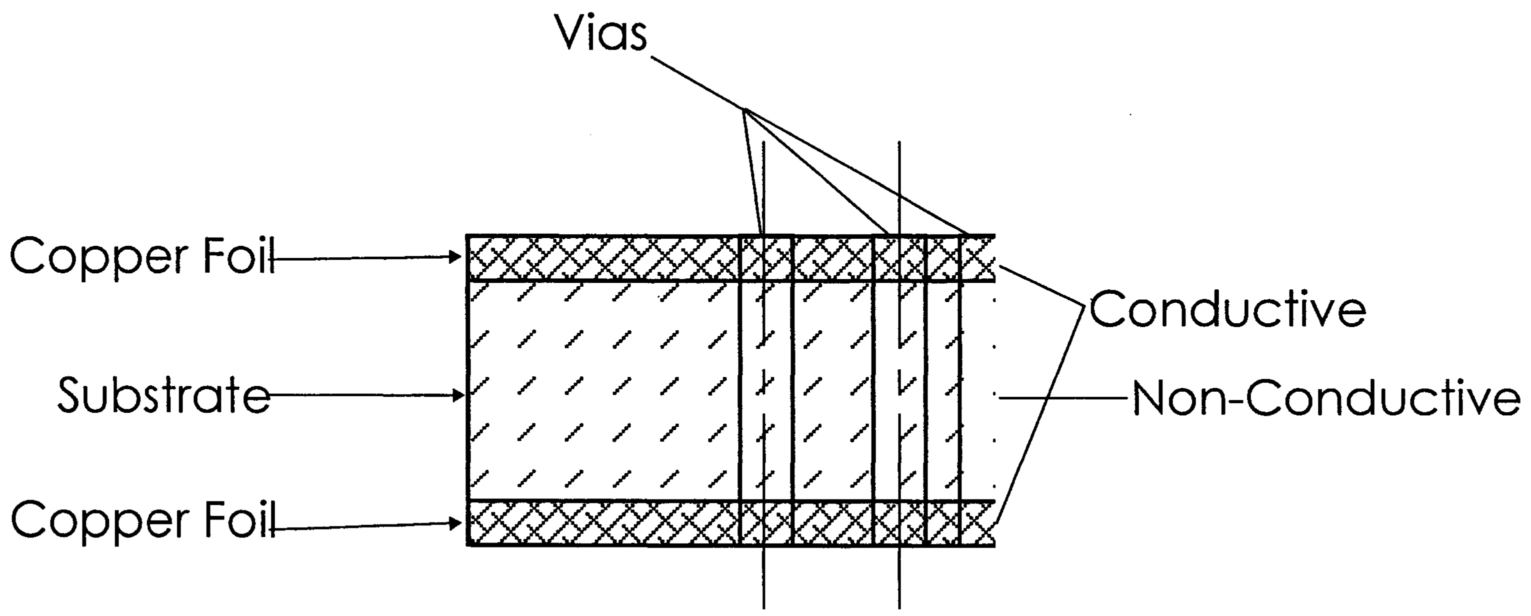

Figure 2.3 - Non-Conductive Holes Through a Printed Circuit Board

Fully designed circuits must meet minimum thickness requirements of 25 micrometers in all areas. Thus, electroless copper plating is only a means of providing conductivity to the inner surface of the vias and is not generally used for the bulk of metals deposition (Coombs, 1996).

Once the holes have been made conductive, the specific circuit pattern that is desired on the final printed circuit board must be plated with conductive material. This must be done without plating the portions of the board that are to have no circuitry. Often, selective plating is accomplished by covering the panel with a material called a photoresist as shown in Figure 2.4. The photoresist covers the non-circuitry portion of the panel, allowing no copper deposition beneath it. Areas that are not covered with photoresist undergo deposition and form the desired circuit pattern. After the boards are plated, the photoresist is removed using a stripping solution and the formation of circuitry is complete. Figure 2.5 shows an example of a completed circuit board.

2.2 – Drag-out

When a bath immersion process is completed and the panel is removed, a film from the bath solution remains on it. This is referred to as 'drag-out'. It is essential to remove drag-out since it otherwise would contaminate the solutions in subsequent processes. Also, drag-out can dry and become detrimental to board surfaces. The drag-out coating is usually removed with a rinsing system. Often the rinse water is discharged directly to the sewer and, in order to do so, it is kept at a low enough concentration to accommodate local sewer by-laws. For example the City of Ottawa

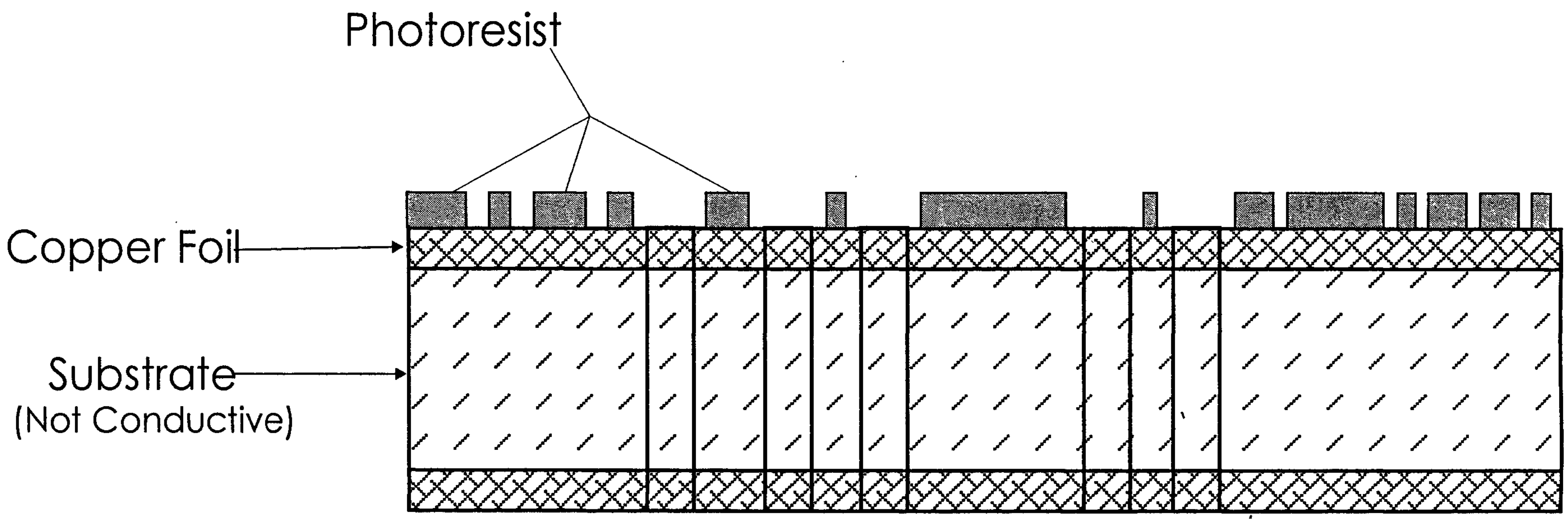

Figure 2.4 - Application of Photoresist for Pattern Plating

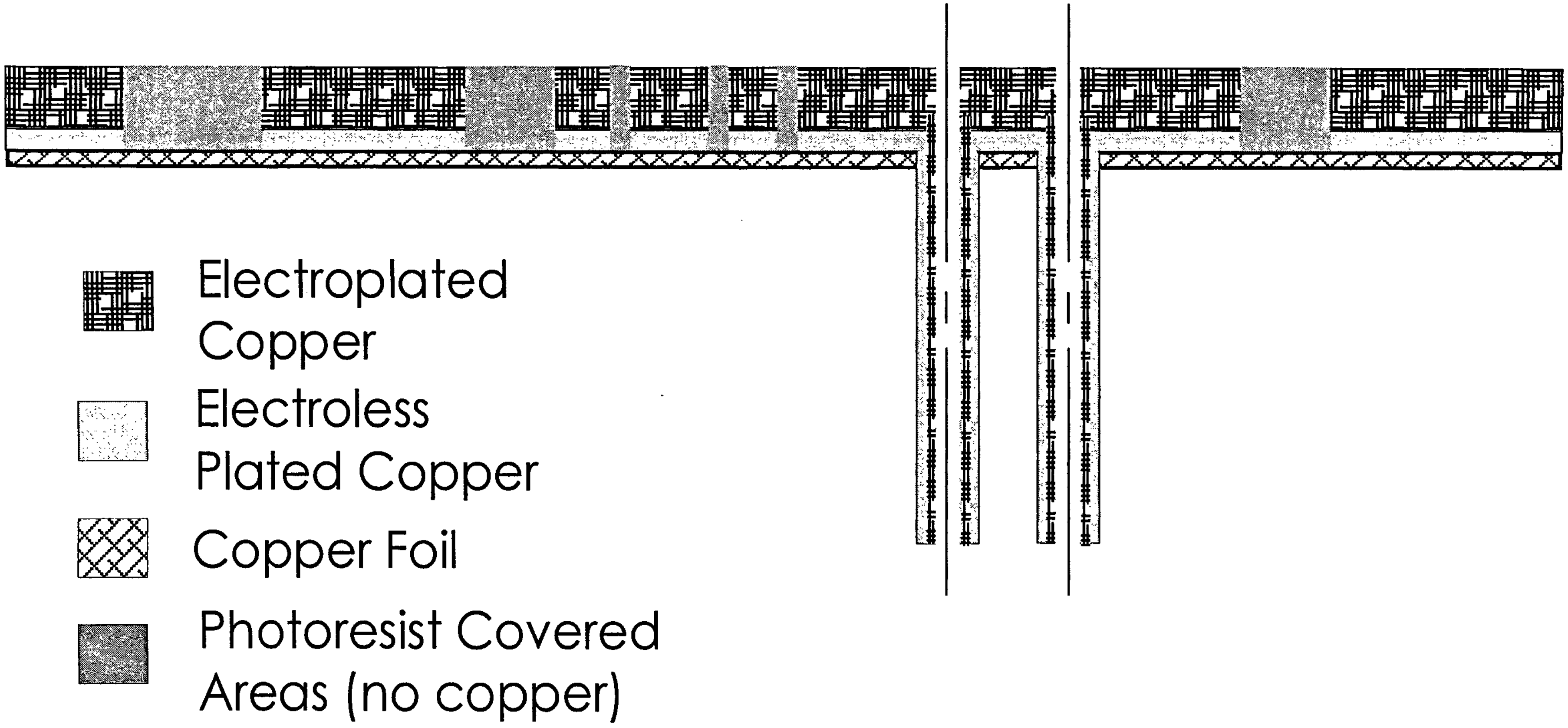

Figure 2.5 - Diagram of Plated Circuit Board (not to scale)

Sewer By-Law limits copper discharges to 3 mg/L while copper concentrations in an electroplating tank are approximately 30,000 mg/L (City of Ottawa, 2000).

2.3 – Rinsing Systems

Rinsing of panels is an essential feature of circuit board manufacturing and is required as an intermediate step between the vast majority of immersion processes. A variety of systems can be used depending on the quality of rinsing required. Some of these systems are illustrated in Figure 2.6.

2.3.1 – Problematic Constituents

The rinsing system must be capable of reducing certain problematic manufacturing contaminants to sufficiently low concentrations to prevent operational problems. The most significant problematic contaminants are calcium, chloride, silica and magnesium. Calcium has a tendency to cause copper oxidation as well as promote line clogging and should be maintained below 4 ppm in the rinsing water. Silica corrodes equipment and forms residues in the PTH line. It should be kept below 6 ppm. In addition, chloride has the tendency to cause roughness on circuit boards unless concentrations are maintained below 2 ppm. Magnesium enhances detrimental copper-copper peeling and must be reduced below 5 ppm (Coombs, 1996). Other constraints in contaminants exist, however these are the most significant.

2.3.2 – Static Rinse

The simplest rinsing system is a static or dump rinse, which involves the use of one or more tanks filled with water. Panels are submerged into a static rinse tank thereby initiating the removal of the film of solution from the previous process. Although

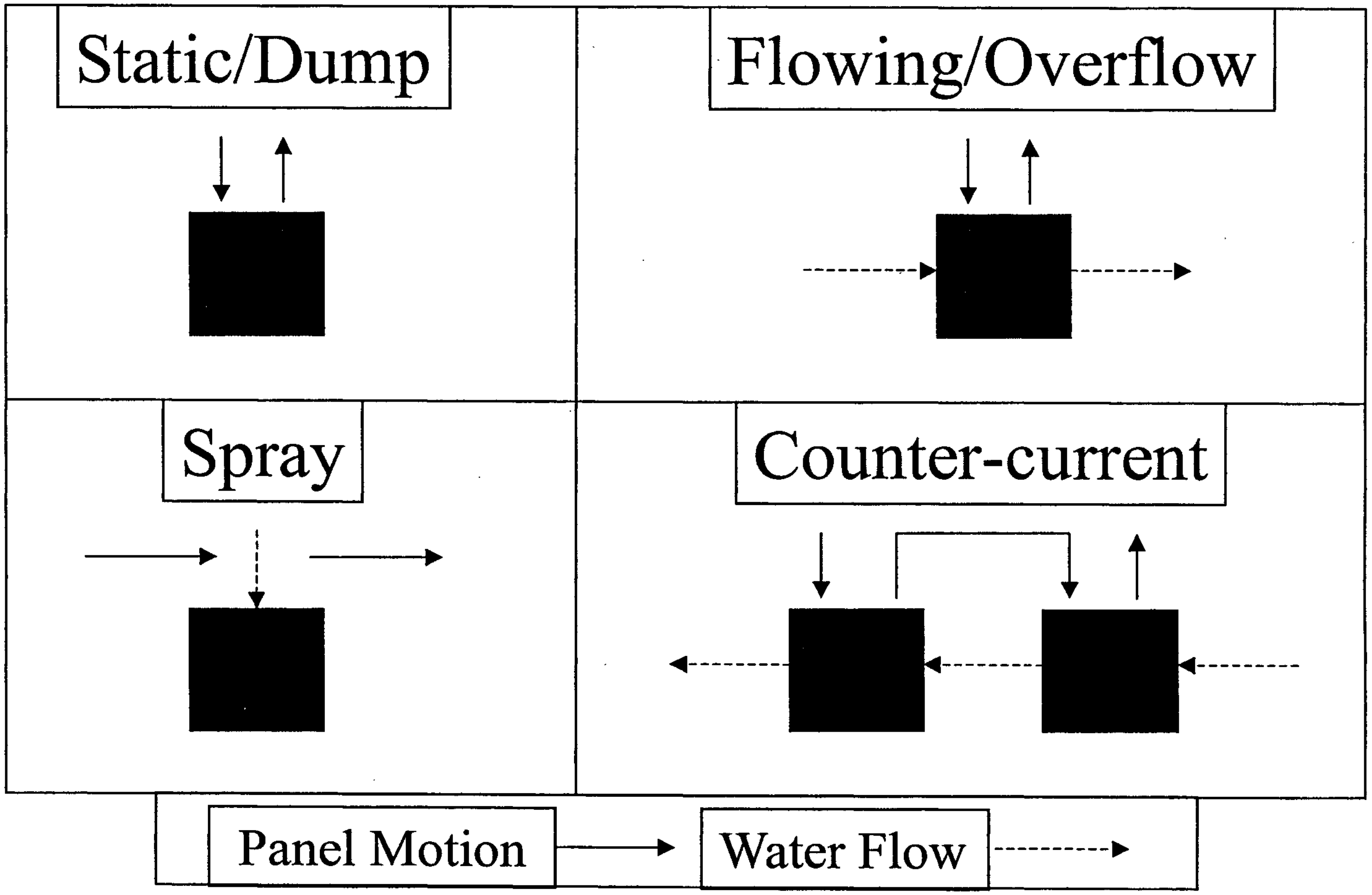

Figure 2.6 - Rinsing Systems

static rinse baths have the advantage of using very little water, there is a significant disadvantage. As the static rinse bath becomes contaminated with the accumulation from panels that have been rinsed, the rate of diffusion of chemicals from the board into the bulk solution is reduced and the quality of rinsing deteriorates. Therefore, the water must be changed once the bath reaches a predetermined level of contamination (Nagy, 2000).

2.3.3 – Flowing Rinse

Flowing rinse baths are used in order to maintain the rate of diffusion from the board into the bulk solution. Flowing rinse systems are employed when it is critical to remove the constituents from the board. This is because they never allow a significant increase in the concentration of contaminants within the rinsing bath and therefore, maintain the diffusion rate and also the quality of rinsing. The problem with this type of rinsing system is that it uses a very large amount of water. By implementing online conductivity meters coupled with a flow control system, the amount of rinse water used can be reduced (Noyes, 1993). The simplest technique is to turn on a flowing rinse tank when it is being used and turn it off at an empirically determined time after the panels have been removed. Flowing rinse systems are often used in groups of 2 or 3 tanks in series. More than 3 is usually not necessary and is not cost-effective.

2.3.4 – Counter-Current Rinse

The most effective use of multiple flowing rinse tanks is in a counter-current system where the rinse water flows from one bath to the next while the work-piece travels in the reverse direction. This way the panels encounter increasingly higher quality water and a concentration gradient is maintained. As a rule, when using 'n' tanks in series, a counter-current system uses about 1/n the amount of water than would be used in a series of co-current flowing rinse tanks to achieve the same degree of rinsing (Nagy, 2000).

2.3.5 – Spray Rinse

Spray rinsing is another technique that can be used. It involves spraying a panel, forcing the residual film off of the board into a drain below. In general, it uses less water than a single flowing rinse tank but more than a 2-stage counter-current system (Mohler, 1983).

2.3.6 – Water Use Reduction

Beyond the rinsing systems themselves, water use reduction can also be achieved through the implementation of controls, such as flow restrictors or monitoring devices. Also, the tanks should be designed to limit short-circuiting and dead space. Increasing the rinse water temperature leads to better rinsing performances, as does the introduction of agitators that increase the water-panel interaction (Noyes, 1993).

2.3.7 – Rinse Water Quality

Using higher quality rinse water leads to better quality rinsing. However, depending on the application, there is usually a point of diminishing returns where it becomes uneconomical to use rinse water of a higher quality. Conductivity and resistance are commonly used to measure water quality since they give a good indication of the ionic load contained within a solution. The quality of water that is used for rinsing varies from municipal drinking water with a resistance of about 0.01 megaohms to ultrapure water with a resistance of greater than 18 megaohms. For most applications where manufacturers do not have fully automated processes, demineralised water with a resistivity of about 0.1-1 mega ohms is sufficient. This corresponds approximately to the limit of dissolved impurities that can exist, such as chloride and silica, before operational problems occur.

2.3.8 – Recycling Flowing Rinse Water

In the printed circuit manufacturing industry, a substantial amount of demineralised water is used in flowing rinse systems. By demineralising flowing rinse effluents and recycling them, the cost of demineralised water can be reduced. Manufacturers that use municipal drinking water as a source for flowing rinse baths can use demineralisers to upgrade the quality of their rinse water and improve rinsing system performance. Demineralisers can also be used to recycle the effluent from static rinse wastewater that has been partially treated using precipitation. In addition, recycling flowing rinse water also reduces the amount of wastewater sent to the sewer and decreases the heavy metals load sent to the wastewater treatment plant.

There are several water treatment technologies that hold the potential to be used for recycling of flowing rinse wastewater within printed circuit board manufacturing. Some examples are solvent (liquid-liquid) extraction, electrodialysis and membrane technologies, however the most commonly applied technology for this application and the one that this document focuses on is ion exchange. Circuit board manufacturers often use ion exchange since it is very well suited for the removal of metals from dilute aqueous solutions and has the ability to produce extremely high quality water (US EPA, 1998). One of the major industrial applications of ion exchange has been in the plating industry for water reuse (Eckenfelder, 2000).

CHAPTER 3 – LITERATURE REVIEW

The ion exchange (IX) process involves subjecting a contaminant, in the aqueous form, to an insoluble exchanger medium where the ionic contaminant replaces ions of a similar charge within the exchanger material. In this fashion, unwanted ions can be removed from solution and replaced with those contained within the exchanger. By definition, for a process to be considered ion exchange, the solid phase must exhibit no substantial change in structure (Etzel and Wachinski, 1997). Exchanger mediums can be designed for cationic or anionic exchange depending on the composition of the wastewater that needs to be treated. The primary advantage of ion exchange is that a specific effluent composition can be achieved through proper design of the system, since the process is quite predictable.

Ion exchange is used to remove hardness from ground water, to conduct demineralisation and to remove dissolved heavy metals such as arsenic, barium, cadmium, chromium, cyanide (free and complexed), lead, mercury, selenium, silver, nickel and copper. It also can be applied to the removal of radium, treatment of nitrate containing ground water, industrial rinsewater treatment, nuclear power plant cooling water treatment, leachate treatment, groundwater remediation as well as metal recovery from industrial effluents (Weber, 1972). The reuse of treated electroplating rinsewaters is a strong economic driving force in the development of ion exchange technologies (Eckenfelder, 2000). It cannot, however, be used for the removal of most organic species in conventional set-ups, although fulvic and humic acids are exceptions (Sengupta, 1995). The phenomenon of ion exchange is dependent upon a concentration gradient between the solution and the fixed medium. Mediums can be natural or synthetic. Most exchanger materials presently used are synthetic polymer resins manufactured for specific applications. The resins are made of high molecular weight polyelectrolytes with fixed ionic groups attached to the solid matrix. Mobile ions are attached to the fixed ionic groups to balance the overall electrostatic charge. An example of this is illustrated in Figure 3.1. This example shows a material set up for cation exchange since the mobile ions are cations. Specifically, this resin contains a polystyrene chain with divinylbenzene (DVB) crosslinks. Na^+ is the mobile cation and SO_3^- is the fixed anion unable to move. Thus, this material could be used to remove any cation that SO_3^- exerts more selectivity toward given the equilibrium conditions. Since Na^+ is the cation that is saturating the medium, the gradient for removal is maximized initially, although eventually, as the sodium is exchanged, the gradient will decrease and exchange will be inhibited. Therefore, there will always be some Na^+ ions left on the medium. An example of an exchanger resin prior to and following an exchange reaction is shown in Figure 3.2: (a) the initial state prior to exchange reaction with cation B^+ and (b) the equilibrium state after exchange reaction with cation B^+ (Haas and Vamos, 1995). The reversible exchange reaction is given by:

$$(R^{-1})A^{+1} + B^{+1}_{(aq)} \rightleftharpoons (R^{-1})B^{+1} + A^{+1}_{(aq)} \qquad (3.1)$$

where R is the fixed ion attached to the polymeric chain.

Treatment systems can be run in batch or columnar styles. Batch treatment involves mixing the solution with the resin in a tank until equilibrium is reached, at which point the two materials are separated. There is limited exchange capacity because the

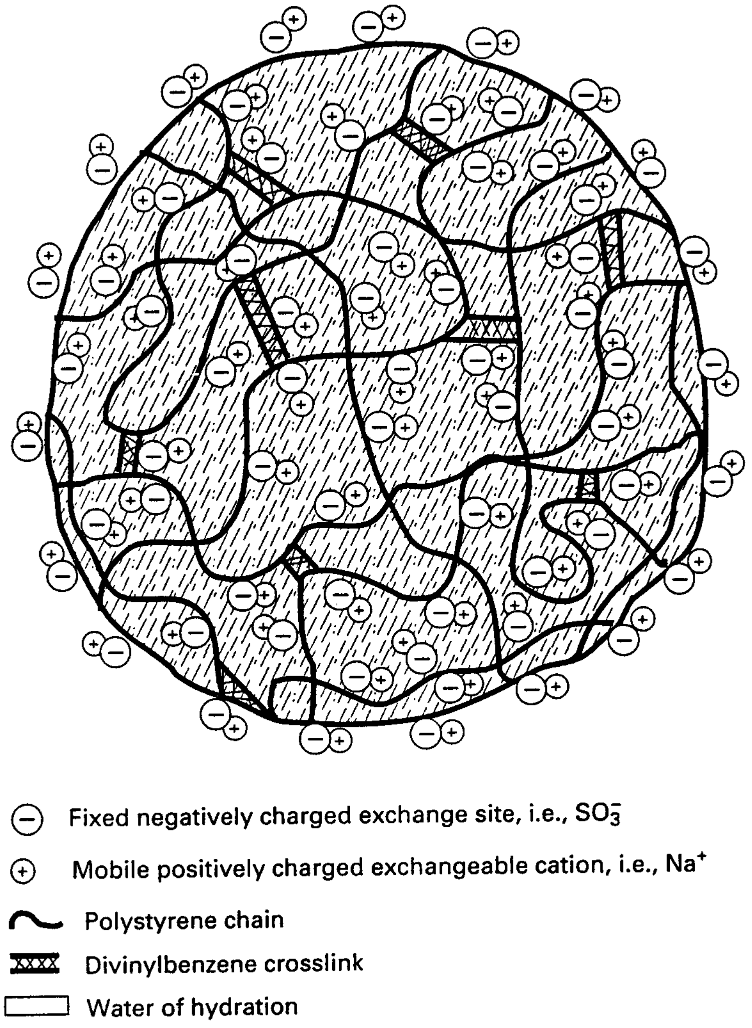

Figure 3.1 – Ion Exchange Resin Close-up (Haas and Vamos, 1995)

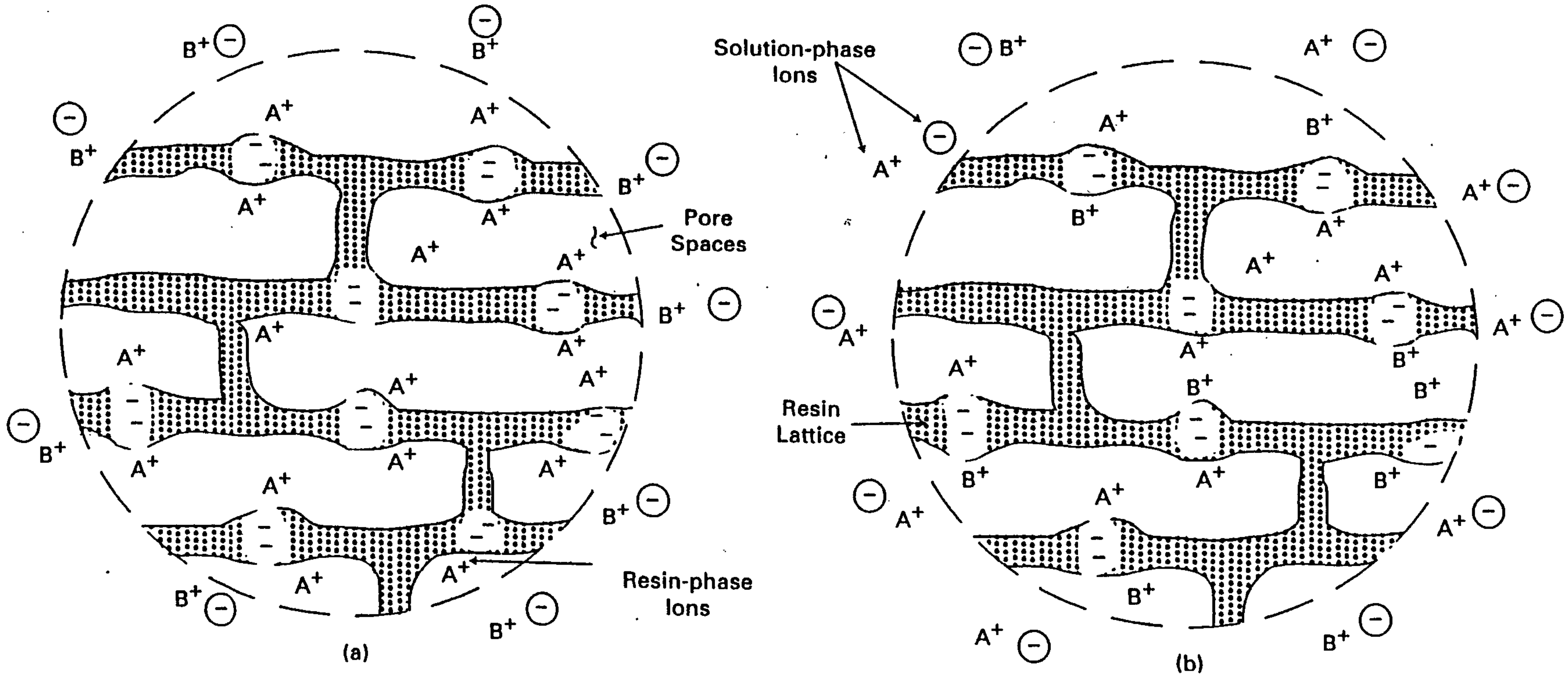

Figure 3.2 – A Cation Exchange Resin Before and After Exchange Takes Place (Haas and Vamos, 1995)

preference the fixed ions exert for the ions in solution decreases as the mobile exchanger ions are released to solution. Batch treatment is inefficient unless selectivity for the target ion in solution is far greater than that for the exchangeable ion on the resin.

Columnar operations treat aqueous streams through a fixed bed of ion exchange materials. Nearly complete separation can be achieved and efficiency is found in column design through complete utilization of the exchanger uptake capacity. This is allowed by the inherent characteristics of columnar flow (see Figure 3.3) Once the initial media at the top of the bed is exhausted, the active ion exchange zone moves down the column to encompass fresh material. In this fashion, a concentration gradient in the active zone is maintained producing consistent treatment. Another advantage of this method is that it allows very efficient regeneration of the exchanger material. An example of a typical full-scale columnar ion exchange unit is shown in Figure 3.4.

3.1 – History

The ancient Greeks used clay to demineralise water although the actual phenomenon of IX was not first observed until in 1850 when a British soil chemist, Thompson, ran a solution of ammonium sulfate through a tube of soil and found that a solution of calcium sulfate came out the bottom (Hill and Lorch, 1987). Shortly thereafter, Way conducted a series of experiments and found that the amount of cation that came out of the bottom was equal to the amount of the original cation that was poured into the top. He concluded that a component of the soil material (aluminosilicate) contains

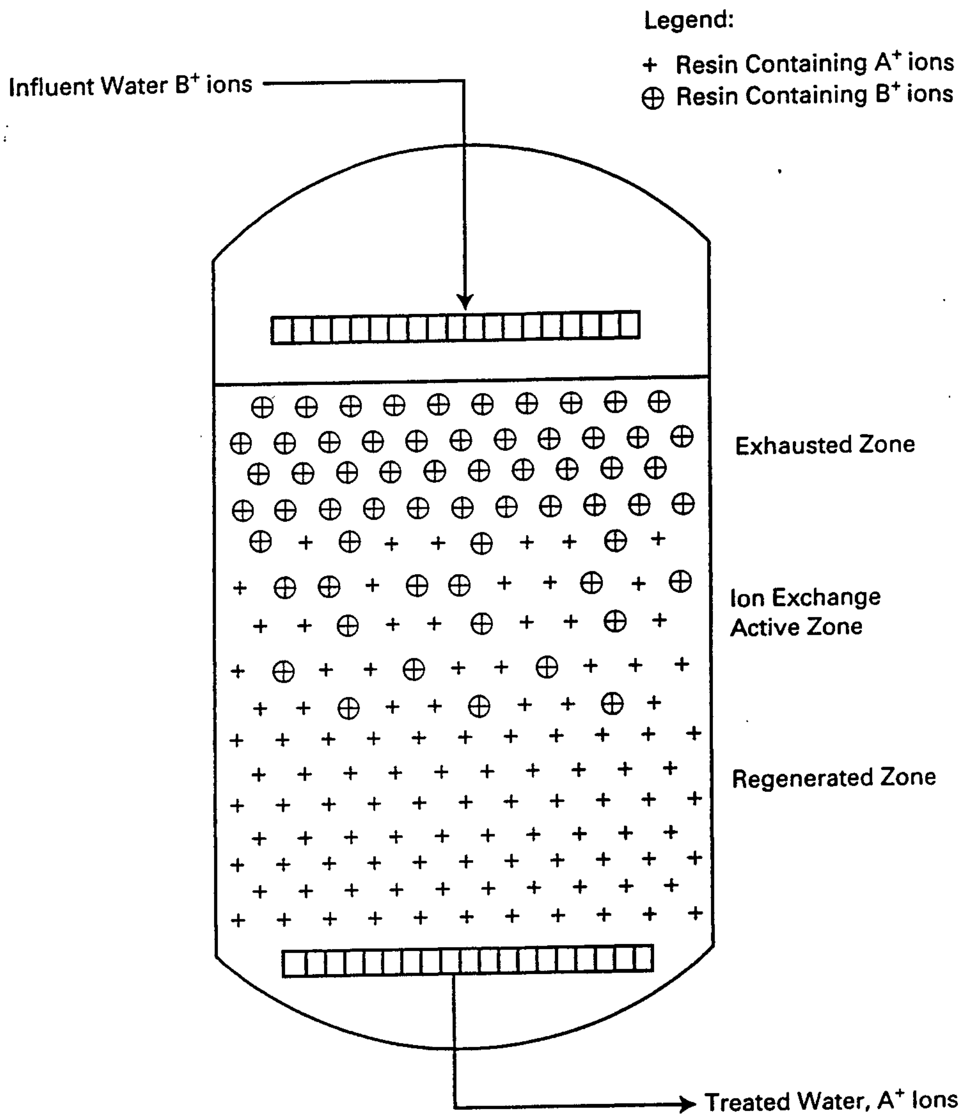

Figure 3.3 – Ion Exchange in Columnar Flow (Haas and Vamos, 1995)

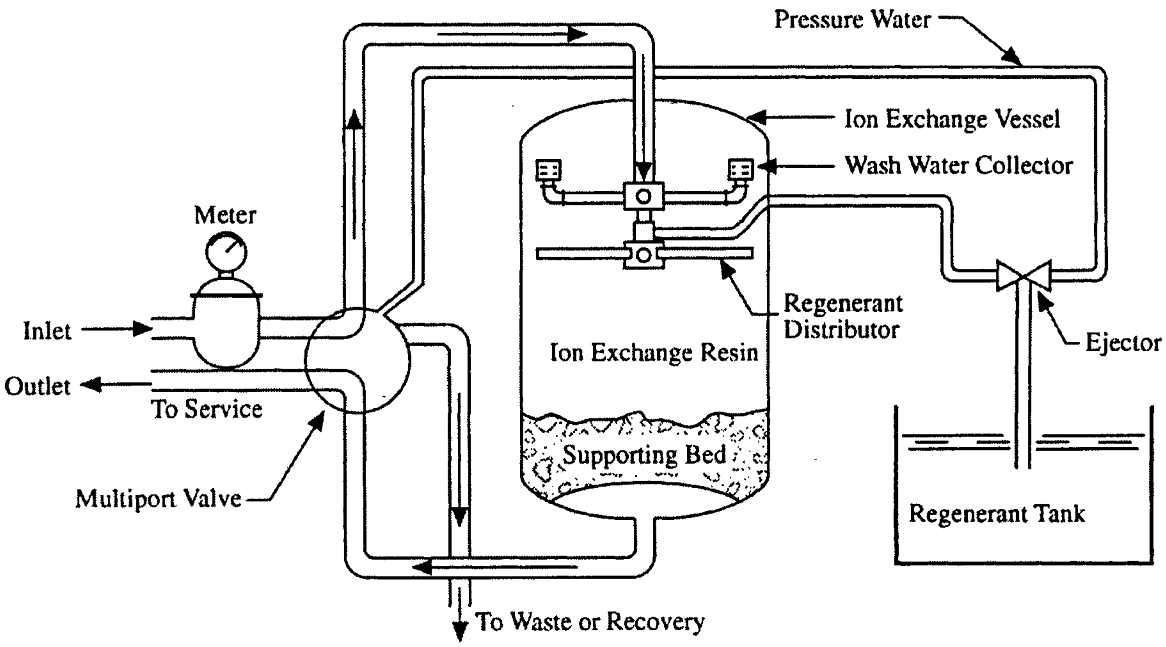

Figure 3.4 - Example of a Full-Scale Ion Exchange System (Etzel and Wachinski, 1997)

mobile cations free to move into the solution. He then produced some aluminosilicate gels to work with. These gels were the first synthetic ion exchangers (Hill and Lorch, 1987).

In 1876 Lemberg transformed the mineral leucite (containing potassium) into analcite (containing sodium), by treating it with a solution of sodium chloride. He then reversed the process by treating the analcite with potassium chloride, thus demonstrating the stoichiometry and reversibility of IX reactions (Hill and Lorch, 1987). This work led to the application of natural aluminosilicate (zeolites) for the removal of hardness from water (Weber, 1972). In 1905 Gans demonstrated that water could be softened by passing it through beds of aluminosilicate that were prepared with sodium chloride. This process was fully reversible. The theory of IX led scientists to believe that if acids and bases could be used to prepare beds, instead of salts, complete deionisation could theoretically be achieved. However, when attempting to use acids, the exchangers could not handle the harsh environment and at that point in time, no anion exchangers were developed.

Adams and Holmes made Bakelite resins in 1934 from crushed phenolic phonographic records that exhibited IX properties. They also invented the first anion exchanger made of phenol-formaldehyde-polyamine condensates (Hill & Lorch, 1987).

About that same time, Liebknecht (from Germany) and Smit (from Holland) simultaneously discovered that the sulphonation of ground coal produced an excellent cation exchanger with good mechanical and chemical stability and a higher capacity than other exchangers of that time. As a result of these discoveries, in 1937 the world's first deionisation plant was constructed in a British brewery. As shown in Figure 3.5, it was made of one column of sulphonated coal followed by a column of anion exchange resin.

In 1944, a new resin was created by d'Alelio. He made a polystyrene sulphonic acid cation exchange resin by copolymerising styrene and divinylbenzene as drops in water to form beads. The beads were then sulphonated and the result was a cation exchange resin with excellent strength and chemical stability with a capacity that more than doubled any other existing resin. Two years later, McBurney invented the corresponding anion exchange resin. He did so by chloromethylating and aminating the same polystyrene beads. All of the previously existing anion exchange resins were weak-base anion exchangers that used amines as the fixed functional groups. They could not remove weak acids, carbon dioxide or silica. In addition to amines, the new polystyrene resins contained quaternary ammonium groups that allowed removal of all these materials. Although these ion exchange materials were invented more than fifty years ago, similar type resins are still used commonly today (Hill & Lorch, 1987).

The sulphonic cation exchange resins required large excesses of acid for regeneration. In the late 1940s many companies introduced weak-acid cation exchangers that could be regenerated with less of an excess of reagent. In the 1950s the next generation of carboxylic resins appeared, cross-linked with acrylic or methacrylic acid. These resins were good for water softening and removal of dissolved solids.

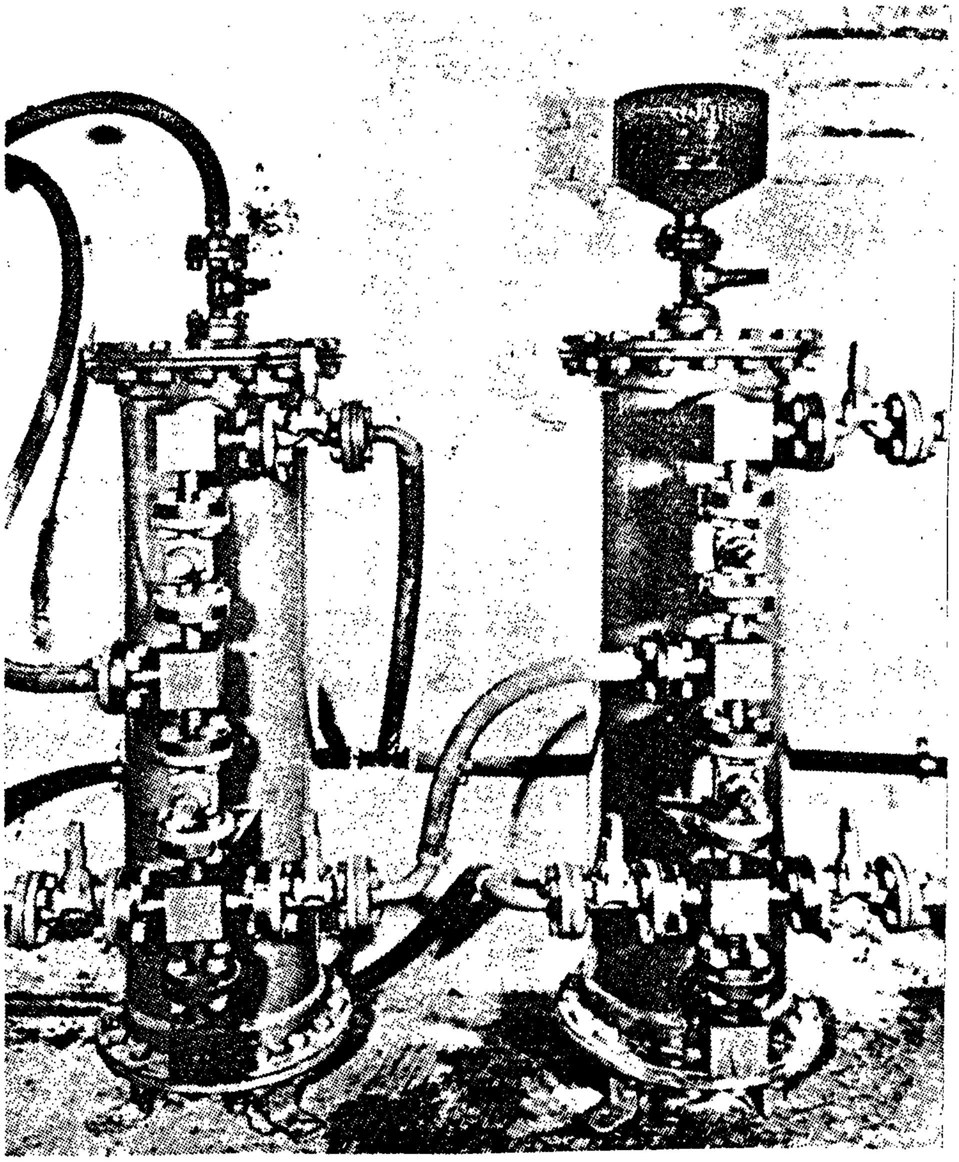

Figure 3.5 – First Demineralisation Plant (Hill and Lorch, 1987)

In 1959 macroporous resins were invented to combat the problems of fouling that occurred during the removal of fulvic and humic acids. The acids could be removed from the water but not effectively removed from the resin during regeneration. The macroporous resins involved used a special matrix that provided an additional system of pore channels through the medium that allowed for the movement of larger particles. These resins showed good resistance to organic fouling, leading to a longer resin lifetime and better water quality. The only problem with the early macroporous resins was that they had low capacities and regeneration efficiencies. Isoporous resins were created in 1965. They had an open gel structure that allowed free passage of larger molecules while maintaining a high capacity and regeneration efficiency. However, in the late 1960s with the invention of high-rate condensate polishing only the macroporous resins had the physical strength and resistance to abrasion that was needed for these applications.

In 1972 the first polyacrylic anion exchange resins were produced. These resins showed excellent resistance to organic fouling, operating capacities 30% greater and chemical efficiencies much higher than the polystyrene counterpart. The quaternary ammonium groups are very stable resulting in a 150% increase in resin life. They are able to reversibly adsorb organics without fouling although they cannot withstand temperatures above 35° C (Hill & Lorch, 1987).

3.2 – Ion Exchange Materials

3.2.1 - Synthetic Resins

Today, copolymers of styrene and divinylbenzene (DVB) are the most common ion exchange resins used. DVB provides the cross-linking in order to keep the resin in an insoluble state (Etzel and Wachinski, 1997).

Exchangers have many characteristics that are pertinent to their performance. Characteristics, such as particle size, density, degree of cross-linking, resistance to oxidation, thermal stability, specific gravity, degree of swelling, moisture content and exchange capacity, provide information on the material in question, which helps designers to determine whether the material is appropriate for a particular application. The capacity is the most important characteristic on the above list. It is the amount of contaminant that can be exchanged per unit of resin. It can be given as dry weight capacity (meq/g) or wet volume capacity (meq/L).

3.2.2 - Classification of Resins

All resins can be classified as cationic or anionic exchangers depending on the nature of the mobile ions of exchange. Also they can be gel resins, which are fairly homogenous mixtures, or macroporous resins, which are more heterogeneous. Some cationic exchangers are referred to as strong or weak acid resins (SAR or WAR), while some anionic exchangers are called strong or weak base resins (SBR or WBR). These names are used to describe the way an acid or base resin gives up a cation or anion, respectively, as the mobile exchange ion.

3.2.3 - Strong Acid Resins

Principal Reaction: $2(R–SO_3H) + Cd^{+2} \rightleftarrows (R–SO_3)_2Cd + 2H^+$ (3.2)

An example of the exchange that occurs within a strong acid resin is shown with the removal of cadmium in the above equation. As shown, the organically fixed anion ($R-SO_3$) gives up two hydrogen ions in exchange for one cadmium ion. Almost all other cations are more attracted to fixed ionic groups than H^+. Using this type of resin practically all of the other cations can be removed from solution, but it can be difficult to regenerate requiring about 4 times the theoretical quantity of regenerant (Rhom and Haas Ion Exchange Laboratory Guide, 2001). This same type of resin is often used in the sodium form, and can be used in any other cation form.

3.2.4 - Weak Acid Resins

Principal Reaction: $2R–COOH + Cd^{+2} \rightleftarrows (R–COO)_2Cd + 2H^+$ (3.3)

Weak acid resins generally contain carboxylic acid groups as the active exchange sites. It is so named because the degree of dissociation is pH dependent. At pH above 9, this resin functions as a strong acid resin, whereas at lower pH the gradient of hydrogen ion concentration is reduced, and consequently very little exchange is achieved. One of the important advantages of using a weak acid is that it can be regenerated with less acid than the strong acid resin. For this type of exchanger, copolymers of acrylic or methacrylic acid are often used with DVB for crosslinking.

3.2.5 - Strong Base Resins (Type I)

These resins generally have quaternary ammonium groups ($R–R_3N^+OH^-$) connected to aromatic rings of styrene-DVB copolymers through methylene groups. Quaternary ammonium groups remain ionised at all pH levels. Type I strong bases are very basic resins but, as with the strong acid resins, they are difficult to regenerate.

3.2.6 - Strong Base Resins (Type II)

Type II strong base resins are similar to type I except they use dimethylethanolamine as the aminating agent. This change in structural composition makes type II resins less chemically stable. Also, the concentration at exchange sites is lower with a lower basicity than type I, however the quantitative requirement for regeneration is less than that for type I resins. Strong base resins can also be produced using polyacrylamide instead of polystyrene as a matrix.

3.2.7 - Weak Base Resins

These exchangers carry amino groups. They can be made with matrix-cross-link pairs of polystyrene-DVB or polyacrylamide-DVB. Other production methods involve step growth or condensation polymerisation to produce phenol-formaldehyde containing amino groups or epoxy polyamines. The use of weak base resins is generally preferred because of the drastically reduced quantity of regenerant required. Often these types of systems are used in conjunction with strong acid exchangers for demineralisation processes. The solution being treated can be passed through a strong acid exchanger where all cations are removed and replaced with hydrogen ions. This solution is then passed through a weak base anion exchanger. Given the low pH level that exists after the cation exchanger, the weak base exchanger exerts maximum exchange capacity and can remove nearly all the contaminant anions from solution. An exception to this is a case where silica must be removed. A strong base resin is necessary for effective removal of silica (Etzel & Watchinski, 1997).

3.2.8 - Chelating Resins

Some exchangers are designed specifically to remove heavy metal cations. These are usually referred to as chelating resins. They contain an imidodiacetic acid similar to the chelating agent ethylenediaminetetraacetic acid (EDTA) that forms strong complexes with heavy metal cations causing a high degree of selectivity for heavy metals (Eckenfelder, 2000). These resins will preferentially remove heavy metals in the presence of other cations although they have the capacity to remove other cations as well.

3.2.9 - Natural Ion Exchange Materials

Although the primary use of IX involves synthetic materials, natural materials exist that exert ion exchange properties. Examples of these natural exchangers include soils, humus, cellulose, wool, protein, coal, activated carbon, lignin, metal oxides, living cells algae and other biomass. Recent studies have shown that some live and dead biomass has a unique ability to selectively remove metals through ion exchange mechanisms. Unfortunately, there are many difficulties in dealing with biomass in an operational context. The U.S. Bureau of Mines has developed immobilized biomass by grinding and blending sphagnum peat moss into porous polysulfone beads. These beads, shown in Figure 3.6, are to be used as ion exchangers (Sengupta, 1995). Of all the natural materials, the most effective exchangers are found in soils containing aluminosilicates. Minerals such as clinoptilolite, analcite, chabazite, hormotome,

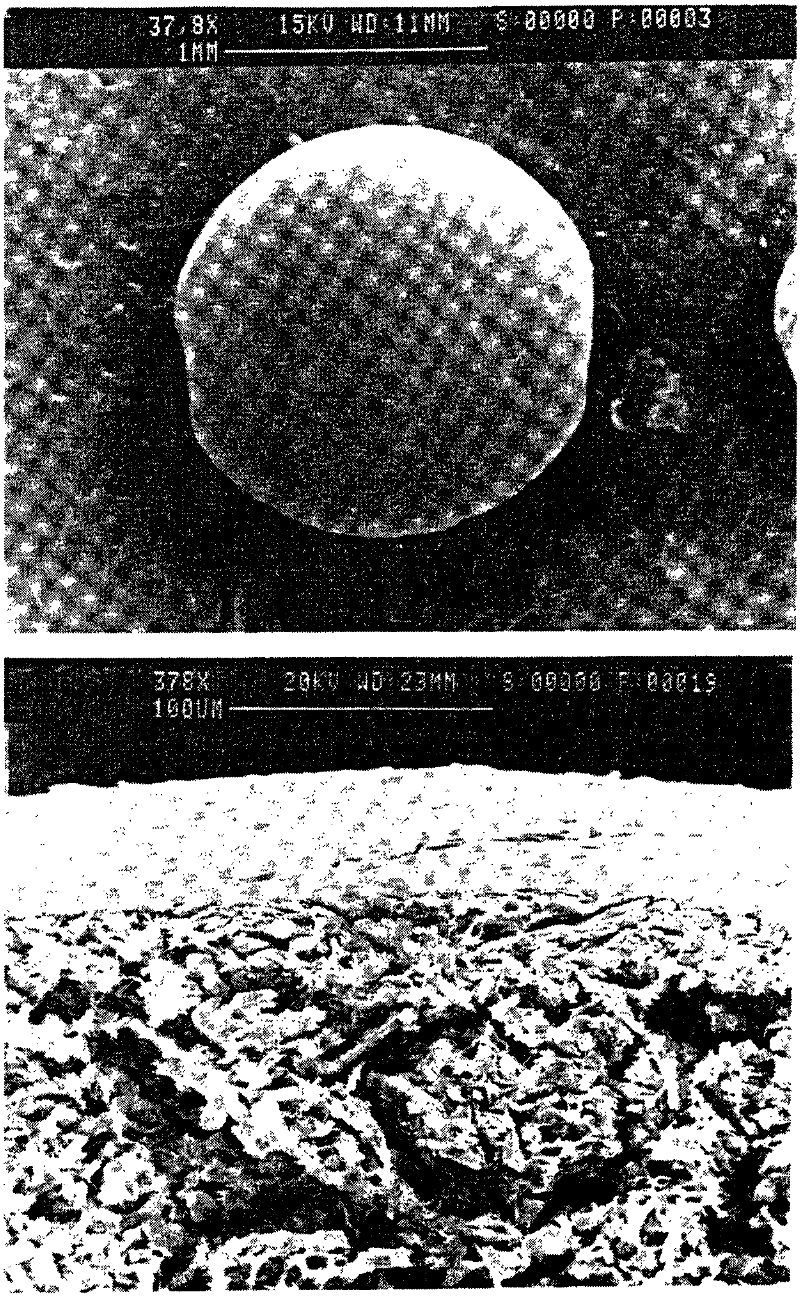

Figure 3.6 - SEM photograph of Immobilized Biomass (Sengupta, 1995)

hevlandite and natrolite act as cation exchangers while apatite and hydroxylapatite act as anion exchangers. Coals act as weak cation exchangers as a result of the carboxylic groups that they contain. Green sand is used for iron and manganese removal and clinoptilolite can be used to treat water with ammonium. Activated alumina is used for the removal of fluoride, arsenic, selenium and phosphate. Presently, there is work being conducted that examines vermiculite for the removal of copper, zinc and nickel from synthetic and natural wastewaters (Etzel & Watchinski, 1997).

3.3 – Ion Exchange Characteristics

Some important factors that are involved in ion exchange processes are discussed in the following sections. These ion exchange characteristics are essential to consider when designing a treatment system. They include ion exchange capacity, leakage, selectivity and kinetics.

3.3.1 – Ion Exchange Capacity

Ion exchange materials can exchange a limited number of ions. Once most of the ion exchange sites have been filled, efficient exchange no longer occurs. The total exchange capacity of a material is a theoretical value that indicates the number of ions exchangeable per unit volume or mass of material. However, this capacity is never reached in practice. In reality, ion exchange columns are judged by their operating capacity, which indicates the amount of ions that can be exchanged before the breakthrough concentration of a contaminant exists in the effluent. This practical value accounts for every aspect of the ion exchange system including: equipment, regeneration specifics, ion exchange material and volume of media bed (Etzel & Wachinski, 1997).

3.3.2 - Leakage

Leakage occurs when a regenerant is formed in the exchanger bed from ion exchange near the top of the media. The regenerant exchanges with contaminant ions further down the bed re-introducing them to the solution. It can be prevented by: a) increasing the excess of regenerant used in regeneration, b) using two columns in series or c) using a mixed bed demineralisation set-up which will be discussed in more detail in section 3.6 (Applebaum, 1964).

3.3.3 - Selectivity

Different ions are attracted to ion exchange resins to varying degrees. The most significant factor that determines the magnitude of the attraction is the ionic charge or valence. For example, a cation exchange resin will selectively choose a Ca^{2+} ion before a Na^+ ion since calcium has a greater valence. Also, when considering two ions of the same charge, competing for the same resin, the one with the larger atomic number will have a greater affinity for the resin. This is because resins are most selective to ions with the smallest hydrated radius. The hydrated radius of an ion (within a group of equally charged ions) is inversely proportional to the ionic radius. In addition, ions in solution (counter ions) that associate more strongly to the fixed ionic groups within the resin are preferentially selected (Weber, 1972). Selectivity is also affected by the degree of cross-linking within a resin, which is a function of the percent divinylbenzene used. Table 3.1 shows the order of selectivity for a typical

Table 3.1 - Table of Cation Exchange Selectivities (Etzel, Wachinski, 1997)

	X4[a]	X8[a]	X16[a]
	Monovalent		
Li	1.00	1.00	1.00
H	1.32	1.27	1.47
Na	1.58	1.98	2.37
NH_3OH	1.90	2.25	3.28
NH_4	1.90	2.55	3.34
K	2.27	2.90	4.50
Rb	2.46	3.16	4.62
Cs	2.67	3.25	4.66
Ag	4.73	8.51	22.9
Tl	6.71	12.4	28.5
	Divalent		
UO_2	2.36	2.45	3.34
Mg	2.95	3.29	3.51
Zn	3.13	3.47	3.78
Co	3.23	3.74	3.81
Cu	3.29	3.85	4.46
Cd	3.37	3.88	4.95
Be	3.43	3.99	6.23
Ni	3.45	3.93	4.06
Mn	3.42	4.09	4.91
Ca	4.15	5.16	7.27
Sr	4.70	6.51	10.1
Pb	6.56	9.91	18.0
Ba	7.47	11.5	20.8
	Trivalent		
Cr	6.60	7.60	10.5
Ce	7.50	10.6	17.0
La	7.60	10.7	17.0

[a] Cross-linking with divinylbenzene at 4, 8, and 16%.

Note: Lithium is arbitrarily set at 1.00.

cation resin (Etzel, Wachinski, 1997). The higher the selectivity value, the greater the affinity that an ion exchange resin exerts for a particular ion. In the table, lithium is used as a reference cation with a value of one. The affinity of other cations is shown as a multiple of the attraction a cation resin exerts toward lithium.

3.3.4 - Kinetics

The mechanism that governs the kinetics of ion exchange depends on the nature of the solution to be treated. The series of mechanisms that must occur in every ion exchange reaction are:

1. Bulk transport from solution to external resin surface
2. Film diffusion into the resin
3. Pore diffusion through the porous structure
4. Ion exchange
5. Pore diffusion of the exchanged ion back to through the porous structure
6. Film diffusion of the exchanged ion to the surface of the resin
7. Bulk transport back into the solution

The ion exchange step is never limiting because it occurs practically instantaneously. If there is sufficient mixing in the reactor, such as in a column set-up, the two bulk transport steps will not be limiting either. The rate of film diffusion is essentially limited by the concentration gradient between a solution and a resin and thus increases with solution concentration. In systems with dilute ionic loads, film diffusion is the mechanism that governs the rate of exchange. When the concentration of a solution increases, pore diffusion governs the reaction because the rate of pore diffusion is inversely proportional to the concentration of ions in a solution (Weber, 1972).

3.4 – Modeling

Ion exchange column performance can be modeled by analyzing both equilibrium data and column performance data. Equilibrium data can be used alone to give an estimate of the operational ion exchange capacity, however it does not take into account mass transfer resistances that occur during column operation. By conducting several column runs with varying concentration one can estimate the performance of an ion exchange system with a model that takes dynamic limitations such as the rate of film diffusion into account (Sengupta, 1995). Only equilibrium models have been presented in this document to give the basic theory of how modeling is approached.

3.4.1 – Local Equilibrium Model

The local equilibrium model is for a single ion and ignores the dynamic mass transfer resistances of ion exchange. It assumes that there is local equilibrium throughout the column. The ion with the greatest affinity for a resin is completely absorbed before any of the ions with the next greatest affinity are absorbed. The same concept is assumed to occur during desorption. Thus, this model predicts breakthrough curves that appear as abrupt wave steps. As a result, all of the ion exchange capacity is taken up by contaminant ions before breakthrough occurs. The equilibrium state that exists throughout the column is defined by a separation factor, α, which characterizes the affinity that different ions have for the resin.

$$\alpha_{a,b} = Y_a X_b / Y_b X_a \tag{3.4}$$

where X and Y are the equivalent fractions of ions (a or b) in the solution and resin phases respectively. Ion a and b refer to two ions being exchanged with each other. Given conditions where the ion to be removed has more affinity for the resin than the co-ion that is attached to the resin, the breakthrough curve has an abrupt transition. This is referred to as compressive behaviour. If the resin phase ion has a greater affinity for the resin than the ion to be removed, such as in the regeneration of an SAR then the column operates under dispersive behaviour. Upstream of the transition front there is a feed plateau where the concentration of the ion is the same as in the feed and downstream there is a presaturation plateau where the ionic concentration is equal to its effluent concentration. A series of partial differential equations representing the behaviour of the column can be derived (Haas and Vamos, 1995). To solve the equation a dimensionless parameter, T, is introduced that is defined as the ratio of the number of equivalents that have exited the column to the number of equivalents of exchange capacity retained by the column for a particular ion.

$$T = Co\,(v - EV) / p_b\, q\, V \tag{3.5}$$

where,

Co – feed solution normality (eqv/L)
v – volume of feed solution exiting the column (L)
V – bed volume (L)
E – packed volume void fraction
q – ion exchange capacity (eqv/g)
p_b – bulk density (g/L)

There are two methods of solution, one for compressive behaviour and one for dispersive behaviour. In most ion exchange examples compressive behaviour occurs. For situations with compressive behaviour,

$$T = (Yf - Yp) / (Xf - Xp) \tag{3.6}$$

where,

Yf – resin phase concentration of species in feed plateau (eqv/L)
Yp – resin phase concentration of species in presaturation plateau (eqv/L)
Xf – solution phase concentration of species in feed plateau (eqv/L)
Xp – solution phase concentration of species in presaturation plateau (eqv/L)

If T can be calculated, equation 3.5 can be solved for v to give the volume of feed that can be passed through the resin be before breakthrough occurs. As a result of the many assumptions that are made using the local equilibrium model it is limited in its ability to accurately predict ion exchange especially since most applications involve a multi-component feed.

3.4.2 –Equilibrium Column Model

The equilibrium column model is similar to the local equilibrium model in that it ignores kinetic resistances. By conducting bottle point tests a Freundlich isotherm can be established to indicate the equilibrium characteristics of an ion exchange resin. Once the Freundlich constants, k and n have been determined to show how the ion exchange equilibrium capacity changes with the solution concentration, the breakthrough time can be predicted by the following equation:

$$t_b = V*q_o/Q*C_o \tag{3.7}$$

where,

t_b – time to breakthrough (min)
V – volume of resin bed (L)

Q – feed flowrate (L/min)
C_o – feed concentration (eqv/L)
q_o – volumetric operational exchange capacity (eqv/L)

This method is particularly useful for quick estimates of the breakthrough time for a specific scenario. If isotherms have not been determined the ion exchange capacity given by the manufacturer can be used as an estimate for q_o.

3.5 - Process Description

There are five steps involved in the operation of every columnar ion exchange treatment unit. They are:

1. Service Run Until Breakthrough Point
2. Backwash
3. Regeneration of Exchanger Medium
4. Slow Water Rinse
5. Rapid Water Rinse

Ion exchange systems run through these five steps continually until their capacity decreases enough to warrant resin replacement. The life of a resin is usually several years.

3.5.1 - Service Run Until Breakthrough Point

The contaminated water is passed through a column packed with an ion exchanger. The ion exchange resin beads have a nominal diameter of 0.5-1.0 mm. Contaminant ions are exchanged for chosen replacement ions and the exchanger is utilized until the effluent concentration reaches the predetermined breakthrough value. Flow is generally downward with contaminated water flowing through the tortuous path of the medium. Flowrates can vary from about 9-27 times the ion exchange bed volume per hour to allow sufficient contact between the two phases. (i.e. empty bed contact times from 2-7 minutes) Manufacturers also recommend minimum bed depths of 30 to 45 cm.

3.5.2 - Backwash

Once the breakthrough concentration is reached, the column is taken off-line and backwashed (reversal of flow) with demineralised water to remove suspended debris and eliminate pathways that may have formed through the bed. Any air entrapped in the media is also removed. The medium should be fully fluidised and will redistribute itself according to the particle size (larger particles at the bottom). For proper fluidisation, the bed must expand 50-100% and this must be accounted for when designing the column. The process takes about 5-30 min with a flowrate that is sufficient to achieve proper fluidisation.

3.5.3 - Regeneration of Exchanger Medium

Regeneration consists of subjecting the exhausted medium to a solution highly concentrated in the original mobile exchange ion. In this manner, it will replace the contaminant ions attached to the exhausted medium. By using relatively high concentrations and slow flowrates (approximately 2-4 bed-volumes per hour) this exchange can be done very efficiently, leaving the contaminant in a much smaller volume than it was previously. Regeneration can be done using co-current or counter-current flow.

3.5.3.1 - Co-current Regeneration:

In co-current regeneration, the flow is in the same direction as in operation (downward). This is the most common type of regenerant flow. The problem inherent in co-current flow is that the media at the bottom receives less regeneration because the regenerant solution has already exerted some of its capacity by the time it reaches the bottom. This can cause problems with leakage of contaminants. Co-current regeneration requires 200-400% of the theoretical stoichiometric mass of regenerant.

3.5.3.2 - Counter-current Regeneration:

Counter-current regeneration is conducted with an upward flow set-up. The medium at the bottom is exposed to the 'freshest' regenerant and thus the leakage problem is not encountered. Counter-current flow is more costly due to the complexity of the equipment and the cost of pumping water. However, the regenerant requirements are greatly reduced with only 125-150% of the theoretical amount of regenerant required. The regeneration process takes about 1-2 hours to complete (Rhom and Haas Ion Exchange Laboratory Guide, 2001).

3.5.4 - Slow Water Rinse

Regeneration must be completed after the final liquid has entered the ion exchange media. This is accomplished by continuing the flow as in regeneration but using demineralised water to displace the last bed volume of regenerant. The volume necessary for this step is usually in the order of 1-2 bed volumes.

3.5.5 - Rapid Flow Water Rinse

Another rinse, with demineralised water and a rapid flowrate is used to remove all of the regenerant within the ion exchange bed. It is conducted for 10-30 min at about 9-27 BV/h, or at a flowrate equivalent to that of the service flow. After this final rinse has been accomplished the system is put back into service although some resins require a second backwash.

3.6 - Ion Exchange Applications

Ion exchange is found in various places throughout industry, laboratories and in homes around the world. Some of the most common applications are discussed in this section.

3.6.1 - Hardness Removal

Water with high levels of hardness (calcium and magnesium) can cause problems when these minerals precipitate in unwanted places. Removing hardness was the first ion exchange application and is its principal application within water treatment (Clifford, 1999). This is a very popular option in the treatment of well water within rural homes. A cation resin in the sodium cycle is used. In other words, the majority of the ion exchange sites are taken up by sodium. Since calcium and magnesium are divalent they exert more affinity to the resin and are exchanged for sodium, which does not precipitate as readily. An example of ideal concentration profiles and breakthrough curves for typical softening and radium removal are shown in Figure 3.7. In the example in the figure, the first contaminant ion to appear in the effluent would be magnesium. In a real softening application, the system would be taken off-

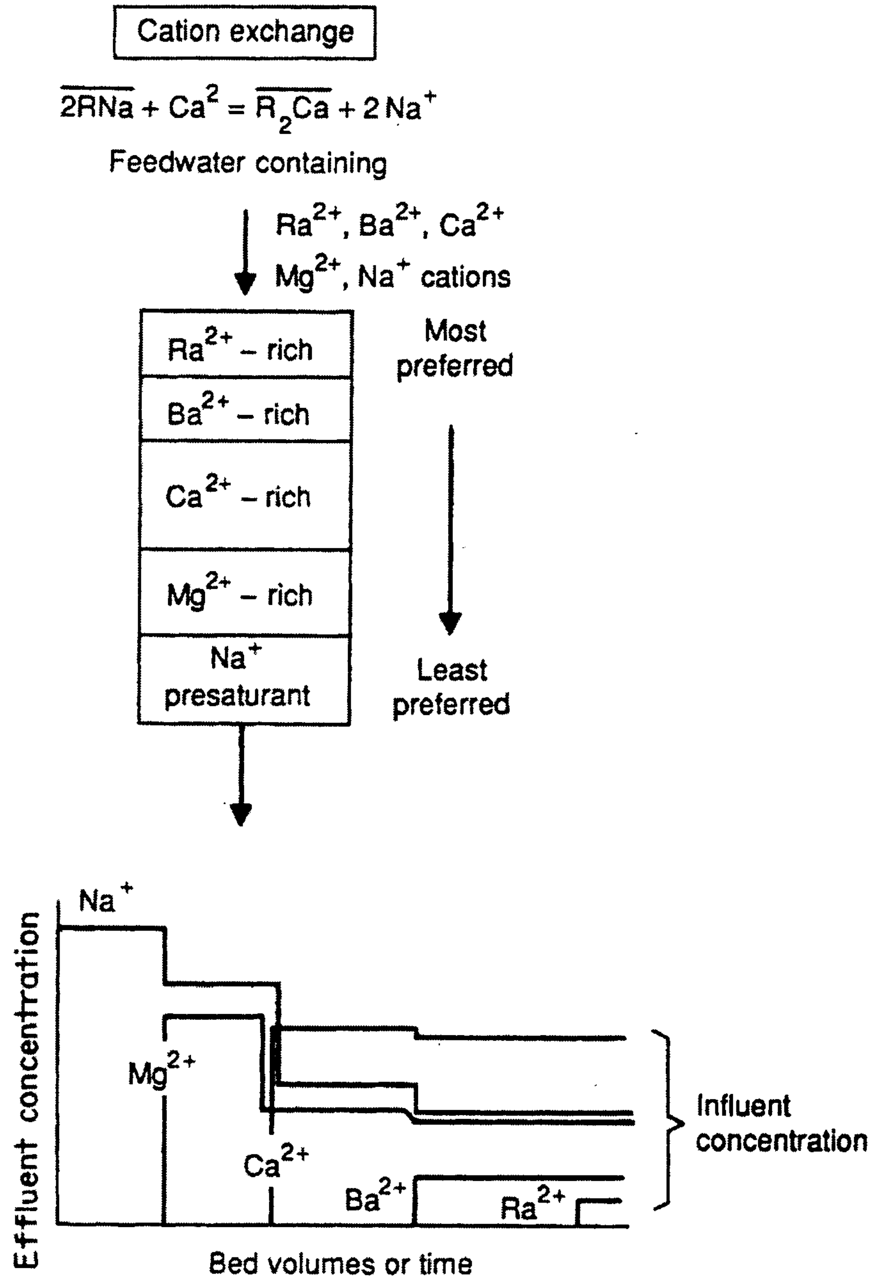

Figure 3.7 - Ideal Resin Concentration Profile (above) and Break-through Curves for Typical Softening and Radium Removal (Clifford, 2000)

line for regeneration once the first contaminant is detected in significant concentrations in the effluent.

3.6.2 - Measurement of Trace Quantities

The ion exchange process is essentially a method of concentrating ions into a smaller volume. The ions from a large volume of water are collected within the resinous matrix during the service run and then released in a much smaller volume of water during regeneration. Therefore, when substances, such as heavy metals, exist in water at a concentration below the detection limits of available equipment, the metals can be concentrated by ion exchange to allow an accurate determination of the original concentration (Rhom and Haas Ion Exchange Laboratory Guide, 2001).

3.6.3 - Metals Recovery

In the metal plating industry a large quantity of wastewater is produced that contains metals. Ion exchange can be used to concentrate and separate these metals solutions. By concentrating them, they can be recovered as metal salts or, sometimes, electrowinning is used, which involves plating the dissolved metals onto a conductive surface to obtain them in their elemental form. An example of this type of system is shown in Figure 3.8. Since each ion in the solution exerts a different affinity for the ion exchange resin, they can be separated. This technique has been used effectively in the recovery of many valuable heavy metals (Dally et al., 1996).

3.6.4 - Industrial Waste Treatment

As effluent guidelines continue to become more stringent, the applications of ion exchange within industrial wastewater treatment are increasing. There are many

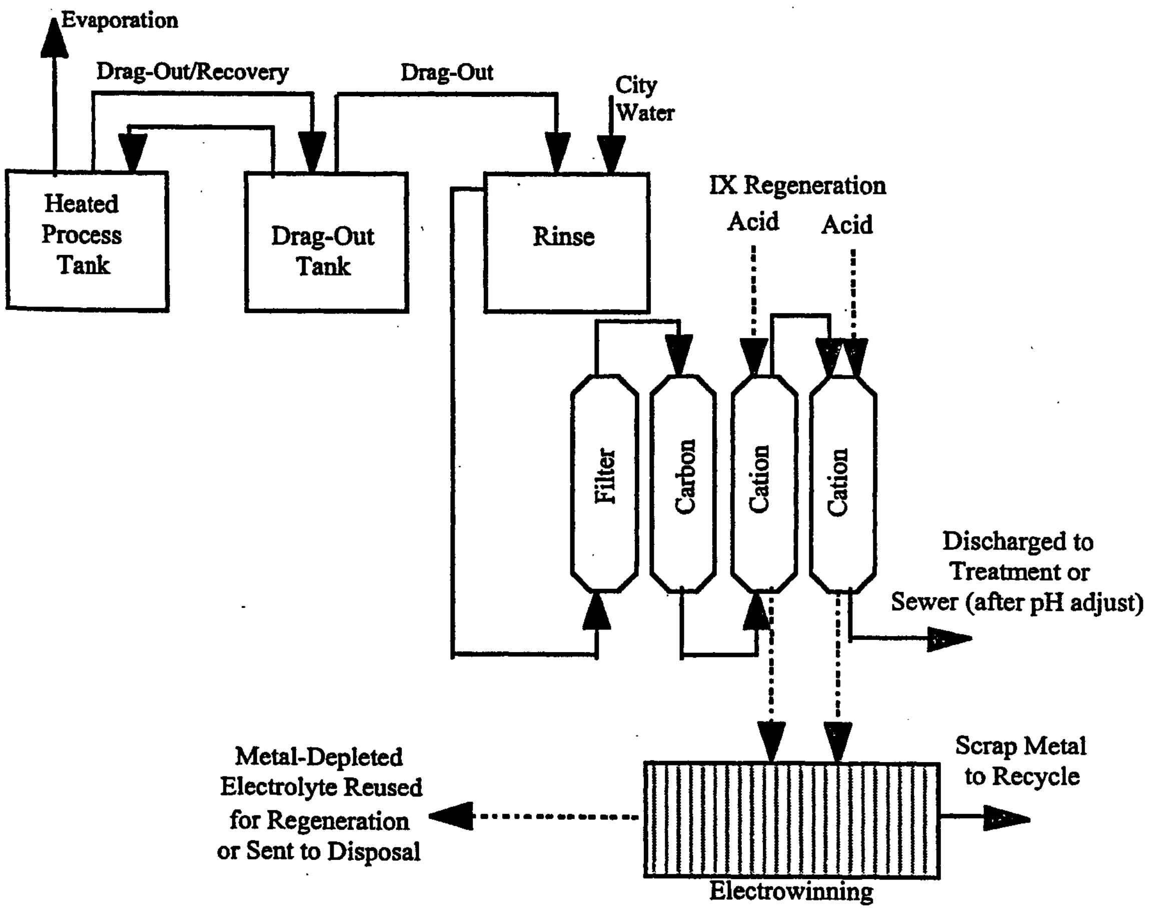

Figure 3.8 – Ion Exchange with Metals Recovery (USEPA, 1998)

restrictions on metals entering sewer systems and ion exchange is excellent for metals removal. Using ion exchange can be somewhat complicated since many industrial wastes contain materials that cause fouling or attack exchange materials. However, synthetic resins are very resistant to chemical and physical attrition and are not soluble in most organic solvents (Weber, 1972).

3.6.5 – Removal of Natural Organic Matter

Natural organic matter (NOM) is found in all surface waters and has been found to be a precursor to disinfectant by-products, such as trihalomethanes. Granular activated carbon (GAC) has been found to be successful as a treatment technology for the removal of NOM. However, GAC systems are not long lasting and the carbon must be removed from the system for its regeneration. Since most humic substances found in surface waters are anionic, studies have been conducted to consider macroporous anion exchange resins for removal of NOM. Some studies have examined using ion exchange in conjunction with GAC to prolong the life of the GAC bed. Figure 3.9 shows the results of a study that compared the life of a GAC bed used for NOM removal with the life of an IX/GAC system. (Sengupta, 1995) The graph shows how the combined IX/GAC system gave a lower level of total organic carbon (TOC) in the effluent than the traditional GAC system after about 2000 bed volumes of cumulative flow. It also shows how the IX/GAC system maintained the higher purity effluent beyond 5000 bed volumes.

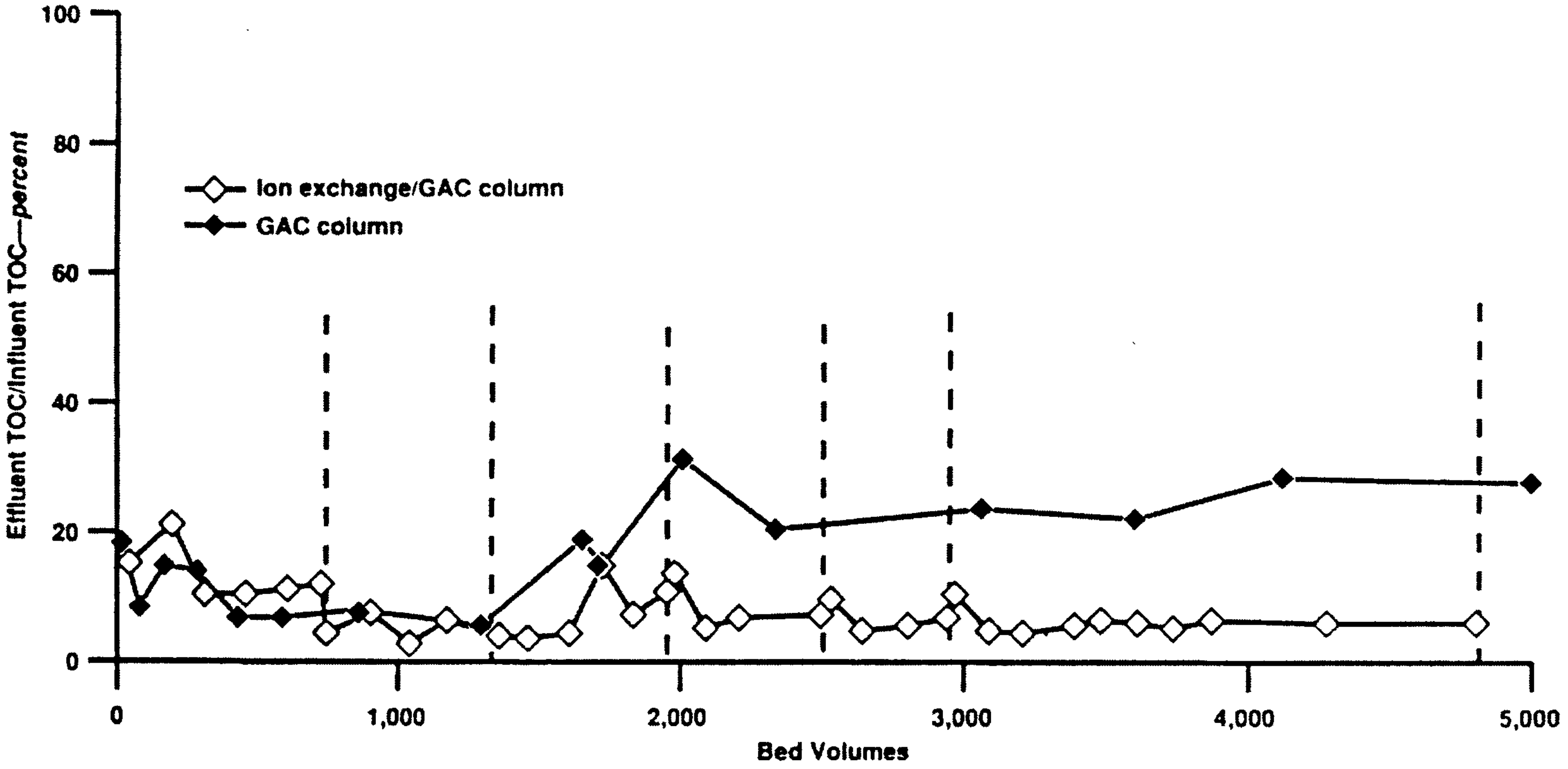

Figure 3.9 - Bed Life of GAC/IX System Compared with Bed Life of Traditional GAC System (Sengupta, 1995)

3.7 – Ion Exchange for Demineralisation

One of the most valuable applications of ion exchange is the demineralisation process. It involves two ion exchange columns in series. The first contains cation resin in the hydrogen form and the second contains anion resin in the hydroxide form. The idea is that all cations in solution are exchanged with hydrogen and all anions exchanged with hydroxide resulting in demineralised water. The process generally contains two-beds with the cation resin ahead of the anion resin as shown in Figure 3.10, although sometimes the order is reversed or the resins are mixed together as in a mixed-bed system (Applebaum, 1964).

3.7.1 - General Considerations

Since ion exchange is never 100% complete and there is always some ion leakage, demineralising systems are designed to treat water to a given degree of leakage. The amount of excess regenerant used (a major operational cost) can be increased in order to reduce ion leakage. The first ion to breakthrough the maximum allowable concentration is usually sodium (from the cation bed) or silica (from the anion bed). When sodium leaks from the cation bed it enters the anion bed where sodium hydroxide is formed. Thus, in a demineralisation system cation leakage results in an increase in effluent pH.

3.7.2 - Counter-flow Regeneration

As discussed in a previous section, counter-flow regeneration can be used to reduce ion leakage. In demineralisation it is used when the influent is high in solids and has

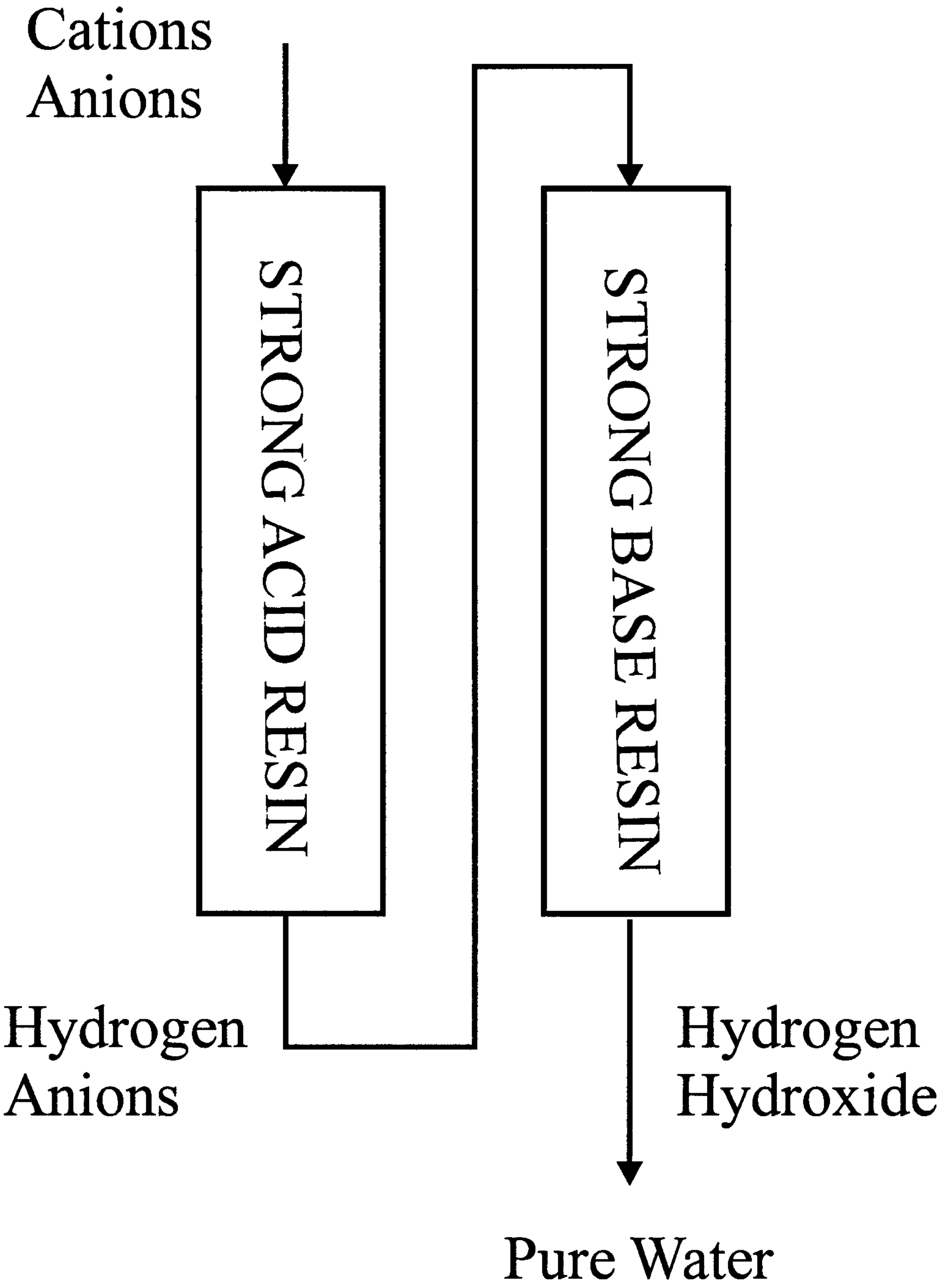

Figure 3.10 - Ion Exchange Demineralisation Set-up

a large amount of sodium. If this is not the case, down-flow regeneration is just as effective and less costly (Applebaum, 1964).

3.7.3 - Four-Bed Demineralisers

To accommodate larger designs where very pure water is required and the amount of excess regenerant needed to achieve the desired level of purity is unreasonable, two systems can be used in series. Thus, the effluent from a demineralisation system is run through another demineralisation system. Once the breakthrough concentration is reached in the first set of columns, they are regenerated and can be brought back on-line as a polisher for the second set of units if the resins are the same type. Sometimes, the second anion exchange column contains a WBR since the few contaminants that a WBR cannot remove (dissolved carbon dioxide and silica) would already be removed using the first anion column with a SBR. A diagram of a four-bed system is shown in Figure 3.11. In this figure SA, WB, SB and D are used to represent a strong acid resin, a weak base resin, a strong base resin and a vacuum degasifier (for removal of dissolved gases).

3.7.4 - Mixed-Bed Demineralisers

Mixed-bed (MB) demineralisers are created by mixing a cation resin and an anion resin within one column. The column acts as a series of many demineralisation systems in a row. There are several advantages offered by a mixed-bed system. The main advantage is a higher purity effluent. MB units are often used as polisher systems after two-stage demineralisers or reverse osmosis. They work well when the influent is very dilute with low solids concentrations and are especially applicable in

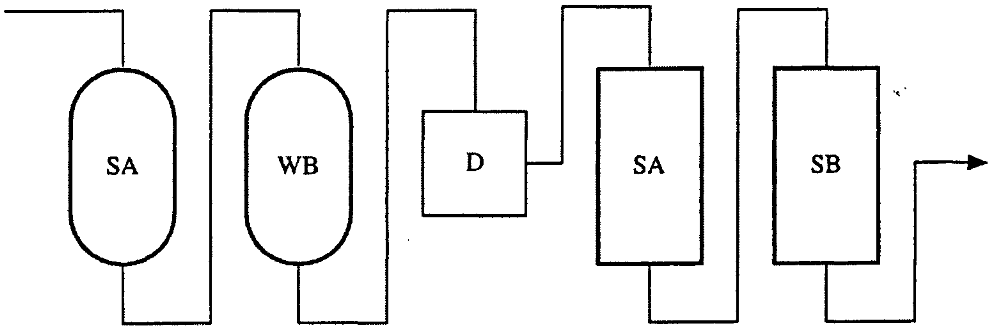

Figure 3.11 - Four-Bed System with Degasification (Etzel and Wachinski, 1997)

situations where simple operation is desirable. The resins are mixed together and must be separated for regeneration because they use different regenerants. Often, MB demineralisers are used until the mixed resin is spent, then the resin is removed to a barrel and replaced to accommodate the following service run. The spent mixed resin can be sent off-site for regeneration or simply disposed of. Some MB systems are set-up to self-regenerate as shown in Figure 3.12. The resins have different densities and can be separated while backwashing.

3.7.5 – Organic Fouling of Demineralisers

In general, it is desirable to remove all organics from a solution before treating it with ion exchange since organics tend to foul ion exchange resins. If cations, that easily form precipitates with hydroxide, are allowed to pass into the anion bed, fouling can also occur. Activated carbon can be used to remove organics from solutions, however, sometimes it is not totally effective. Organic traps are anion exchange resins that are regenerated with sodium chloride. They can be very effective in removing organics and are sometimes used as a pre-treatment for demineralisation systems (Hill and Lorch, 1987). Macroreticular resins are more porous and facilitate elution of organics during regeneration to reduce fouling. They can be used for the uptake of target non-polar organics.

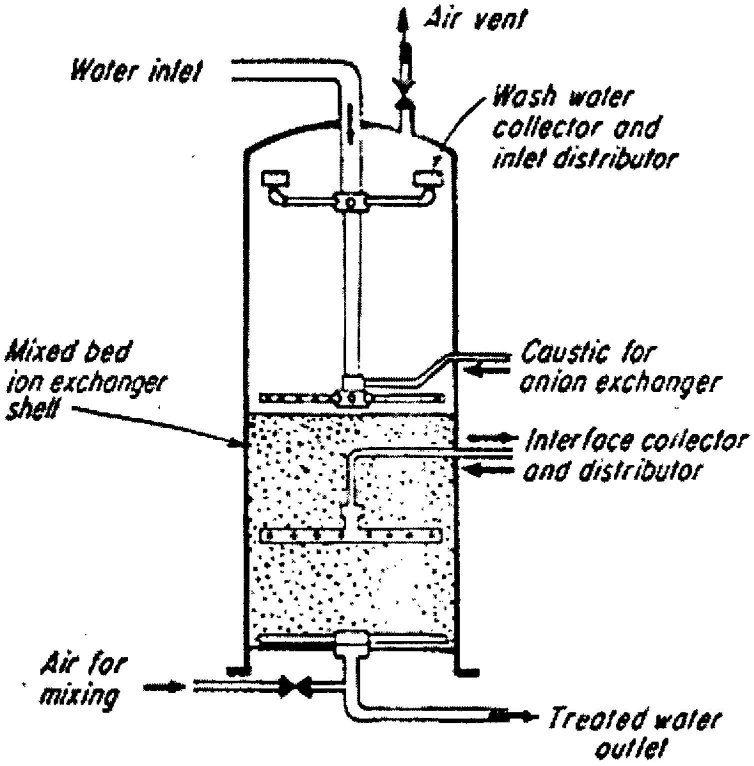

Figure 3.12 – Self-Regenerating Mixed-Bed System (Applebaum, 1968)

CHAPTER 4 – EXPERIMENTAL METHODS

Filtran Microcircuits Incorporated (FMI) is a relatively small printed circuit board manufacturer. They produce boards for many different applications and use mostly conventional plating technologies. Filtran has over 25 flowing rinse baths within their plating operations. The source of water currently used for these flowing rinses is municipal drinking water. These baths all have different flowrates, different concentrations and different contaminant constituents, since they follow a variety of process baths in the manufacturing line. One of the goals of this project was to analyse all flowing rinse baths and try to quantify an overall flowrate as well as the concentration of each constituent. This was done in order to create a solution that represented water that would be created if all the flowing rinse bath effluents were mixed together. This allowed the creation of a synthetic wastewater that could be used as a feed for treatment experiments.

The five main process lines that were analysed include two copper plating lines, an electroless copper line or PTH line and two gold plating lines that include nickel and copper as a sub-surface coating. Schematics of each of these process lines are shown in Figure 4.1. Many of the baths include proprietary chemistry making it very difficult to find out what constituents are present and in what concentrations. This was especially true for organic brighteners that are present in many of the plating baths. A photo of a copper plating bath is shown in Figure 4.2. There are 25 individual flowing rinse baths supporting the five manufacturing lines in the analysis. In addition to the flowing rinses, there are 36 process baths where various chemical

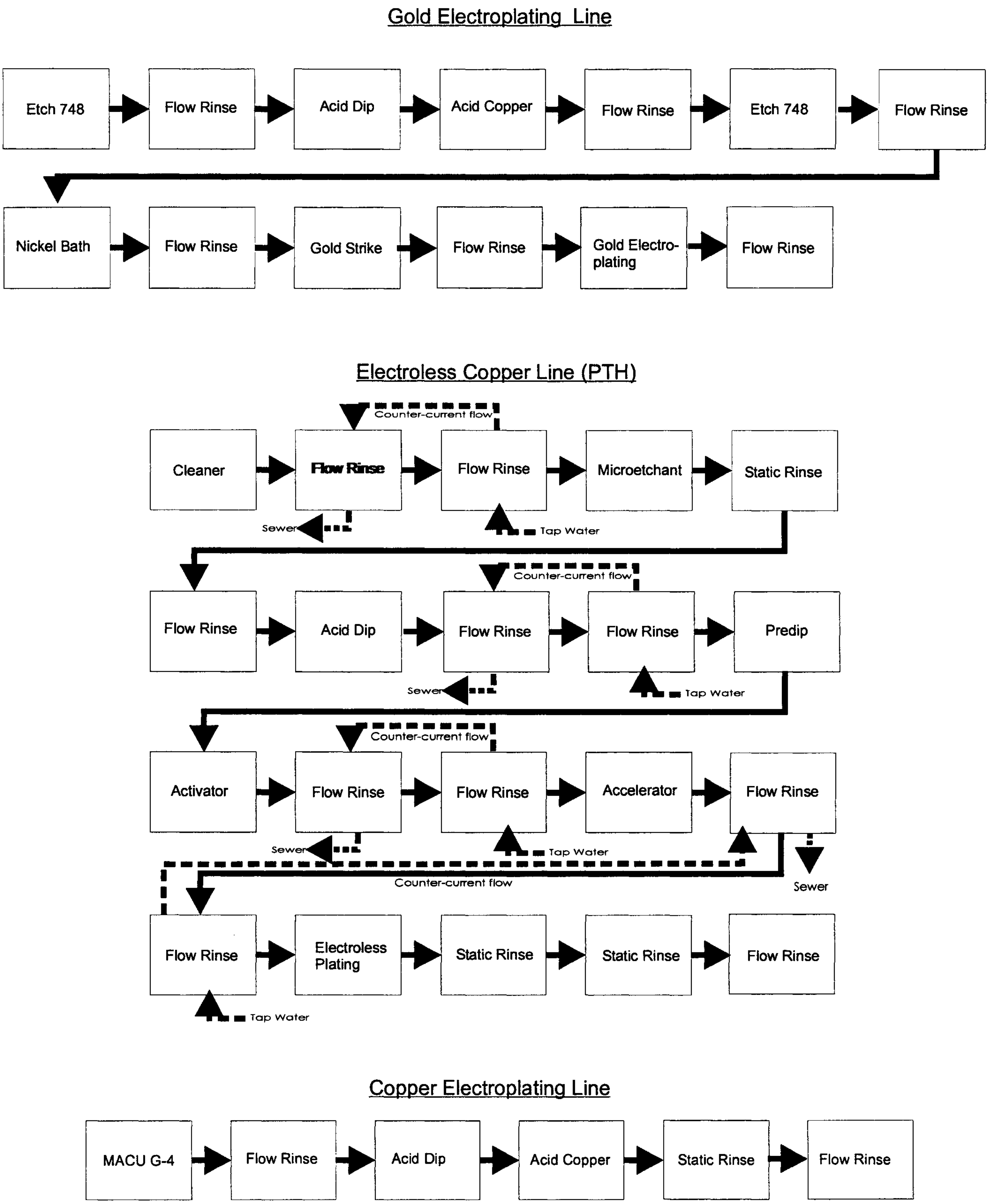

Figure 4.1 - Process Flow Diagrams

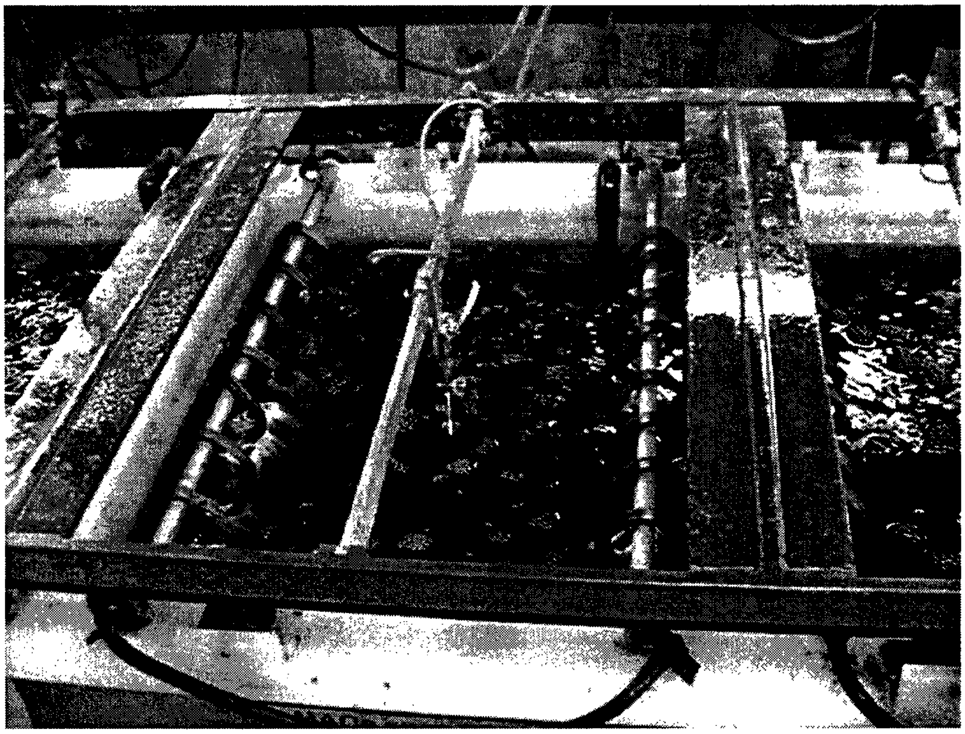

Figure 4.2 – Photograph of Copper Plating Tank

and electrochemical reactions take place. The two gold plating and two copper plating lines are designed to process only one panel at a time. However, in the PTH line many panels are processed simultaneously, using a panel rack as shown in Figure 4.3. The flowing rinse baths vary greatly in volume with 265 L each in the PTH line and only 16 L each within the gold line. The copper line flowing rinse baths each have a volume of about 60 L.

An ongoing literature review was being conducted during the project, to allow the determination of a treatment system that would be appropriate for the given situation. In order to give focus to the search for an appropriate treatment technology, some preliminary sampling was necessary to have an idea of the magnitudes of the concentrations in the flowing rinse baths.

4.1 – Preliminary Sampling

The sampling was conducted in two phases. The preliminary phase included sampling from only two flowing rinse baths (in the PTH line) and analyzing them for copper, the predominant metal used in printed circuit board manufacturing. These data were used primarily to test the atomic adsorption (AA) spectrometer at FMI against an inductively coupled plasma (ICP) spectrometer at the University of Ottawa and to compare the results using glass and polypropylene sample containers. The comparison between glass and polypropylene was performed because copper has the tendency to adsorb onto glass surfaces (Standard Methods for the Examination of Water and Wastewater, 1998).

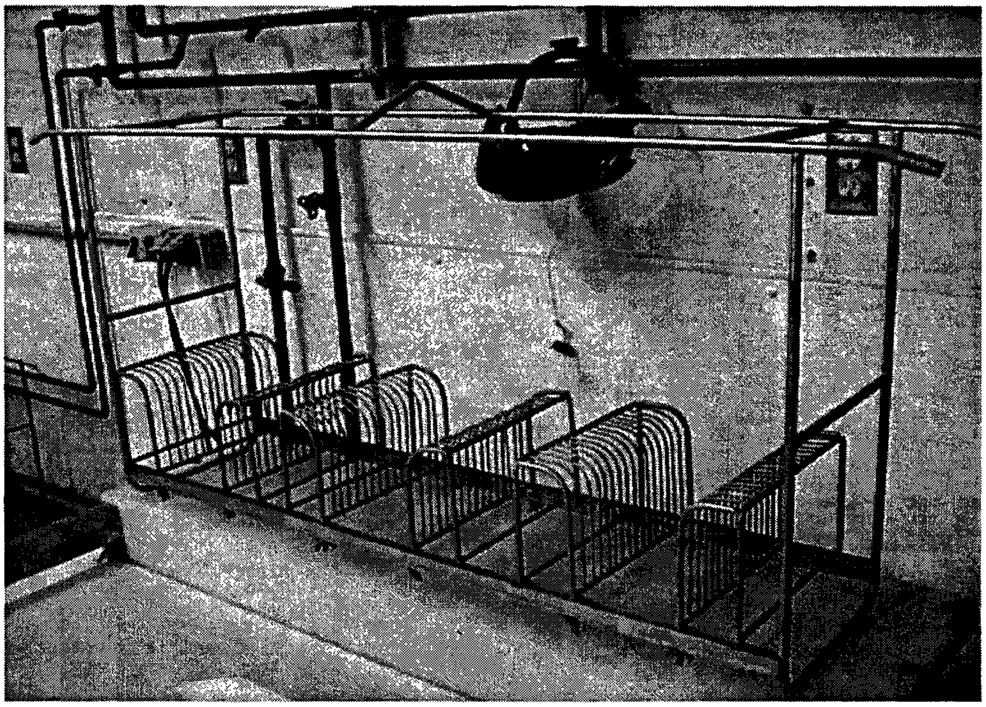

Figure 4.3 – Photograph of Panel Rack

When a panel or a rack of panels is immersed into a flowing rinse bath, there is an initial concentration peak. The concentration then diminishes according to complete mixed basin dynamics until it is negligible. In the first phase of preliminary sampling this phenomenon was observed by taking samples of the same rinsing bath every ten minutes, beginning at the moment the panels were removed.

The AA unit that was used is a Varian 220FS (Varian Systems Inc., Palo Alto, California) and standard method 3111-B was used. The AA unit gave results that were almost identical to those generated by the ICP using standard method 3120-B at the University of Ottawa. The results from samples taken in glass and polypropylene containers over time are given in Figure 4.4. The glass containers did not show any signs of adsorbing copper, at least not any more than the polypropylene containers since on average their copper concentrations were slightly higher. Thus, both glass and polypropylene sampling vessels were used throughout the sampling in the second phase. As can be seen in the graph, the copper concentrations peaked at about 1 mg/L and decayed to about 0.4 mg/L after 30 minutes. The question, then, became whether to design a system based on the peaking concentration since that value is the extreme situation that may be faced by a treatment system. However, the nature of the manufacturing process is such that the panels run from the beginning of the line to the end and a situation where all the flowing rinse baths were peaking in concentration simultaneously would never occur. Although the concentrations of copper in the flowing rinse wastewater were found to be very low (well below the local sewer copper limit of 3 mg/L), when recycling the water for reuse in rinsing applications it is necessary to eliminate several key ions that can be problematic in the

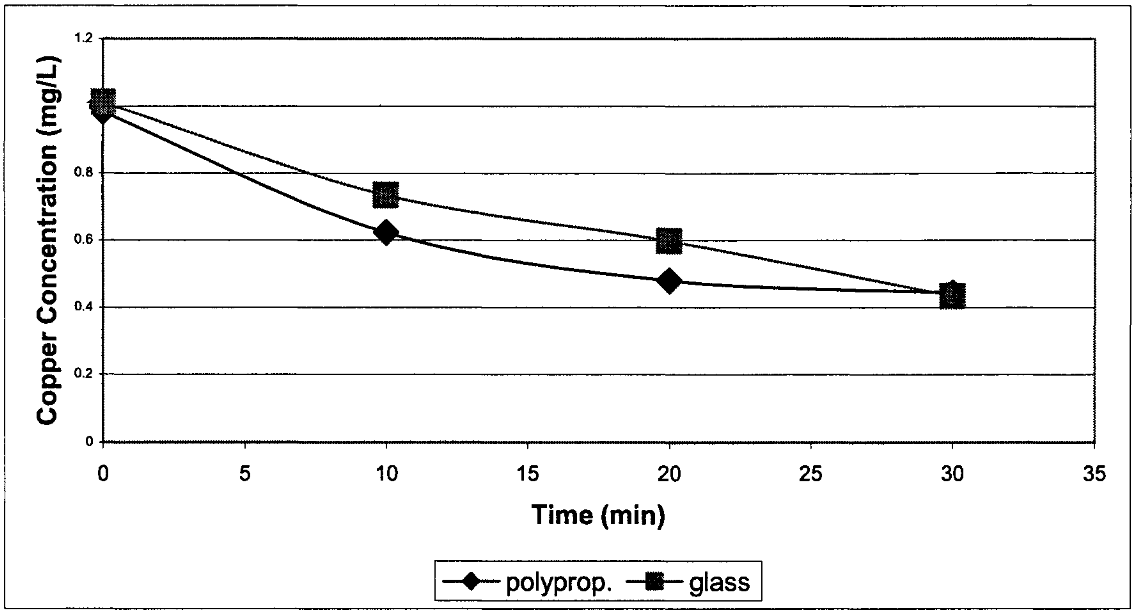

Figure 4.4 – Post-Immersion Copper Concentration for Glass and Polypropylene Sampling Containers

manufacturing process. These ions were discussed in section 2.3.1 and include chloride, magnesium, calcium and silica among others.

4.2 – Flowrate Determination

The determination of flowrates for the 25 baths was performed in several different ways. Some flowing rinse baths have an influent hose that could simply be shifted to flow into a graduated container and timed. Other baths have an influent hole at the bottom of the tank, and it was necessary to empty the bath and then measure its volume and the time it took for it to reach the overflow level. However, one measurement of each bath was not sufficient because none of the influent flowrates are controlled and thus, they vary over time depending on how much water is being used in the building at a particular time. To obtain a meaningful value for each bath, the flowrates were measured many times and an average was taken. In addition, it was found that some of the process lines are only operated for 8 hours per day while others are operated for close to 16 hours per day. These values also depend greatly on market demand. It was found that, when all of the flowing rinse baths are running they use about 110 L/min. When market conditions are at their peak, all the processes may be used for an average of 16 hours per day, translating into over 100 m^3/d. Table 4.1 shows the results of the flowrate analysis. Note that EC, GP and CP refer to electroless copper plating, gold plating and electrolytic copper plating lines respectively and the numbers refer to the order of the flowing rinse baths along the process train. The flowrates range from 320 mL/min to 12.5 L/min. Note that the flowing rinses within the two gold lines (GPa total and GPb total) have very different flowrates. This is because they were constructed at different times. The newer line is

Table 4.1 – Flowrate Analysis of Flowing Rinse Baths

Flowing Rinse Bath Code	Flowrate (L/min)
EC1/2	2.6
EC3	2.9
EC4	3.3
EC5/6	4.3
EC7/8	5
EC9	4
EC Total	**22.1**
GP1	0.68
GP2	0.69
GP3	1.9
GP4	5.5
GP5	0.35
GP6	0.52
GPa Total	**9.64**
GP7	7
GP8	6.3
GP9	9.6
GP10	10
GP11	6.8
GP12	13
GPb Total	**52.7**
CP1	6.4
CP2	3.6
CP3	1
CP4	2.5
CP5	2.8
CP Total	**16.3**
Total	**100.74**

supported by much higher flowrates ensuring a more complete rinse. The gold plating baths incorporate a manual spray rinse for the panels before they are sent to the flowing rinse bath.

It was noted that many of the flowing rinse baths were run continuously for the duration of the day but were only used occasionally. By introducing the flow when rinsing is required and turning it off a predetermined time afterward, a significant amount of water could be saved.

4.3 – Composite Sampling

The second phase of the sampling was much more in depth. Composite samples were taken including a small amount from each of the 25 flowing rinse baths. The volume taken from each bath was proportional to the average flowrate that was determined for it. Thus, a composite sample that was representative of a mixture of all the flowing rinse baths could be analysed using the AA unit at Filtran. These samples were analysed for copper, nickel, gold and some samples were taken to the University of Ottawa for TOC analysis to obtain an approximate of the organic load using a Rosemount (Dohrmann) DC-180 Total Organic Carbon Analyzer (Rosemount, Santa Clara, Ca) employing standard method 5310c. TOC vaComposite samples were taken routinely, over the course of 2 weeks at a time when market conditions were relatively slow. Table 4.2 shows the results of the composite sampling analysis. The average copper concentration was found to be 0.65 mg/L with the peak concentration being 2.1 mg/L. Gold and nickel were found in much smaller concentrations with the exception of 3 samples where nickel was found to be greater than 1 mg/L. This is

Table 4.2 – Composite Sampling Analysis for Copper, Gold and Nickel within FMI Flowing Rinse Baths

Date	Time	Cu	Au	Ni
		mg/L	mg/L	mg/L
18-Jun	10:00	2.116	n.d.	n.d.
19-Jun	1:15	1.065	n.d.	n.d.
19-Jun	2:15	0.818	n.d.	n.d.
19-Jun	2:50	0.367	n.d.	1.573
25-Jun	8:00	0.18	n.d.	n.d.
25-Jun	9:00	0.627	n.d.	n.d.
25-Jun	10:00	0.366	n.d.	n.d.
25-Jun	11:00	0.307	n.d.	n.d.
26-Jun	1:00	0.042	n.d.	0.067
26-Jun	2:00	0.34	n.d.	1.023
26-Jun	3:00	0.757	n.d.	0.037
27-Jun	9:00	0.425	n.d.	n.d.
29-Jun	11:15	0.201	0.03	n.d.
29-Jun	12:00	0.895	0.03	n.d.
29-Jun	1:15	0.452	n.d.	n.d.
3-Jul	1:30	0.308	0.02	n.d.
3-Jul	2:30	1.059	0.04	n.d.
5-Jul	9:00	1.072	0.02	n.d.
5-Jul	10:00	0.424	0.02	n.d.
5-Jul	11:00	0.572	0.01	1.803
5-Jul	12:45	1.202	0.02	n.d.
6-Jul	9:00	1.43	n.d.	n.d.
Average Concentration		0.68	0.02	0.9
Maximum Concentration		2.12	0.04	1.803

probably due to the small volume and low flowrates of some of the flowing rinse tanks within the gold line (where the only nickel baths are located). No associated gold peaks were found probably because panels are spray rinsed over the gold plating bath to remove much of the valuable gold before the panels are sent to the flowing rinse.

4.4 – Materials Acquisition

The acquisition of materials for the construction of a bench-scale system was undertaken fairly early in the project to ensure that there was sufficient time for the materials to arrive, while still allowing an adequate time period for construction of the apparatus and for the bench-scale testing. Many companies were contacted to request samples of ion exchange resins in August and September 2001 but, unfortunately, due to delays in shipping, some materials took an inordinate amount of time to arrive. The last sample was not received until March, 2002. However, some ion exchange resin was received in October, 2001 and the preliminary runs, for trouble-shooting the system, could be performed. A list of the materials used in the experiments is given in Table 4.3.

Three ion exchange resin companies provided free samples: Purolite (Purolite Resin), Rhom & Haas (Amberlite Resin) and Bayer (Lewatit Resin). These companies sent their recommended resins for demineralisation of a wastewater containing metals and typical ionic constituents, characteristic of tap water. Unfortunately, at the time, the design of a synthetic wastewater feed was not complete and thus, an analysis of the exact wastewater could not be provided. GAC was used as a pre-filter primarily for

Table 4.3 – List of Experimental Materials

Column Materials	Supplier, Location
Amberlite IRC 748 chelating cation exchange resin	Rhom & Haas, Philadelphia, N.J
Amberlite IRA 400cl strong base anion exchange resin	Rhom & Haas, Philadelphia, N.J
Purolite S-930 chelating cation exchange resin	The Purolite Co., Bala Cynwyd, PA
Purolite A-100 strong base anion exchange resin	The Purolite Co., Bala Cynwyd, PA
Lewatit MonoPlus S 100 strong acid cation exchange resin	Bayer Inc., Pointe-Claire, QC
Lewatit MonoPlus M 500 strong base anion exchange resin	Bayer Inc., Pointe-Claire, QC
Serfilco MBD-10 mixed bed resin	Serfilco Ltd., Northbrook, IL
Calgon granular activated carbon CPG – LF 12 x 40	Calgon Carbon Corp., Catlettsburg, KY

organics removal. The GAC used was from Calgon Carbon Corporation with an iodine number of 960 mg/g. Detailed information data sheets for all media used in the columns are given in the Appendix A.

4.5 – Apparatus

Glass was chosen as the material for the columns used in the apparatus since there is a glass blower at the University of Ottawa who could construct the columns and was also available for adjustments and repairs when necessary. The apparatus was first constructed in October 2001, however, it was improved constantly as the experimental work was carried out. A photograph of the existing set-up in February, 2002 is shown in Figure 4.5. A schematic of the experimental set-up is shown in Figure 4.6.

4.5.1 - Columns

The column design was based on schematics from Etzel and Wachinski (Etzel and Wachinski, 1997). The columns varied slightly in length but were about 110 cm with an internal diameter of 22 mm. The media in the columns was supported with a coarse sintered glass disk. The sintered disks were used because the columns are so long that it was difficult to remove glass wool from the bottom. The sintered glass had a tendency to clog over time. To clean them they were soaked overnight in 50% hydrochloric acid. The flow pattern through the columns was observed during each run as copper was exchanged with hydrogen. It caused the resin to turn blue and demonstrated that equal exchange was occurring evenly over the entire bed and no flow channelling was evident.

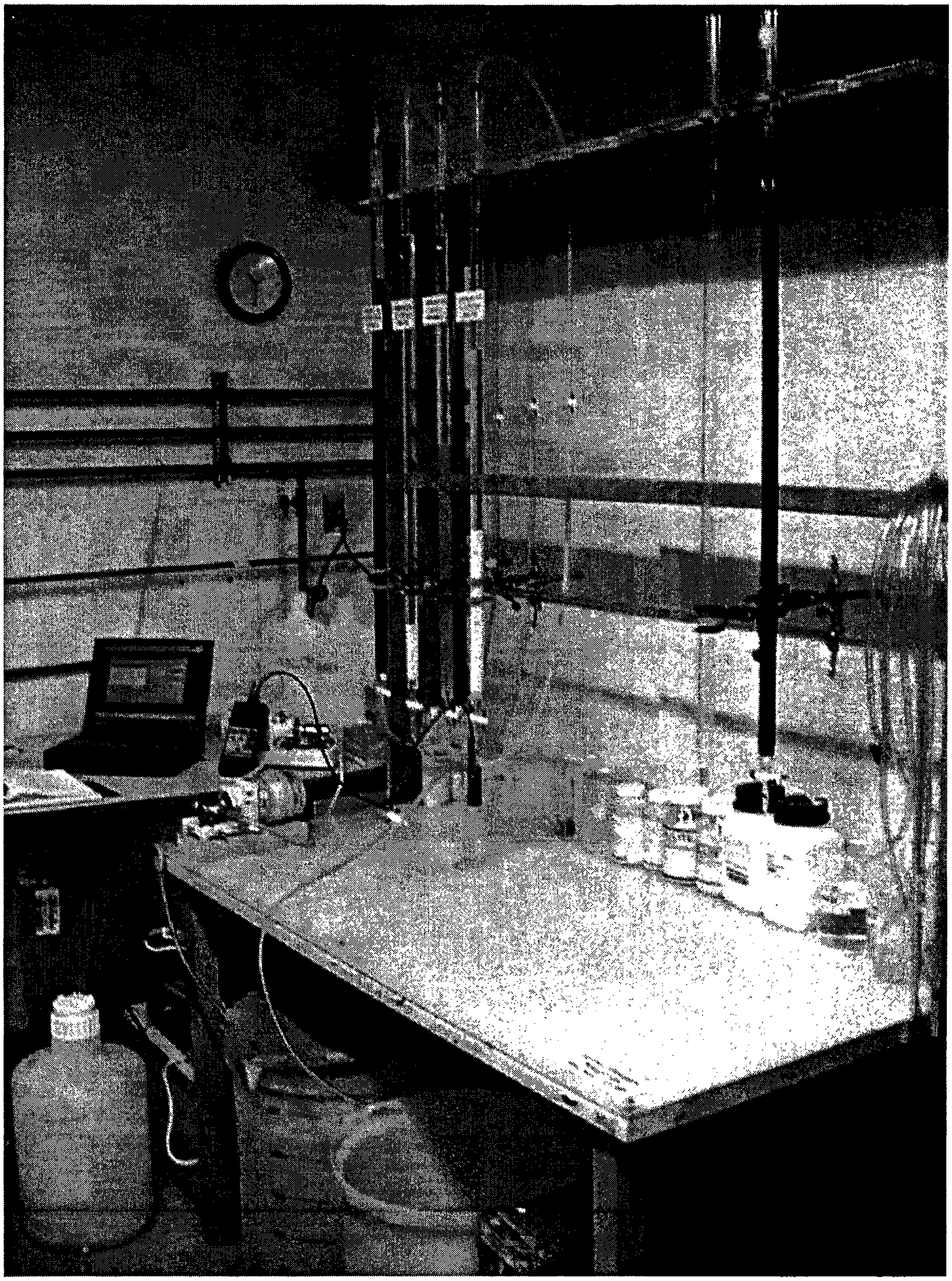

Figure 4.5 – Experimental Apparatus

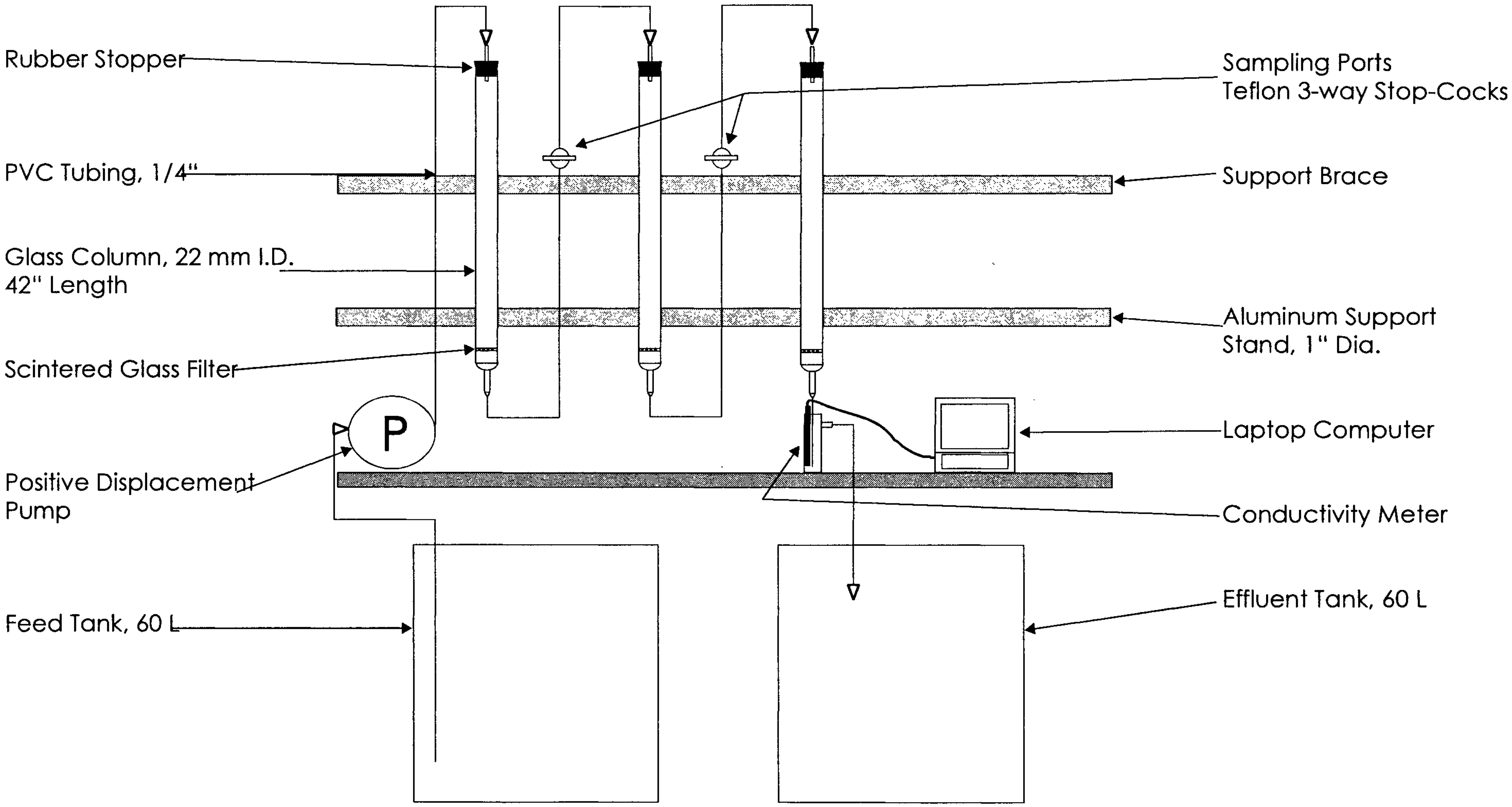

Figure 4.6 - Schematic of Experimental Apparatus

4.5.2 - Pumps

Two positive displacement pumps (model# JB2RO64N, Fluid Metering Inc., Syosset, NY) were used throughout the experiments for the service flow as well as backwashing, regeneration and rinsing cycles. They are capable of producing 1-140 mL/min. It would have been beneficial, in retrospect, to have pressure gauges incorporated in the system so that, during an experimental run, the pressure could be monitored to prevent any unwanted build-ups.

4.5.3 - Conductivity Meter

Since there are a multitude of ionic constituents in the waste flowing rinse water that must be removed, conductivity was used as a surrogate parameter for monitoring removal instead of measuring each constituent. Since the composition of the feed and effluent were fairly consistent, a correlation between conductivity and TDS concentration was made and a conductivity of 30 uS/cm was chosen as the upper limit of acceptable effluent water quality. A hand held conductivity meter (model# 21800-012, VWR, Mississauga, Ontario) was used and incorporated into the apparatus as shown in the photograph in the previous figure. It has the ability to report real-time data to a computer and was set-up in this fashion for the majority of the experiments, ensuring accurate periodic readings.

4.5.4 - Other Materials

Sampling ports were provided, using 3-way stopcocks. They were placed in between each column at a height approximately equal to the top of the resin bed. Two 65 L barrels were used as feed and effluent tanks, however, when demineralised water was being produced it was sent to a 20 L deionised water tank that was used for the backwashing and rinsing cycles as well as to dilute regenerants to their appropriate concentrations. The 6.35 mm PVC tubing was attached to the top of the columns through glass tubes that were inserted into rubber stoppers that served to plug the columns, rendering them airtight. Teflon stopcocks were attached to the bottom of the columns by the glass blower and their tips were burred to facilitate the constant attachment and detachment of tubing that was necessary during the various ion exchange process stages.

4.6 – Feed Preparation

It was very difficult to produce a feed that was consistent using flowing rinse baths, since their concentrations of contaminants vary significantly over time. Thus, to prepare a feed, a sample was taken from each of the process baths that occurs in the manufacturing train immediately before each flowing rinse bath. Flowing rinse baths rinse the film of process bath solution off of the work piece. A small amount of solution was taken from each of the process baths and were mixed and diluted to such an extent that the copper concentration of the mixture matched the maximum copper concentration found from the composite samples of the flowing rinse baths. Three mL from each process bath was diluted into 60 L of tap water, since tap water is used for all the flowing rinse systems at FMI. This produced the final synthetic feed with approximately 2 mg/L copper. Four of the flowing rinse baths in the gold lines were categorized as "low use" or "spray rinse" baths and only half of the amount was taken from these process baths to compensate for low usage. The process bath solutions are monitored and maintained daily and provided a much more consistent feed than could be created from the flowing rinse baths themselves.

4.6.1 - Feed Consistency

To further increase the consistency, enough solution from each process bath was collected and mixed to produce several litres of concentrated feed that could conveniently be diluted to quickly produce a synthetic feed of any concentration. Unfortunately, when combining the pure process bath solutions, they reacted to form a milky precipitate and thus the concentrated solution could not be used. To prevent this, a small bottle was filled with each different process solution and kept separately as shown in Figure 4.7. These bottles could then be accessed easily and the appropriate amount of each could be dispensed into the feed tank dilution water when necessary using a digital micropipette. Each of the thirteen bottles was given a code indicating which process bath it was taken from.

4.6.2 – Constituent Analysis

At that time, a full analysis had not been conducted because the first feed had just been produced. However, many other measurements had been taken to define the constituents of the feed. First of all, as was mentioned earlier, copper, nickel and gold were measured using an AA spectrometer. In the feed solution the copper concentration was about 2 mg/L. The gold and nickel concentrations were about 0.2 and 0.4 mg/L, respectively. Also, it was known that in most cases when copper is added to solutions it is in the form of copper sulphate. Gold is added as gold cyanide and nickel as nickel chloride. Thus, using stoichiometric equivalents many of the

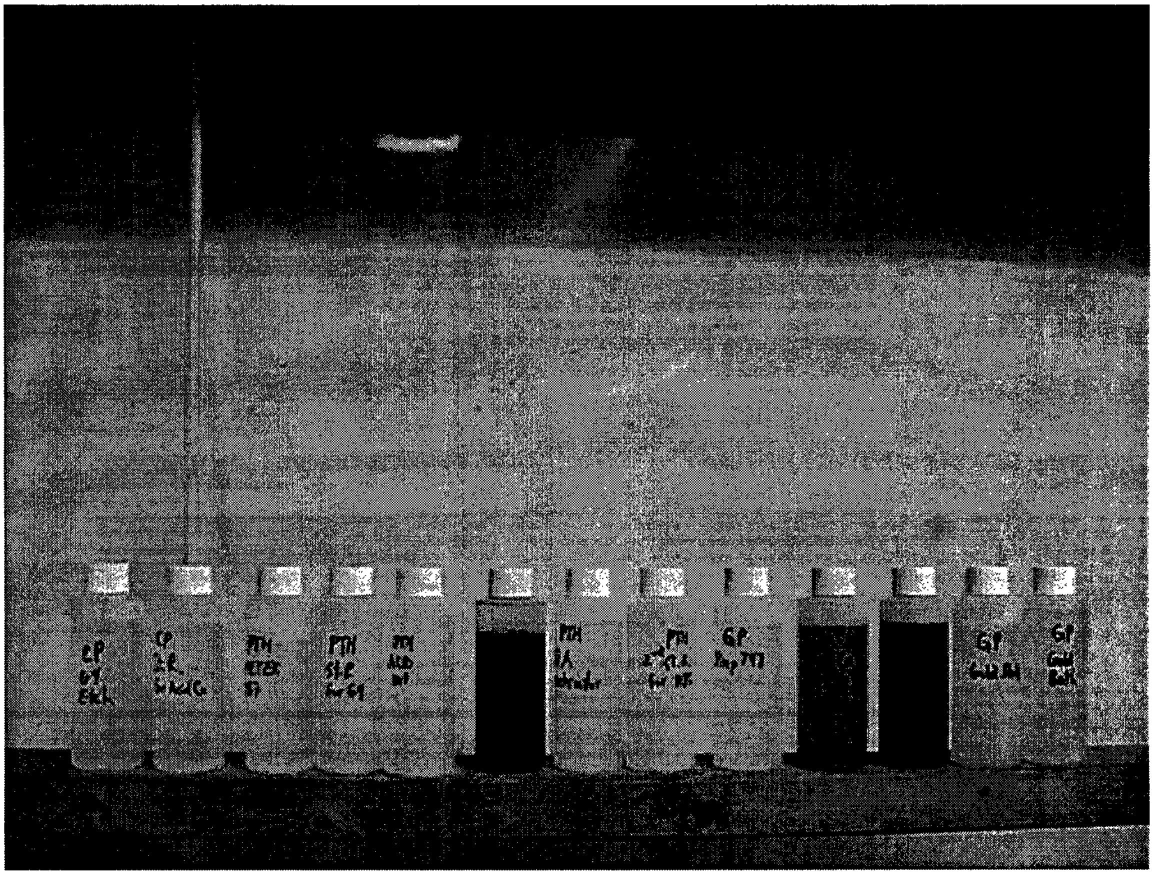

Figure 4.7 – Sample Bottles Containing Various Process Solutions

constituents could be inferred. In addition, data were obtained from the local water treatment plant (see Appendix B) giving the concentration ranges of all constituents in the raw tap water.

CHAPTER 5 – RESULTS

5.1 – Preliminary Experimental Runs

Once the apparatus was set-up as discussed above, deionised water was pumped through the empty columns to check for loose fittings and make sure the pumps could perform appropriately. Upon reading the literature that accompanied the first resin (from Rhom and Haas) it was found that a minimum bed depth of 45 cm should be used in columns. The columns could support a media bed of that height but there was not sufficient room for proper backwashing, so the columns were taken to the glass blower and lengthened to about 110 cm. Rhom & Haas supplied two resins: IRC 748 strong acid cation resin and IRA 400cl strong base anion resin. The IRC 748 resin is a chelating resin selective for metals and will be discussed in more detail later. These two resins were conditioned using 8% HCl for the cation resin and 4% NaOH for the anion resin. This put the resins into the form for a demineralisation set-up. To maintain consistency, the total theoretical exchange capacity of each bed was matched at 240 meq. For example, given two resins with theoretical exchange capacities of 1 meq/L and 2 meq/L respectively. The volume of the latter resin bed would be one half of the former to maintain 240 meq of total theoretical exchange capacity. In this way resins could be compared with each other more easily.

5.1.1 – The First Run

The first run was not successful. Figure 5.1 shows the curve of effluent conductivity versus time. The maximum acceptable effluent conductivity of 30 uS/cm was reached within twenty minutes and the conductivity continued to increase over time,

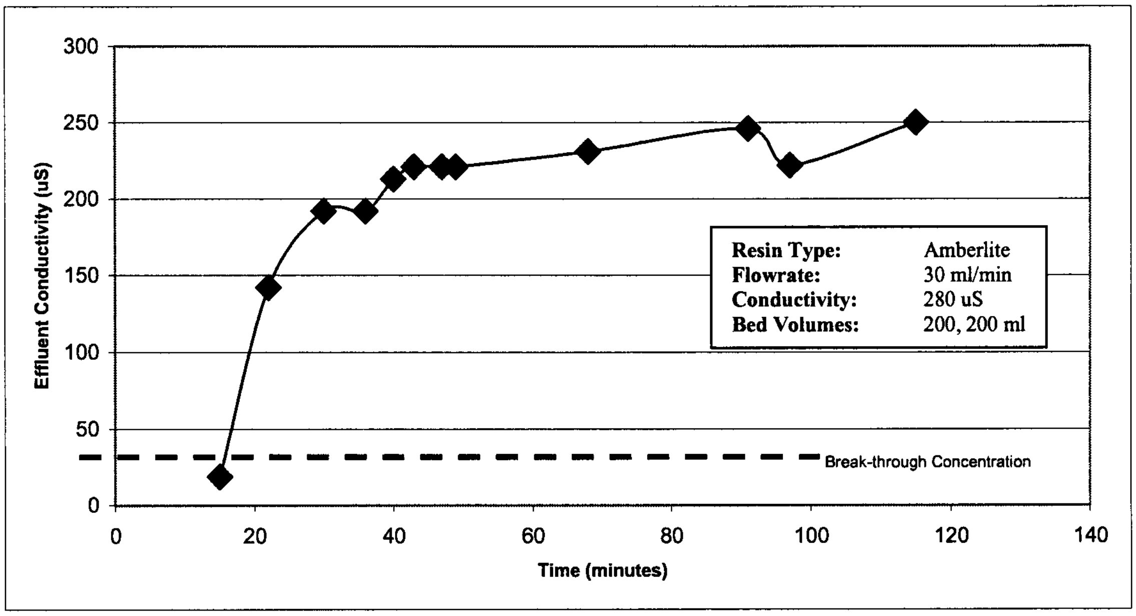

Figure 5.1 – First Run Effluent Conductivity vs Time

indicating that there was a problem with the system. There was an amine smell coming from the anion bed during rinsing, so it was thought that perhaps the anion resin was not conditioned properly. However, after consulting with the technical representatives at both Purolite and Rhom & Haas it was found that the amine smell is normal for anion resins when in the hydroxide form. After rinsing the bed with a few bed volumes of demineralised water the smell disappeared.

5.1.2 - Troubleshooting

The system was regenerated again and re-run and the results were identical: high pH and high conductivity. Since the pH was high, it was known that there was more OH^- being exchanged than H^+ and thus, it was hypothesized that the cation bed was not working effectively. Upon consulting with the technical representative from Purolite, it was suggested that more excess regenerant acid be used for regenerating the cation bed since it seems to be limited. During the next run the amount of excess acid was increased to 150% of the recommended dose given in the resin technical data sheet but the results were as before. This time it was noted that the conductivity of the effluent from the cation bed kept increasing over time while the conductivity of the anion bed remained fairly constant. This is illustrated by the breakthrough curve in Figure 5.2. These data reinforced the hypothesis of an ineffective cation bed.

In order to investigate this hypothesis several steps were taken. To make sure the source of the problem was not the cation resin itself, the feed was run through a different set of resins. The second set of resins was donated by Purolite and they included the S-930 chelating strong acid cation resin and the A-100 weak base anion

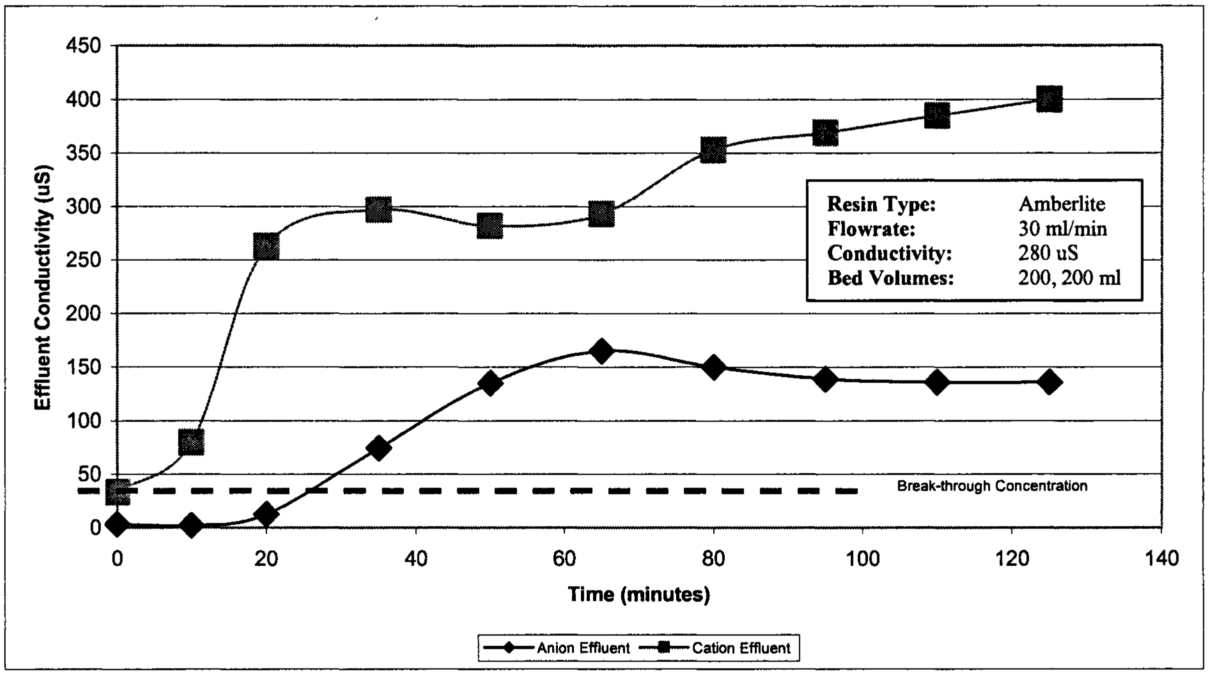

Figure 5.2 – Second Run Effluent Conductivity vs Time

resin. As it turned out, the results achieved using the Purolite resins were identical to the results using the Amberlite resins. As another trouble shooting measure, a different configuration was used where the anion resin bed (or column) preceded the cation resin bed. Since it seemed that the cation bed was not working properly, it was thought that there might have been some anions that have a tendency to complex the cations preventing them from being removed in the cation bed. If the wastewater was sent through the anion bed and exchanged for OH^- first, the complexing anions could be removed and the cations could be exchanged more successfully without these anions present. However, when trying to run the solution through the anion column first, problems were encountered early on, with precipitation of calcium causing the bed to clog and the run could not be continued. As a third measure, samples were taken for analysis to obtain a better idea of the feed constituents and to gauge how the system was performing. The feed samples were sent to ARECO Canada, a company in Ottawa, where a general water chemistry analysis was performed on the synthetic feed. The methods used in the analysis are included in the full report, which can be found in Appendix C.

5.1.3 - Full Feed Analysis

Table 5.1 shows a condensed version of the results from ARECO that includes only those constituents with a significant concentration. The main cations present in order of decreasing concentration were calcium, potassium, sodium, copper and magnesium. All of these cations should be easily removable using a SAR. The main anions present were sulphate, chloride and fluoride. These anions should be readily removable using a SBR. The only analyte found in concentrations greater than 1

Table 5.1 – Summary of Full Feed Analysis

Constituent	Concentration		Constituent	Concentration
Cations	**(mg/L)**		**Anions**	**(mg/L)**
Copper	2.57		Sulphate	66.8
Magnesium	2.0		Chloride	12.6
Calcium	14.9		Fluoride	1.2
Potassium	14.9		**Organics**	**(mg/L)**
Sodium	8.2		DOC	9

mg/L that could cause problems with an ion exchange demineralisation system was the dissolved organic carbon (DOC). However, the GAC bed should have removed most of the 9 mg/L of DOC that was found and the effects of organic fouling would not affect the quality of effluent so early in the run. In addition, the analysis did not include silica, which is both a common constituent in tap water and a problematic contaminant for printed circuit board manufacturing.

A second set of samples was sent out for analysis, this time samples were taken of the tap water, the synthetic feed, from both sampling ports and of the effluent. They were analysed for the major monovalent ions present (sodium, potassium, chloride and fluoride) as well as cyanide, sulphate and silica. The results are shown in Table 5.2. This sampling and analysis took place in January, 2002. It can be seen that everything was being removed successfully except for the cations, which showed zero removal. This proved that the cation bed was not functioning properly.

5.2 – Three-Bed System Experiments

If there was an anionic constituent in the feed solution, that was responsible for attracting the cations more strongly than the resin and 'pulling' them through the cation bed, then the cations should be readily removable once that anionic constituent has been removed. To test this theory, a few litres of effluent from the two-bed demineralisation system was sent through a cation bed again. The cation bed worked successfully in this context and a formal experiment was prepared where the cation resin of the demineralisation system was split into two columns with half of the cation resin before the anion bed and half of it after the anion bed. A portion of the cation

Table 5.2 – Analysis of Samples Taken at Different Stages in the Treatment System

	Concentration, mg/L				
Constituent	**Tap**	**Feed**	**Post GAC**	**Post Cation**	**Effluent**
Fluoride	0.8	1.1	0.9	1.0	ND
Chloride	5.0	11.5	11.1	11.0	0.9
Cyanide	ND	0.013	ND	0.024	ND
Sulphate	23.4	70.9	78.4	94.4	ND
Sodium	2.9	6.8	7.1	6.6	6.9
Potassium	ND	12.6	13.5	11.4	13.1
Silica	5.7	5.7	5.6	5.7	ND

bed was left in front of the anion bed to prevent the precipitation problems from occurring as in the previous experiments with the anion first and the cation second. Figure 5.3 shows the breakthrough curve for the experimental run. It seemed that the cation resin functioned properly when the anions had been removed. Although it was not exactly understood why, a demineralisation system with a cation bed before and after the anion bed demineralised the water successfully.

A series of experiments were then run that involved manipulating the balance of cation resin before and after the anion bed. Three cation balances were used. The first consisted of 25% of the total cation resin before the anion bed and 75% after (25:75). The other two balances used were 50:50 and 75:25. Since the operating flowrates suggested by the manufacturer varies over a wide range, 3 different flowrates were used to determine how flowrate affects performance. Also, three concentrations of feed were used, corresponding to conductivities of about 300, 500 and 1000 uS/cm. This led to 7 different experimental runs that are outlined in Table 5.3. For the runs where the concentration was varied, a flowrate of 60 mL/min and a cation configuration of 60:40 were used. When varying the flowrate, the feed concentration corresponded to 480 uS/cm and the cation configuration was once again 60:40. It should be noted that most of these runs suffered periodic pressure build-ups that caused many operational problems. They were caused by calcium passing through the cation bed and entering the high pH environment of the anion bed, where it had a tendency to precipitate and clog the anion bed. Most of the experiments involving flowrate and concentration as variables had to be stopped as a

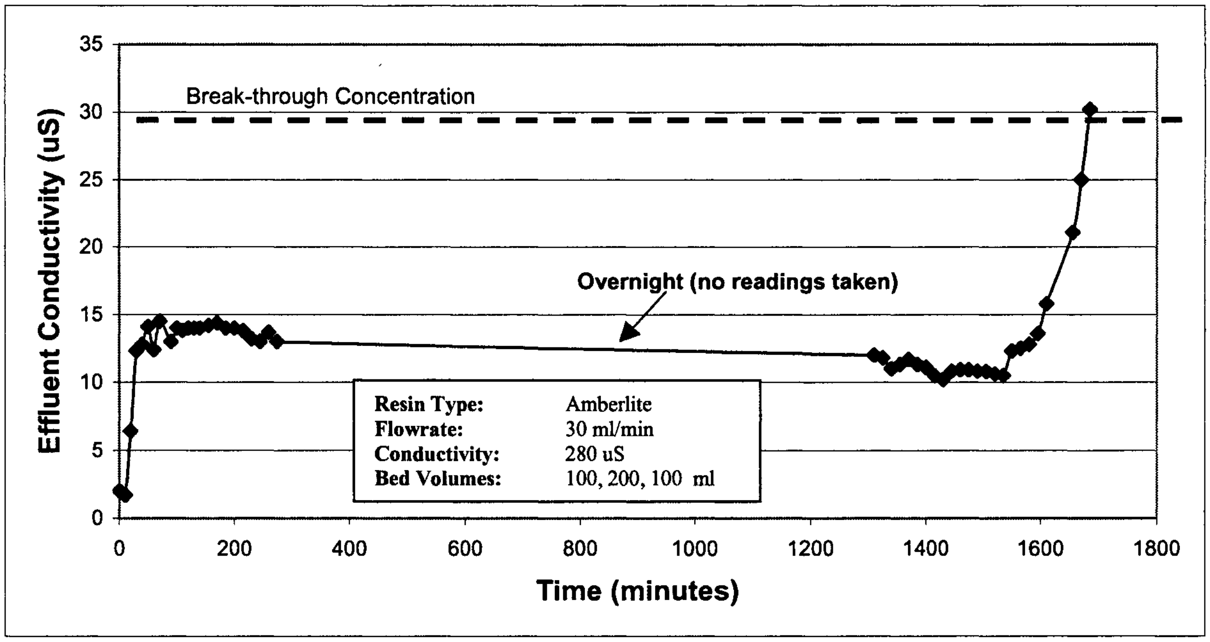

Figure 5.3 – Breakthrough Curve for First 3-Bed Run

Table 5.3 – Summary of 3-Bed Experiments Performed

Run #	Flowrate (mL/min)	Conductivity (uS)	Configuration (Cation1:Cation2)
1	60	480	25:75
2	60	480	50:50
3	60	480	75:25
4	60	260	60:40
5	60	900	60:40
6	30	480	60:40
7	90	480	60:40

result of pressure build-up. The rubber stoppers sealing the top of the columns were forced out of the column several times.

For the cation balance experiments, an ionic concentration corresponding to 470 uS/cm was used with a flowrate of 60 mL/min (18 BV/h) for all three runs. The results are shown in Figure 5.4. The results of manipulating the cation balance show that as the amount of resin is increased in the second cation bed, the exchange capacity of the system is increased. The 25:75 set-up successfully treated 250 meq of ions before breakthrough, while the 50:50 and 75:25 set-up treated only about 175 and 100 meq, respectively, before breakthrough. The average effluent quality was also better for the 25:75 set-up at about 11 uS/cm while the 50:50 and 75:25 showed average effluent conductivities of about 12 and 16 uS/cm, respectively.

The cation bed seemed to work consistently when placed after an anion bed, but the cation bed before the anion resin seemed to be ineffective. The total amount of cation resin in the system was always the same, but when more was placed after the anion bed, the operational exchange capacity of the system increased. This led to the reinforcement of the hypothesis that there was a problematic anionic constituent, preventing effective cation exchange. It was thought that the removal of this anion using a SBR allowed the cation bed to work properly. The problematic constituent was thought, at first, to be a complexing organic, such as EDTA. However, upon close examination of the feed it was found that given the 9 mg/L DOC concentration, there were not enough organics present to complex the amount of cations that were passing through, in fact, it was found that the only anion that existed in sufficient

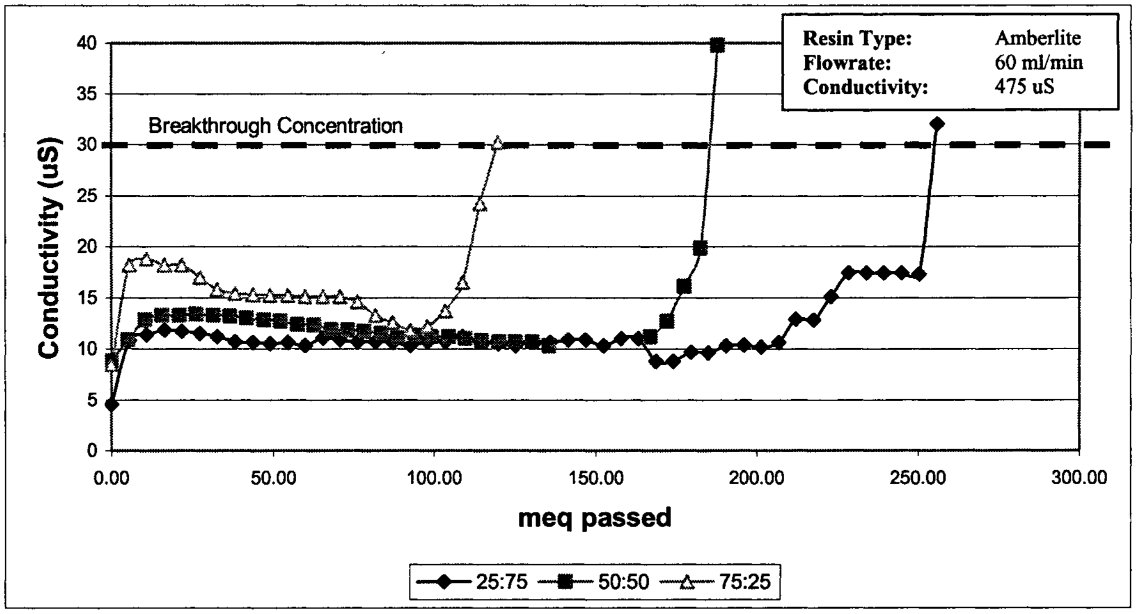

Figure 5.4 – Breakthrough Curves for Three Different Cation Balances

quantities to effect the cation exchange column was sulphate, which accounted for more than half of all anions.

5.3 – The Sulphate Experiment

An experimental set-up, as shown in Figure 5.5, was created to test the cation resin for sodium removal in the presence of sulphate. Solutions of about 20 mg/L NaCl and Na_2SO_4 were made and each was passed through a Purolite cation bed. As shown in the figure, the two set-ups were identical although they were conducted at a smaller scale than the majority of the experimental runs. The influent and effluent of each column were sent for analysis and the results showed that there was zero removal from both beds. Since each solution contained only one cation and one anion there could be no competitive exchange or complexing of cations. Since sodium is known to be removable by cation exchange, this showed that there must be a problem with the cation exchange resin and that sulphate was not causing problems with the process. However, when entering a cation bed after anion exchange, the cation resin worked much better producing an effluent with a conductivity less than 15 uS/cm.

The only difference between the feed entering the cation bed directly and it entering after being run through the anion bed seemed to be the pH level. Since the anion bed exchanges all anions for hydroxide, the pH rises to about 11. A high pH influent creates a large gradient between the cation resin and the solution since the cation resin is hydrogen loaded. Thus, it was concluded that the Amberlite and Purolite cation resins that were used for the experiments do not perform well unless the feed has a high pH. It appeared that the problem had to be the resins themselves.

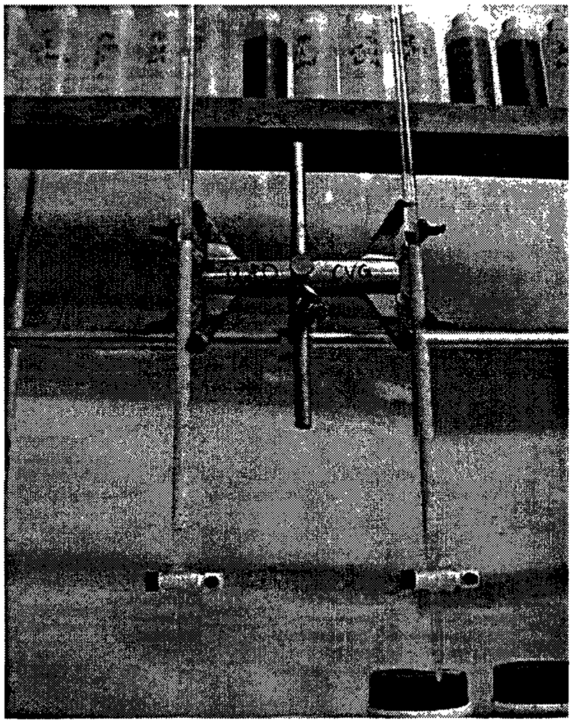

Figure 5.5 – Sulphate Experiment Set-up

5.4 - Lewatit Demineralisation

At the time the sulphate experiment was being conducted, the third set of resins (Lewatit) finally arrived, after six months wait. The Lewatit resins were then put into the same two-bed demineralisation set-up that was used in the preliminary experiments to observe if they exhibited the same problems as the other two resins. The results were very different from before. Unlike the Amberlite and Purolite resins, the Lewatit system worked with a simple two-bed system. There was no clogging but the effluent conductivity was consistently higher than desired at 45 uS/cm. When tap water (130 uS/cm) was run through the two-bed system it was treated to 14 uS/cm. The feed (500 uS/cm) was treated to a conductivity of 45 uS/cm, about a 50% higher conductivity than the established breakthrough concentration of 30uS/cm.

The Lewatit cation resin was not a chelating resin. The problems that were encountered during the experiments with Amberlite and Purolite resins were due to the fact that the Amberlite and Purolite were both chelating resins, highly selective for heavy metals. The experiments that were undertaken show that chelating resins are ineffective for demineralisation operations.

The experiments that were proposed for testing ion exchange demineralisation as a treatment method for flowing rinse wastewater included investigating three demineralising resin sets and one mixed-bed resin, however, two of the resin sets (Amberlite and Purolite) were not appropriate for demineralisation and the third set of resins (Lewatit) did not produce an effluent low enough in conductivity, although it did prove that ion exchange resins can be used to successfully remove all relevant ionic constituents. The last set of experiments was performed using a mixed-bed (MB) resin, containing SAR and SBR mixed together.

5.5 - Mixed-Bed Experiments

MB resins are generally used for polishing when ultrapure water is required; however, there is a practical advantage to using them alone for demineralisation, given the simplicity of a system where no regeneration steps are required. The operator simply replaces the spent resin with fresh material. Upon discussing options with the chemistry laboratory supervisor, it was decided that a mixed-bed system is a valid option, despite the higher operational costs.

The final experiments, using the Serfilco MBD-10 MB resin, showed again that ion exchange is an appropriate technology for this scenario. A photograph showing the mixed-bed resin set-up is shown in Figure 5.6. The photograph shows the two distinctly different resins (light and dark) that are mixed within the same column. The same type of resin was used for each of the experiments. The mixed-bed system worked very well with an effluent conductivity in the range of 5 uS/cm. Several runs were conducted to check the effect of altering the flowrate and concentration of the feed. Four runs were conducted to check the effect of altering the flowrate from 30 mL/min to 75 mL/min. For the first two runs at 75 and 60 mL/min, a bed volume of 200 mL was used. In order to allow the subsequent flowrate runs to be finished within one working day (to maintain consistent column operation), it was necessary to reduce the bed volume of the 45 and 30 mL/min runs to 100 mL. The results of the

Figure 5.6 – Photo of Mixed-Bed Resin Column

flowrate testing using mixed-bed resins are shown in Figure 5.7. The graph shows that altering the flowrate within the manufacturers range does not have a significant impact on the operational exchange capacity of the system. An operational capacity of about 1 meq/mL of resin was achieved for all flowrates.

The experiments that were conducted to observe the effect of altering the concentration were run at 45 mL/min and used a 100 mL bed volume. Three experimental runs were completed using feed concentrations corresponding to conductivities of 315, 470 and 990 uS/cm. The results illustrated in Figure 5.8 show that all of these runs were capable of reducing the effluent conductivity to below 5 uS/cm however there is no clear pattern since the middle concentration feed had a higher operational capacity than the higher concentration feed, but the lowest concentration feed showed the lowest operation capacity. This shows that altering the concentration does not have a large effect on the operational capacity of the resin column. According to ion exchange kinetic theory, at such a low feed concentration the governing mechanism for exchange is film diffusion. Thus, it would be expected that the highest concentration feed would achieve the greatest operational capacity.

5.6 – Modeling

Since it is expected that the governing mechanism of exchange is film diffusion, a single mass transfer resistance model is appropriate for modeling column performance. However, given that no equilibrium testing was conducted an isotherm has not been made and a kinetic analysis has not been attempted.

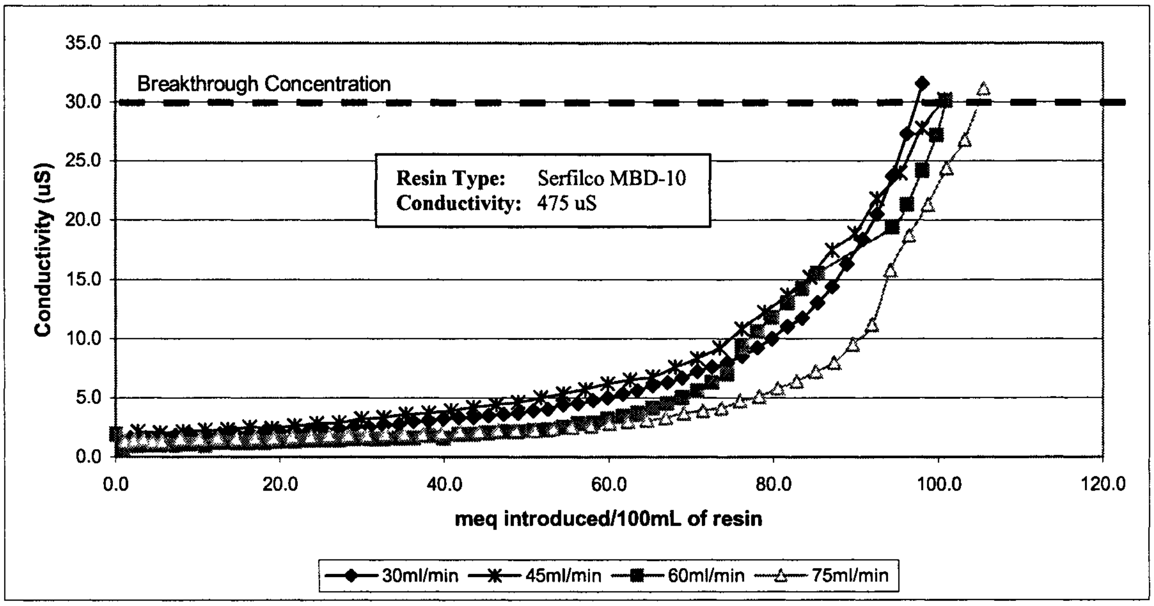

Figure 5.7 – Mixed-Bed Breakthrough Curves for Four Different Flow Rates

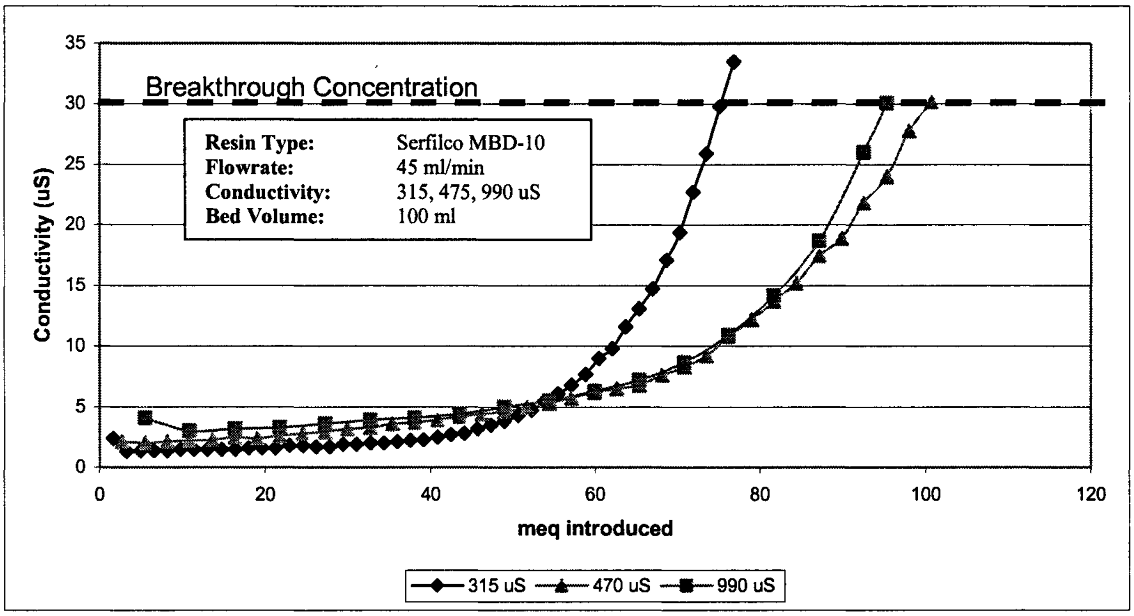

Figure 5.8 – Mixed-Bed Breakthrough Curves for Three Different Concentrations

A simplified approach has been taken that involves the use of the equilibrium column model. The equilibrium column model is based on the assumption that there is no mass transfer resistance and thus, there is no mass transfer zone. Contaminant ions are exchanged instantaneously within the column bed until the exchange capacity of the resin, according to equilibrium, is reached. This creates a square shaped wave front of effluent contaminant concentration because it assumes that no contaminant ion passes through the column until the bed is completely utilized.

One experimental run was conducted with the Amberlite IRC 748 chelating cation resin with a feed solution prepared with 640 mg/L of copper. The concentration of copper in the effluent was analyzed over time. Unfortunately, the test was only continued until the effluent copper concentration was 70 mg/L so the entire breakthrough curve was not captured. However, based on the equilibrium column model the breakthrough time is predicted by:

$$t_b = (q_o * V)/(Q * C_o) \tag{5.1}$$

t_b = breakthrough time (min)
q_o = ion exchange capacity of the resin (eq/L)
V = volume of resin bed (L)
Q = flowrate of feed solution (L/min)
C_o = concentration of feed solution (eq/L)

$t_{b(\text{copper run})} = (1.25 * 0.189) / (0.03 * 20.14)$
$t_{b(\text{copper run})} = 390.6$ min

Figure 5.9 shows the comparison between the collected data showing the beginning of the breakthrough curve and the theoretical breakthrough curve based on the equilibrium column model. It can be seen from the figure that the calculated theoretical breakthrough time is not an unreasonable estimate if it is assumed that the

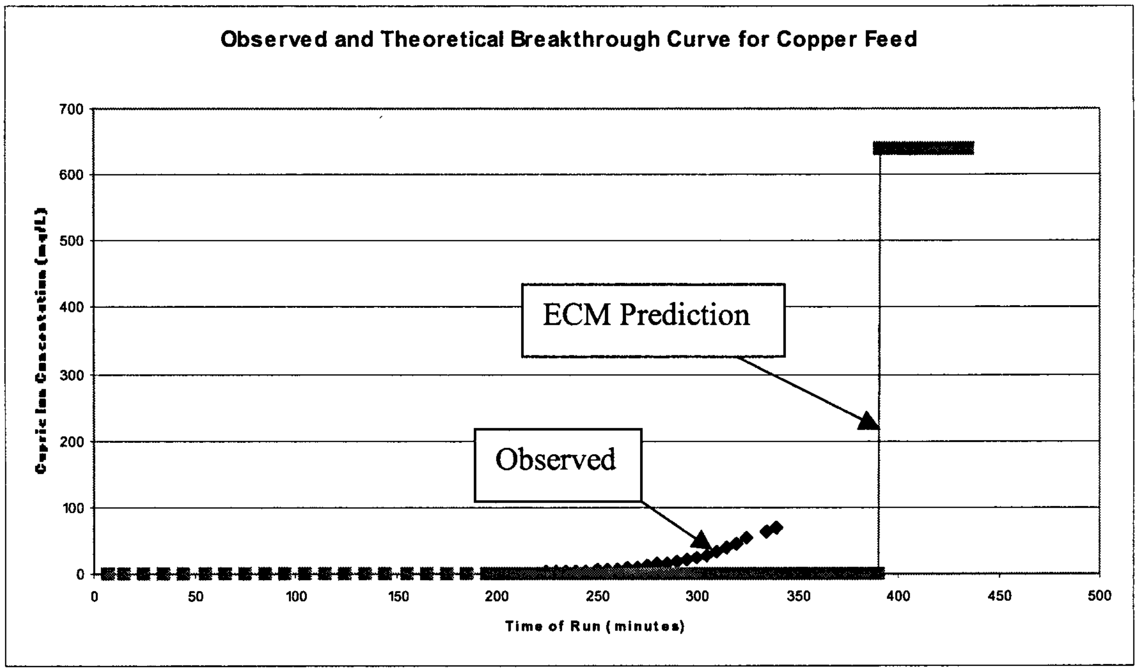

Figure 5.9 – Equilibrium Column Model for Run With Copper Solution

true breakthrough curve would be a symmetrical S-shaped curve where the calculated breakthrough time corresponds to the middle of the S-shaped curve.

For the experimental runs that were conducted using a multi-component feed solution that was prepared to simulate the rinse wastewater, it is not possible to model because only the conductivity of the effluent was measured. It is recommended that in future work where column testing is conducted that at least one run is completed where samples are taken over time and analyzed for each individual ion so that the effluent concentration of each ion is known. The run should be continued until the influent and effluent concentrations of each ion are equal. This allows for a kinetic modeling approach. For the runs conducted with the Amberlite and Purolite resins, the cation resins were ineffective. This prevents the possibility of modeling the performance of these resins. However, to give an example of how the equilibrium column model can be used to estimate breakthrough curves Figure 5.10 shows the theoretical breakthrough curves for the anions presented in Table 5.1. The calculations are based on a two-bed demineralisation system with equivalent cation and anion capacities of 200 meq. The breakthrough times are calculated using equation 5.1 and it is assumed that each ion has an independent wave front that occurs in the order of increasing preference with respect to the resin. Thus fluoride appears in the effluent first, followed by chloride, silica and sulphate.

5.7 – Discussion

The feed used in the experiments was more concentrated than expected for the actual wastewater. This was done to allow experiments to be completed within a reasonable

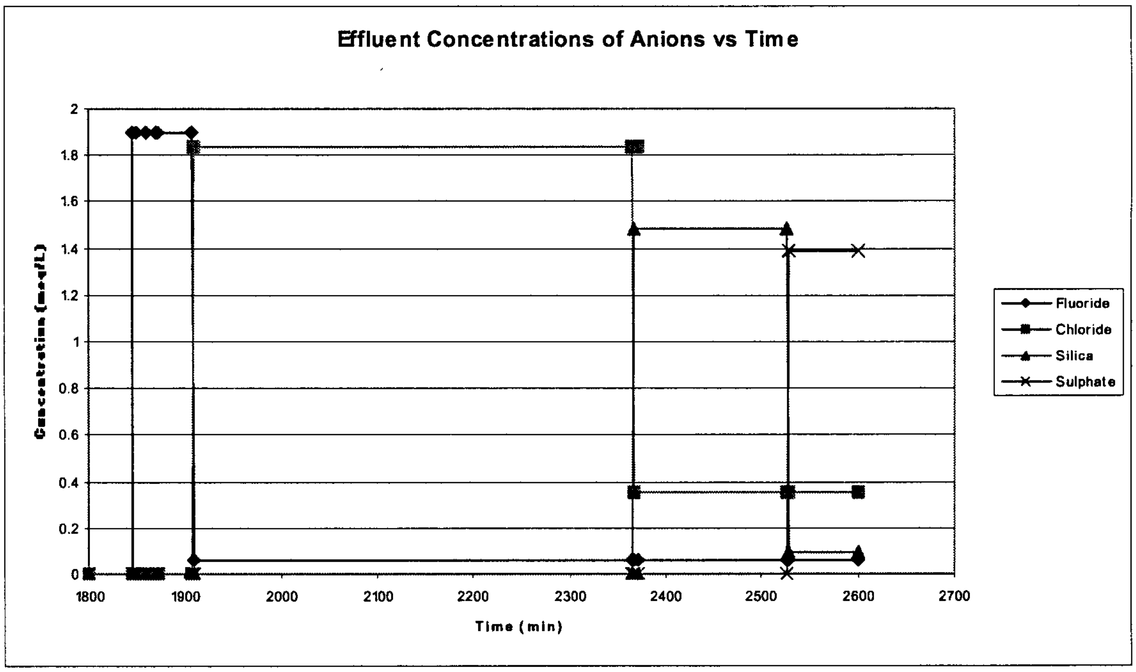

Figure 5.10 – Equilibrium Column Model For Anionic Species Given Hypothetical Two-Bed System

time frame. The lowest concentration that was used in the experiments (280 uS/cm) corresponds approximately to the highest concentration expected in the combined flowing rinses. The actual wastewater is expected to have an average ionic load that is equivalent to about 200 uS/cm of conductivity. However, the municipal drinking water alone, which is used as a feed for the flowing rinse tanks, has about 150 uS/cm of conductivity leaving only 50 uS/cm of conductivity associated with contaminants introduced through the rinsing operations. Thus, if demineralised water (10 uS/cm) is used as a feed for the rinse tanks instead of tap water, the wastewater is expected to measure an average of only about 60 uS/cm. Many of the experiments that were conducted included variation of the feed concentration to allow an understanding of the effects that concentration has on operational capacity. The results seem to indicate that there is no strong relationship between the removal of ionic species and feed concentration, indicating that the data collected in the experiments are relevant for the more dilute feed in an actual system. However, film diffusion is the governing mechanism of ion exchange at low concentrations and therefore it is expected that reducing the concentration further would result in a slight decrease in the operational ion exchange capacity.

The feed was made to replicate wastewater that originated as municipal drinking water. There are many constituents present in the municipal water that would not require removal if one were to use a demineralised water feed for the flowing rinse baths. For example, silica is present in the local municipal water at concentrations up to 5.7 mg/L. If a demineralisation system were used as the source for the flowing rinses, there would be no silica in the wastewater. Without silica present in the wastewater, it may be possible to use a weak base anion resin, which is less expensive than a strong base anion resin for anion exchange.

For all experiments except for the MB systems, the volume of resin used in each bed was based on the calculated volume that corresponded to 240 meq of theoretical exchange capacity. Thus, many of the bed volumes were different. This includes differences between the cation and anion resin within any particular demineralisation set-up. Resin manufacturers give recommended flowrate ranges in the units of bed volumes per time, thus, from this perspective, the flowrates were slightly different for the cation and anion bed in many of the experimental set-ups, however the absolute flowrates, given in mL/min were consistent.

As a rough cost estimate, given a mixed-bed resin cost of $13.13/L and an operational treatment capacity of approximately 165 L per litre of resin (from the experimental results), if the wastewater is expected to have only 60 uS/cm of ionic loading (about 1/8 of the experimental loading) then it would cost approximately $8.50/m^3 of water treated (see Appendix D for more detailed calculations). This is about six times the cost of municipal drinking water, which is only $1.50/m^3. However, there are many other benefits of having a mixed bed demineralisation system that could reduce other manufacturing costs at Filtran. For example, there is currently a small demineralisation unit for process make-up water since the process water must be of high purity. This system would no longer be necessary since there would be a consistent supply of demineralised water. In addition, the static rinse wastewater is treated using a precipitation system and the sludge is then filter pressed. The treated water has copper concentrations in the order of 2-3 mg/L. The effluent from this treatment system could also be sent to the demineralisation process and recycled preventing it from entering the sewer and ensuring that the City of Ottawa requirement for less than 3 mg/L of copper in the sewer is followed.

Although FMI uses municipal drinking water as a source for their flowing rinse operations, it is recommended in the literature that demineralised or ultrapure water be used for rinsing circuit boards. (Coombs, 1996) The cost analysis has shown that it would cost FMI about six times as much to maintain a mixed-bed demineralisation system for recycling of their flowing rinse water than it would to continue to use municipal drinking water. However, if they were to begin using demineralised water for their flowing rinse applications then it would be less expensive to recycle the water rather than continually treat tap water to this level.

CHAPTER 6 – CONCLUSIONS

6.1 – Conclusions

The main objective of this work has been achieved. A synthetic feed that replicates a mixture of the flowing rinse effluents from FMI was created and treated using a number of ion exchange demineralisation set-ups. As a result of the experiments the following conclusions have been drawn.

1- An ion exchange demineralisation system can be effective for the continual recycling of this water. Of the resins tested, the mixed-bed system showed the best performance and it is estimated that the operational cost of this type of system would be approximately $8.65 per cubic meter treated. However, other systems such as those recommended for future work within the following section are expected to be much less expensive and should be investigated. Other ion exchange demineralisation set-ups exist that were not tested and may prove to be the best option for Filtran.

2- The preliminary sampling that was conducted along with the determination of flowrates within the flowing rinse baths has provided FMI with detailed knowledge of their flowing rinse processes in terms of the quality and quantity of wastewater being generated. It was found during the flowrate analysis that many of the baths are left flowing for lengthy intervals without use. Water use and the associated costs could be reduced through the implementation of systems for preventing these excessive flows from occurring. These types of water reduction measures are presented in Section 3.3.6.

3- A significant amount of time was spent testing the Amberlite and Purolite resins within a demineralisation context. Unfortunately, the chelating resins that were sent by the manufacturers proved to be ineffective for demineralisation. It was shown that the Amberlite IRC 748 and Purolite S-930 chelating resins are not effective for demineralisation since they do not remove most cations effectively unless the influent has a pH of approximately 11 or higher. These chelating resins are, however, very effective at selectively removing heavy metals in the presence of other cations.

4- The experiments involving 3-bed systems showed that effective removal could be achieved using the chelating resins at the cost of operational performance. Many problems with resin beds clogging occurred during these experiments. This type of set-up is not recommended.

6.2 – Recommendations and Future Work

Future work could involve investigating a 4-bed Lewatit demineralisation system. Although the capital cost of a 4-bed system is much higher than that of a two-bed system, the effluent quality should be much better and in many cases, even when a two-bed system suffices, four beds are used to allow the treatment system to work effectively while part of the system is out of service for maintenance. In addition, further testing of standard (not chelating) Amberlite and Purolite strong acid resins within a two-bed context should be performed. The anion resins from these manufacturers seemed to perform well given the 3-bed system results that included the chelating cation resins and strong base anion resins. From these results, it seems that using a regular strong acid cation resin with the anion resins could lead to better performance than the Lewatit demineralisation set-up.

Further experiments should be also be undertaken that examine using a weak base anion resin in place of the strong base resin. The source of the small amount of silica (5 mg/L) that was found in the feed was the municipal drinking water, not the processes at Filtran. Wastewater that does not contain silica can be treated using a weak base resin following a strong acid resin. The experiments should be conducted using demineralised water as dilution for the process solutions instead of tap water.

Other testing could be conducted to analyse the effectiveness of using an organic trap (a strong base anion resin in the chloride form) for up-front removal of organics. This could be compared with GAC to determine which of these organic removal systems is more effective for the particular organic species present.

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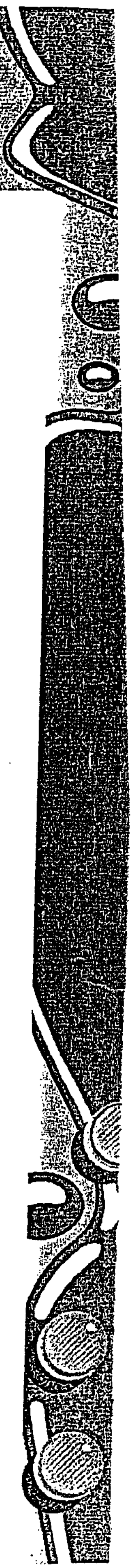
APPENDIX A – Detailed Media Data Sheets

AMBERLITE® IRC748

Industrial Grade Chelating Resin for Metals Removal



PRODUCT DATA SHEET

AMBERLITE IRC748 is an iminodiacetic acid chelating cation exchange resin with high selectivity for calcium, magnesium and strontium in chloralkali brines. Amberlite IRC748 also exhibits high selectivity for heavy metal cations over alkali metal ions found in various process and waste streams. Selectivity is achieved by the iminodiacetic acid functionality chemically bound to a macroreticular resin matrix. Because of the high preference of Amberlite IRC748 for metals and excellent kinetic performance, this resin can remove metals from solutions even in the presence of high concentrations of sodium or calcium salts, with very low metal leakage. The macroreticular structure of Amberlite IRC748 is highly resistant to osmotic shock and has excellent physical stability. The typical properties of Amberlite IRC748 are shown below.

TYPICAL PROPERTIES

Matrix	Macroporous styrene divinylbenzene
Functional groups	Iminodiacetic acid
Physical form	Opaque, beige beads
Ionic form as shipped	Na^+
Total exchange capacity	≥ 1.25 eq/L (Na^+ form)
Moisture holding capacity	60.0 to 65.0 % (Na^+ form)
Bulk density	685 to 760 g/L (Na^+ form)
Particle size	
Harmonic mean size	500 - 650 µm
Uniformity coefficient	≤ 1.7
< 0.300 mm	1.0% max
> 1.100 mm	5.0% max
Typical reversible swelling	$H^+ \rightarrow Na^+$: 30 %

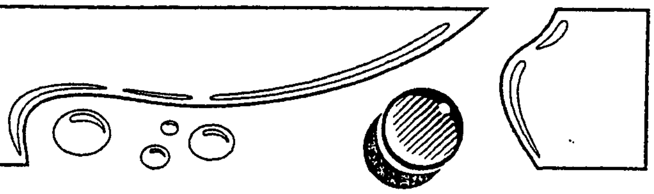
SUGGESTED OPERATING CONDITIONS

Maximum operating temperature	90 °C (Na^+ form)
pH range	1.5 to 14 (depending on applications)
Service flow rate	6 to 32 BV/h
Regenerant	HCl or H_2SO_4
Concentration	5 to 10 %
Flow rate	2 to 4 BV/h
Sodium form conversion	1 - 4 % NaOH, Flow rate : 2 to 4 BV/h
Pressure drop (at 20 °C)	11 kPa/m bed depth per 10 m/h 0.75 psi/ft bed depth at 4.1 gpm/ft^2

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

ROHM
HAAS

ION EXCHANGE RESINS



AMBERLITE® IRA400 Cl

STRONGLY BASIC ANION EXCHANGE RESIN

AMBERLITE® IRA400 Cl is a type 1, gelular, premium grade, strongly basic, anion exchange resin. It is based on crosslinked polystyrene and has high regeneration efficiency and excellent rinse performance. It is used in co-flow regeneration and conventional counterflow systems with downflow loading and upflow regeneration with air or water hold-down. Combined with a strong acid cation exchanger, AMBERLITE IRA400 Cl resin reduces both strong and weak acid concentrations to extremely low levels. Its main use is water demineralization. Other fields of application include the treatment of electroplating waste and the isolation of anionic metals.

PROPERTIES	
Matrix	Polystyrene divinylbenzene copolymer
Functional groups	Quaternary Ammonium
Physical form	Pale yellow translucent beads
Ionic form as shipped	Chloride
Total exchange capacity	1.4 meq/ml (Cl^- form)
Moisture holding capacity	44 to 48 % (Cl^- form)
Shipping weight	45 lbs/ft^3
Mean Size	0.60 to 0.75 mm
Uniformity coefficient	1.6 maximum
Screen Grading (Wet)	16 to 50 mesh (US Standard Screens)
Screen Analysis	5% maximum on 16 mesh (US Standard Screens) 3 % maximum thru 50 mesh
Maximum Reversible Swelling	$Cl^- \rightarrow OH^-$: approximately 30 %

SUGGESTED OPERATING CONDITIONS	
Optimum pH range	0 to14
Maximum operating temperature	140°F (OH^- form) / 170°F (Cl^- form)
Minimum bed depth	24 inches
Service flow rate	1 to 3 gpm/ft^3
Regenerant (100% basis)	**NaOH**
Flow rate (gpm/ft^3)	0.25 to 0.5
Concentration (%)	2 to 4
Level (lbs/ft^3)	2 to 12
Minimum contact time (minutes)	30
Rinse Flow Rate	0.25 to 0.5 gpm/ft^3 initially, to displace regenerant , then 1.5 gpm/ft^3
Rinse Water Requirements	75 gal/ft^3 (approximate)

LIMITS OF USE

AMBERLITE IRA400 Cl 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 Company in order to determine the best resin choice and optimum operating conditions.

PUROLITE®
ION EXCHANGE RESINS

S-930
Macroporous Iminodiacetic Chelating Resin

(For the selective removal of heavy metals from aqueous solutions)

Technical Data

Section IV. **PRODUCT DESCRIPTION**

Purolite S-930 is a macroporous polystyrene based chelating resin, with iminodiacetic groups designed for the removal of cations of heavy metals from industrial effluents. These cations may be separated from high concentrations of univalent cations (typically sodium) and also from common divalent cations (such as calcium). Removal can be achieved both from weakly acidic and weakly basic solutions depending on the metals to be removed.

Purolite S-930 finds use in processes for extraction and recovery of metals from ores, galvanic plating solutions, pickling baths, and effluents even in the presence of alkaline earth metals (calcium and magnesium).
Further important uses include the refining of the salt solutions of transition and precious metals and for the cleaning and purification of various organic or inorganic chemical products by removal of heavy metals contamination (usually from aqueous solution).

Typical Chemical & Physical Characteristics

Polymer Matrix Structure		Macroporous Styrene-divinylbenzene
Physical form & Appearance		Opaque Beige Spheres
Whole Bead Count		>90%
Functional Groups		Iminodiacetic
Ionic Form (as shipped)		Na^+
Shipping Weight		710 - 745 g/l (44.5 - 46.5 lb/ft^3)
Screen Size range (British Standard Screen)		14-52 mesh, wet
Particle Size range		+ 1.0mm <10%, -0.3mm <1%
Moisture Retention, H^+ Form		55-65%
Reversible Swelling, ($H^+ \rightarrow Na^+$)		<20%
Specific Gravity, Moist H^+ Form		1.17
Total Exchange Capacity, H^+ Form (wet, volumetric)		1.1 eq./l., min.
	H^+ Form	35g of Cu^{++}/l., 2.2 lb/ft^3 min.
	Na^+ Form	0.94 eq./l., min.
	Na^+ Form	30g of Cu^{++}/l., 1.9 lb/ft^3 min.
Max. Operating Temperature, H^+ Form		70°C (158°F)
*p*H Range (operating) H^+ Form		2-6
	Na^+ Form	6-11

PUROLITE
ION EXCHANGE RESINS

FEB 99

A-100

Macroporous Weak-Base Anion-Exchange Resin

(FOR THE DEMINERALISATION OF WATER)

Technical Data

PRODUCT DESCRIPTION

Purolite A-100 is a macroporous poly(vinylbenzyl) tertiary amine type exchange resin, primarily used for the removal of anions of strong acids in a two-bed deionization process. Because of its structure, it has excellent mechanical and osmotic stability, and is able to remove high molecular weight organic materials from the influent water, thus protecting a following strong-base resin from fouling. The organics are readily eluted, and the regenerated resin shows good rinse behaviour, and a very acceptable operating capacity on relatively high-TDS waters.

While there are several other specially-tailored macroporous intermediate-base resins in the **Purolite A-100** series, **Purolite A-100** itself is probably the most generally useful. A suitably-graded version, **Purolite A-100DL**, is recommended for use in conjunction with **Purolite A-200DL** or **A-400DL** in layered-bed DOUBLITE anion exchange systems.

Typical Chemical and Physical Characteristics

Polymer Structure	Macroporous polystyrene crosslinked with divinylbenzene
Appearance	Spherical beads
Functional Groups	Tertiary amino
Ionic Form - as shipped	FB form
Total Capacity (FB Form)	1.3 eq/l min
Strong Base Capacity	10-20 % of total
Moisture Retention (Cl^- Form)	53-60%
Bead Size Range (microns)	+1200 <5 %, -300 <1%
Screen Size Range (U.S. Standard Screen)	16-50 mesh
Reversible Swelling (FB → Cl^-)	20%
Specific Gravity (FB Form)	1.04
Shipping Weight	655-685 kg/m^3 (41-43 lb/ft^3)
Temperature Limit (FB Form)	60°C (140°F)
(Cl^- Form)	100°C (212°F)
pH Limits (stability)	0-14
(operating)	0-9

SYBRON
CHEMICALS INC.
A Bayer Company

Lewatit MonoPlus S 100

*Lewatit MonoPlus S 100 is a strongly acidic, gel-type ion exchange resin of uniform particle size (monodispersed) based on a styrene-divinylbenzene copolymer. The monodispersed resin beads are chemically and osmotically highly stable. The optimized kinetics lead to an increased operating capacity compared to ion exchange resins with heterodispersed bead size distribution. **MonoPlus S 100** is also available in hydrogen form (**MonoPlus S 100 H**).

Lewatit MonoPlus S 100 applications:

softening, demineralization, condensate polishing*

Physical and chemical properties		**US Units**		**International Units**	
Ionic form as shipped			Na^+		Na^+
Mean bead size	> 90%	mm	0.6 +- 0.05	mm	0.6 +- 0.05
Uniformity cofficient		max.	1.1	max.	1.1
Shipping weight		lbs/ft³	51.0	g/l	820
Density				g/l	1.28
Water retention		% weight	42 - 48	%	42 - 48
Total capacity, min.		kg $CaCO_3$ / ft³	43.6	eq/l	2
Volume change	Na^+ >> H^+	max. %	8	max. %	8
Stability	temperature range	°F	14 - 250	°C	-10 - 120
	pH range		0 - 14		0 - 14
Storability	of product	min years	2	min. years	2
	temperature range	°F	14 -	°C	-10 - 40

MSDS: Material Safety Data Sheets are available for all Sybron/Bayer products. The MSDS contain pertinent information that ed to ensure safe handling and use of our products. It is recommended that copies of MSDS be obtained by calling 1-800-678-0020 or 1-800-662-2927.

Contact Us:
Sybron Chemicals Inc.
A Bayer Company
Birmingham Road
Birmingham, NJ 08011
Phone: 1-800-678-0020
Fax: 609-894-8641

www.ionexchange.com

Contact Us:
Sybron Chemicals Inc.
A Bayer Company
100 Bayer Road
Pittsburgh, PA 15205
Phone: 1-800-662-2927
Fax: 412-777-4109

www.ionexchange.com

SYBRON
CHEMICALS INC.
A Bayer Company

Lewatit MonoPlus M 500

*Lewatit MonoPlus M 500 is a strongly basic, gel-type ion exchange resin of uniform particle size (monodispersed) based on a styrene-divinylbenzene copolymer. The monodispersed resin beads are chemically and osmotically highly stable. The optimized kinetics lead to an increased operating capacity compared to ion exchange resins with heterodispersed bead size distribution. **MonoPlus M 500** is also available in hydroxide form (**MonoPlus M 500 OH**).

Lewatit MonoPlus M 500 applications:

demineralization, mixed bed / condensate polishing*

Physical and chemical properties		US Units		International Units	
Ionic form as shipped			Cl^-		Cl^-
Mean bead size	> 90%	mm	0.6 +- 0.05	mm	0.6 +- 0.05
Uniformity cofficient		max.	1.1	max.	1.1
Shipping weight		lbs/ft³	42	g/l	670
Density				g/l	1.08
Water retention		% weight	50 - 60	%	50 - 60
Total capacity, min.		kg $CaCO_3$ / ft³	26	eq/l	1.2
Volume change	Cl^- >> OH^-	max. %	22	max. %	22
Stability	temperature range	°F	34 - 212	°C	1 - 100
	pH range		0 - 14		0 - 14
Storability	of product	min years	2	min. years	2
	temperature range	°F	34 - 104	°C	1 - 40

MSDS: Material Safety Data Sheets are available for all Sybron/Bayer products. The MSDS contain pertinent information that may be required to ensure safe handling and use of our products. It is recommended that copies of MSDS be obtained by calling 1-800-678-0020 or 1-800-662-2927.

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Contact Us:
Sybron Chemicals Inc.
A Bayer Company
100 Bayer Road
Pittsburgh, PA 15205
Phone: 1-800-662-2927
Fax: 412-777-4109

www.ionexchange.com

BULLETIN
R-203B
SEPT. 2001

SERFILCO® ION EXCHANGE RESINS

For: *High purity water / Precious metal recovery Recirculated rinses / Waste treatment Heavy metal removal*

MIXED BED RESIN

FOR MAKE-UP WATER AND RECIRCULATED RINSES

Mixed bed resin is designed for use in a single column or multiple columns in series to provide water to a 20,000 ohm endpoint (25 ppm). Average quality less than 0.1 ppm prior to breakthrough. Use to demineralize make-up water such as for plating and EDM.

When used in recirculating rinses, the estimated capacity per cu. ft. is 470,000 divided by the MMHOS or 235,000 divided by ppm TDS.

When regenerated and reused, the capacity will only be 50 to 70% of the virgin resin.

DESCRIPTION	TYPE	PART NO. *
Mixed bed resin	MBD-10	1328
Mixed bed resin w/Indicator dye	MBD-10D	1328D

Specially blended resin for pure recirculation EDM systems. Provides maximum capacity for metallic ions. Not recommended for raw make-up water. Requires monitoring with a conductivity meter.

Specially blended resin for EDM recirc. systems	MBD-MAG	1306

ANION RESINS

For gold and silver recovery from rinse water.

Can hold as much as 120 ounces per cu. ft., but is typically used up to only 50 to 75% of capacity.

Silver photographic solutions can be regenerated in a two-step operation using dilute sulfuric acid and tap water rinse which causes the silver to precipitate in the resin. After up to 10 cycles the silver is recovered by incineration.

Resin for acid gold recovery and silver recovery from photographic solution	SBG1	1322

An anion resin in the OH form, maintains a high pH and helps prevent formation of hydrogen cyanide gas. Capacity for gold is 100 ounces per cu. ft. maximum. This anion resin is also used in two-step demineralization systems with the cation resin in the hydrogen form.

Resin for alkaline gold or silver recovery	SBG1-OH	1316

CATION RESINS

Supplied in the sodium form, will remove heavy metals from rinse waters for discharge. It will also remove calcium and magnesium which will reduce its capacity for copper, nickel trivalent chromium. We suggest the use of softened rinse water.

DESCRIPTION	TYPE	PART NO. *
Sodium form	CG8-Na	1375

Same function as the sodium form, but the discharge will be acidic. The cation resin in the hydrogen form is used with the anion resin in the OH form (SBG1-OH) in two-step demineralization processes.

Hydrogen form	CG8-H	1376

SPECIFIC ION RESINS

Specific ion resins have the capacity to remove specific types of substances from waste streams in the presence of other ions that would normally exhaust the resin. This ability allows the treatment of much larger volumes than with ordinary non-specific resins. Consult the Sales Department for specific details.

Heavy metals removal - copper, nickel, chrome, zinc, lead as cations at pH's above 5.	SIR-300	1307
Mercury removal as cation or anion.	SIR-200	1308
Precious metal removal from acid streams including aqua regia at pH 0-6, non-regenerable. Also for mercury removal.	SIR-400	1309
Heavy metal removal from waste streams.	SIR-500	1310

* Price per cubic foot.
Consult Sales Department for quantity pricing and special packaging.

To order .5 cu. ft. bag - add .5B to Part No.
To order .9 cu. ft. bag - add .9B to Part No.

F.O.B. Northbrook, Illinois

SERFILCO®, LTD.
1777 Shermer Road
Northbrook, IL 60062-5360 U.S.A.
847-559-1777
800-323-5431
Email: sales@serfilco.com
FAX: 847-559-1995
www.serfilco.com

Distributed by

CALGON
CALGON CARBON CORPORATION

Calgon Carbon Corporation, Big Sandy Plant PO Box 664,
Catlettsburg, KY 41129-0664
Fax: (606)739-6741

Certificate of Analysis

Date: 11/15/2001
Customer Order: 45121895
Delivery / Item: 80103584 / 000040
Sales Order: 10076398
Ship Date: 11/16/2001
Page: 1 of 1

Customer Number: 30051

BRENNTAG CANADA INC
6395 NORTHWEST DRIVE
MISSISSAUGA ON L4V 1K2

Attention: Ms, Karen Knuude
FAX 416-233-7706

Customer Specific Information
Material:

NSF
Certified to
ANSI/NSF 61

Material: 18003140 / CPG-LF 12x40 - 55LB-BAG (STK)

activated Carbon.

Batch S01B09WK7 / Quantity 8,800.000 LB

Specification	Unit	Value	Lower Limit	Upper Limit
ABRASION NUMBER TM9	Unit	86	78	—
ACID SOLUBLE ASH TM17	%	0.1	—	0.5
ACID SOLUBLE IRON TM18	%	0.01	—	0.01
IODINE NUMBER TM4/ASTM D4607	mg/g	951	950	—
MOISTURE TM1 / ASTM D2867	%	0	—	3
MOLASSES NUMBER TM3	Unit	220	210	—
MEAN PARTICLE DIAMETER TM23	mm	1.3	1.2	1.4
US SIEVE SERIES ON 10	%	1	—	5
US SIEVE SERIES -40 MESH	%	0.1	—	0.5
EXTRACTABLE PH TM15/ASTMD3838	Unit	7	5	8

cc: Ms. Rohinee Singh FAX 905-677-0445

Contact: Martha Chapman
Phone: 606-739-2319

APPENDIX B – City of Ottawa Quarterly Report on Drinking Water Quality

Central Supply:

Summary Table for 2nd Quarter 2001

The results for Britannia and Lemieux Water Plants are shown separately, although most results are very similar since the source water (Ottawa River) and treatment processes are the same for both plants. Since the distribution system is blended between the two plants, a single column is shown that represents average water quality measured at routine test locations throughout the distribution network.

For reference, beside the result column is shown the number of samples taken during the quarter. The frequency of testing varies with the nature of the Parameter being tested. For comparison against the water quality results, the drinking water standards are included to indicate the maximum allowable concentration (MAC) for the various substances.

The table is split into sections based on the nature of the analysis performed: microbiological, operational, volatile organics, inorganics, and pesticides/PCB's. It is important to note that many other Parameters are sampled and tested but are not reported in this quarterly summary report. They are however presented in the annual water quality report which is available to the public upon request, and posted on the regional web-site for drinking water.

City of Ottawa Drinking Water Quality - Central Supply
Sampling & Analysis Results for 2nd Quarter 2001 (Apr-Jun)

Results for Britannia / Lemieux Island
Water Purification Plants & Distribution System
(average results expressed in mg/L unless otherwise stated)

Microbiological

Parameter	Britannia Treated Water Results (# of results above limit)	# of Tests	Lemieux Treated Water Results (# of results above limit)	# of Tests	Distribution System Results (# of results above limit)	# of Tests	Drinking Water Standard*	Compliance with Drinking Water Standards?
Total Coliform Bacteria (cfu/100mL)	0	361	0	359	1	620	0	YES
E.coli (cfu/100mL)	0	361	0	359	1	620	0	YES
Heterotrophic Plate Count (cfu/mL)	0	48	0	52	2	432	500	YES

Operational Parameters

Parameter	Britannia Treated Water	# of	Lemieux Treated Water	# of	Distribution System	# of	Drinking Water	Compliance with Drinking

	Results (average)	Tests	Results (average)	Tests	Results (average)	Tests	Standard*	Water Standards?
Turbidity (NTU)	0.51	177	0.38	182	0.31	598	1.0, 5.0 (a)	YES
Chlorine Residual (Total)	1.24	177	1.25	182	1.02	602	3.00 (e)	YES
Fluoride	0.78	177	0.80	177	0.78	183	150 (b)	YES

Volatile Organics

Parameter	Britannia Treated Water Results (average)	# of Tests	Lemieux Treated Water Results (average)	# of Tests	Distribution System Results (average)	# of Tests	Drinking Water Standard*	Compliance with Drinking Water Standards?
Benzene	not detected	1	not detected	1	N/A	2	0.005	YES
Carbon Tetrachloride	not detected	1	not detected	1	N/A	2	0.005	YES
1,2-Dichlorobenzene	not detected	1	not detected	1	N/A	2	0.2	YES
1,4-Dichlorobenzene	not detected	1	not detected	1	N/A	2	0.005	YES
1,2-Dichloroethane	not detected	1	not detected	1	N/A	2	0.005	YES
1,1-Dichloroethylene	not detected	1	not detected	1	N/A	2	0.014	YES
Dichloromethane	not detected	1	not detected	1	N/A	2	0.05	YES
Ethylbenzene	not detected	1	not detected	1	N/A	2	0.0024 (c)	YES
Monochloro-benzene	not detected	1	not detected	1	N/A	2	0.08	YES
Tetrachloro-ethylene	not detected	1	not detected	1	N/A	2	0.03	YES
Trichloro-ethylene	not detected	1	not detected	1	N/A	2	0.05	YES
Toluene	not detected	1	not detected	1	N/A	2	0.024 (c)	YES
Trihalomethanes	0.040	4	0.037	4	0.042	4	0.100	YES
Vinyl Chloride	not detected	1	not detected	1	N/A	2	0.002	YES
Xylene	not detected	1	not detected	1	N/A	2	0.30 (c)	YES

Inorganics

Parameter	Britannia Treated Water Results (average)	# of Tests	Lemieux Treated Water Results (average)	# of Tests	Distribution System Results (average)	# of Tests	Drinking Water Standard*	Compliance with Drinking Water Standards?
Arsenic	not detected	1	*not detected*	1	N/A	-	0.025	YES
Barium	0.014	1	0.015	1	N/A	-	1.00	YES

Boron	not detected	1	not detected	1	N/A	-	5.0	YES
Cadmium	not detected	1	not detected	1	N/A	-	0.005	YES
Chromium	not detected	1	not detected	1	N/A	-	0.05	YES
Copper	not detected	1	0.006	1	N/A	-	1.0 (c)	YES
Iron	0.024	1	0.025	1	N/A	-	0.30 (c)	YES
Lead	not detected	1	not detected	1	not detected	2	0.01	YES
Manganese	0.006	1	0.007	1	N/A	-	0.05 (c)	YES
Mercury	0.0002	1	0.0003	1	N/A	-	0.001	YES
Nitrate	0.16	13	0.18	11	N/A	-	10.0	YES
Nitrite	not detected	13	not detected	11	N/A	-	1.0	YES
Selenium	not detected	1	not detected	1	N/A	-	0.01	YES
Sodium	3.31	1	3.22	1	N/A	-	20, 200 (d)	YES
Uranium	not detected	1	not detected	1	N/A	-	0.10	YES

Next

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APPENDIX C – Analytical Reports

REPORT OF ANALYSIS

ARECO CANADA - A Division of Caduceon Enterprises Inc., 40 CAMELOT DR., NEPEAN, ONTARIO, K2G 5X8
TELEPHONE: (613) 228-1145 FACSIMILE: (613) 228-1148

LABORATORY I.D.:	11912-13	CLIENT:	FILTRAN
SAMPLE MATRIX:	Water	JOB/PROJECT NO.:	F10746-3
REPORT NUMBER:	145501401	DATE SUBMITTED:	19-Dec-01
REPORT TO:	Francis Lai	DATE REPORTED:	14-Jan-02

PARAMETERS	UNITS	M.D.L.	ODWS		RESULTS		
			Objective	Type of Objective	WS 1		
Hardness(as $CaCO_3$)	mg/L	1	80-100	OG	54		
Alkalinity(as $CaCO_3$)	mg/L	1	30-500	OG	ND		
Conductivity	µS/cm	1			303		
pH		0.00-14.00	6.5-8.5	OG	3.96		
Fluoride	mg/L	0.1	1.5	MAC	1.2		
Chloride	mg/L	1.0	250	AO	12.6		
Cyanide	mg/L	0.005			0.068		
Nitrite(N)	mg/L	0.1	1.0	MAC	ND		
Nitrate(N)	mg/L	0.1	10.0	MAC	0.6		
Sulphate	mg/L	1.0	500	AO	66.8		
Calcium	mg/L	1.0			14.9		
Magnesium	mg/L	1.0			2.0		
Sodium	mg/L	1.0	200	AO	8.2		
Potassium	mg/L	1.0			14.9		
Ammonia(N)	mg/L	0.01			0.36		
Tannins	mg/L	0.1			0.9		
Dissolved Org. Carbon	mg/L	1	5.0	AO	9		
Iron	mg/L	0.01	0.30	AO	0.07		
Manganese	mg/L	0.005	0.05	AO	0.009		
Anion Sum	meq/L				1.86		
Cation Sum	meq/L				1.85		
% Difference	%				0.36		
Ion Ratio	AS/CS				1.01		
SAR					0.49		
Conductivity (calc.)	µS/cm				230		
TDS (ion sum calc.)	mg/L		500	AO	127		
EC(calc.)/EC(actual)					0.76		
TDS(calc.)/EC(actual)					0.42		
Langelier Index	S.I.				-		

ODWS = Ontario Drinking Water Standards, August 2000
AO = Aesthetic Objective
MAC = Maximum Acceptable Concentration
OG = Operational Guideline
Results in **BOLD** are in exceedance of the drinking water objectives

- = Not Requested/Analyzed
ND = Not Detected
M.D.L. = Method Detection Limit

Certified by
Greg Clarkin, B.Sc., C.Chem.
Laboratory Director

Address all Inquiries to the Laboratory Director/Manager.

CLIENT: FILTRAN
ADDRESS: 2475 Don Reid Dr.
Ottawa,Ontario
K1H 1E2

CLIENT JOB NUMBER: F10746-3

ATTENTION: Francis Lai

REPORT DATE: 14-Jan-02

ANALYTICAL REPORT

ARECO LABORATORY I.D.: 11912-13

REPORT NUMBER: 145501401

DATE RECEIVED: 19-Dec-01

TIME RECEIVED: 2:05 PM

SAMPLE MATRIX: Water
OF SAMPLES RECEIVED: 1

ANALYSES	ANALYST	QTY	DATE EXTRACTED	DATE ANALYZED	TIME ANALYZED	ANALYTICAL METHOD	METHOD REFERENCE
Hardness (as $CaCO_3$)	A.S.P.	1	NA	20-Dec-02	11:00 AM	ICP-AES	EPA 200.7
Alkalinity (as $CaCO_3$)	S.L.	1	NA	20-Dec-01	12:13 PM	Colorimetric/Electrode	EPA 310.2
Conductivity	T.H.	1	NA	07-Jan-02	8:35 AM	Conductivity Meter	EPA 120.1
pH	T.H.	1	NA	07-Jan-02	8:35 AM	pH Meter	EPA 150.1
Anions	D.S.	1	NA	20-Dec-01	5:00 PM	Ion Chromatography	EPA 300.0
Metals - Cations	A.S.P.	1	NA	20-Dec-01	11:00 AM	ICP-AES	EPA 200.7
Tannins	S.L.	1	NA	08-Jan-02	10:41 AM	Colour-Automated	SM 5500B
Dissolved Org. Carbon	D.S.	1	NA	09-Jan-02	4:00 PM	Combustion/IR	EPA 415.1
Nitrogen - Ammonia (N)	S.L.	1	NA	19-Dec-02	5:02 PM	Colour-Automated	EPA 350.2
Metals - Heavy	A.S.P.	1	NA	20-Dec-01	1:30 PM	ICP-AES	EPA 200.7

- = Not Requested/Analyzed
NA = Not Applicable

Greg Clarkin, B.Sc., C.Chem.
Laboratory Director
ARECO CANADA INC

REPORT OF ANALYSIS

ARECO CANADA - A Division of Caduceon Enterprises Inc., 40 CAMELOT DR., NEPEAN, ONTARIO, K2G 5X8

TELEPHONE: (613) 228-1145 FACSIMILE: (613) 228-1148

LABORATORY I.D.:	11912-13	CLIENT:	FILTRAN
SAMPLE MATRIX:	Water	JOB/PROJECT NO.:	F10746-3
REPORT NUMBER:	145501401	DATE SUBMITTED:	19-Dec-01
REPORT TO:	Francis Lai	DATE REPORTED:	14-Jan-02

PARAMETERS	UNITS	M.D.L.	RESULTS			ODWS	
			WS 1			Objective	Type of Objective
Inorganics - Metals:							
Aluminum	mg/L	0.05	0.10			0.10	OG
Arsenic	mg/L	0.002	0.035			0.025	IMAC
Barium	mg/L	0.01	0.01			1.0	MAC
Boron	mg/L	0.01	0.86			5.0	IMAC
Cadmium	mg/L	0.005	ND			0.005	MAC
Calcium	mg/L	1.0	14.9				
Chromium	mg/L	0.01	ND			0.05	MAC
Copper	mg/L	0.01	2.57			1.0	AO
Iron	mg/L	0.01	0.07			0.30	AO
Lead	mg/L	0.001	<0.01			0.01	MAC
Magnesium	mg/L	1.0	2.0				
Manganese	mg/L	0.005	0.009			0.05	AO
Potassium	mg/L	1.0	14.9				
Selenium	mg/L	0.005	<0.01			0.01	MAC
Sodium	mg/L	1.0	8.2			200	AO
Uranium	mg/L	0.0001	<0.001			0.10	MAC
Zinc	mg/L	0.02	0.08			5.0	AO

ND = Not Detected
tr = Trace amounts detected
M.D.L. = Method Detection Limit
ODWS = Ontario Drinking Water Standards, August 2000
AO = Aesthetic Objective
OG = Operational Guideline
MAC = Maximum Acceptable Concentration
IMAC = Interim Maximum Acceptable Concentration

<0.001 = MDL's elevated due to dilutions performed as a result of matrix interferences.

Certified by,
Greg Clarkin, B.Sc., C.Chem.
Laboratory Director

Address all Inquiries to the Laboratory Director/Manager.

CLIENT: FILTRAN
ADDRESS: 2475 Don Reid Dr.
Ottawa,Ontario
K1H 1E2

CLIENT JOB NUMBER: F10746-3

ATTENTION: Francis Lai

REPORT DATE: 14-Jan-02

ANALYTICAL REPORT

ARECO LABORATORY I.D.: 11912-13

REPORT NUMBER: 145501401

DATE RECEIVED: 19-Dec-01

TIME RECEIVED: 2:05 PM

SAMPLE MATRIX: Water
OF SAMPLES RECEIVED: 1

ANALYSES	ANALYST	QTY	DATE EXTRACTED	DATE ANALYZED	TIME ANALYZED	ANALYTICAL METHOD	METHOD REFERENCE
Metals - Heavy	M.G.	1	NA	20-Dec-01	1:30 PM	ICP-AES	EPA 200.7
Metals - Cations	M.G.	1	NA	20-Dec-01	11:00 AM	ICP-AES	EPA 200.7
Metals - Arsenic	M.G.	1	NA	11-Jan-02	4:28 PM	GFAAS	EPA 206.2
Metals - Lead	M.G.	1	NA	11-Jan-02	4:28 PM	GFAAS	EPA 239.2
Metals - Selenium	M.G.	1	NA	11-Jan-02	4:28 PM	GFAAS	EPA 270.2

- = Not Requested/Analyzed
NA = Not Applicable

Greg Clarkin, B.Sc., C.Chem.
Laboratory Director
ARECO CANADA INC

APPENDIX D – Cost Calculations

Calculations for Estimate of Cost

Cost of MB resin = \$13.13/L resin

Operating Capacity = 165L water treated/L resin

Conductivity of Actual Wastewater = 60 uS

Conductivity of Experimental Wastewater = 480 uS

Average Effluent Conductivity = 10 uS

Ratio of Ionic Uptake = (480-10)/(60-10) = 9.4

Predicted Operational Capacity of Low Actual Wastewater

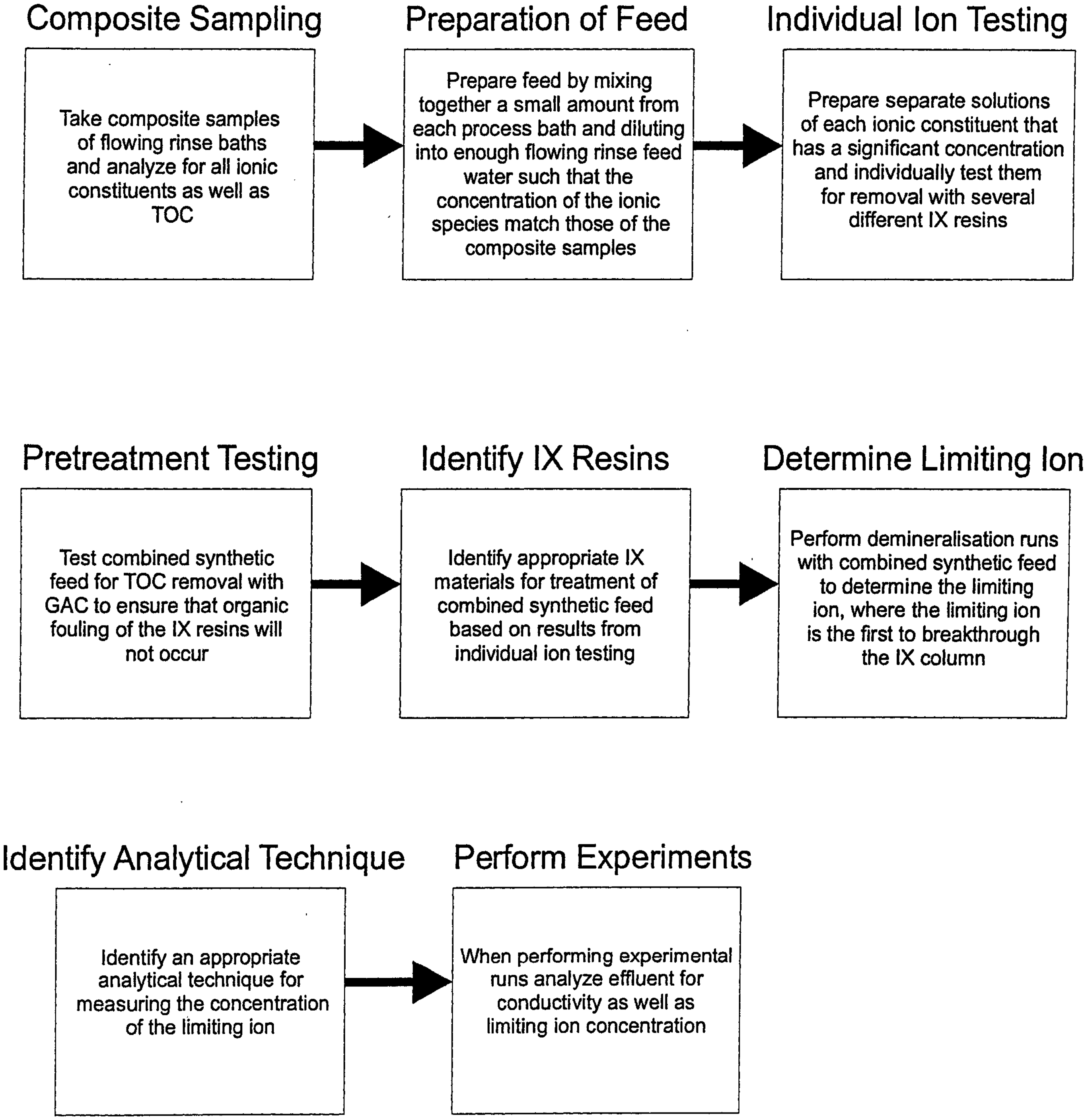
= 9.4 * 165 L water treated/L resin = 1551L water treated/L resin

invert: 1 L resin/ 1.551 m^3 water treated = 0.645 L resin/m^3 water treated

0.645 L resin * \$13.13/L resin = **\$8.47/ m^3 water treated**

APPENDIX E – Miscellaneous Data

Flow Chart of Method for Testing Feasibility of Ion Exchange for Recycling of Wastewater



Composite Sampling

Take composite samples of flowing rinse baths and analyze for all ionic constituents as well as TOC

Preparation of Feed

Prepare feed by mixing together a small amount from each process bath and diluting into enough flowing rinse feed water such that the concentration of the ionic species match those of the composite samples

Individual Ion Testing

Prepare separate solutions of each ionic constituent that has a significant concentration and individually test them for removal with several different IX resins

Pretreatment Testing

Test combined synthetic feed for TOC removal with GAC to ensure that organic fouling of the IX resins will not occur

Identify IX Resins

Identify appropriate IX materials for treatment of combined synthetic feed based on results from individual ion testing

Determine Limiting Ion

Perform demineralisation runs with combined synthetic feed to determine the limiting ion, where the limiting ion is the first to breakthrough the IX column

Identify Analytical Technique

Identify an appropriate analytical technique for measuring the concentration of the limiting ion

Perform Experiments

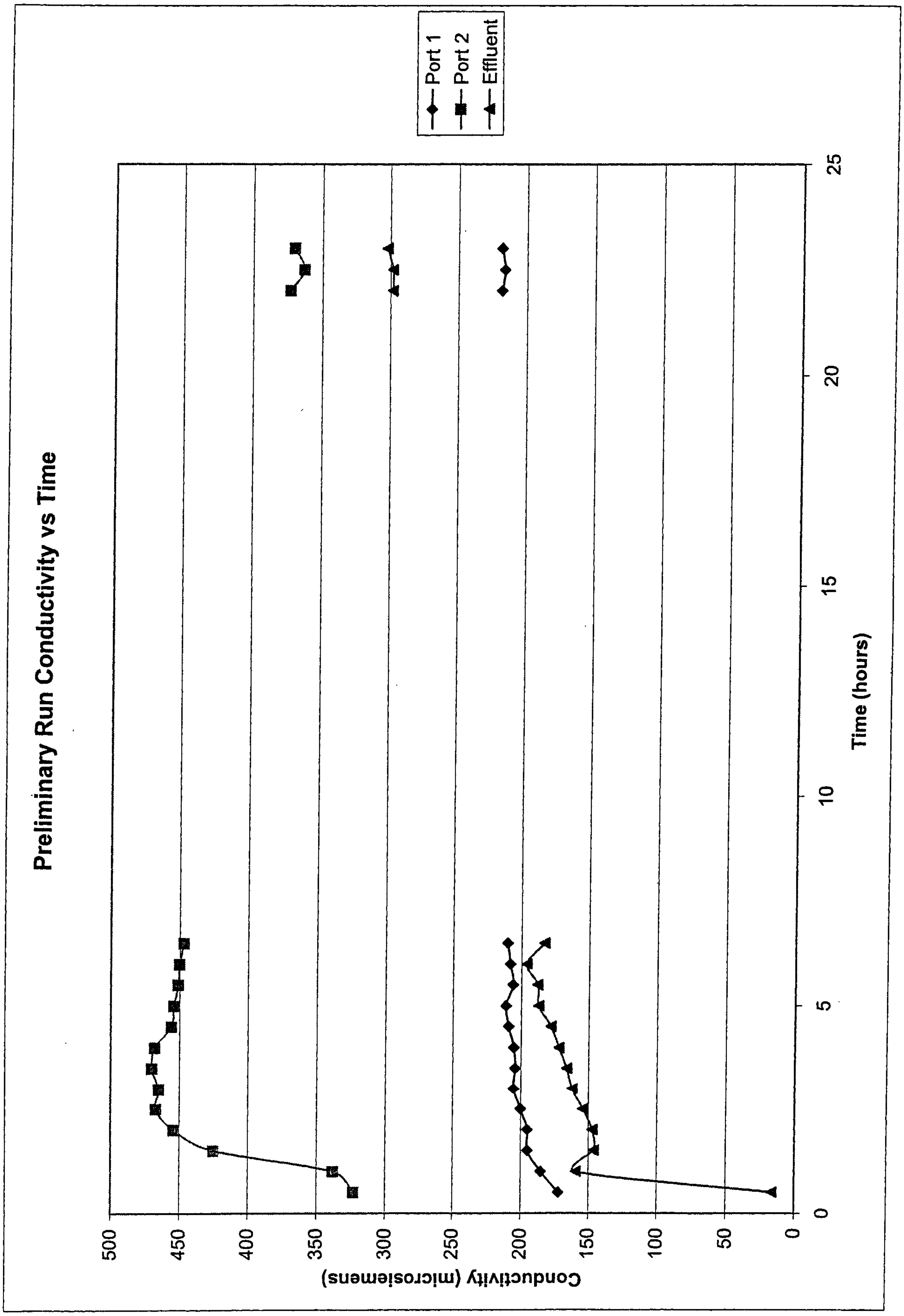
When performing experimental runs analyze effluent for conductivity as well as limiting ion concentration

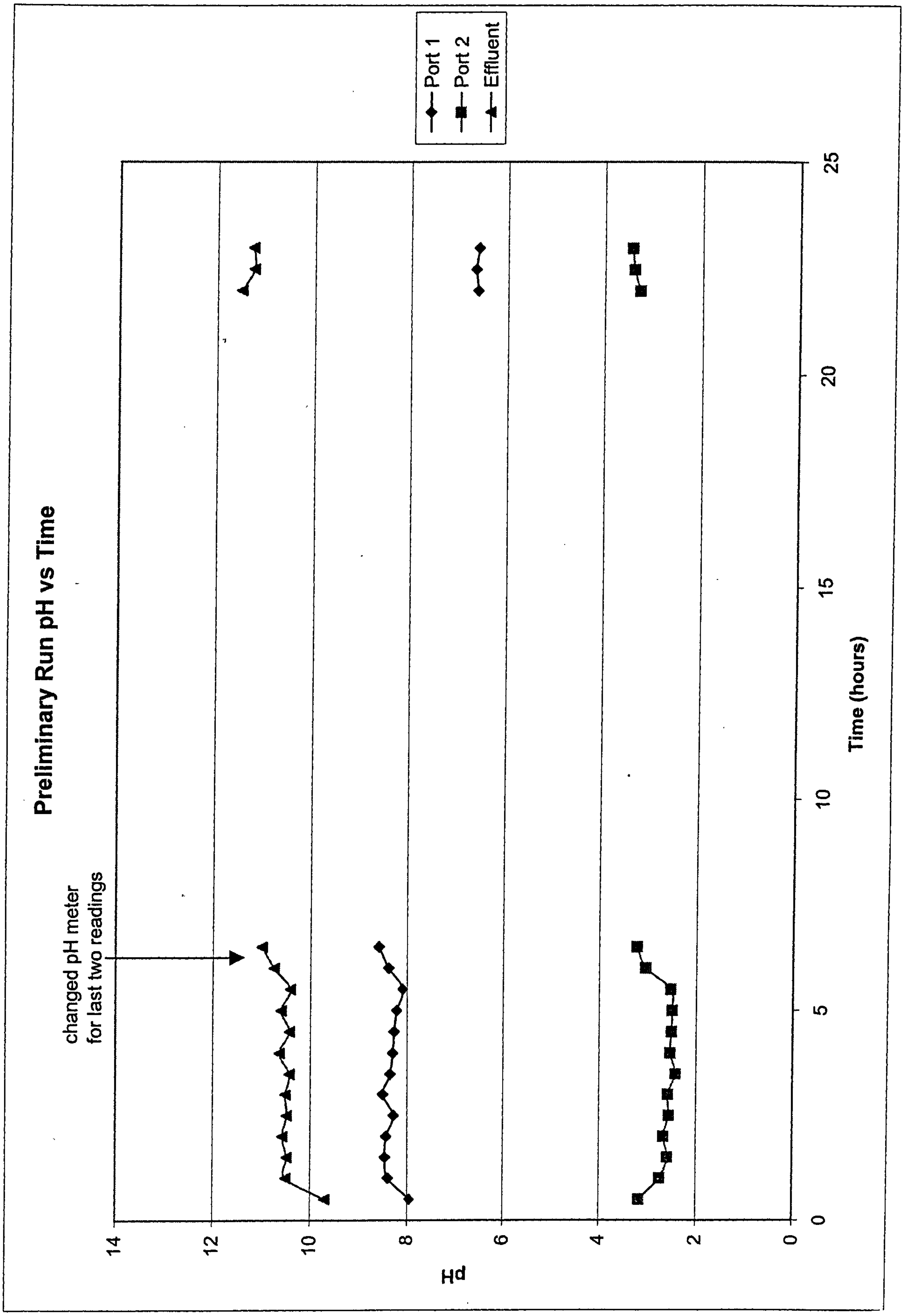
Table of Preliminary Runs (October 2001 - February 2002)

Date	Feed Conductivity (uS/cm)	Flowrate mL/min	Resin Set-up	Comments
10/25/01	280	33.3	Amberlite CIX-AIX	high conductivity and pH in effluent early in run
10/26/01	295	30	Amberlite CIX-AIX	high conductivity and pH in effluent early in run
11/27/01	309	30	Amberlite CIX-AIX	high conductivity and pH in effluent early in run
12/10/01	297	30	Amberlite CIX-AIX	high conductivity and pH in effluent early in run
12/13/01	copper sol'n 640 ppm	30	Amberlite CIX-AIX	copper exchange effective fully removed until breakthorugh
1/16/01	226	30	Amberlite CIX-AIX	high conductivity and pH in effluent early in run
1/17/01	240	30	Purolite CIX-AIX	high conductivity and pH in effluent early in run
1/24/01	300	30	Purolite CIX-AIX	high conductivity and pH in effluent early in run
1/29/01	300	30	Purolite CIX-AIX	high conductivity and pH in effluent early in run
2/6/01	282	30	Amberlite CIX-AIX-CIX	produced acceptable quality for 24 hours (approx. 15 uS/cm)

Preliminary Run

Time	Conductivity				pH							
	Port 1	Port 2	Effluent	% removal	Port 1	$[H^+]_{Port 1}$	Port 2	$[H^+]_{Port 2}$	$[OH^-]$	Effluent	$[H^+]_{Effluent}$	$[OH^-]$
0												
0.5	172	323	16.3	94.7%	7.95	1.1E-08	3.17	6.8E-04	1.5E-11	9.7	2.0E-10	5.0E-05
1	185	338	159	48.5%	8.4	4.0E-09	2.75	1.8E-03	5.6E-12	10.5	3.2E-11	3.2E-04
1.5	195	425	146	52.8%	8.46	3.5E-09	2.59	2.6E-03	3.9E-12	10.48	3.3E-11	3.0E-04
2	195	454	147	52.4%	8.44	3.6E-09	2.67	2.1E-03	4.7E-12	10.57	2.7E-11	3.7E-04
2.5	200	467	154	50.2%	8.29	5.1E-09	2.56	2.8E-03	3.6E-12	10.48	3.3E-11	3.0E-04
3	205	465	162	47.6%	8.51	3.1E-09	2.58	2.6E-03	3.8E-12	10.51	3.1E-11	3.2E-04
3.5	204	470	166	46.3%	8.36	4.4E-09	2.43	3.7E-03	2.7E-12	10.43	3.7E-11	2.7E-04
4	205	468	172	44.3%	8.31	4.9E-09	2.54	2.9E-03	3.5E-12	10.64	2.3E-11	4.4E-04
4.5	209	456	178	42.4%	8.28	5.2E-09	2.51	3.1E-03	3.2E-12	10.43	3.7E-11	2.7E-04
5	211	454	187	39.5%	8.23	5.9E-09	2.5	3.2E-03	3.2E-12	10.6	2.5E-11	4.0E-04
5.5	206	451	188	39.2%	8.1	7.9E-09	2.53	3.0E-03	3.4E-12	10.41	3.9E-11	2.6E-04
6	208	450	196	36.6%	8.4	4.0E-09	3.05	8.9E-04	1.1E-11	10.75	1.8E-11	5.6E-04
6.5	210	447	183	40.8%	8.6	2.5E-09	3.23	5.9E-04	1.7E-11	11	1.0E-11	1.0E-03
22	218	373	298	3.6%	6.62	2.4E-07	3.28	5.2E-04	1.9E-11	11.5	3.2E-12	3.2E-03
22.5	216	363	298	3.6%	6.66	2.2E-07	3.4	4.0E-04	2.5E-11	11.25	5.6E-12	1.8E-03
23	218	370	302	2.3%	6.6	2.5E-07	3.44	3.6E-04	2.8E-11	11.26	5.5E-12	1.8E-03


Preliminary Run Conductivity vs Time
Conductivity (microsiemens)
500
450
400
350
300
250
200
150
100
50
0
Time (hours)
0
5
10
15
20
25
Port 1
Port 2
Effluent


Preliminary Run pH vs Time
changed pH meter for last two readings
pH
0
2
4
6
8
10
12
14
Time (hours)
0
5
10
15
20
25
Port 1
Port 2
Effluent

Amberlite Cation Configuration Data

Date	2/26/2001		3/5/2001		3/7/2001		3/12/2001		3/14/2001		3/26/2001		3/21/2001	
Concentration, meq/L	6.05		6.05		5.8		3.28		11.34		5.92		5.29	
Flow rate, ml/min	60		60		60		60		60		30		90	
	Conductivity (uS/cm) and milliequivalents introduced													
Time (min)	1a	meq	2a	meq	3a	meq	4a	meq	5a	meq	6a	meq	7a	meq
0	4.5	0.00	8.5	0.00	8.8	0.00	13.8	0.00	8.6	0.00	22.9	0.00	11.6	0.00
15	10.8	5.45	18.2	5.45	10.9	5.22	8.5	2.95	21.4	10.21	8.2	2.66	11.4	7.14
30	11.4	10.89	18.8	10.89	12.8	10.44	9.9	5.90	22.6	20.41	11.2	5.33	12.5	14.28
45	11.8	16.34	18.2	16.34	13.3	15.66	10.7	8.86	20.9	30.62	13.5	7.99	12	21.42
60	11.7	21.78	18.2	21.78	13.3	20.88	11.2	11.81	19.5	40.82	14	10.66	11.4	28.57
75	11.5	27.23	17	27.23	13.4	26.10	11.5	14.76	18.8	51.03	15.9	13.32	10.7	35.71
90	11.2	32.67	15.8	32.67	13.3	31.32	11.6	17.71	18.3	61.24	15.8	15.98	10.2	42.85
105	10.7	38.12	15.4	38.12	13.2	36.54	11.8	20.66	17.7	71.44	15.5	18.65	9.9	49.99
120	10.6	43.56	15.3	43.56	13	41.76	12	23.62	17.6	81.65	15.2	21.31	9.8	57.13
135	10.5	49.01	15.2	49.01	12.8	46.98	12.2	26.57	17.3	91.85	14.9	23.98	9.6	64.27
150	10.6	54.45	15.2	54.45	12.7	52.20	12.9	29.52	17	102.06	14.5	26.64	9.4	71.42
165	10.3	59.90	15.1	59.90	12.4	57.42	13.1	32.47	16.6	112.27	14.2	29.30	9.1	78.56
180	11.1	65.34	15.1	65.34	12.3	62.64	13.2	35.42	16.5	122.47	14	31.97	9.4	85.70
195	10.9	70.79	15.1	70.79	11.9	67.86	13	38.38	16.3	132.68	13.8	34.63	9.9	92.84
210	10.7	76.23	14.6	76.23	11.8	73.08	13	41.33	15.8	142.88	13.5	37.30	10	99.98
225	10.7	81.68	13.3	81.68	11.7	78.30	12.9	44.28	15.8	153.09	13.4	39.96	10.8	107.12
240	10.6	87.12	12.6	87.12	11.5	83.52	12.8	47.23	15.7	163.30	13.3	42.62	13.4	114.26
255	10.3	92.57	11.8	92.57	11.1	88.74	12.3	50.18	15.6	173.50	13.1	45.29	16	121.41
270	10.7	98.01	12.2	98.01	11.3	93.96	13	53.14	15.6	183.71	12.9	47.95	20.2	128.55
285	10.7	103.46	13.7	103.46	11.2	99.18	12.6	56.09	15.6	193.91	12.8	50.62	26.1	135.69
300	11.2	108.90	16.5	108.90	11.2	104.40	12.8	59.04	15.8	204.12	12.8	53.28	30.2	142.83
315	10.7	114.35	24.2	114.35	11	109.62	12.3	61.99	15.3	214.33	12.7	55.94		
330	10.5	119.79	30.2	119.79	10.8	114.84	12.6	64.94			12.6	58.61		
345	10.3	125.24			10.7	120.06	12.9	67.90			12.5	61.27		
360	10.7	130.68			10.7	125.28	12.9	70.85			12.6	63.94		
375	10.6	136.13			10.7	130.50	11.3	73.80			12.4	66.60		
390	10.9	141.57			10.3	135.72	11.2	76.75			12	69.26		
405	10.9	147.02				140.94	12.6	79.70			12	71.93		
420	10.3	152.46				146.16	12.2	82.66			12	74.59		
435	11	157.91				151.38	12.2	85.61			12	77.26		
450	11	163.35				156.60	11.8	88.56			12	79.92		
465	8.8	168.80				161.82	12	91.51			12	82.58		
480	8.8	174.24			11.2	167.04	12	94.46			12	85.25		
495	9.7	179.69			12.7	172.26		97.42			12.2	87.91		
510	9.6	185.13			16.1	177.48		100.37			12.1	90.58		
525	10.3	190.58			19.9	182.70		103.32			12	93.24		
540	10.4	196.02			39.8	187.92		106.27			12	95.90		
555	10.2	201.47						109.22			12	98.57		
570	10.6	206.91					24	112.18			12	101.23		
585	12.9	212.36									12	103.90		
600	12.8	217.80									12	106.56		
615	15.1	223.25									12	109.22		
630	17.4	228.69									12	111.89		
645	17.4	234.14									12	114.55		
660	17.4	239.58									12	117.22		
675	17.4	245.03									12	119.88		
690	17.3	250.47									12	122.54		
705	32	255.92									12	125.21		
720											11.7	127.87		
735											13.8	130.54		
750											11	133.20		
765											10.2	135.86		
780											9.6	138.53		
795											9.2	141.19		
810											8.8	143.86		
825											8.4	146.52		
840											8.4	149.18		
855											8.8	151.85		
870											9.3	154.51		
885											10.1	157.18		