Base Metal Equilibrium Prediction on Ion Exchange Resin

by

Moegamat Zain Rejaldien

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Supervisor: JW Coetzee

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DECLARATION

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

MZ Rejaldien

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ABSTRACT

This study is the first phase of an investigation into an alternative process to recover base metals from solution, namely ion exchange. An identified ion exchange resin was employed to study the recovery of copper, nickel and cobalt from electrolytic solutions. The main focus of the investigation was the prediction of equilibrium conditions in this multi-component system using a batch configuration.

In order to predict equlibrium conditions, existing multi-component isotherms such as Fritz and Schleunder were tested. It has been shown that traditional isotherms did not accurately predict equilibrium conditions, hence the need for development of new isotherms. Essentially two approaches were followed in the development of new isotherms namely, an effective concentration approach as well as a heat transfer approach. Both yielded positive outcomes with the effective concentration approach proving to be the most accurate. In addition to these two approaches a thermodynamical approach was also tested which also showed favourable predictions for Cu loading

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

The loss of metals in effluent streams in the mining industry is common and results in financial losses as well as environmental problems. Current recovery/separation processes for Cu, Ni and Co involve selective leaching which could be problematic and the separation procedure is usually labour intensive. and hazardous to health (especially where strong acids are used as the leaching medium). It is proposed to improve the separation procedure by a total leach followed by ion exchange using a synthetic resin.

This study is the first phase towards proposing an ion exchange process i.e. the accurate prediction of equilibrium conditions. A sodium based synthetic resin (Amberlite IRC748) was evaluated to determine its adsorptive capacity in aqueous solutions containing the elements copper. nickel and cobalt.

Adsorption isotherms and/or equilibrium data are the basic design requirements of any adsorption system. Experimental results were therefore compared to existing isotherms and alternative isotherms were also developed when required.

The literature review focuses on ion exchange. ion exchange resins. base metals and equilibrium isotherms as the most important aspects of the study.

1.1 Elementary Principles of Ion Exchange

Ion exchangers are insoluble solid materials which carry exchangeable cations or anions [1]. These ions can be exchanged for an equivalent amount of other ions of the same charge when the ion exchanger is in contact with electrolytic solutions. Ion exchangers capable of both cation and anion exchange are called amphoteric ion exchangers.

Ion exchangers owe their properties to the nature of their structure. They consist of a framework, which is held together by chemical bonds or lattice energy. The framework carries a surplus electric charge, which is countered by ions of opposite sign (counter-ions). The counter-ions are free to move in the framework and can be replaced by ions of the same charge. The counter-ion content of ion exchangers, or its ion exchange capacity, is a constant and is solely determined by the magnitude of the framework charge [2].

When an ion exchanger is placed in an electrolytic solution, an exchange of counter-ions takes place. After a certain time ion exchange equilibrium is obtained and both the ion exchanger as well as the electrolyte contain both counter-ion species (electrolyte and ion exchanger counter ions). The pores of the ion exchanger however not only contain counter ions but also solutes and solvents.

Uptake of solvent may result in swelling of the ion exchanger. Uptake of solutes is essentially a distribution of the solute between liquid phases i.e. the pore liquid and the solution outside. Sorption of an electrolyte increases counter-ion content and the sorbed counter ions are accompanied by an equivalent number of co-ions. The co-ions are mobile ions with charges of the same sign as the ion exchanger framework charge. Thus, the counter ion content of an ion exchanger depends not only on the framework charge magnitude but on the co-ion content as well [1].

Ion exchangers prefer certain species to others and this preference can be attributed to:

- The electric interactions between the charged framework and the counter ions depend on the size and valence of the counter ion

- In addition to electrostatic forces, other interactions between the ions and their environment are effective
- Large counter ions may be sterically excluded from the narrow pores of the ion exchanger

This ability of an ion exchanger to distinguish between various counter ions is called selectivity [1].

1.2 Structure and Properties of Ion Exchangers

Many natural and synthetic products show ion exchange properties. The most important ion exchangers are :

- mineral ion exchangers
- synthetic inorganic ion exchangers
- ion exchange coals
- ion exchange resins

1.2.1 Mineral Ion exchangers

Most mineral ion exchangers are crystalline alumosilicates with cation exchange properties [3]. Characteristic representatives are the zeolites which have a relatively open three-dimensional structure with channels and interconnecting cavities in the alumosilicate lattice.

The zeolites are relatively soft minerals and not very abrasion resistant. They swell very little and the counter ions in their pores are not very mobile. Their small and uniform pore size gives rise to a sieve action where large non-electrolyte molecules cannot be accommodated and smaller species can be exchanged.

Their practical use is restricted to a narrow pH range (around 7) and they are only moderately stable in solutions of very low silica or salt content.

1.2.2 Synthetic Inorganic Ion Exchangers

The first inorganic cation exchangers were prepared by fusion of mixtures of soda, potash, feldspar, kaolin and other similar components [2]. These ion exchangers resemble zeolites, except for their more irregular structure

Inorganic cation exchangers were later prepared by precipitation with caustic from acidic solutions of aluminium sulphate and sodium silicate [4]. The drying of the gelatinous precipitate produced the gel ion exchanger resembling zeolites except for its irregular shape. Their irregular shape resembles that of silica gel and ion exchange resins. Regular structured zeolites have been synthesised in recent years but as ion exchangers they are of little practical importance.

Synthesised cation exchangers with much more satisfactory properties have been prepared by combining group IV oxides with more acidic oxides of group V and VI. They have high capacities, high rates of ion exchange and are superior to organic resins regarding thermal stability and resistance to radiation. However, these tend to loose their fixed ionic groups at high pH and are not readily prepared in mechanically stable particle form.

1.2.3 Ion Exchange Coals

Many coals contain carboxylic and other weak acid groups, enabling them to be used as cation exchangers [5]. These swell excessively, are easily decomposed by alkali and tend to peptize and therefore need to be stabilized before use. Stabilization methods include treatment with metal solutions, treatment with acidic/alkali solutions, sulfonation, thermal activation and treatment with oxygen and nitrous gases.

Sulfonation is the conversion of coal into strong-acid cation exchangers by contacting it with fuming sulfuric acid. The sulfuric acid treatment results in the coal being gelified, thereby improving its chemical and mechanical stability. The sulfonated coals resemble resins but their composition is less uniform and their mechanical and chemical stability is inferior [3].

1.2.4 Ion Exchange Resins

Synthetic ion-exchange resins consist of an inert polymeric hydrocarbon matrix to which functional groups are attached. The polymer matrix is a three-dimensional network that swells when in contact with aqueous solutions [1].

Ion exchange resins are tightly cross-linked structures containing fixed polar anionic groups whose negative charges are balanced by cations [6]. The chemical, thermal and mechanical stability as well as the ion exchange behaviour of resins depend chiefly on the structure and degree of crosslinking of the matrix and on the nature and number of fixed ionic groups.

Chemical and thermal stability of resins are not limited. Resin deterioration are mainly caused by thermal and chemical degradation of the matrix (oxidation) and loss of fixed ionic groups (hydrolysis). Most present commercial resins are stable in all common solvents except in the presence of oxidizing or reducing agents and withstand temperatures up to 100 degrees C.

Anion exchange resins are produced when amines are used to react with the chloromethylated resin matrix. The active groups in anion exchange resins are either quaternary ammonium groups for strong base resins, or primary, secondary or tertiary for weak base resins.

The rates of the exchange reactions are therefore high. Reactions are reversible and generally diffusion controlled, and the selectivity of the resins for one ion over the other is predominantly a function of the size, charge, and polarizability of the ions.

Cation exchange resins are described as polymers containing phenolic, sulphonic, carboxylic and phosphonic acid groups as an integral part of the resin and equivalent amount of cations [7]. Irrespective of their method of manufacture, ion exchange resins are all cross-linked gels, containing a high proportion of water as an essential part of their structure.

Two types of resin exist [1]:

- the gel type
- the macroporous or macroreticular type

The gel type offers a high exchange capacity while the macroporous type offers physiochemical durability and faster loading kinetics.

Selectivity of resins are determined by the nature of their fixed ionic groups. For example, resins with sulphonic acid groups prefer Ag^+ while resins with carboxylic acid groups prefer alkaline-earth cations, and resins with chelating groups prefer certain heavy-metal cations [1].

Innumerable types of ion exchange resins with different properties can be prepared. The nature and number of the fixed ionic groups as well as the composition and the cross-linking of the matrix can be varied in order to adapt to certain applications.

1.3 Preparation of Ion Exchangers

Synthetic resins have become the most efficient and widely used ion exchangers [4]. Ion exchange resins can be obtained from manufacturing companies. Most companies prefer to buy resins from these companies due to the difficulty in preparing them.

Synthesis of ion exchange resins must yield a three-dimensional. cross-linked matrix of hydrocarbon chains carrying fixed ionic groups. The matrix can be formed by polycondensation or addition polymerization. The fixed ionic groups can be introduced to the monomers, which make up the resin or can also be introduced into the cross-linked resin after polymerization.

The resin should be insoluble and able to swell. Too many cross-links inhibits swelling and reduces the mobility of counter ions, hence cross-linking should be formed at appropriate levels.

1.4 Equilibria

Equilibria between ion exchangers and solutions have been subjected to extensive experimental and theoretical research [1]. Most of earlier investigations focused on the distribution of different competing counter ion species between the ion exchanger and solution. Swelling and sorption equilibria received little attention until organic ion exchange resins were studied.

Several equilibria theories between ion exchangers and solutions have been developed and are in good agreement with experimental results.

1.4.1 Theoretical Approaches and Models

Equilibria between ion exchangers and solutions can be explained by means of rigorous thermodynamics [8]. This treatment is regarded as correct and universal but yields a minimum of information about the physical causes of the phenomena to which it is applied. The quantities involved in this treatment cannot be determined by measurement and can neither be predicted without using thermodynamic assumptions.

Models with particular properties resembling those of the ion exchanger have therefore been introduced for deriving equations to explain various physical forces. With such models the effect of changes on the system can be analysed.

Commitment to a model however can mean deviation from rigorous thermodynamics. Relations derived from specific models are meaningful only when the properties of the actual system are aptly represented by the model. Certain models involve several parameters which can be chosen within wide limits so as to fit experimental results. A better criterion for models is its ability to predict system behaviour based in fundamental data [9].

The behaviour of ion exchangers depends on an overwhelming variety of factors. One or the other of these factors may be the most or least important and accordingly so the numerous theories will be affected.

1.5 Swelling

1.5.1 Principles

Ion exchange resins are able to sorb solvents. The resin then usually expands to a limited degree. Ion exchange resins can also swell in water and polar solvents.

Swelling equilibrium is a balance of forces where equilibrium is obtained when the elastic forces of the matrix balance the dissolution tendency of 'he resin. The extent of swelling therefore depends on [4]:

- nature of the solvent
- degree of cross-linking
- nature of the fixed ionic groups
- capacity
- nature of the counter ion

- ion-pair formation and association
- solution concentration

Swelling is favoured by:

- polar solvents
- high resin capacity
- strong solvation tendency of the fixed ionic groups
- large and strongly solvated counter ions
- low valence of the counter ion
- complete dissociation in the resin
- low concentration of the external solution [5]

This information is particularly important in column operations. An ion exchange column can burst when a resin swells and excessive shrinking favours channeling, particularly at column walls.

1.6 Water of Hydration and Free Water

Water uptake by an initially dry resin is accompanied in the initial stages by a volume contraction of the system [10]. Later it is taken up without any significant change in system volume . Hydration shells are more tightly packed than free water and it can therefore be concluded that as long as the total system volume contracts, hydration shells are formed and additional water is taken up as free water.

Free water content does not necessarily parallel total water content or the expansion of the resin. Swelling of a resin increases when a counter ion is replaced by another larger one in its hydrated state. The more swollen resin together with the higher swelling pressure squeezes out free water thereby reducing resin free water content.

Many experimental results are easier explained in terms of free water content than in terms of total water content.

1.7 Sorption of Solutes

Ion exchangers can sorb solutes from solutions they are in contact with. The solute then can be removed from the resin by washing with pure solvent.

The sorption behaviour of strong electrolytes is different from that of weak or non-electrolytes. Weak and non-electrolytes are sorbed by ion exchangers in a similar way as non-ionic adsorbents. Strong electrolytes are exposed to forces arising from the presence of fixed ionic groups and counter ions in the resin.

The result is a Donnan type sorption equilibrium unique to ionic sorbents.

1.8 Sorption Isotherms and Distribution Coefficients

1.8.1 Sorption Isotherms

Sorption isotherms describe the dependence of the equilibrium concentration of the solute in the sorbent on the concentration of the external solution. For ion exchangers it is preferable to relate the concentrations in terms of the ion exchanger and the solution. The sorption isotherm is therefore either of the two functions [1]:

$$m_{i,r} = f(m_{i,s})$$

$$C_{i,r} = g(C_{i,s})$$

The molal isotherm is used when a distinction is made between the pore liquid and the matrix while the molar isotherm is used when the sorbent is treated as a single phase.

1.8.2 Distribution Coefficients

The distribution coefficient of solutes is defined as the ratio of the concentrations of the solute in the sorbent and solution [1]:

$$i = \frac{m_{i,r}}{m_{i,s}} \quad \text{(molal distribution)}$$

$$i = \frac{C_{i,r}}{C_{i,s}} \quad \text{(molal distribution)}$$

Only in the case of a linear isotherm will the distribution coefficient be independent of concentration.

1.9 Sorption of Non-electrolytes

1.9.1 Ionic Solvation and Salting Out

The fixed ionic groups and counter ions in the ion exchanger form solvation shells and tie up solvent molecules. Only a fraction of the solvent is 'free' and only the free solvent can dissolve non-electrolyte.

In the absence of any other interactions. one must expect the concentration of free solution to equal the concentration in the resin. The molality which refers to the total solvent including ionic solvation shells is thus lower in the resin than in the free solvent. The non-electrolyte is then salted out in the same way as in liquid-liquid equilibria when two liquids come into contact with one liquid containing a salt or higher concentration of salt [7].

Salting out effects are most effective when only a small fraction of the solvent is free. This is the case when the resin is highly cross-linked and counter ions are strongly hydrated. Molal distribution of the solute thus decreases with an increase in cross-linking and solvation number of the counter ion.

1.10 Sorption of Strong Electrolytes

Equilibria of ion exchangers with electrolytic solutions are more complex than those with non-electrolytes. Two essential aspects differentiates between electrolytic and no-electrolytic sorption:

- The ion exchanger contains counter ions prior to sorption and the sorbed ions are indistinguishable from the original ones
- Mobile ions are subject to electrostatic forces of the system

1.11 The Donnan Potential

To understand the origin of electrostatic forces in the system. consider a cation exchanger being placed in a dilute solution of a strong electrolyte. The cation concentration is larger in the ion exchanger and the anion concentration is larger in the solution.

If the ions carried no electrical charge. the concentration difference would be leveled out by simple diffusion. Such a process would however disturb electroneutrality. Migration of cations into the positively charged solution and anions into the ion exchanger would result in an accumulation of positive charge in the solution and negative charge in the ion exchanger [11].

The first few ions that diffuse would thus build up and electrical potential difference between the ion exchanger and solution. The potential difference is called the Donnan Potential. The Donnan potential pulls cations back into the ion exchanger and anions back into the solution.

An equilibrium is established when the tendency of the ions to level out the concentration differences is balanced by the electric forces [1]. For this reason the ion exchanger has a much higher counter ion concentration and a much lower co-ion concentration than the external solution. The same occurs with anion exchangers but the Donnan potential is of opposite sign.

The Donnan potential has one immediate consequence for electrolyte sorption. It repels co-ions from the ion exchanger and prevents the internal co-ion concentration from exceeding an equilibrium value which is far smaller than the concentration in the external solution.

The higher the Donnan potential, the increase in co-ion exclusion and the smaller the electrolyte uptake. The Donnan potential in turn depends on the ionic concentrations and valences. The Donnan potential is greater with an increase in concentration difference between the ion exchanger and the external solution. The absolute value of the Donnan potential also increases with a decreasing external and increasing internal counter ion concentration [11]. This also results in an increase in the efficiency of electrolyte exclusion.

The force with which an electric field acts on an ion is proportional to the ionic charge. The Donnan potential thus decreases with an increase in counter ion valence and electrolyte exclusion efficiency decreases.

Various kinds of interactions in the ion exchanger can strongly affect electrolytic sorption. Association or ion-pair formation between the counter ions and the fixed ionic groups localizes the counter ions in the ion exchanger and decreases the Donnan potential. Weak acid cation exchangers in H^+ form are very little ionized and hence do not exclude acids [8]. The acids are taken up according to/following Langmuir or Freundlich isotherms rather than the Donnan-type principle. This is also true for sorption of bases by weak-base anion exchangers.

Even more conspicuous deviations from Donnan type isotherms occur when multi-valent ions associate strongly with fixed ionic groups. The rules for Donnan type exclusion may even be reversed in such cases.

1.12 Ion Exchange Equilibria

Ion exchange equilibrium is obtained when an ion exchanger is placed in an electrolytic solution containing an ion different to that of the ion exchanger and the counter ions exchange positions until there is no longer a driving force present to promote ion exchange [1]. Using the example that the ion exchanger contains counter ion A and the solution contains counter ion B the following is observed:

$$A_{\text{ion exchanger}} + B_{\text{solution}} \Leftrightarrow B_{\text{ion exchanger}} + A_{\text{solution}}$$

The exchange as a rule is reversible and therefore it makes no difference whether A is exchanged for B. or B for A.

1.13 Copper

- **Standard State**: solid at 298 K
- **Colour**: copper. metallic
- **Symbol**: Cu

- **Atomic Number:** 29
- **Molar Mass:** 63.546
- **Group Number:** 11
- **Period Number:** 4
- **Atomic Diameter:** 2.551×10^{-10}m
- **Density at 293K:** 8.94×10^3 kg/m^3
- **Melting Point:** 1356K
- **Boiling Point:** 2868K
- **Valence States:** 2 & 1
- **Heat of Fusion:** 134kJ/kg
- **Heat of Vaporization:** 3630kJ/kg

Copper (Cu), is a reddish metallic element with a bright metallic lustre and is widely used in many applications [12]. Copper is one of the transition elements on the periodic table with an atomic number of 29.

Copper was first used by man over 10,000 years ago. A copper pendant discovered in what is now northern Iraq has been dated about 8700 B.C. For nearly five millennia copper was the only metal known to man, and was thus used in all metal applications. By 5000 BC, the dawn of metallurgy had arrived, as evidence exists of the smelting of simple copper oxide ores such as malachite and azurite.

Because of its many desirable properties, such as its conductivity of electricity and heat, its resistance to corrosion, its malleability and ductility, and its beauty, copper has long been used in a wide variety of applications [9]. The principal use is electrical because of coppers' extremely high conductivity, which is second only to that of silver.

Pure copper is soft but can be hardened somewhat by further processing. Alloys of copper, which are far harder and stronger than the pure metal, have higher resistance and so cannot be used for electrical purposes. They do, however, have corrosion resistance almost as good as that of pure copper and are very easily worked in machine shops. The two most important alloys are brass (a zinc alloy) and bronze (a tin alloy).

Both tin and zinc are sometimes added to the same alloy, and no sharp dividing line can be drawn between brass and bronze. Both are used in enormous quantities. Copper is also alloyed with gold, silver, and nickel, and is an important constituent of alloys such as monel metal, gunmetal and German silver.

Copper forms two series of chemical compounds: *cuprous*, in which the copper has a valency of 1, and *cupric*, in which the copper has a valency of 2 [12]. Cuprous compounds are easily oxidized to cupric, in many cases by mere exposure to air while cupric compounds are stable.

1.13.1 Sources

Coppers' flow through the economy starts at mining companies, which process vast quantities of low-grade ore, mostly from open-pit mines in order to produce copper.

The production of copper can be broken up in the following stages:

- Mining
- Crushing
- Grinding/Milling
- Concentrating
    - Leaching and Electrowinning, or
    - Smelting and Electrolytic Refining

1.13.1.1 Mining, Crushing

Copper is obtained by mining sulfide and oxide ores through digging or blasting and then crushing it to walnut-sized pieces.

1.13.1.2 Grinding

Crushed ore is ball or rod-milled in large, rotating, cylindrical machines until it becomes a powder usually containing less than 1 percent copper. Sulfide ores are moved to a concentrating stage, while oxide ores are routed to leaching tanks.

1.13.1.3 Concentrating

Minerals are concentrated into a slurry that is about 15% copper. Waste slag is removed and water is recycled. Tailings (left-over earth) containing copper oxide are routed to leaching tanks or are returned to the surrounding terrain.

Once copper has been concentrated it can be turned into pure copper cathode in two different ways: Leaching & electrowinning or smelting and electrolytic refining.

1.13.1.3a Leaching and Electrowinning

Oxide ore and tailings are leached by a weak acid solution, producing a weak copper sulfate solution.

The copper-laden solution is treated and transferred to an electrolytic process tank. When electrically charged, pure copper ions migrate directly from the solution to starter cathodes made form pure copper foil [12]. Precious metals can be extracted from the solution.

1.13.1.3b Smelting and Electrolytic Refining

Several stages of melting and purifying the copper content result, successively, in matte, blister and, finally, 99% pure copper. Recycled copper begins its journey to finding another use by being resmelted.

Anodes cast from the nearly pure copper are immersed in an acid bath [12]. Pure copper ions migrate electrolytically from the anodes to "starter sheets" made from pure copper foil where they deposit and build up into a 300-pound cathode. Gold, silver and platinum may be recovered from the used bath.

1.13.1.4 End Product

Cathodes of 99.9% purity may be shipped as melting stock to mills or foundries. Cathodes may also be cast into wire rod, billets, cakes or ingots, generally, as pure copper or alloyed with other metals. Cathode is converted to:

- Wire Rod - Coiled rod about 1/2" in diameter is drawn down by wire mills to make pure copper wire of all gages.
- Billet - 30' logs, about 8" diameter, of pure copper are sawed into these shorter lengths which are extruded and then drawn as tube, rod and bar stock of many varied sizes and shapes. Rod stock may be used for forging.
- Cake - Slabs of pure copper, generally about 8" thick and up to 28' long, may be hot- and cold-rolled to produce plate, sheet, strip and foil.
- Ingot - Bricks of pure copper may be used by mills for alloying with other metals or used by foundries for casting.

Most copper production is based on sulphide ores containing little copper but significant amounts of iron. New cleaner technologies are now important with older processes present major environmental problems. Complex procedures are used initially to form copper sulphide appropriate for final reduction via a copper(I) oxide [7]

The resulting crude copper is purified using an electrolytic procedure involving plating onto pure copper cathodes.

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

Notably, the purification step leaves an "anode slime" which contains useful amounts of silver and gold.

The metallurgy of copper varies with the composition of the ore [5]. Native copper is crushed, washed, and cast in bars. Oxides and carbonates are reduced with carbon. The most important ores, the sulfides, contain not more than 12 percent, sometimes as little as 1 percent, of copper and must first be crushed and concentrated by flotation.

The concentrates are smelted in a reverberatory furnace, which yields crude metallic copper, approximately 98 percent pure. Crude copper is further purified by electrolysis, yielding bars exceeding 99.9 percent purity.

Copper ore normally is crushed, ground, and concentrated, usually by flotation, to produce a beneficiated ore containing about 25% copper. The ore concentrates are reduced to the metallic state, most often by a pyrometallurgical process. Traditionally, the concentrated ore is processed in a primary smelting reactor to produce a copper sulfide-iron sulfide matte, up to 60 percent copper.

At present, reverberatory technology is rapidly being replaced by oxygen/flash smelting, which greatly reduces the volume of off-gases [9]. Sulfuric acid is manufactured from the sulphur dioxide contained in these off-gases, reducing air pollution by 95% or more and providing an important co-product of copper smelting.

The matte is oxidized in a converter to convert the iron sulfides to iron oxides, which separate out in a slag, and to reduce the copper sulfide to blister copper, which contains at least 98.5 percent copper. Current technology combines the converting step with the preceding smelting step. Fire refining of blister copper then removes most of the oxygen and other impurities, leaving a product of at least 99.5 percent purity, which is cast into anodes. Finally, most anode copper is electrolytically refined, usually to a purity of at least 99.95 percent.

The resulting cathodes are the normal end product of the producer companies and are a common item of commerce. In recent years, many producers have installed continuous-cast rod mills to directly convert cathode copper to wire rod wire and cable mills [12]. Primary producers may also convert the cathode to cakes or billets of copper for sale to brass mills.

Hydrometallurgical processing is an increasingly important alternative to pyrometallurgy, particularly for nonsulfide ores, such as oxides, silicates, and carbonates. Weak acid is percolated through ore or waste dumps of rejected materials. Copper is leached out of the ore by the acid solution extraction, to produce an electrolyte suitable for electrowinning, wherein copper is extracted electrolytically much as anode copper is electrorefined. Electro-won copper is equal in quality to that produced by electrolytic refining [12].

1.13.2 Uses of Copper

Because copper is very ductile, it can be drawn into wires of any diameter from about 0.025 mm (about 0.001 in) upward. The tensile strength of drawn copper wire is about 4200 kg/sq cm (about 60,000 lb/sq in). It can be used in outdoor power lines and cables, as well as in house wiring, lamp cords, and electrical machinery such as generators, motors, controllers, signaling devices, electromagnets, and communications equipment .

Copper has been used for coins throughout recorded history and has also been fashioned into cooking utensils, vats, and ornamental objects. Copper was at one time used extensively for sheathing the bottom of wooden ships to prevent fouling. Copper can easily be electroplated, by itself or as a base for other metals. Large amounts are used for this purpose, particularly in making electrotypes, reproductions of type for printing.

The copper industry has two main segments:

- producers-mining, smelting, refining companies
- fabricators-wire mills, brass mills, foundries, powder plants.

The end products of the producers, the most important of which are refined cathode copper and wire rod, are sold almost entirely to the copper fabricators [12]. The end products of the fabricators consist of :

- electrical wire
- strip
- sheet
- plate
- rod
- bar
- mechanical wire
- tube
- forgings
- extrusions
- castings
- powder

These products are sold to a wide variety of users: mainly the construction industry, manufacturing industries, and the government. Certain mill products, chiefly wire, cable, and most tubular products, are used without further metalworking. On the other hand, most flat-rolled products, rod, bar, mechanical wire, forgings, castings and powder go through multiple forming, machining, finishing, and assembling operations before emerging as finished products.

Copper wire mill products are destined for use as electrical conductors [2]. Starting with wire rod, these mills cold draw the wire (with necessary anneals) to final dimensions through a series of dies. The individual wires may be stranded and normally are insulated before being gathered into cable assemblies.

Brass mills melt and alloy feedstock to make strip, sheet, plate, tube, rod, bar, mechanical wire, forgings, and extrusions. Somewhat less than half the copper input is refined and the rest is scrap. Fabricating processes, such as hot rolling, cold rolling, extrusion, and drawing are employed to convert the melted and cast feedstock into mill products.

About 45% of the output of US brass mills is unalloyed copper and high-copper alloys, chiefly in such forms as plumbing and air conditioning tube, busbar and other heavy-gage, flat products for electrical use, strip for auto radiator and other heat-exchanger fins, and roofing sheet [12].

Copper alloys comprise the remaining 55%. Free-cutting brass rod, which exhibits outstanding machinability and good corrosion resistance, and brass strip, which has high strength, corrosion resistance, excellent formability, and good electrical properties, together constitute about 80% of the total tonnage of copper alloys shipped from US brass mills.

Other alloy types of major commercial significance include:

- copper-nickels, which are strong and particularly resistant to seawater and used for coinage
- tin bronzes (phosphor bronzes), which are noted for their excellent cold forming behavior and strength
- tin brasses, known for outstanding corrosion resistance
- nickel silvers, which combine a silvery appearance with good formability and corrosion resistance

- beryllium coppers, which provide outstanding strength when hardened
- aluminum bronzes, which have high strength along with good resistance to oxidation, chemical attack, and mechanical abrasion.

Foundries use pre-alloyed ingot, scrap, and virgin metal as raw materials. Their chief products are shaped castings for many different industrial and consumer goods, the most important of which are plumbing products and industrial valves. Centrifugal and continuous cast copper alloy products find major application as bearings, cylinders, and other symmetrical components [7].

Powder plants produce powder and flake for further fabrication into powder metallurgy parts, chiefly small sintered bronze bushings, and other uses. Certain copper solutions have the power of dissolving cellulose, and large quantities of copper are for this reason used in the manufacture of rayon. Copper is also used in many pigments and in insecticides fungicides although it is being largely replaced by synthetic organic chemicals for these purposes.

1.13.3 Markets

Despite popular belief that copper is a material that is always on the defensive and being substituted for, analysis shows the opposite to have been true over the last ten or fifteen years. In the late 1960's and early 1970's, copper was indeed the object of considerable substitution, particularly by aluminum in wire mill products [9]. This aluminum penetration resulted in copper reaching its lowest market share at 71.9% of the total insulated wire and cable market in 1974, with particularly sharp aluminum inroads into power cable, building wire, and magnet wire (used to wind motors and transformers).

Building wiring and plumbing have been the two top markets in recent years. Both have benefited from an increasing intensity of use (more electrical loads and more bathrooms in new homes). Plastics are an ongoing threat to copper in plumbing applications but their usage is still held back by their susceptibility to permeation by gasoline and other organics and to mechanical damage. They also do not exhibit copper's bacteriostatic properties.

Automotive applications, copper's third largest market, is the source of the most serious current substitution threat-aluminum in the radiator [2]. Copper's answer to this threat is new soldering materials, better radiator designs, and new automated production techniques.

Though aluminum has made inroads into the radiator, copper has gained far more due to the dramatic increase in wiring and electronics within the average car. Today, the use of copper and copper alloys in an average US-built passenger car is about 50 pounds, versus 36 pounds in 1980.

Telecommunications, on the other hand, has dropped from the number 2 spot to number 4 in less than a decade. Fiber optics is the popular explanation for this decrease, but in fact it accounted for little of it prior to 1990. Other technological factors are responsible, such as subscriber carrier (piggybacking of many phone conversations on a single pair of copper wires) and the use of wires of smaller cross-section. This is a textbook example of copper applications being engineered for ever-increasing efficiency of use, which results in decreased poundage. However, optical fibers are indeed a real threat for the future. Whether that threat is realized may depend more on cost factors than technical considerations.

Copper also goes head-to-head with aluminum in power utilities [12]. Aluminum's light weight is its one advantage in current-carrying applications and it is used almost exclusively in overhead transmission and distribution cable. The advent of high temperature superconductors, today's hottest technical area, opens new vistas of possibility. Superconductors need to be surrounded by "shunt" materials, which can carry heavy currents around faults that occasionally occur in the superconductor. The mini-materials battle between copper and aluminum for the best such material for current-technology superconductors such as niobium-titanium has been won by copper.

Superconductivity could be an important new market for copper, particularly in transmission lines, energy storage devices, and other applications not yet contemplated.

A fact that is surprising to many is that when the markets are put on a usage-intensity basis-that is, pounds of copper used per unit of measure of each industry (use per housing start, per vehicle, per ton of air-conditioner capacity, etc.), copper has shown increasing use in the last ten years. This is in contrast to the often quoted statement that the intensity of use of copper and other "mature" metals is falling rapidly [12].

Copper's healthy maintenance of markets and its promise to gain new ones, such as superconductivity applications, new marine uses such as ship hulls and sheathing of offshore platforms, electric vehicles, earth-coupled heat pumps, solar energy (which will inevitably re-emerge at some point when oil supplies tighten), fire sprinkler systems, and nuclear waste disposal canisters, to name a few, must be balanced against its prospects of future availability. Of the world's reserves of copper about one-quarter of the deposits are economically recoverable now or in the near future.

There are wide variations in the energy used to recover metals from the earth's crust. Copper ranks near the middle for energy required for extraction-higher than iron, zinc or lead, but at considerable advantage to aluminum, titanium and magnesium, which require much larger quantities of energy to break down the ore (or seawater and brines in the case of magnesium) into metallic form [13].

For all metals the recycling of scrap is considerably more energy-efficient than recovery from ores, and here copper's high recycling rate-higher than any other engineering metal-makes it the material of choice.

Each year in the USA more copper is recovered and put back into service from recycled material than is derived from newly mined ore. Copper's recycle value is so great that premium-grade scrap normally has at least 95% of the value of primary metal from newly mined ore.

This concludes that copper will continue its 10.000-year history of usefulness many millennia into the future.

1.14 Cobalt

Symbol:	Co
Atomic Number:	27
Molar Mass:	58.933200
Group Number:	9
Period Number:	4

Cobalt (Co) is a silvery-white magnetic metallic element used chiefly for making alloys. The atomic number of cobalt is 27 and it is one of the transition elements on the periodic table. Cobalt was discovered in 1735 by the Swedish chemist George Brandt. It has a relatively low strength and little ductility at normal temperatures. but is ductile at high temperatures. Cobalt melts at about 1495° C and boils at about 2870° C. It has a specific gravity of 8.9 and the atomic weight of cobalt is 58.933.

Of several known cobalt isotopes. the radioactive cobalt-60 is the most important. It has a half-life of 5.7 years and produces intensive gamma radiation [5]. Cobalt-60 is used extensively in industry and in radioisotope therapy.

Thermally resistant alloys. called superalloys. containing cobalt are used in industry and aircraft gas turbine engines. An alloy with steel known as cobalt steel is used for making permanent magnets. With tungsten carbide. cobalt forms Carboloy. a hard material used for cutting and machining steel: alloyed with chromium. cobalt produces Stellite. used for the same purpose. Cobalt is also used in ceramics and paint driers and as a catalyst [12].

1.14.1 Sources

Cobalt is about the 30th most abundant element in crustal rocks. Cobalt occurs as:

- arsenide $CoAs_2$, known as smaltite or speiss cobalt
- as cobalt sulfarsenide (CoAsS), known as cobalt glance orcobaltite
- and as a hydrated arsenate of cobalt ($Co(AsO_4)_2 \cdot 8H_2O$), known as cobalt bloom or erythrite.

The chief commercial sources of cobalt are the cobaltite ores of Ontario in Canada, and the central African nations of the Democratic Republic of the Congo (DRC, formerly Zaire) and Zambia, which, along with Canada, are the world's leading producers of the metal [12].

It is not normally necessary to make cobalt in the laboratory as it is available readily commercially. Industrially, however, it is normally produced as a byproduct from the production of copper, nickel and lead.

Normally the ore is "roasted" to form a mixture of metals and metal oxides. Treatment with sulphuric acid leaves metallic copper as a residue and disolves out iron, cobalt and nickel as the sulphates [3]. Iron is obtained by precipitation with lime (CaO) while cobalt is produced as the hydroxide by precipitation with sodium hypochlorite (NaOCl)

$$2Co^{2+}(aq) + NaOCl(aq) + 4OH^-(aq) + H_2O \rightarrow 2Co(OH)_3(s) + NaCl(aq)$$

The trihydroxide $Co(OH)_3$ is heated to form the oxide and then reduced with carbon (as charcoal) to form cobalt metal.

$$2Co(OH)_3(\text{heat}) \rightarrow Co_2O_3 + 3H_2O$$

$$2Co_2O_3 + 3C \rightarrow 4Co + 3CO_2$$

1.15 Nickel

Symbol:	Ni
Atomic Number:	28
Molar Mass:	58.6934
Group Number:	10
Period Number:	4

Nickel is a silvery white metal that takes on a high polish and is used chiefly in making alloys. It is hard, malleable, ductile, somewhat ferromagnetic, and a fair conductor of heat and electricity [5].

Nickel was used as coinage in nickel-copper alloys for several thousand years, but was not recognized as an elemental substance until 1751 when the Swedish chemist Baron Axel Frederic Cronstedt isolated the metal from niccolite ore [12].

1.15.1 Properties

Nickel is a hard, malleable, ductile metal, capable of taking a high polish. It is magnetic below 345° C (653° F) and exists in five stable isotopic forms. Metallic nickel is not very active chemically. It is soluble in dilute nitric acid and becomes passive (nonreactive) in concentrated nitric acid and it does not react with alkalies. Nickel melts at about 1455° C (about 2651° F), boils at about 2730° C (about 4946° F) and has a specific gravity of 8.9.

1.15.2 Sources

A rich deposit of nickel was discovered in 1957 in northern Québec and most of the world supply of nickel is mined in Canada. Cuba, the former Union of Soviet Socialist Republics (USSR), China and Australia are next in importance as nickel producers [12].

World mine production (nickel content) in 1991 totaled about 923,000 metric tons. The United States has no large deposits of nickel and accounts for less than 1 percent of the annual world output. Most of the nickel that is used in the United States must be imported and approximately 30 percent of annual U.S. consumption is recycled.

Nickel is found as a constituent in most meteorites and often serves as one of the criteria for distinguishing a meteorite from other minerals. Iron meteorites, or siderites, may contain iron alloyed with from 5% to nearly 20% nickel [12].

Combined with other elements, it occurs in minerals such as garnierite, millerite, niccolite, pentlandite, and pyrrhotite, the latter two minerals being the principal ores of nickel. Nickel ranks about 22nd in natural abundance among elements in crustal rock.

It is not normally necessary to make nickel in the laboratory as it is available readily commercially. Small amounts of pure nickel can be isolated in the laborotory through the purification of crude nickel with carbon monoxide. The intermediate in this process is the highly toxic nickel tetracarbonyl, $Ni(CO)_4$. The carbonyl decomposes on heating to about 250°C to form pure nickel powder [5].

$$Ni + 4CO(50°C) \rightarrow Ni(CO)_4(230°C) \rightarrow Ni + 4CO$$

The $Ni(CO)_4$ is a volatile complex which is easily flushed from the reaction vessel as a gas leaving the impurities behind.

Industrially, the Mond process uses the same chemistry. Nickel oxides are reacted with "water gas", a mixture of $CO + H_2$. Reduction of the oxide with the hydrogen results in impure nickel. This reacts with the CO component of the water gas to make $Ni(CO)_4$ as above. Thermal decomposition leaves pure nickel metal.

1.15.3 Nickel Production

Nickel ores usually contain impurities, chief among which is copper. Sulfide ores, such as pentlandite and nickeliferous pyrrhotite, are usually smelted in a blast furnace and shipped in the form of a matte of copper and nickel sulfide to refineries, where the nickel is removed by various processes. In the electrolytic process, the nickel is deposited in pure metallic form after the copper has been preferentially removed by deposition at a different voltage and in a different electrolyte [12].

In the Mond process, copper is removed by dissolution in dilute sulfuric acid and the nickel residue is reduced to impure metallic nickel [7]. Carbon monoxide is passed over the impure nickel, forming nickel carbonyl ($Ni(CO)_4$), a volatile gas. The nickel carbonyl is heated to 200° C (392° F) and decomposes, depositing pure metallic nickel. Nickel carbonyl, [$Ni(CO)_4$] is an extremely toxic gas and exposure should not exceed 0.007 mg m^{-3}.

1.15.4 Uses of Nickel

Nickel is used as a protective and ornamental coating for metals, particularly iron and steel, that are susceptible to corrosion. The nickel plate is deposited by electrolysis in a nickel solution. Finely divided nickel absorbs 17 times its own volume of hydrogen and is used as a catalyst in many processes, including the hydrogenation of oils.

Nickel is used chiefly in the form of alloys. It imparts great strength and corrosion resistance to steel. Nickel steel, containing about 2 to 4 percent nickel, is used in automobile parts such as axles, crankshafts, gears, valves, rods, machine parts and in armor plate. Some of the most important nickel-containing alloys are German silver, Invar, Monel metal, Nichrome, and Permalloy. The nickel coins used for currency are an alloy of 25 percent nickel and 75 percent copper. Nickel is also a key component of nickel-cadmium batteries [12].

1.15.4.1 Nickel Compounds

I. Nickel forms primarily divalent (nickelous) compounds, although examples of compounds with formal oxidation states ranging from -1 to +4 are known. Most of the salts of nickel, such as nickel chloride ($NiCl_2$), nickel sulfate ($NiSO_4$) and nickel nitrate ($Ni(NO_3)_2$), are green or blue in color and they are most commonly hydrated.

II. Nickel ammonium sulfate ($NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) is used in nickel-electroplating solutions. Nickel compounds are often identified by adding an organic reagent, dimethylgloxime, which reacts with nickel to form a red flocculent precipitate.

1.16 Isotherms

1.16.1 The Ion Exchange Isotherm

Ion exchange equilibrium can be characterized by the 'ion exchange isotherm' [9]. The isotherm gives a graphical representation which covers all experimental conditions at a given temperature. Equilibrium can be described in terms of the following quantities:

- separation factor
- selectivity coefficient
- distribution coefficient

These quantities vary with temperature and any of their specific values corresponds to only one point on the isotherm surface. The ion exchange isotherm shows the ionic composition of the ion exchanger as a function of experimental conditions. Various representations can be used but as a rule the equivalent ionic fraction x_{Ar} of the counter ion A in the ion exchanger is plotted as a function of the equivalent ionic fraction x_{As} in the solution while the other variables are kept constant. The equivalent ionic fraction is calculated as follows:

$$x_A = \frac{z_A m_A}{z_A m_A + z_B m_B}$$

or

$$X_A = \frac{z_A m_A}{\Sigma z_i m_i}$$

The dependence of x_{Ar} on the total solution concentration can be shown in a three dimensional representation in which the isotherm is a curved surface. In a system where the ion exchanger shows no preference for counter ions, the equivalent ionic fraction for the ion exchanger is the same as that for the solution and the ion exchange isotherm will thus be linear.

1.16.1.1 The Separation Factor

If ion A is preferred to ion B in the above-mentioned example, the isotherm is negatively curved and if B is preferred, the isotherm is positively curved. The preference of ion exchangers for one counter ion is often expressed by the separation factor [1].

The separation factor is the quotient of the concentration ratios of the two counter ions in the ion exchanger and in the solution

$$\text{Separation factor} = \frac{x_{Ar}\,x_{Bs}}{x_{As}\,x_{Br}}$$

The separation factor is usually not constant and depends on solution concentration, temperature and the equivalent fraction [10].

1.16.1.2 Selectivity Coefficient

The selectivity coefficient can be used instead of the separation factor to describe ion exchange equilibria. The equation describing selectivity coefficients is similar to that of the separation factor but the selectivity constant equation incorporates the ionic valences as exponents:

$$\text{Selectivity constant} = \frac{m_{Ar} Z_B m_{Bs} Z_A}{m_{Br} Z_A m_{As} Z_B}$$

$$\text{or} \qquad \frac{C_{Ar} z_B C_{Bs} z_A}{C_{Br} z_A C_{As} z_B}$$

$$\text{or} \quad \frac{x_{Ar} z_B x_{Bs} z_A}{x_{Br} z_A x_{As} z_B}$$

where it is preferable to use absolute values for the ionic valences

1.16.1.3 Distribution Coefficient

Equilibrium can also be conveniently expressed in terms of distribution coefficients of the counter ions [10]:

$$\text{Distribution coefficient} = \frac{m_{Ar}}{m_{As}} = \frac{x_{Ar} m_r}{x_{As} m_s}$$

$$\text{and} \qquad \frac{C_{Ar}}{C_{As}} = \frac{x_{Ar} C_r}{x_{As} C_s}$$

The use of distribution coefficients is particularly advantageous when the species is a trace component.

The concentration ratio of the counter ions in the ion exchanger is usually different to that in solution as the ion exchanger selects one counter ion in preference to the other [10]. This ion exchanger characteristic is called its selectivity.

1.16.2 Single component isotherms

The most commonly used single solute isotherms in aqueous solutions are:

- Linear isotherm: $q_e = AC_e$
- Freundlich isotherm: $q_e = AC_e^{\,n}$ [13]
- Langmuir isotherm: $q_e = \dfrac{AC_e}{\sum_{i=1}^{n} B_i C_e}$ [14]

The linear isotherm should only be used at very low adsorbate concentrations [11]. The Freundlich isotherm has been widely used to describe the adsorption of solutes from single solute solutions but a disadvantage of the isotherm is that it does not approach linearity at low concentrations. The Langmuir isotherm is based on the assumption that maximum adsorption takes place when a single layer of adsorbate covers the adsorbent surface and that the adsorption energy is constant. At very low concentrations the Langmuir isotherm reduces to a linear form.

1.16.3 Multi-component isotherms

The adsorption of a component in a multi-component solution is determined not only by its concentration but also by the competitive effect of the other components in solution.

The single component Freundlich isotherm may be extended to incorporate more than one adsorbing species:

$$q_{e,i} = A_i C_{e,i} \left[C_{e,i} + \sum_{j=1}^{N} B_{i-j} C_{e,j} \right]^{n_i - 1}$$

The Langmuir isotherm can be extended as follows to account for multi-component systems:

$$q_{e,i} = \frac{A_i C_{e,i}}{1 + \sum_{j=1}^{N} A_j C_{e,j}}$$

Fritz and Schleunder suggested a general empirical equation for calculating the adsorption equilibria of components in aqueous solutions [15]:

$$q_{e,i} = \frac{A_i C_{e,i}^{\,n_i}}{D_i + \sum_{j=1}^{N} A_j C_{e,j}^{\,n_j}}$$

1.17 Significance of the literature study

- Ion exchange by resin is a complex process to describe and model
- Cu. Ni and Co are produced in large quantities and have a wide application area
- Cu substitution by other metals such as aluminium is notable. hence the need for effective and efficient Cu recovery thereby reducing production costs.
- Hydromatallurgy has become an alternative to pyrometallurgical processes

CHAPTER 2

EXPERIMENTAL

All experimental work was performed in a stirred 1litre glass beaker in which the 1 litre solution was contacted with 5ml of IRC748 resin. The volume of resin used in the experiments was determined from its capacity (>1.25 eq/l) and by measuring it in a small volumetric cylinder. Properties of the resin can be seen in Appendix 1. Cu, Ni and Co solutions were made up by mixing distilled water with respective metal sulphates.

The concentration of the single component solutions ranged between 2000ppm and 50ppm while the two component mixtures had concentration variations of the two components ranging between 1000ppm and 50ppm. Cu, Ni and Co concentrations also ranged between 50 and 1000ppm in the three component solutions

Samples were taken via a syringe which was rinsed with the sample solution before a sample was taken. Two to four samples were taken at 1 hour intervals and the experiment was allowed to run for 4 hours. Before hourly samples were taken, the pH of the solution was 'corrected' to a pH of 3 by either adding H_2SO_4 or NaOH solution. This is essential in that equilibrium is affected by solution pH.

Analysis of the samples was done on an Atomic Adsorption Spectrophotometer. The samples were first diluted (1 in 100 or 1in 1000 depending on the sample concentration) before being analysed and the necessary adjustments were made in calculating the sample concentrations. The amounts of metal on the resin was determined by a mass balance over the system.

The values/concentrations obtained for the samples taken at the same sampling times for respective experiments were averaged to obtained one sample concentration at that specific time. The average concentration was then 'corrected' by accounting for losses in solution during sampling and rinsing.

CHAPTER 3

ACCURACY OF EXISTING ISOTHERMS

This chapter describes the experimental results obtained and the accuracy of existing isotherms in predicting experimentally generated equilibrium conditions.

3.1 Single Component Experiments

3.1.1 Copper

Aqueous solutions containing copper were prepared by dissolving copper sulphate in distilled water. Solutions with the following copper concentrations were prepared and contacted with Amberlite IRC748 resin:

- 50ppm
- 100ppm
- 500ppm
- 1000ppm

Samples of the copper solutions were taken after their pH was corrected and the amount of acidic or basic solution added as well as solution lost during rinsing was included in determining sample concentrations:

$$\text{Actual conc} = \frac{\text{sample conc} \times (\text{prev vol} + \text{prev vol added} - \text{prev vol lost} + \text{vol added})}{\text{previous vol} + \text{prev vol added} - \text{previus volume lost}}$$

So for the 50ppm solution at t = 1, the actual Cu concentration equals:

$$\frac{4.52\text{x}(1000+1.4-40+0.95)}{(1000+1.4-40)} = 4.53\text{ppm}$$

All the Cu experiments followed the same trend as shown in Fig 3.1 and results obtained from the above-mentioned can be seen in Table 3.1.

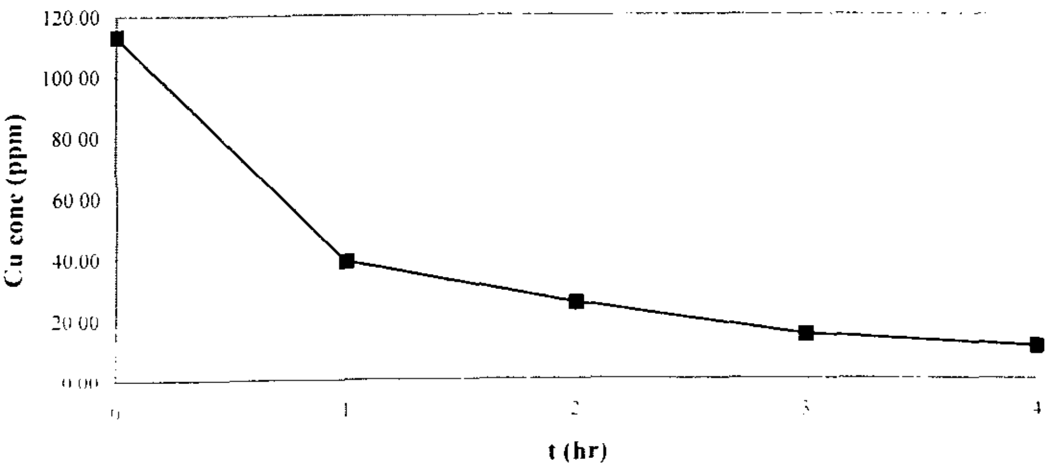

Graph showing the decrease in Cu in a 100ppm soln when contacted with an Amberlite IRC748 resin

Fig 3.1

Sample no.	C_o (mg/l)	C_e (mg/l)	Resin volume (ml)	q_e (mg/l)	$l_n\ q_e$	$l_n\ C_e$
1	2014.92	1837.64	5	35.45	3.57	7.52
2	1162.16	869.67	5	58.50	4.07	6.77
3	610.58	387.00	5	44.72	3.80	5.96
4	113.19	10.70	5	20.50	3.02	2.37
5	56.91	0.75	5	11.23	2.42	-0.29

Table 3.1 Cu Single Component Experimental Data

3.1.2 Nickel

Aqueous solutions containing nickel were prepared by dissolving nickel sulphate in distilled water. Solutions with the following nickel concentrations were prepared and contacted with Amberlite IRC748 resin:

- 50ppm
- 100ppm
- 250ppm
- 500ppm
- 1000ppm

Sample procedures and concentration calculation methods were the same as those used for copper solution samples. All the Ni experiments followed the same trend as shown in Fig 3.2 and experimental results obtained can be seen in Table 3.2

Graph showing the conc change in a 100ppm Ni soln when contacted with an Amberlite IRC748 resin

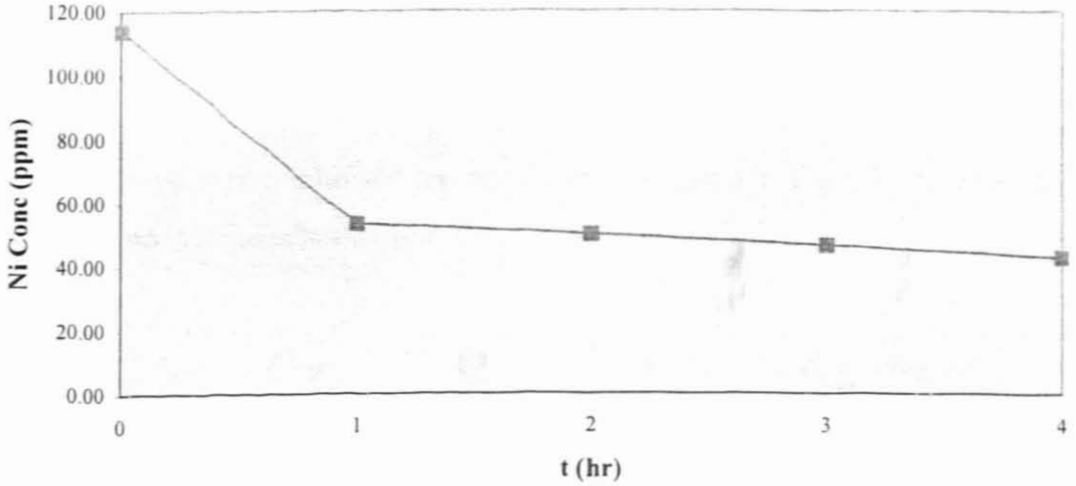


Fig 3.2

Sample No.	C_o (mg/l)	C_e (mg/l)	resin volume (ml)	q_e (mg/l)	$\ln q_e$	$\ln C_e$
1	1047.30	959.11	5	17.638	2.87	6.95
2	617.62	521.68	5	19.188	2.95	6.43
3	251.56	191.57	5	11.998	2.48	5.53
4	114.08	43.01	5	14.214	2.65	4.74
5	56.03	13.33	5	8.54	2.14	4.03

Table 3.2 Ni Single Component Experimental Data

3.1.3 Cobalt

Aqueous solutions containing cobalt were prepared by dissolving cobalt sulphate in distilled water. Solutions with the following cobalt concentrations were prepared and contacted with Amberlite IRC748 resin:

- 50ppm
- 500ppm
- 1000ppm
- 2000ppm

All the Co experiments followed the same trend as shown in Fig 3.3 and experimental results obtained can be seen in Table 3.3

Graph showing the decrease in concentration of a 50ppm Co solution when contacted with an Amberlite IRC748 resin

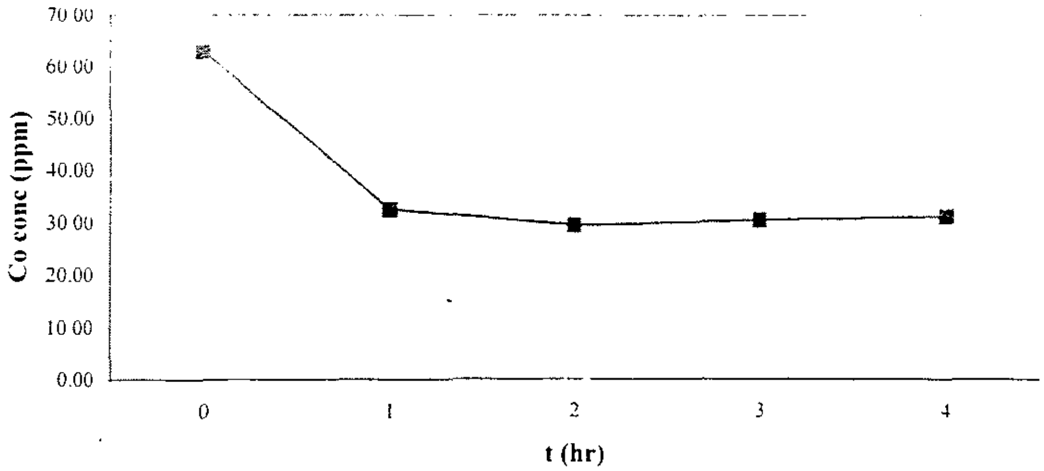


Fig 3.3

Sample no.	C_o (mg/l)	C_e (mg/l)	resin volume (ml)	q_e (mg/l)	$L_n q_e$	$l_n C_e$
1	1971.36	1884.93	5	17.47	2.86	7.59
2	829.83	672.65	5	31.44	3.45	6.72
3	513.21	471.91	5	8.26	2.11	6.24
4	62.78	31.25	5	6.31	1.84	4.14

Table 3.3 Co Single Component Experimental Data

3.1.4 Summary of Single Component Experiments

In the single component experiments, 5ml of resin showed an increase in % element recovery with a decrease in solution concentration for all three elements and an increase in element loading with an increase in solution concentration.

The resin displayed a selectivity for copper with a 98.68% recovery for copper, 76.20% for nickel and 50.27% for cobalt in their respective 50ppm solutions. This selectivity was confirmed when the above-mentioned equations to calculate selectivity coefficients were tested on the experimental data. The copper experiments displayed the highest selectivity coefficients while the cobalt experiments displayed the lowest (See Table 3.4).

Selectivity Coefficients			
Sample	Cu	Ni	Co
2000	5.26	-	0.073
1000	6.54	0.4	0.316
500	9.75	0.68	0.023
250	-	0.054	-
100	11.49	1.06	-
50	17.7	0.97	0.161

Table 3.4 Single Component Experimental Selectivity Coefficients

The results obtained for the single component experiments were also fitted to the Freundlich isotherm and the resultant plots shown below:

Graph of lnqe vs lnCe for Cu, Ni and Co - Single Component Experiments

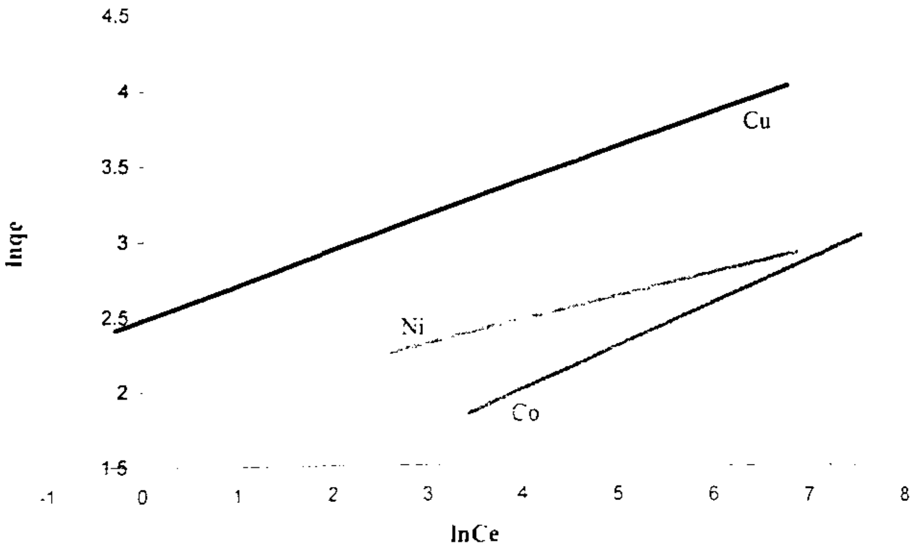


Fig 3.4

It was concluded that the loading of Cu, Ni and Cobalt onto the Amberlite IRC748 resin in the single component experiments could be described by the following Freundlich equations:

$$qe_{Cu} = 11.94Ce_{Cu}^{0.23}$$

$$qe_{Ni} = 6.33Ce_{Ni}^{0.16}$$

$$qe_{Co} = 4.34Ce_{Co}^{0.44}$$

From the above isotherms it can be seen that the highest 'A-value' is obtained in the Cu isotherm. The A-value is an indication of high element loading on the resin in relation to low solution concentration at equilibrium. The large A-value obtained in the Cu isotherm indicates high q_e values will be obtained at low Ce values, further confirming the resin's selectivity for copper.

Large 'n-values' indicates that the final element loading on the resin is very dependent on the solution concentration at equilibrium. From the above single component isotherms it can be seen that the loading of cobalt is very much dependent on the concentration of the cobalt solution at equilibrium.

3.2 Two Component Experiments

Mixtures/solutions containing Cu and Ni, Cu and Co, and Ni and Co were prepared and contacted with Amberlite IRC748 resin to determine the effect of the elements on each other's ion exchange in a two component system.

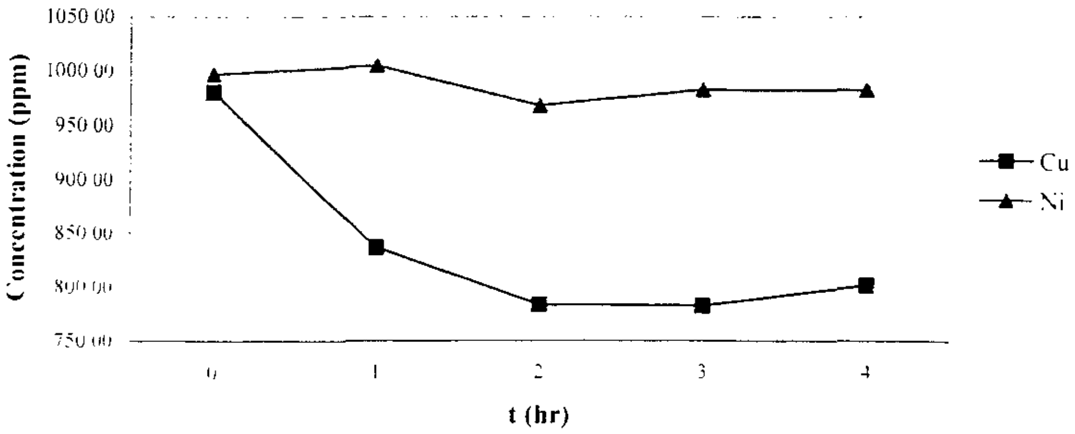
3.2.1 Cu/Ni Experiments

Cu/Ni solutions of the following concentrations were prepared and contacted with 5ml of resin for 4 hours:

- 1000ppm Cu/1000ppm Ni

- 250ppm Cu/1000ppm Ni
- 50ppm Cu/1000ppm Ni
- 1000ppm Cu/50ppm Ni
- 1000ppm Cu/100ppm Ni
- 500ppm Cu/100ppm Ni
- 50ppm Cu/50ppm Ni

The ion exchange followed the trend as shown in Fig 3.5 and results obtained for these experiments can be seen in Table 3.5.



Graph showing the change in concentration of Ni and Cu in a 1000 ppm Cu and 1000 ppm Ni solution when contacted with an Amberlite IRC748 resin

Fig 3.5

Sample no.	**C_o (mg/l)**		**C_e (mg/l)**		**q_e (mg/l)**		**l_n q_e**		**l_n C_e**	
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
1	980.76	996.79	802	982	35.75	2.89	3.58	1.06	6.69	6.89
2	263.74	973.51	122	912	28.35	12.26	3.34	2.51	4.80	6.82
3	66.49	938.58	14	845	10.50	18.70	2.35	2.93	2.64	6.74
4	917.37	50.58	741	40	35.27	2.11	3.56	0.75	6.61	3.69
5	973.20	265.03	796	154	35.44	22.20	3.57	3.10	6.68	5.04
6	491.06	101.33	309	105	36.41	1.00	3.59	0.00	5.73	4.65
7	50.71	49.37	1	31	9.96	3.77	2.30	1.33	-0.11	3.43

Table 3.5 Two Component (Cu/Ni) Experimental Data

3.2.2 Ni/Co Experiments

Ni/Co solutions of the following concentrations were prepared and contacted with 5ml of resin for 4 hours:

- 1000ppm Ni/1000ppm Co
- 1000ppm Ni/250ppm Co
- 250ppm Ni/1000ppm Co
- 100ppm Ni/1000ppm Co
- 1000ppm Ni/100ppm Co
- 1000ppm Ni/50ppm Co
- 50ppm Ni/1000ppm Co
- 500ppm Ni/100ppm Co
- 100ppm Ni/500ppm Co
- 50ppm Ni/50ppm Co

The ion exchange followed the trend shown in Fig 3.6 and the results obtained for these experiments can be seen in Table 3.6.

Graph showing the change in concentration of Co and Cu in a 1000 ppm Ni and 1000 ppm Co mixture when contacted with an Amberlite IRC748 resin

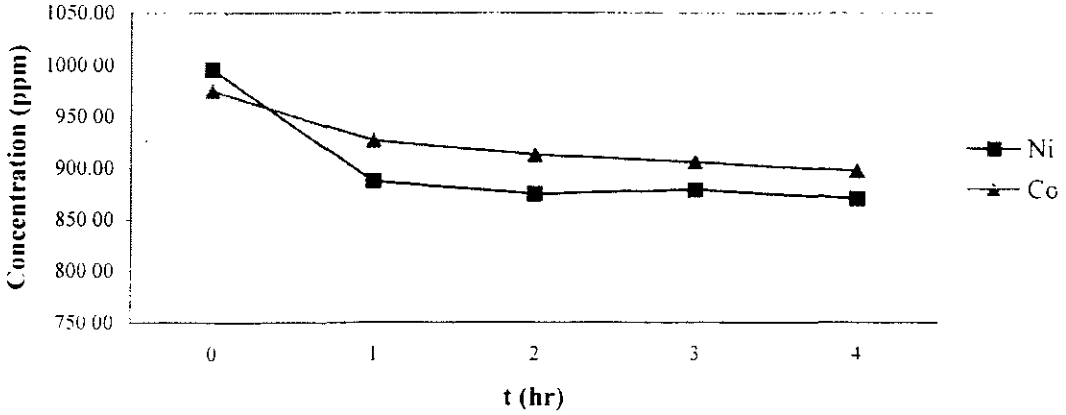


Fig 3.6

Sample no.	C_o (mg/l)		C_e (mg/l)		q_e (mg/l)		$l_n q_e$		$l_n C_e$	
	Ni	Co	Ni	Co	Ni	Co	Ni	Co	Ni	Co
1	995.93	975.25	870.70	25.05	897.71	15.51	6.77	3.22	6.80	2.74
2	1002.07	272.11	886.11	23.19	250.53	4.32	6.79	3.14	5.52	1.46
3	266.45	995.02	201.50	12.99	933.50	12.30	5.31	2.56	6.84	2.51
4	109.07	1003.60	70.01	7.81	915.61	17.60	4.25	2.06	6.82	2.87
5	934.25	116.09	778.18	31.21	106.52	1.91	6.66	3.44	4.67	0.65
6	994.20	68.55	812.59	36.32	62.01	1.31	6.70	3.59	4.13	0.27
7	63.04	994.20	43.51	3.91	906.16	1.00	3.77	1.36	6.81	0.00

Table 3.6 Two Component (Ni/Co) Experimental Data

3.2.3 Cu/Co Experiments

Cu/Co solutions of the following concentrations were prepared and contacted with 5ml of resin for 4 hours:

- 1000ppm Cu/1000ppm Co
- 1000ppm Cu/250ppm Co
- 250ppm Cu/1000ppm Co
- 100ppm Cu/1000ppm Co
- 1000ppm Cu/100ppm Co
- 1000ppm Cu/50ppm Co
- 50ppm Cu/1000ppm Co
- 50ppm Cu/50ppm Co
- 500ppm Cu/100ppm Co
- 100ppm Cu/500ppm Co
- 250ppm Cu/100ppm Co
- 100ppm Cu/250ppm Co

The above-mentioned ion exchange experiments followed a trend as shown in Fig. 3.7 and the results obtained for these experiments can be seen in Table 3.7

Graph showing the change in concentration of Co and Cu in a 1000 ppm Cu and 1000 ppm Co solution when contacted with an Amberlite IRC748 resin

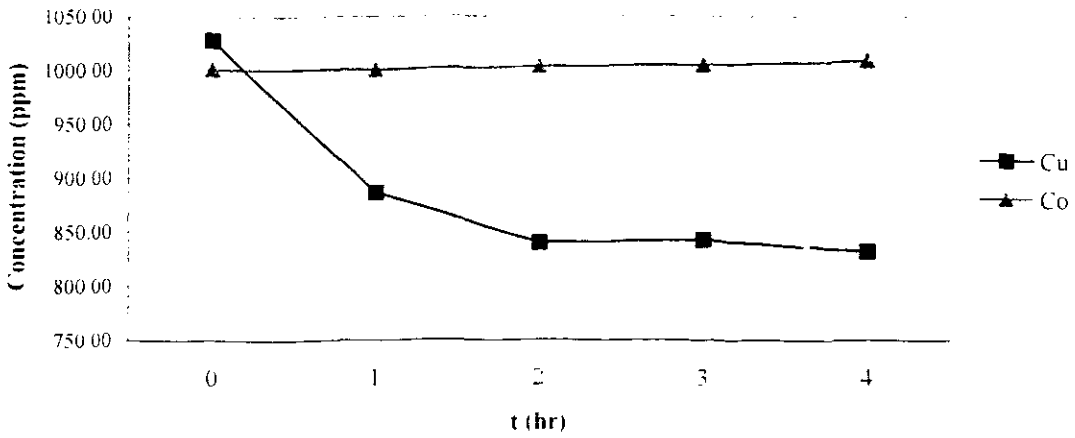


Fig 3.7

Sample no.	**C_o (mg/l)**		**C_e (mg/l)**		**Q_e (mg/l)**		**l_n q_e**		**l_n C_e**	
	Cu	Co	Cu	Co	Cu	Co	Cu	Co	Cu	Co
1	1028.28	1001.27	832.19	1008.3	39.22	-1.49	3.67	-	6.72	6.92
2	974.39	244.43	791.76	241.03	36.53	0.68	3.60	-0.38	6.67	5.48
3	288.23	997.80	133.41	971.58	30.96	5.24	3.43	1.66	4.89	6.88
4	984.26	95.06	790.09	91.51	38.83	0.71	3.66	-0.34	6.67	4.52
5	103.42	975.45	26.51	915.21	15.38	12.05	2.73	2.49	3.28	6.82
6	989.36	58.71	794.59	56.01	38.95	0.54	3.66	-0.62	6.68	4.03
7	50.37	964.34	2.50	874.15	9.57	1.00	2.26	0.00	0.92	6.77
8	51.36	56.36	4.33	24.00	9.40	6.47	2.24	1.87	1.47	3.18
9	496.85	102.07	310.04	97.51	37.36	0.91	3.62	-0.09	5.74	4.58
10	101.75	509.41	39.00	462.05	12.55	9.47	2.53	2.25	3.66	6.14
11	248.51	101.74	101.52	93.52	29.40	1.64	3.38	0.50	4.62	4.54
12	100.74	243.17	20.00	202.05	16.15	8.22	2.78	2.11	3.00	5.31

Table 3.7 Two Component (Cu/Co) Experimental Data

3.2.4 Summary of Two Component Experiments

The results obtained in the two component mixtures/experiments confirmed the resin's selectivity shown in the single component experiments. It was found that nickel and cobalt had very little effect on the adsorption of copper in their respective solutions while the presence of copper reduced both the adsorption of nickel and cobalt. Nickel and cobalt had very little effect on each other in their experiments.

The two component experiment results were plotted and compared to those obtained in the single component experiments. The results obtained for each component were compared against the single component Freundlich isotherm and only the results obtained for copper in the copper-nickel and copper-cobalt mixtures fitted the isotherm (See Fig 3.8 and Fig 3.9 respectively) which confirms the very small effect that cobalt and nickel has on the adsorption of copper in their respective mixtures. In the nickel-cobalt mixtures the results obtained also fitted the Freundlich isotherm (See Fig 3.10) and this also confirms the small competition between the two in their mixtures.

Graph of lnqe vs lnCe for Cu data obtained in Cu/Ni experiments

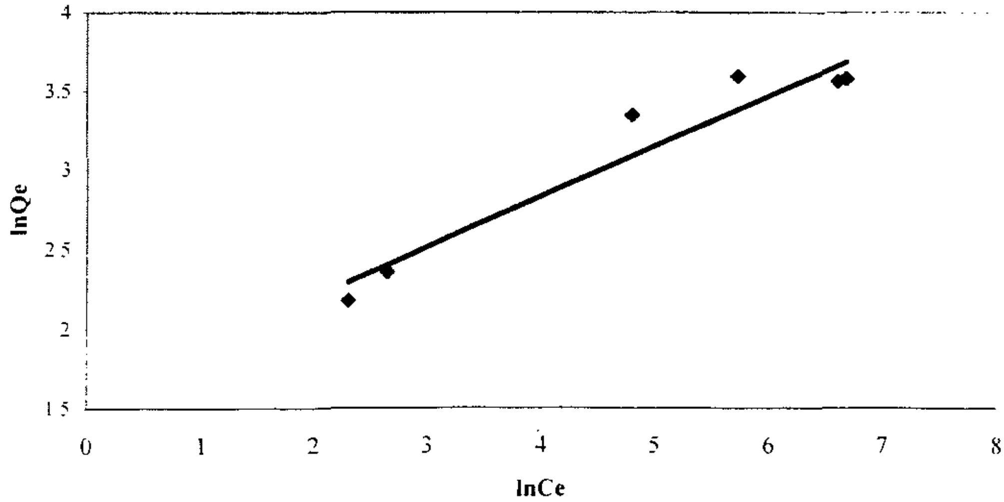


Fig 3.8

Graph of lnqe vs lnCe for Cu data obtained in Cu/Co experiments

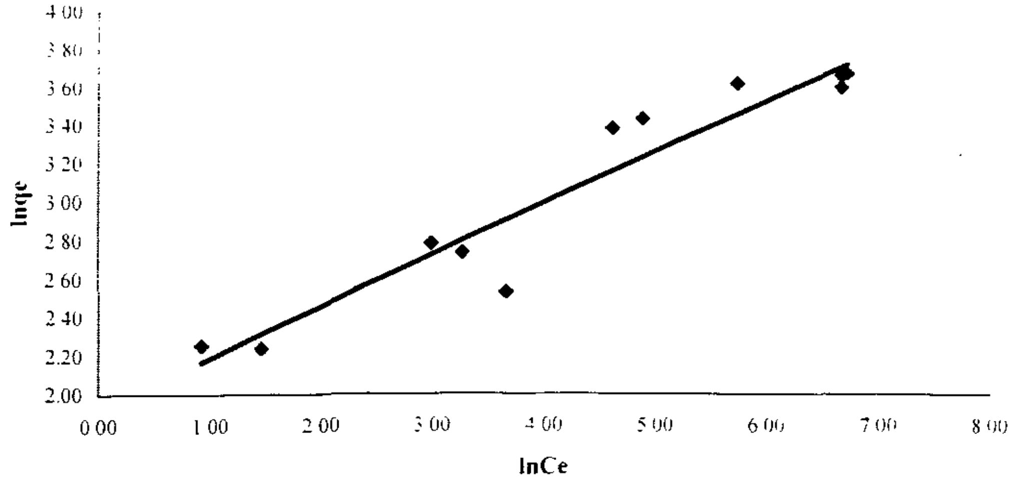


Fig 3.9

Graph of lnqe vs lnCe for Ni and Co data obatained in Ni/Co experiments

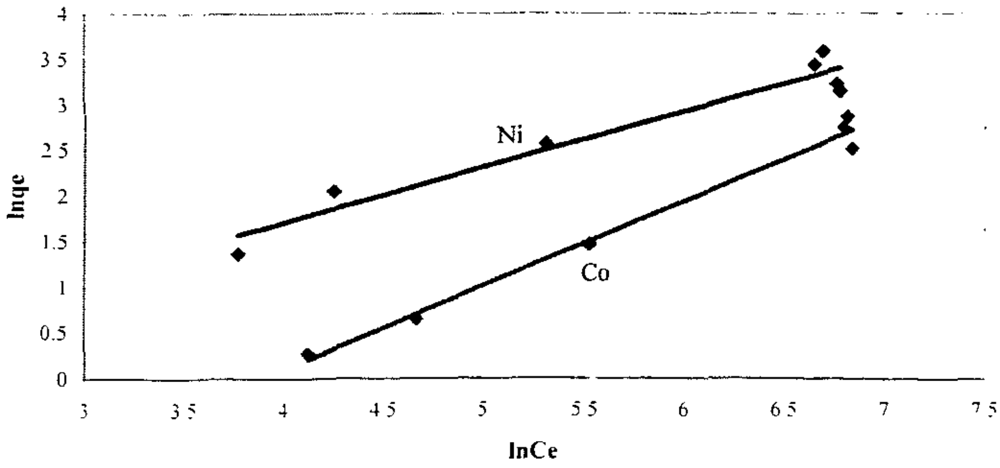


Fig 3.10

The following was therefore concluded:

For copper-nickel solutions.

$$q_{eCu} = 4.8C_{eCu}^{0.32}$$

and copper-cobalt solutions.

$$q_{eCu} = 6.85C_{eCu}^{0.27}$$

For nickel cobalt solutions it was concluded that:

$$q_{eNi} = 2.04C_{eNi}^{0.6}$$

$$q_{eCo} = 36.91C_{eCo}^{0.92}$$

Where the results did not fit the Freundlich isotherm, an isotherm **based** on the

Freundlich isotherm was developed to interpret the data obtained:

$q_{e1} = AC_{e1}^{n1}$ - single component (1)

$q_{e1} = (AC_{e1}^{n1})^{m}.C_{e2}^{x}$ - two components, where Ce^{x} Ce_{2x} is introduced as a competition factor (2)

From (2)

$$\ln q_{e1} = \ln(AC_{e1}^{n1})^{m} + \ln C_{e2}^{x}$$

$$\ln q_{e1} = m \ln(AC_{e1}^{n1}) + x \ln C_{e2}^{x}$$

$$\frac{\ln q_{e1}}{\ln C_{e2}} = m \quad \frac{\ln(AC_{e1}^{n1}) + x}{\ln C_{e2}}$$

$\frac{\ln q_{e1}}{\ln C_{e2}}$ vs $\frac{\ln(AC_{e1}^{n1})}{\ln C_{e2}}$ was plotted to model the adsorption in the two component experiments and the resultant graphs can be seen in Fig 3.11 and 3.12

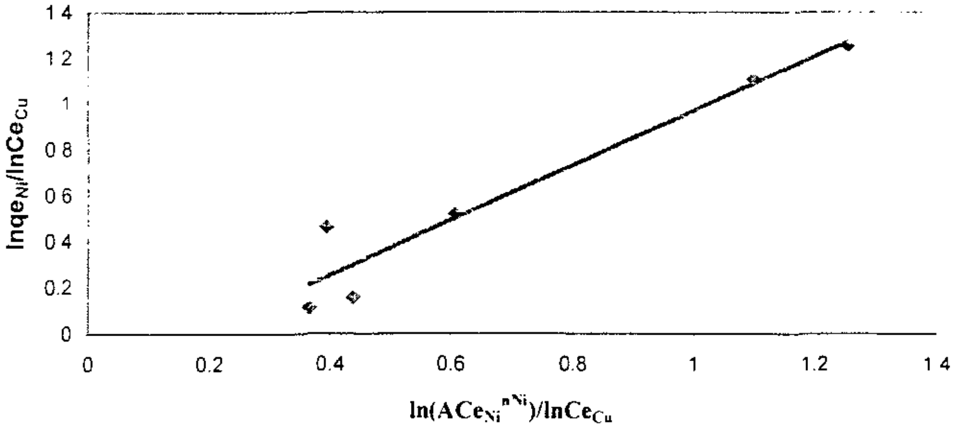

Graph of $\ln q_{e_{Ni}}/\ln Ce_{Cu}$ vs $\ln(ACe_{Ni}^{n_{Ni}})/\ln Ce_{Cu}$ for Ni data obtained in Cu/Ni experiments

Fig 3.11

Thus for copper-nickel solutions: $q_{eNi} + (6.33C_{eNi}^{0.16})^{1.1953}C_{eCu}^{-0.225}$

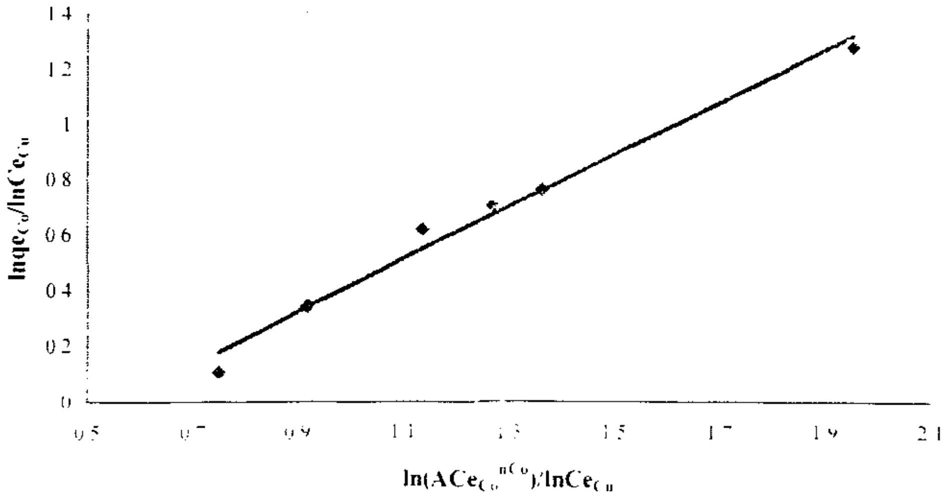

Graph of $\ln q e_{Co}/\ln Ce_{Cu}$ vs $\ln(ACe_{Co}^{n_{Co}})/\ln Ce_{Cu}$ - Cu/Co experiments

Fig 3.12

Thus for copper–cobalt solutions it was concluded that:

$$q_{eCo} = 4.34C_{eCo}^{0.44})^{0.9424} C_{eCo}^{-0.78}$$

3.3 Three Component Experiments

Mixtures/solutions containing Cu, Ni and Co were prepared and contacted with Amberlite IRC748 resin to determine the effect of the elements on each other's ion exchange in a three component system.

Solutions containing Cu, Ni and Co with the following concentrations were prepared and contacted with 5ml of resin for 4 hours:

- 1000ppm Cu/1000ppmNi/1000ppm Co
- 50ppm Cu/50ppm Ni/1000ppm Co
- 50ppm Cu/1000ppm Ni/50ppm Co
- 50ppm Cu/1000ppm Ni/250ppm Co
- 50ppm Cu/50ppm Ni/50ppm Co
- 50ppm Cu/250ppm Ni/1000ppm Co
- 100ppm Cu/500ppm Ni/500ppm Co
- 500ppm Cu/100ppm Ni/250ppm Co
- 1000ppm Cu/50pm Ni/100ppm Co
- 500ppm Cu/250ppm Ni/100ppm Co

The results obtained from the above-mentioned experiments are tabulated in Table 3.8.

Sample no.	**C_o (mg/l)**			**C_e (mg/l)**			**q_e (mg/l)**			**L_n q_e**			**l_n C_e**		
	Cu	Ni	Co	Cu	Ni	Co	Cu	Ni	Co	Cu	Ni	Co	Cu	Ni	Co
1	1011.61	954.57	1002.60	815.19	917.21	985.73	39.28	7.47	3.38	6.70	6.82	6.89	3.67	2.01	1.22
2	55.53	51.53	53.03	3.50	31.01	43.51	10.41	4.10	1.90	1.25	3.43	3.77	2.34	1.41	0.64
3	54.53	53.53	966.58	11.50	41.51	902.71	8.61	2.40	12.77	2.44	3.73	6.81	2.15	0.88	2.55
4	54.53	246.65	989.09	6.50	201.05	922.71	9.61	9.12	13.28	1.87	5.30	6.83	2.26	2.21	2.59
5	47.53	998.60	260.16	7.00	899.71	253.06	8.11	19.78	1.42	1.95	6.80	5.53	2.09	2.98	0.35
6	45.53	996.10	63.04	6.50	912.71	60.51	7.81	16.68	0.50	1.87	6.82	4.10	2.05	2.81	-0.68
7	96.06	485.29	487.79	33.51	429.60	473.61	12.51	11.14	2.84	3.51	6.06	6.16	2.53	2.41	1.04
8	494.80	102.06	252.15	317.07	94.52	244.56	35.54	1.51	1.52	5.76	4.55	5.50	3.57	0.41	0.42
9	990.09	51.53	105.06	799.68	49.51	103.52	26.06	0.07	0.14	6.68	3.90	4.64	3.26	-2.67	-1.97
10	499.30	236.64	106.06	328.08	181.54	102.02	34.24	11.02	0.81	5.79	5.20	4.63	3.53	2.40	-0.21

Table 3.8 Three Component Experimental Data

For the purpose of 3-component equilibrium modelling, the multi-component Langmuir and Fritz and Schleunder isotherms were selected. The Freundlich multi-component isotherm was not selected due to its application being more suitable for two-component systems.

3.3.1 Determining the Optimum Solution

Due to the number of variables to be solved for, a C++ computer program was developed to find the best solution by using a sum of squares of errors criteria. Of utmost importance is the selection of various starting points by the program so as to avoid a result based on a local minimum (See Fig 3.13). A "nuclear bomb to destroy an ant" approach was followed so as to avoid solutions that are not necessarily the optimum solution to the equilibrium isotherm. Numerical techniques were avoided as these are often unstable in the optimum region.

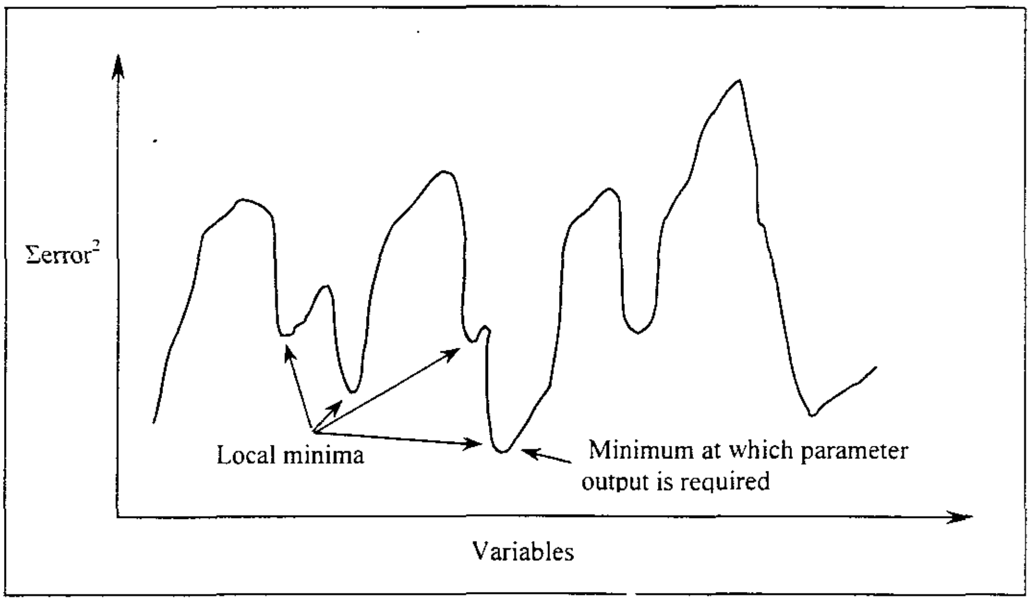


Fig. 3.13 Figure showing difference in local minima and required minimum

3.3.2 Computer Program Overview.

An array of the adsorption data obtained for each three component experiment was defined in the above-mentioned program and one vector for each species (Cu, Ni, Co) declared in the constructor (See Appendix 2). The program consists of an inner and outer loop into which the adsorption data array is 'inserted'.

The inner loop finds the minimum sum of squares of errors by individually incrementing or decrementing the parameters of the isotherms by the specified increments. The outer loop changes the initial conditions to the conditions obtained in the inner loop to obtain a new sum of squares of errors until the minimum sum of squares of errors is found. This prevents the program from giving a solution at a local minimum.

3.3.3 Accuracy of two existing isotherms

From the parameters obtained in the computer program described above, the following Langmuir and Fritz & Schleunder isotherms can be generated for the Amberlite IRC748 resin:

Langmuir

$$q_{eCu} = \frac{6.35C_{eCu}}{1 + 0.15C_{eNi} + 1.3C_{eCo}}$$

$$q_{eNi} = \frac{2.55C_{eNi}}{1.15.3C_{eCu} + 0.1C_{eCo}}$$

$$q_{eCo} = \frac{1.5C_{eCo}}{1 + 7.7C_{eCu} + 0.25C_{eNi}}$$

Fritz and Schleunder

$$q_{eCu} = \frac{8C_{eCu}^{0.6}}{1.33 + C_{eNi}^{0.3} + C_{eCo}^{0.3}}$$

$$q_{eNi} = \frac{7.95C_{eNi}^{0.495}}{6.35 + 1.05C_{eCu}^{0.305} + 1.05C_{eCo}^{0.305}}$$

$$q_{eCo} = \frac{8C_{eCo}^{0.695}}{29.6 + 5.05C_{eCu} + 5.05C_{eNi}^{0.505}}$$

The experimental values (final concentrations) obtained for the respective components were inserted in the respective isotherms to determine how accurate the Langmuir and Fritz & Schleunder isotherms predicted component loading and to compare the two isotherms as well (See Tables 3.9 to 3.11).

qe_{Cu} (mg/l)				
Experimental	Calculated		$error^2$	
	Langmuir	Fritz & Schleunder	Langmuir	Fritz & Schleunder
39.4	1.85	29.83	1410.31	91.55
10.4	0.24	2.38	103.29	64.43
8.6	0.42	2.99	66.89	31.55
9.6	0.06	1.91	90.98	59.34
8.2	0.01	1.87	67.00	38.92
7.8	0.01	2.11	60.62	32.52
12.4	0.15	4.97	150.16	56.89
35.6	6.05	24.21	873.00	128.30
38	29.17	49.80	77.99	563.59
34.2	3.35	25.46	951.52	77.04
			3851.76	**1144.12**

Table 3.9 Comparison between experimental and calculated qe_{Cu} values when using the multi-component Langmuir and Fritz & Schleunder Isotherms

qe_{Ni}(mg/l)				
Experimental	calc		$error^2$	
	Langmuir	Fritz & Schleunder	Langmuir	Fritz & Schleunder
7.6	0.003	8.62	57.71	1.04
4.2	0.062	2.91	17.12	1.65
2.4	0.009	2.45	5.72	0.00
9.2	0.005	5.40	84.54	14.44
19.4	0.019	13.11	375.64	39.51
16.6	0.073	14.90	273.15	2.88
11	0.049	8.02	119.93	8.91
1.4	0.883	3.49	0.27	4.37
0.4	5.247	2.46	23.50	4.25
11	2.179	5.11	77.82	34.69
			1035.40	**111.74**

Table 3.10 Comparison between experimental and calculated qe_{Ni} values when using the multi-component Langmuir and Fritz & Schleunder Isotherms

qe_{Co}(mg/l)				
Experimental	Calc		error^2	
	Langmuir	Fritz & Schleunder	Langmuir	Fritz & Schleunder
3.4	0.31	2.87	9.53	0.28
1.8	1.57	1.92	0.05	0.01
12.8	15.80	12.94	9.03	0.02
13.2	7.37	8.68	33.95	20.42
1.4	0.52	1.98	0.78	0.33
0.4	0.12	0.73	0.08	0.11
2.8	1.47	3.69	1.78	0.79
1.4	0.25	2.26	1.32	0.74
0.2	0.04	0.99	0.02	0.63
0.8	0.10	1.09	0.49	0.08
			57.03	**23.43**

Table 3.11 Comparison between experimental and calculated qe_{Co} values when using the multi-component Langmuir and Fritz & Schleunder Isotherms

It was discovered that both isotherms were not a good representation of the ion exchange taking place with respect to copper and that the Fritz & Schleunder was more accurate than the Langmuir isotherm for all three components.

The Fritz and Schleunder isotherm gave relatively accurate predictions for nickel and cobalt when compared to experimental loading values obtained.

CHAPTER 4

DEVELOPING ALTERNATIVE ISOTHERMS FOR MULTI-COMPONENT EQUILIBRIA

Due to the relatively inaccurate results obtained using the multi-component Langmuir and Fritz and Schleunder isotherms, different/other approaches were also investigated with the aim of developing isotherms to predict more accurate equilibrium conditions for the 3-component systems.

4.1. An effective concentration approach to multi-component system equilibria

Copper, nickel and cobalt equilibrium loading is well explained by a single component isotherm as was shown in Chapter 3. In multi-component systems, interaction between the dissolved species occurs as competition for active sites on the resin surface. It was therefore decided to test a theory in which it is assumed that a dissolved species contributes less than its actual solution concentration to the mass transfer driving force. The solution concentration of the species under consideration thus becomes an 'effective' concentration.

Two models were tested:

- The effective concentration is affected linearly by the other dissolved species:

$$\text{effective concentration} = \frac{C_{ei}}{\sum_{i=1}^{N=1} B_j C_{ej}}$$

$$\text{hence} \quad q_e = A_i \left[\frac{C_{ei}}{\sum_{j=1}^{N=1} B_j C_{ei}} \right]^{ni}$$

- The effective concentration is affected non-linearly by the other dissolved species:

$$\text{effective concentration} = \frac{C_{ei}}{\sum_{j=1}^{N=1} C_{ej}^{nj}}$$

$$\text{hence} \quad q_{ei} = A_i \left[\frac{C_{ei}}{\sum_{j=1}^{N=1} C_{ej}^{ni}} \right]$$

4.1.1 Effective concentration isotherm with linear competition

The unknown parameters were also solved via a C++ program (See Appendix 2 and 3) and the following isotherms were generated:

$$q_{eCu} = 14.3 \left[\frac{C_{eCu}}{0.021C_{eNi} + 0.121C_{eCo}} \right]^{0.3}$$

$$q_{eNi} = 4.3 \left[\frac{C_{eNi}}{0.344C_{eCu} + 0.003C_{eCo}} \right]^{0.25}$$

$$q_{eCo} = 1.7 \left[\frac{C_{eCo}}{0.462C_{eCu} + 0.035C_{eNi}} \right]^{0.4}$$

4.1.2 *Effective concentration isotherm with non-linear competition*

The unknown parameters were also solved via a C++ program (See Appendix 2 and 3) and the following isotherms were generated:

$$q_{eCu} = 4.4\left[\frac{C_{eCu}}{C_{eNi}^{0.05} + C_{eCo}^{0.05}}\right]^{0.4}$$

$$q_{eNi} = 4.8\left[\frac{C_{eNi}}{C_{eCu}^{0.75} + C_{eCo}^{0.45}}\right]^{0.3}$$

$$q_{eCo} = 4.9\left[\frac{C_{eCo}}{C_{eCu}^{2.2} + C_{eNi}}\right]^{0.8}$$

Both the linear and non-linear multi-component isotherms gave much better results for copper when compared to Langmuir and Fritz & Schleunder isotherms. The non-linear isotherm predicted better values than the linear isotherm thereby confirming that the competition between copper and the other components is a non-linear function when linked to concentration. Both isotherms also predicted relatively accurate equilibrium loading for Ni and Co (See Table 4.2 and 4.3).

qe_{Cu} (mg/l)				
Experimental	Calculated from effective concentration approach		$error^2$	
	Linear	non-linear	Linear	non-linear
39.4	25.19	44.47	201.86	25.68
10.4	12.68	5.58	5.19	23.23
8.6	7.35	8.37	1.55	0.05
9.6	6.16	6.74	11.83	8.16
8.2	7.95	6.85	0.06	1.84
7.8	9.59	6.96	3.19	0.71
12.4	11.70	12.79	0.49	0.15
35.6	28.55	31.47	49.72	17.03
38	48.52	46.02	110.57	64.31
34.2	35.28	32.22	1.17	3.91
			385.63	**145.08**

Table 4.1 Comparison between experimental and calculated qe_{Cu} values when using an effective concentration approach

qe_{Ni} (mg/l)				
Experimental	Calculated from effective concentration approach		$error^2$	
	Linear	non-linear	Linear	non-linear
7.6	5.58	7.71	4.08	0.01
4.2	8.79	7.12	21.11	8.54
2.4	5.85	5.43	11.91	9.19
9.2	8.95	8.88	0.06	0.10
19.4	16.01	15.97	11.50	11.76
16.6	18.02	18.24	2.03	2.69
11	9.80	10.66	1.45	0.11
1.4	4.13	4.93	7.47	12.45
0.4	2.80	3.40	5.78	8.97
11	4.84	6.03	37.99	24.70
			103.39	**78.53**

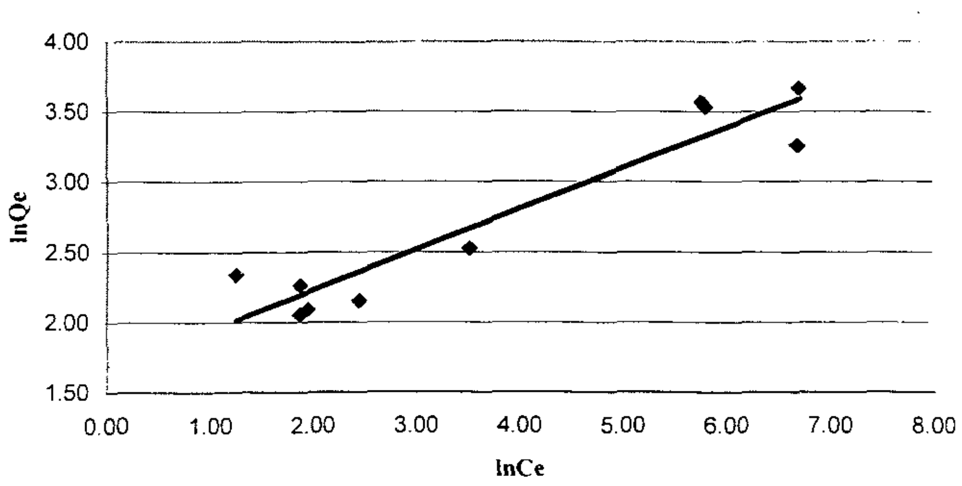
Table 4.2 Comparison between experimental and calculated qe_{Ni} values when using an effective concentration approach

qe_{Co} (mg/l)				
Experimental	calc		error^2	
	Linear	non-linear	Linear	non-linear
3.4	2.32	0.01	1.17	11.51
1.8	5.02	4.28	10.38	6.15
12.8	11.87	12.55	0.87	0.06
13.2	10.28	12.97	8.54	0.05
1.4	3.76	1.67	5.58	0.07
0.4	2.12	0.53	2.95	0.02
2.8	5.08	1.19	5.18	2.58
1.4	2.07	0.02	0.45	1.92
0.2	1.02	0.00	0.68	0.04
0.8	1.43	0.01	0.39	0.63
			36.20	**23.03**

Table 4.3 Comparison between experimental and calculated qe_{Co} values when using an effective concentration approach

4.2. A Single Component Approach

Knowing that the resin was copper selective, a single component Fruendlich isotherm approach was also investigated with respect to predicting copper loading on IRC748 resin. The resultant graph can be seen in Fig 4.1.



Graph of lnqe vs lnCe for Cu data obtained in Cu/Ni/Co experiments

Fig4.1

The same C++ approach was used to generate A and n values (See Appendix 2 and 3) based on the three component experimental values obtained and the following isotherm was obtained:

$$q_{eCu} = 4.8C_{eCu}^{0.32}$$

It can be seen that this is exactly the same isotherm generated for copper in the copper-nickel experiments (two component experiments). This behaviour of the resin in respect of copper loading in a three component system of various Ni and Co concentrations once again confirms the selectivity of the resin for copper as well as the little effect Co and Ni has on Cu loading.

The results obtained for copper loading predictions from this isotherm (Appendix 3) was even better than that obtained from the non-linear isotherm mentioned above.

It can therefore be shown that when a resin is highly selective for a species, a single component isotherm can be used to obtained good equilibrium predictions of the dominant species. When compared to the isotherm obtained in the single component experiment for copper:

$$q_{eCu} = 11.94C_{eCu}^{0.23}$$

it is noted that that the A and n values for Cu have changed considerably. A decrease in the A-value for Cu was obtained in the three component system thus showing smaller element loading on the resin in relation to low solution concentration at equilibrium.

A higher n-value was obtained for Cu in the three component system indicating that final element loading on the resin is even more dependent on the Cu concentration at equilibrium. This can be attributed to the loading of the other components on the resin as well as the resultant competition exerted.

4.3. A Heat Transfer Approach

A heat transfer approach to predict equilibrium component loading was also investigated. From the heat transfer equation:

$$Q = UA\Delta t$$

The following mass transfer equation was generated:

$$L = mA\Delta C$$

Change in concentration is not homogenous as change in temperature but if a term could be developed to explain driving force in ion exchange, this type of approach could be useful.

The driving force in the system would thus be:

$$DF = [\text{solution}] - \text{loading}$$

At equilibrium DF = 0 and therefore:

$$[\text{solution}] - \text{loading} = 0$$

thus, assuming non-linear solution driving force:

$$\left(C_{e1}^{\;n1} + C_{e2}^{\;n2} + C_{e3}^{\;n3}\right) = \left(q_{e1} + q_{e2} + q_{e3}\right) = q_{etot}$$

A C++ program was once again used to determine n values based on the experimental equilibrium values (See Appendix 2 and 3) obtained and the following isotherm was obtained:

$$\left(C_{eCu}^{\;0.5} + C_{eNi}^{\;0.4} + C_{eCo}^{\;0.4}\right) = q_{etot}$$

The experimental values (final concentrations) obtained for the components were inserted in the above isotherm to determine how accurate the isotherm predicted the total loading. Positive results were obtained (See Table 4.4) when compared to actual loadings but these however can only be compared to the other isotherms as far as total component loading is concerned and not the individual components.

qe_{tot} (mg/l)		
Experimental	Heat transfer approach	error^2
50.4	61.32	119.20
16.41	10.49	35.01
23.81	23.14	0.45
32.01	26.34	32.18
28.91	26.99	3.70
24.81	23.11	2.90
26.31	28.90	6.69
38.34	33.02	28.35
26.66	39.48	164.23
46.04	32.49	183.66
		576.38

Table 4.4 Comparison between experimental and calculated qe_{tot} values when using a heat transfer approach

4.4 A Probabilistic Thermodynamical Approach

In the three-component system under consideration, the following ion exchange reactions are possible:

$$Cu^{2+} + R-2Na^{+} \Leftrightarrow R-Cu^{2+} + 2Na^{+} \quad (1)$$

$$Ni^{2+} + R-2Na^{+} \Leftrightarrow R-Ni^{2+} + 2Na^{+} \quad (2)$$

$$Co^{2+} + R-2Na^{+} \Leftrightarrow R-Co^{2+} + 2Na^{+} \quad (3)$$

$$Cu^{2+} + R-Co^{2+} \Leftrightarrow R-Cu^{2+} + Co^{2+} \quad (4)$$

$$Cu^{2+} + R-Ni^{2+} \Leftrightarrow R-Cu^{2+} + Ni^{2+} \quad (5)$$

$$Co^{2+} + R-Ni^{2+} \Leftrightarrow R-Co^{2+} + Ni^{2+} \quad (6)$$

Hence, 6 reversable reactions totalling 12 exchange reactions.

4.4.1 *Hypothesis*

At equilibrium the sums of the probability that a reaction will occur and the probability that a collision has taken place are equal for all possible exchange reactions.

$$P_{R1} \times P_{C1} = P_{R2} \times P_{C2} = \ldots\ldots\ldots\ldots P_{Rn} \times P_{Cn}$$

where: P_R = probability that the reaction will occur after the collision

P_C = probability that a collision will occur

The probability that a reaction will occur is linked to the Gibbs free energy approach while the probability of a collision occurring is the sum of the species concentrations taking part in the specified reaction as illustrated by the collision theory.

Thus, for reversable reaction 1:

$$P_F \times K_1\left[Cu^{2+}\right]\left[R - 2Na^{+}\right] = P_R \times K_2\left[Na^{+}\right]^2\left[R - Cu^{2+}\right]$$

where: F = Forward reaction

R = Reverse reaction

$K_{1,2}$ = Constants

It is also assumed that there are no intermediate reactions.

4.4.2 *Formulation and Constant Determination*

Microsoft Excel's 'Solver' function was employed in order to determine the accuracy of this proposed approach. Resultant probability and constant values obtained can be seen in Table 4.5.

Reaction	P_F	P_R	K_1	K_2
1	0.5	0.05	0.2	0.1
2	0.2	0.1	0.1	0.1
3	0.1	$1\text{x}10^{-6}$	0.1	0.1
4	0.62	0.14	0.32	0.1
5	0.01	$1\text{x}10^{-7}$	0.1	0.1
6	$2\text{x}10^{-5}$	$1\text{x}10^{-5}$	0.28	0.18

Table 4.5 Probability and Constant Values obtained from Microsoft Excel's Solver

From the results obtained, the following equations can be generated:

$$0.1\left[Cu^{2+}\right]\left[R-2Na^{+}\right]=0.005\left[Na^{+}\right]^{2}\left[R-Cu^{2+}\right]=$$

$$0.02\left[\mathrm{Ni}^{2+}\right]\left[\mathrm{R}-2\mathrm{Na}^{+}\right]=0.01\left[\mathrm{Na}^{+}\right]^{2}\left[\mathrm{R}-\mathrm{Ni}^{2+}\right]=$$

$$0.01\left[\mathrm{Co}^{2+}\right]\left[\mathrm{R}-2\mathrm{Na}^{+}\right]=1\times10^{-7}\left[\mathrm{Na}^{+}\right]^{2}\left[\mathrm{R}-\mathrm{Co}^{2+}\right]=$$

$$0.19\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{R}-2\mathrm{Co}^{2+}\right]=0.014\left[\mathrm{Co}^{2+}\right]\left[\mathrm{R}-\mathrm{Cu}^{2+}\right]=$$

$$0.001\left[Cu^{2+}\right]\left[R-Ni^{2+}\right]=1\times10^{-8}\left[Ni^{2+}\right]\left[R-Cu^{2+}\right]=$$

$$5\times10^{-6}\left[\mathrm{Ni}^{2+}\right]\left[\mathrm{R}-\mathrm{Co}^{2+}\right]=2\times10^{-6}\left[\mathrm{Co}^{2+}\right]\left[\mathrm{R}-\mathrm{Ni}^{2+}\right]$$

From the above results obtained and the resultant equations, qe values were calculated and compared to experimental data. Based on a sum of squares of errors approach, only q_e values obtained for copper were favourable and these can be seen in Tables 4.6 – 4.8.

qe_{Cu} (mg/l)		
Experimental	Thermodynamical approach	error^2
39	37.7	1.70
8.6	10.9	5.22
7.8	9.1	1.65
8.1	9.5	1.87
10.4	11.1	0.48
9.6	10.9	1.58
12.5	19.2	44.52
35.6	8.4	740.69
38	7.3	941.61
34.2	36.4	4.74
		1744.06

Table 4.6 Comparison between experimental and calculated qe_{Cu} values when using a thermodynamical approach

Qe_{Ni} (mg/l)		
Experimental	Thermodynamical approach	error^2
7.6	180.60	29927.62
2.5	10.65	66.48
16.6	199.12	33312.50
21.6	199.51	31652.23
4.1	10.26	37.89
9.2	49.32	1609.38
11	96.57	7322.72
1.5	16.36	220.77
0.4	0.10	0.09
11.1	43.22	1031.57
		105181.24

Table 4.7 Comparison between experimental and calculated qe_{Ni} values when using a thermodynamical approach

qe_{Co} (mg/l)		
Experimental	Thermodynamical approach	error^2
3.4	4.44	1.08
12.8	140.32	16260.85
0.5	11.42	119.22
1.4	48.60	2227.52
1.9	8.30	40.93
13.2	171.54	25070.53
2.8	76.66	5455.98
1.4	15.02	185.53
0.3	3.63	11.10
0.8	0.10	0.49
		49373.23

Table 4.8 Comparison between experimental and calculated qe_{Co} values when using a thermodynamical approach

With reference to the Cu values above, the qe predictions were relatively accurate except for two instances. Favourable predictions obtained for Cu and not for the other two components could be attributed to the resin's high selectivity for Cu.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

- It was found that it is not a simple procedure to predict accurate equilibrium estimates for multi-component systems.
- An effective concentration approach was more accurate for Cu in multi-component systems than more frequently used multi-component isotherms.
- A single component Freundlich isotherm can effectively be used to predict equilibrium estimates for the component for which the resin is highly selective for in multi-component systems .
- The heat transfer approach to mass transfer should be investigated further as it could lead to predicting individual ion exchange profiles accurately.
- The thermodynamical approach only seems to give favourable predictions for the component for which a resin is highly selective.

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NOMENCLATURE

Δt : change in temperature (K)

ΔC : change in concentration (mg/l)

A : area (m^2) or equilibrium constant

$B_{i\text{-}j}$: competition factor

Ce : equilibrium solution concentration (mg/l)

C_i : total concentration of counter ion 'i' in system (moles/l)

C_{ir} : concentration of counter ion 'i' in ion exchanger (moles/l)

C_{is} : concentration of counter ion 'i' in solution (moles/l)

CO : Carbon Monoxide

Co^{+} : Cobalt ion

CO_2 : Carbon Dioxide

$Co(OH)_3$: Cobalt Hydroxide

Co_2O_3 : Cobalt Oxide

Cu_2O : Copper Oxide

Cu_2S : Copper Sulphide

D : constant

i : distribution coefficient

m : mass transfer coefficient (m^{-2})

m_i : total concentration of counter ion 'i' in system (moles/kg)

m_{ir} : concentration of counter ion 'i' in ion exchanger (moles/kg)

m_{is} : concentration of counter ion 'i' in solution (moles/kg)

n : equilibrium constant

$NaOCl$: Sodium Hypochlorite

O_2 : Oxygen

q_e : equilibrium loading (mg/l)

Q : heat load (W)

SO_2 : Sulphur Dioxide

U : heat transfer coefficient (W/m^2K)

X_{AR} : Ionic Fraction of counter ion 'A' in ion exchanger

X_{AS} : Ionic Fraction of counter ion 'A' in solution

X_{BR} : Ionic Fraction of counter ion 'B' in ion exchanger

X_{BS} : Ionic Fraction of counter ion 'B' in solution

z_n : ionic valency of ion 'n'

AMBERLITE® IRC748

ROHM
AA

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*

SELECTIVITY

The apparent selectivity of any ion exchange resin for a given metal depends upon concentration, the presence of other species and pH. This makes absolute selectivities very difficult to determine, especially for waste treatment applications. Because of this, laboratory testing is essential when a resin is required to remove one or more types of metal ions selectively. In general the selectivity follows the following order:

$Na^{+} << Ca^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Cd^{2+} < Zn^{2+} < Ni^{2+} < Pb < Cu$
$< Hg^{2+} < Fe^{3+}$

The affinity for H^{+} at pH 4 is situated between Pb and Cu^{2+}. Consequently, for the metals with selectivities less than Cu^{2+}, the resin should be in the salt form (for example in the Na^{+} form) to minimize metal leakage. At a pH of 2, the resin will be extensively in the H^{+} form and will only efficiently remove Fe^{3+}, Cu^{2+} and Hg^{2+}. Selectivity at various pH conditions for Amberlite IRC748 are given below:

pH = 2

Metal ion	$K_{M/Ca}$
Fe^{3+}	325 000
Cu^{2+}	130 000
Hg^{2+}	> 43 000

pH = 4

Metal ion	$K_{M/Ca}$
Hg^{2+}	2 800
Cu^{2+}	2 300
Pb^{2+}	1 200
Ni^{2+}	57
Zn^{2+}	17
Cd^{2+}	15
Co^{2+}	6.7
Fe^{2+}	4.0
Mn^{2+}	1.2
Ca^{2+}	1.0

pH = 9*

Metal ion	$K_{M/Ca}$
Ni^{2+}	30
Cd^{2+}	14
Cu^{2+}	10
Zn^{2+}	3
Ca^{2+}	1.0

*** very high ammonium background, (200 g/L $(NH_4)_2SO_4$).**

APPLICATIONS

AMBERLITE IRC748 is used in the following special applications :

- Purification of brine in the chloralkali industry.
- Electronics industry (printed wiring boards).
- Purification of process streams containing trace metals.
- Electroplating industry.
- Recovery of heavy metals from hydrometallurgical leach streams.

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H FILE

```
#include <vector>

#ifndef _ISOTHERM_H_
#define _ISOTHERM_H_

class equilibrium
{
public:
equilibrium();
~equilibrium();
void langmuir(const vector<double> VC, const vector<double> VN, const vector<double> VCo);
void  fritz (const vector<double> VC, const vector<double> VN, const vector<double> VCo);
void effective_1 (const vector<double> VC, const vector<double> VN, const vector<double> VCo);
void effective_2 (const vector <double> VC, const vector <double> VN, const vector <double> VCo);
void driving (const vector<double> VC, const vector <double> VN, const vector <double> VCo);
void single (const vector <double> VC);

private:
double A1, A2, A3;
double n1, n2, n3, D;
double E, m, C2, C3;
double A,n, ACu, nCu, nNi, nCo;
double SOSCu, SOSNi, SOSCo, ACu1, ACu2, ACu3, ANi1, ANi2, ANi3, ACo1, ACo2, ACo3;
double nCu1, nCu2, nCu3, nNi1, nNi2, nNi3, nCo1, nCo2, nCo3, D1, D2, D3;
double ECu, ENi, ECo, mCu, mNi, mCo, CCu2, CCu3, CNi1, CNi3, CCo1, CCo2;
};

#include "i.cpp"
#endif
```

CPP FILE LINKED TO H FILE

```
#include <vector>
#include "math.h"
#include <fstream>
#include <iomanip>

//Constructor for class equilibrium
equilibrium :: equilibrium()
{
double array[] = {815, 39.4, 4, 10.4, 12, 8.6, 7, 9.6, 7, 8.2, 7, 7.8, 34, 12.4, 317, 35.6, 800, 38, 328,
34.2, 917, 7.6, 31, 4.2, 42, 2.4, 201, 9.2, 900, 19.4, 913, 16.6, 430, 11, 95, 1.4, 50, 0.4, 182, 11,
986, 3.4, 44, 1.8, 903, 12.8, 923, 13.2, 253, 1.4, 61, 0.4, 474, 2.8, 245, 1.4, 104, 0.2, 102, 0.8};
//Create 3 vectors, one for each component
vector<double> VC;
vector<double> VN;
vector<double> VCo;
for (int i = 0; i < 20; i++)
        VC.push_back(array[i]);
for (int i= 20;i<40;i++)
        VN.push_back(array[i]);
for (int i= 40;i<60 ;i++)
        VCo.push_back(array[i]);
langmuir(VC, VN, VCo);
}

//Destructor for class equilibrium
equilibrium :: ~equilibrium()
{
cout<<"You will find the results in the following files in this directory"<<endl;
cout<<"langresults, fritzresults, effective1, effective2, driving and single"<<endl;
cout<<"Have a nice day"<<endl;
cout<<"Any character to exit ";
char e;
cin>>e;
}

//Function to solve for parameters in Langmuir isotherm
void equilibrium :: langmuir (const vector<double> VC, const vector<double> VN, const
vector<double> VCo)
{
ofstream out("Langresult.txt");
out<<"A1"<<"    "<<"A2"<<"    "<<"A3"<<"    "<<"SOS"<<endl;
A1 = 3;
A2 = 2;
A3 = 1;
SOSCu = 1000000;
SOSNi = 1000000;
SOSCo = 1000000;
int i;
int j(1);
int count;
double c1, c2, c3;
//Declare duplicate vectors
vector<double> V1(20), V2(20), V3(20);
double qu, qd;
double Totalu, Totald, Erroru, Errord, SOS;
//Declare and initialise adjustments to original parameter estimates
int Adj1(1), Adj2(0),Adj3(0);
```

```
//Outer loop : each time starting with new initial values for the parameters
while (j < 13)
        {
//Initialise all values for outer loop
        i = 1;
        count = 1;
        c1 = 0.05;
        c2 = 0;
        c3 = 0;
        Totalu = 0;
        Totald = 0;
        SOS = 100000;
        V1 = VC;
        V2 = VN;
        V3 = VCo;
//Inner loop : determines minimum(local) sum of squares of errors
        while (i < 500)
        {
//Run through vector and determine SOSOE
                for (int j = 0; j < 19; j += 2)
                { //1
//Obtain q by incrementing a parameter
                qu = ((A1 + c1) * V1[j])/(1 - ((A2 +c2)* V2[j]) + ((A3 +c3)* V3[j]));
//Compare to actual and determine total error for this senario
                Erroru = pow((qu - V1[j+1]),2);
                Totalu += Erroru;
//Ensure that no parameters are negative and decrement a parameter to obtain q
                if ((A1-c1 > 0.1) && (A2-c2 > 0.1) && (A3-c3 > 0.1))
                { //2
                qd = ((A1-c1) * V1[j])/(1 - ((A2-c2) * V2[j]) + ((A3-c3) * V3[j]));
                Errord = pow((qd - V1[j+1]),2);
                Totald += Errord;
                } //2
                else Totald = SOS - 10;
                } //1
//Establish whether a lower sum of squares of errors have been obtained and adjust parameters
                if ((SOS > Totalu) || (SOS > Totald))
                { //3
                if (Totalu < Totald)
                { //4
                SOS = Totalu;
                A1 += c1;
                A2 += c2;
                A3 += c3;
                } //4
                else
                { //5
                SOS = Totald;
                A1 -= c1;
                A2 -= c2;
                A3 -= c3;
                } //5
                } //3
//Change increment/decrement setting
                if (c1 == 0.05)
                { //6
                c1 = 0;
                c2 = 0.05;
                } //6
                else if (c2 == 0.05)
```

```
        { //7
        c2 = 0;
        c3 = 0.05;
        } //7
        else
        { //8
        c3 = 0;
        c1 = 0.05;
        } //8
        i++;
        if ((i == 499) && (count != 1) && (count != 2))
        { //9
        if (SOS < SOSCo)
        { //10
        SOSCo = SOS;
        ACo3 = A1;
        ACu3  = A2;
        ANi3  = A3;
        } //9
        } //10
//Initialise vectors for next set of iterations and determine best scenario so far
        if ((i == 499) && (count < 3))
        { //11
        if (count == 1)
        { //12
        V1 = VN;
        V2 = VCo;
        V3 = VC;
        if (SOS < SOSCu)
        { //13
        SOSCu = SOS;
        ACu1  = A1;
        ANi1  = A2;
        ACo1  = A3;
        } //13
        } //12
        else
        { //14
        V1 = VCo;
        V2 = VC;
        V3 = VN;
        if (SOS < SOSNi)
        { //15
        SOSNi = SOS;
        ANi2  = A1;
        ACo2  = A2;
        ACu2  = A3;
        } //15
        } //14
        i = 1;
        count ++;
        out<<setprecision(2)<<A1<<"  "<<setprecision(2)<<A2<<"
        "<<setprecision(2)<<A3<<"  "<<setprecision(4)<<SOS<<endl;
//Make adjustments to initial values and reset other values
        SOS = 100000;
        A1 = 3 + Adj1;
        A2 = 2 + Adj2;
        A3 = 1 + Adj3;
        c1 = 0.05;
        c2 = 0;
```

```
                c3 = 0;
                } //11
                Totalu = 0;
                Totald = 0;
                } //WHILE I
        out<<A1<<"  "<<A2<<"   "<<A3<<"   "<<setprecision(4)<<SOS<<endl;
        out<<"=============================================="<<endl;
//Reset adjustments
        if ((j==1) || (j==4) || (j==7) || (j==10))
        Adj1 += 2;
        else if ((j==2) || (j==5) || (j==9) || (j==11))
        Adj2 += 2;
        else Adj3 += 2;
        j++;
        } //WHILE J
out<<"BEST RESULT OBTAINED"<<endl;
out<<"Copper"<<endl;
out<<"SOS   "<<SOSCu<<endl;
out<<"ACu   "<<ACu1 <<endl;
out<<"ANi   "<<ANi1 <<endl;
out<<"ACo   "<<ACo1 <<endl;
out<<"Nickel"<<endl;
out<<"SOS   "<<SOSNi<<endl;
out<<"ANi   "<<ANi2 <<endl;
out<<"ACo   "<<ACo2 <<endl;
out<<"ACu   "<<ACu2 <<endl;
out<<"Cobalt"<<endl;
out<<"SOS   "<<SOSCo<<endl;
out<<"ACo   "<<ACo3 <<endl;
out<<"ACu   "<<ACu3 <<endl;
out<<"ANi   "<<ANi3 <<endl;
fritz (VC, VN, VCo);
}


//Function to solve Fritz & Schleunder isotherm
void equilibrium ::  fritz (const vector<double> VC, const vector<double> VN, const vector<double>
VCo)
{
ofstream out("Fritzresult.txt");
out<<"A1"<<"   "<<"A2"<<"   "<<"A3"<<"   "<<"n1"<<"   "<<"n2"<<"   "<<"n3"<<"   "<<"D"<<"
"<<"SOS"<<endl;
A1 = 5;
A2 = 2;
A3 = 1;
n1 = 0.5;
n2 = 0.2;
n3 = 0.2;
D = 3;
SOSCu = 1000000;
SOSNi = 1000000;
SOSCo = 1000000;
int i;
int j(1);
int count;
double c1, c2, c3, c4, c5, c6, c7;
vector<double> V1(20), V2(20), V3(20);
double qu, qd;
double Totalu, Totald, Erroru, Errord, SOS;
int Adj1(1), Adj3(0), Adj5(0), Adj7(0);
```

```
double Adj2(0), Adj4(0), Adj6(0);
while (j < 29)
        {
        i = 1;
        count = 1;
        c1 = 0.05;
        c2 = 0;
        c3 = 0;
        c4 = 0;
        c5 = 0;
        c6 = 0;
        c7 = 0;
        Totalu = 0;
        Totald = 0;
        SOS = 10000;
        V1 = VC;
        V2 = VN;
        V3 = VCo;
        while (i < 500)
                {
                for (int j = 0; j < 19; j += 2)
                { //1
                qu = ((A1 + c1) * pow(V1[j], (n1 + c4)))/((D + c7) +
                ((A2 + c2) * pow(V2[j], (n2 + c5))) + ((A3 + c3) * pow(V3[j], (n3 + c6))));
                Erroru = pow((qu - V1[j+1]), 2);
                Totalu += Erroru;
                if ((A1-c1 > 0.1) && (A2-c2 > 0.1) && (A3-c3 > 0.1) && (n1-c4 > 0.1)
                && (n2-c5 > 0.1) && (n3-c6 > 0.1) && (D-c7 > 0.1))
                { //2
                qd = ((A1 - c1) * pow(V1[j], (n1 - c4)))/((D - c7) +
                ((A2 - c2) * pow(V2[j], (n2 - c5))) + ((A3 - c3) * pow(V3[j], (n3 - c6))));
                Errord = pow((qd - V1[j+1]), 2);
                Totald += Errord;
                } //2
                else Totald = SOS + 10;
                } //1
                if ((SOS > Totalu) || (SOS > Totald))
                { //3
                if (Totalu < Totald)
                { //4
                SOS = Totalu;
                A1 += c1;
                A2 += c2;
                A3 += c3;
                n1 += c4;
                n2 += c5;
                n3 += c6;
                D += c7;
                } //4
                else
                { //5
                SOS = Totald;
                A1 -= c1;
                A2 -= c2;
                A3 -= c3;
                n1 -= c4;
                n2 -= c5;
                n3 -= c6;
                D -= c7;
                } //5
```

```
} //3
if (c1 == 0.05)
{ //6
c1 = 0;
c4 = 0.005;
} //6
else if (c4 == 0.005)
{ //7
c4 = 0;
c2 = 0.05;
} //7
else if (c2 == 0.05)
{ //8
c2 = 0;
c5 = 0.005;
} //8
else if (c5 == 0.005)
{ //9
c5 = 0;
c3 = 0.05;
} //9
else if (c3 == 0.05)
{ //10
c3 = 0;
c6 = 0.005;
} //10
else
{ //11
c6 = 0;
c7 = 0.05;
} //11
i++;
if ((i == 499) && (count != 1) && (count != 2))
{ //12
if (SOSCo > SOS)
{ //13
SOSCo = SOS;
ACo3 = A1;
ACu3 = A2;
ANi3 = A3;
nCo3 = n1;
nCu3 = n2;
nNi3 = n3;
D3 = D;
} //13
} //12
if ((i == 499) && (count < 3))
{ //14
if (count == 1)
{ //15
V1 = VN;
V2 = VCo;
V3 = VC;
if (SOS < SOSCu)
{ //16
SOSCu = SOS;
ACu1 = A1;
ANi1 = A2;
ACo1 = A3;
nCu1 = n1;
```

```
        nNi1 = n2;
        nCo1 = n3;
        D1 = D;
        } //16
        } //15
        else
        { //17
        V1 = VCo;
        V2 = VC;
        V3 = VN;
        if (SOS < SOSNi)
        { //18
        SOSNi = SOS;
        ANi2 = A1;
        ACo2 = A2;
        ACu2 = A3;
        nNi2 = n1;
        nCo2 = n2;
        nCu2 = n3;
        D2 = D;
        } //18
        } //17
        i = 1;
        count++;
        out<<setprecision(2)<<A1<<"  "<<setprecision(2)<<A2 <<"
        "<<setprecision(2)<<A3 <<"  "<<setprecision(2)<<n1
        <<"  "<<setprecision(2)<<n2<<"  "<<setprecision(2)<<n3<<"
        "<<setprecision(2)<<D<<"  "<<setprecision(4)<<SOS<<endl;
        SOS = 100000;
        A1 = 5 + Adj1;
        A2 = 1 + Adj3;
        A3 = 1 + Adj5;
        n1 = 0.5 + Adj2;
        n2 = 0.3 + Adj4;
        n3 = 0.3 + Adj6;
        D = 1 + Adj7;
        c1  = 0.05;
        c2 = 0;
        c3 = 0;
        c4 = 0;
        c5 = 0;
        c6 = 0;
        c7 = 0;
        } //14
        Totalu = 0;
        Totald = 0;
        } //WHILE I
out<<setprecision(2)<<A1<<"  "<<setprecision(2)<<A2 <<"  "<<setprecision(2)<<A3 <<"
"<<setprecision(2)<<n1
<<"  "<<setprecision(2)<<n2<<"  "<<setprecision(2)<<n3<<"  "<<setprecision(2)<<D<<"
"<<setprecision(4)<<SOS<<endl;
out<<"=================================================="<<endl;
if ((j==1) || (j==8) || (j==15) || (j==22))
Adj1 += 2;
else if ((j==2) || (j==9) || (j==16) || (j==23))
Adj2 += 0.1;
else if ((j==3) || (j==10) || (j==17) || (j==24))
Adj3 += 2;
else if ((j==4) || (j==11) || (j==18) || (j==25))
Adj4 += 0.1;
```

```
        else if ((j==5) || (j==12) || (j==19) || (j==26))
        Adj5 += 2;
        else if ((j==6) || (j==13) || (j==20) || (j==27))
        Adj6 += 0.1;
        else Adj7 += 2;
        j++;
        } //WHILE J
out<<"BEST RESULT"<<endl;
out<<"Copper"<<endl;
out<<"SOS   "<<SOSCu<<endl;
out<<"ACu   "<<ACu1 <<endl;
out<<"ANi   "<<ANi1 <<endl;
out<<"ACo   "<<ACo1 <<endl;
out<<"nCu   "<<nCu1<<endl;
out<<"nNi   "<<nNi1<<endl;
out<<"nCo   "<<nCo1<<endl;
out<<"D   "<<D1<<endl;
out<<"Nickel"<<endl;
out<<"SOS   "<<SOSNi<<endl;
out<<"ANi   "<<ANi2<<endl;
out<<"ACo   "<<ACo2<<endl;
out<<"ACu   "<<ACu2<<endl;
out<<"nNi   "<<nNi2<<endl;
out<<"nCo   "<<nCo2<<endl;
out<<"nCu   "<<nCu2<<endl;
out<<"D   "<<D2<<endl;
out<<"Cobalt"<<endl;
out<<"SOS   "<<SOSCo<<endl;
out<<"ACo   "<<ACo3<<endl;
out<<"ACu   "<<ACu3<<endl;
out<<"ANi   "<<ANi3<<endl;
out<<"nCo   "<<nCo3<<endl;
out<<"nCu   "<<nCu3<<endl;
out<<"nNi   "<<nNi3<<endl;
out<<"D   "<<D3<<endl;
effective_1 (VC, VN, VCo);
}

//Function to optimise isotherm based on effective concentration.1
void equilibrium :: effective_1(const vector<double> VC, const vector<double> VN, const
vector<double> VCo)
{
ofstream out ("effective1.txt");
out<<"E"<<"      "<<"m"<<"      "<<"C1"<<"      "<<"C2"<<"      "<<"SOS"<<endl;
SOSCu = 1000000;
SOSNi = 1000000;
SOSCo = 1000000;
E = 5;
m = 0.3;
C2 = 0.001;
C3 = 0.001;
int i;
int j(1);
int count;
double c1, c2, c3, c4;
vector<double> V1(20), V2(20), V3(20);
double qu, qd;
double Totalu, Totald, Erroru, Errord, SOS;
int Adj1(1);
double  Adj2(0), Adj3(0), Adj4(0);
```

```
while (j < 17)
        {
        i = 1;
        count = 1;
        c1 = 0.1;
        c2 = 0;
        c3 = 0;
        c4 = 0;
        Totalu = 0;
        Totald = 0;
        SOS = 1000000;
        V1 = VC;
        V2 = VN;
        V3 = VCo;
        while (i < 500)
                {
                for (int j = 0; j < 19; j += 2)
                { //1
                qu = (E + c1) * pow(V1[j]/(((C2 + c3) * V2[j]) + ((C3 + c4) * V3[j])), (m + c2));
                Erroru = pow((qu - V1[j+1]), 2);
                Totalu += Erroru;
                if ((E-c1 > 0.1) && (m-c2 > 0.001) && (C2 - c3 > 0.001) && (C3 - c4 > 0.001))
                { //2
                qd = (E - c1) * pow(V1[j]/(((C2-c3) * V2[j]) + ((C3 - c4) * V3[j])), (m-c2));
                Errord = pow((qd - V1[j+1]), 2);
                Totald += Errord;
                } //2
                else Totald = SOS + 10;
                } //1
                if ((SOS > Totalu) || (SOS > Totald))
                { //3
                if (Totalu < Totald)
                { //4
                SOS = Totalu;
                E += c1;
                m += c2;
                C2 += c3;
                C3 += c4;
                } //4
                else
                { //5
                SOS = Totald;
                E -= c1;
                m -= c2;
                C2 -= c3;
                C3 -= c4;
                } //5
                } //3
                if (c1 == 0.1)
                { //6
                c1 = 0;
                c2 = 0.05;
                } //6
                else if (c2 == 0.05)
                { //7
                c2 = 0;
                c3 = 0.005;
                } //7
                else if (c3 == 0.005)
                { //8
```

```
c3 = 0;
c4 = 0.005;
} //8
else
{ //9
c4 = 0;
c1 = 0.1;
} //9
i++;
if ((i == 499) && (count != 1) && (count != 2))
{ //10
if (SOS < SOSCo)
{ //11
SOSCo  = SOS;
ECo  = E;
mCo  = m;
CCu3 = C2;
CNi3 = C3;
} //1
} //10
if ((i == 499) && (count < 3))
{ //12
if (count == 1)
{ //13
V1 = VN;
V2 = VCo;
V3 = VC;
if (SOS < SOSCu)
{ //14
SOSCu = SOS;
ECu = E;
mCu = m;
CNi1 = C2;
CCo1 = C3;
} //14
} //13
else
{ //15
V1 = VCo;
V2 = VC;
V3 = VN;
if (SOS < SOSNi)
{ //16
SOSNi = SOS;
ENi = E;
mNi = m;
CCo2 = C2;
CCu2 = C3;
} //16
} //15
i = 1;
count ++;
out<<setprecision(2)<<E<<"  "<<setprecision(3)<<m<<"
"<<setprecision(3)<<C2<<
"  "<<setprecision(3)<<C3<<"  "<<setprecision(4)<<SOS<<endl;
SOS = 1000000;
E = 5 - Adj1;
m = 0.3 + Adj2;
C2 = 0.01 + Adj3;
C3 = 0.01 + Adj4;
```

```
                c1 = 0.1;
                c2 = 0;
                c3 = 0;
                c4 = 0;
                } //12
                Totalu = 0;
                Totald = 0;
                } //WHILE I
        out<<setprecision(2)<<E<<" "<<setprecision(3)<<m<<" "<<setprecision(3)<<C2<<
        " "<<setprecision(3)<<C3<<" "<<setprecision(4)<<SOS<<endl;
        out<<"=============================================================="<<endl;
        if ((j==1) || (j==5) || (j==9) || (j==13))
        Adj1 += 1;
        else if ((j==2) || (j==6) || (j==10) || (j==14))
        Adj2 += 0.1;
        else if ((j==3) || (j==7) || (j==11) || (j==15))
        Adj3 += 0.002;
        else Adj4 += 0.002;
        j++;
        } //WHILE J
out<<"BEST RESULT"<<endl;
out<<"Copper"<<endl;
out<<"SOS   "<<SOSCu<<endl;
out<<"E   "<<ECu<<endl;
out<<"m   "<<mCu<<endl;
out<<"CNi   "<<CNi1<<endl;
out<<"CCo   "<<CCo1<<endl;
out<<"Nickel"<<endl;
out<<"SOS   "<<SOSNi<<endl;
out<<"E   "<<ENi<<endl;
out<<"m   "<<mNi<<endl;
out<<"CCo   "<<CCo2<<endl;
out<<"CCu   "<<CCu2<<endl;
out<<"Cobalt"<<endl;
out<<"SOS   "<<SOSCo<<endl;
out<<"E   "<<ECo<<endl;
out<<"m   "<<mCo<<endl;
out<<"CCu   "<<CCu3<<endl;
out<<"CNi   "<<CNi3<<endl;
effective_2(VC, VN, VCo);
}

//Function to solve isotherm based on effective concentration.2
void equilibrium :: effective_2(const vector<double> VC, const vector<double> VN, const
vector<double> VCo)
{
ofstream out ("effective2.txt");
out<<"E"<<"    "<<"m"<<"    "<<"C1"<<"    "<<"C2"<<"    "<<"SOS"<<endl;
E = 4;
m = 0.3;
C2 = 0.1;
C3 = 0.1;
int i;
int j(1);
int count;
double c1, c2, c3, c4;
vector<double> V1(20), V2(20), V3(20);
double qu, qd;
double Totalu, Totald, Erroru, Errord, SOS;
int Adj1(1);
```

```
double  Adj2(0), Adj3(0), Adj4(0);
        while (j < 17)
        {
        i = 1;
        count = 1;
        c1 = 0.1;
        c2 = 0;
        c3 = 0;
        c4 = 0;
        Totalu = 0;
        Totald = 0;
        SOS = 1000000;
        V1 = VC;
        V2 = VN;
        V3 = VCo;
                while (i < 500)
                {
                for (int j = 0; j < 19; j+= 2)
                { //1
                qu = (E + c1) * pow (V1[j]/(pow (V2[j], (C2 + c3)) + pow (V3[j], (C3 + c4))), (m +
                c2));
                Erroru = pow((qu - V1[j+1]), 2);
                Totalu += Erroru;
                if ((E-c1 > 0.1) && (m-c2 > 0.01) && (C2 - c3 > 0.01) && (C3 - c4 > 0.01))
                { //2
                qd = (E - c1) * pow(V1[j]/(pow(V2[j], (C2-c3)) + pow(V3[j], (C3-c4))),(m-c2));
                Errord = pow((qd - V1[j+1]), 2);
                Totald += Errord;
                } //2
                else Totald = SOS + 10;
                } //1
                if ((SOS > Totalu) || (SOS > Totald))
                { //3
                if (Totalu < Totald)
                { //4
                SOS = Totalu;
                E += c1;
                m += c2;
                C2 += c3;
                C3 += c4;
                } //4
                else
                { //5
                SOS = Totald;
                E -= c1;
                m -= c2;
                C2 -= c3;
                C3 -= c4;
                } //5
                } //3
                if (c1 == 0.1)
                { //6
                c1 = 0;
                c2 = 0.05;
                } //6
                else if (c2 == 0.05)
                { //7
                c2 = 0;
                c3 = 0.05;
                } //7
```

```
else if (c3 == 0.05)
{ //8
c3 = 0;
c4 = 0.05;
} //8
else
{ //9
c4 = 0;
c1 = 0.1;
} //9
i++;
if ((i == 499) && (count != 1) && (count != 2))
{ //10
if (SOS < SOSCo)
{ //11
SOSCo  = SOS;
ECo  = E;
mCo  = m;
CCu3 = C2;
CNi3 = C3;
} //11
} //10
if ((i == 499) && (count < 3))
{ //12
if (count == 1)
{ //13
V1 = VN;
V2 = VCo;
V3 = VC;
if (SOS < SOSCu)
{ //14
SOSCu = SOS;
ECu = E;
mCu = m;
CNi1 = C2;
CCo1 = C3;
} //14
} //13
else
{ //15
V1 = VCo;
V2 = VC;
V3 = VN;
if (SOS < SOSNi)
{ //16
SOSNi = SOS;
ENi = E;
mNi = m;
CCo2 = C2;
CCu2 = C3;
} //16
} //15
i = 1;
count ++;
out<<setprecision(2)<<E<<"  "<<setprecision(3)<<m<<"
"<<setprecision(3)<<C2<<
"  "<<setprecision(3)<<C3<<"  "<<setprecision(4)<<SOS<<endl;
SOS = 1000000;
E = 4 + Adj1;
m = 0.3 + Adj2;
```

```
			C2 = 0.1 + Adj3;
			C3 = 0.1 + Adj4;
			c1 = 0.1;
			c2 = 0;
			c3 = 0;
			c4 = 0;
			} //12
			Totalu = 0;
			Totald = 0;
			} WHILE I
out<<setprecision(2)<<E<<"  "<<setprecision(3)<<m<<"  "<<setprecision(3)<<C2<<
"  "<<setprecision(3)<<C3<<"  "<<setprecision(4)<<SOS<<endl;
out<<"==============================================================="<<endl;
if ((j==1) || (j==5) || (j==9) || (j==13))
Adj1 += 1;
else if ((j==2) || (j==6) || (j==10) || (j==14))
Adj2 += 0.1;
else if ((j==3) || (j==7) || (j==11) || (j==15))
Adj3 += 0.05;
else Adj4 += 0.05;
j++;
} WHILE J
out<<"BEST RESULT"<<endl;
out<<"Copper"<<endl;
out<<"SOS   "<<SOSCu<<endl;
out<<"E   "<<ECu<<endl;
out<<"m   "<<mCu<<endl;
out<<"CNi   "<<CNi1<<endl;
out<<"CCo   "<<CCo1<<endl;
out<<"Nickel"<<endl;
out<<"SOS   "<<SOSNi<<endl;
out<<"E   "<<ENi<<endl;
out<<"m   "<<mNi<<endl;
out<<"CCo   "<<CCo2<<endl;
out<<"CCu   "<<CCu2<<endl;
out<<"Cobalt"<<endl;
out<<"SOS   "<<SOSCo<<endl;
out<<"E   "<<ECo<<endl;
out<<"m   "<<mCo<<endl;
out<<"CCu   "<<CCu3<<endl;
out<<"CNi   "<<CNi3<<endl;
driving (VC, VN, VCo);
}


//Function to solve equilibrium based on driving force
void equilibrium ::driving (const vector<double> VC, const vector<double> VN, const vector<double>
VCo)
{
ofstream out ("driving.txt");
out<<"n1"<<"    "<<"n2"<<"    "<<"n3"<<"    "<<"SOS"<<endl;
SOSCu  = 1000000;
n1  = 0.1;
n2  = 0.1;
n3  = 0.1;
int i;
int j(1);
double c1, c2, c3;
vector<double> V1(20), V2(20), V3(20);
V1 = VC;
```

```
V2 = VN;
V3 = VCo;
double qu, qd;
double Totalu, Totald, Erroru, Errord, SOS;
double Adj1(0),  Adj2(0), Adj3(0);
        while (j < 17)
        {
        i = 1;
        c1 = 0.05;
        c2 = 0;
        c3 = 0;
        Totalu = 0;
        Totald = 0;
        SOS = 1000000;
                while (i < 500)
                {
                for (int j = 0; j < 19; j+= 2)
                { //1
                qu = (pow(V1[j], (n1 + c1)) + pow( V2[j], (n2 + c2)) + pow (V3[j], (n3 + c3))) -
                (V1[j+1] + V2[j+1] + V3[j+1]);
                Erroru = pow (qu, 2);
                Totalu += Erroru;
                if ((n1-c1 > 0.1) && (n2-c2 > 0.01) && (n1 - c3 > 0.01))
                { //2
                qd = (pow (V1[j], (n1 - c1)) + pow (V2[j], (n2 - c2)) + pow (V3[j], (n3 - c3))) -
                (V1[j] + V2[j] + V3[j]);
                Errord = pow (qd, 2);
                Totald += Errord;
                } //2
                else Totald = SOS + 10;
                } //1
                if ((SOS > Totalu) || (SOS > Totald))
                { //3
                if (Totalu < Totald)
                { //4
                SOS = Totalu;
                n1 += c1;
                n2 += c2;
                n3 += c3;
                } //4
                else
                { //5
                SOS = Totald;
                n1 -= c1;
                n2 -= c2;
                n3 -= c3;
                } //5
                } //3
                if (c1 == 0.05)
                { //6
                c1 = 0;
                c2 = 0.05;
                } //6
                else if (c2 == 0.05)
                { //7
                c2 = 0;
                c3 = 0.05;
                } //7
                else
                { //8
```

```
        c3 = 0;
        c1 = 0.05;
        } //8
        i++;
        if (i == 499)
        { //9
        if (SOS < SOSCu)
        { //10
        SOSCu = SOS;
        nCu = n1;
        nNi = n2;
        nCo = n3;
        } //10
        out<<setprecision(2)<<n1<<"  "<<setprecision(2)<<n2<<"
        "<<setprecision(2)<<n3<<
        "  "<<setprecision(4)<<SOS<<endl;
        SOS = 1000000;
        n1 = 0.1  + Adj1;
        n2 = 0.1 + Adj2;
        n3 = 0.1  + Adj3;
        c1 = 0.05;
        c2 = 0;
        c3 = 0;
        } //9
        Totalu = 0;
        Totald = 0;
        } //WHILE I
    out<<"======================================================"<<endl;
    if ((j==1) || (j==4) || (j==7) || (j==10))
    Adj1 += 0.1;
    else if ((j==2) || (j==5) || (j==8) || (j==11))
    Adj2 += 0.1;
    else
    Adj3 += 0.1;
    j--;
    } WHILE J
out<<"BEST RESULT"<<endl;
out<<"SOS   "<<SOSCu<<endl;
out<<"nCu   "<<nCu<<endl;
out<<"nNi   "<<nNi<<endl;
out<<"nCo   "<<nCo<<endl;
single (VC);
}

//Function to solve single component Freundlich isotherm for component 1
void equilibrium ::single (const vector<double> VC )
{
ofstream out ("single.txt");
out<<"A"<<"    "<<"n"<<"    "<<"SOS"<<endl;
SOSCu = 1000000;
A = 3;
n = 0.2;
int i;
int j(1);
double c1, c2;
vector<double> V1(20);
V1 = VC;
double qu, qd;
double Totalu, Totald, Erroru, Errord, SOS;
double Adj1(1),  Adj2(0);
```

```
while (j < 9)
{
i = 1;
c1 = 0.1;
c2 = 0;
Totalu = 0;
Totald = 0;
SOS = 1000000;
        while (i < 500)
        {
        for (int j = 0; j < 19; j+= 2)
        { //1
        qu = (A + c1) * pow (V1[j], (n + c2));
        Erroru = pow ((qu - V1[j+1]), 2);
        Totalu += Erroru;
        if ((A-c1 > 0.1) && (n-c2 > 0.01))
        { //2
        qd = (A - c1) * pow (V1[j], (n - c2));
        Errord = pow ((qd - V1[j+1]), 2);
        Totald += Errord;
        } //2
        else Totald = SOS + 10;
        } //1
        if ((SOS > Totalu) || (SOS > Totald))
        { //3
        if (Totalu < Totald)
        { //4
        SOS = Totalu;
        A += c1;
        n += c2;
        } //4
        else
        { //5
        SOS = Totald;
        A -= c1;
        n -= c2;
        } //5
        } //3
        if (c1 == 0.1)
        { //6
        c1 = 0;
        c2 = 0.02;
        } //6
        else
        { //7
        c1 = 0.1;
        c2 = 0;
        } //7
        i++;
        if (i == 499)
        { //8
        out<<setprecision(3)<<A<<"  "<<setprecision(3)<<n<<"
        "<<setprecision(3)<<SOS<<endl;
        out<<"=========================================="<<endl;
        if (SOS < SOSCu)
        { //9
        SOSCu = SOS;
        ACu = A;
        nCu = n;
        } //9
```

```
                SOS = 1000000;
                A = 3  + Adj1;
                n = 0.2 + Adj2;
                c1 = 0.1;
                c2 = 0;
                } //8
                Totalu = 0;
                Totald = 0;
                } WHILE I
        if ((j==1) || (j==3) || (j==5) || (j==7))
        Adj1 += 1;
        else
        Adj2 += 0.1;
        j++;
        } WHILE J
out<<"BEST RESULT"<<endl;
out<<"SOS   "<<SOSCu<<endl;
out<<"A   "<<ACu<<endl;
out<<"n   "<<nCu<<endl;
}
```

MAIN PROGRAM

```
#include <iostream>
#include "isotherm.h"

int main ()
{
        equilibrium a;
        return 0;
}
```

CAPE PENINSULA