THE RECOVERY OF METAL CYANIDES BY ION EXCHANGE RESINS

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DECLARATION

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

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1 December 2000

ABSTRACT

Cyanide is used extensively in the mining industry to leach gold and silver from their ores. Cyanide, in the form of sodium or potassium cyanide, is added in excess to that required theoretically due to equilibrium and kinetic considerations in the leaching step. This results in free cyanide and various other cyanide complexes reporting to the effluent streams of these operations. In this study the removal of these species from solution by means of ion exchange resins was investigated. Equilibrium conditions, kinetic parameters and the competitive exchange nature of the process was evaluated.

The experimental work focused on contacting the various resins individually in a batch reactor with free cyanide, iron cyanide and copper cyanide complexes. The experimental data obtained was found to be well explained by the Freundlich-type multi- and single-component isotherms. Furthermore, mass transfer parameters were investigated revealing that certain cyanide species outperform others kinetically in the ion exchange process. During this study it was shown that ion exchange processes could be effective in effluent clean-up of those streams containing cyanide complexes.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Cyanide

The term cyanide can refer to the anion CN^- or to its acidic form hydrocyanic acid, HCN. The oxidation of cyanide produces cyanogen, C_2N_2, whereas a simple cyanide compound dissociates to the cyanide anion (CN^-) and a cation (H^+). An organic compound, which consists of a cyanide and a cyanogen is refered to as a nitrile. During metabolism, the cyanide anion is liberated by the nitrile and produces the biological effects of the cyanide ion.[1]

Cyanide consists of a carbon and nitrogen polyatomic anion containing a triple bond. The cyanide ion is found rarely in this form, usually forming complexes with transition metals or ionic bonds with alkali metals and alkali earth metals. Researchers have categorised inorganic compounds of cyanide into subsets, grouped together on the basis of similiar chemical characteristics:

- **Free cyanide**
- **Simple cyanide compounds**
- **Weak acid dissociable (W.A.D) cyanides**
- **Moderately strong cyanide complexes**

Cyanide can also form hydrocarbon chains resulting in a number of organic molecular combinations.

1.1.1 Free cyanide

The simplest form of cyanide is "free cyanide". There are only two species, hydrogen cyanide and the anionic cyanide molecule. Free cyanide is the ionic cyanide released into aqueous solutions by the dissolution and dissociation of cyanide compounds and complexes.[1] An example of this is the potassium salt:

$$\mathbf{KCN + H_2O \Rightarrow K^+ + CN^-} \qquad \mathbf{pK_a \approx \infty}$$

The reaction between the cyanide ion and water is expressed by the following equation:

$$\mathbf{CN^- + H_2O \Rightarrow HCN + OH^-} \qquad \mathbf{pK_a = 2.03 \times 10^{-10}}$$

The solubility of hydrocyanic gas in water is very low and it also readily dissociates into hydrogen and anionic cyanide at low pH. Cyanide solutions as a rule should be kept at high pH to prevent the formation of hydrocyanic gas. The formation of hydrocyanic gas at a low pH is used in many processes for the removal of cyanide from solution by means of acidification and volatilisation. Hydrocyanic gas is colourless and has an almond smell and can be detected even at low concentrations.

1.1.2 Simple cyanide compounds

These compounds consist of a cyanide polyatomic anion and alkali earth metals. The compounds are electrically neutral and are consequently capable of existing in the solid form. When they are placed in an aqueous environment they dissociate into the alkali earth metals and free cyanide[1]. e.g.

$$\mathbf{NaCN \Rightarrow Na^+ + CN^-}$$

1.1.3 Weak acid dissociable (W.A.D.) cyanides

These complex metal cyanides are discernable from their counter parts for their tendency to break down into free cyanide and a transition metal when exposed to a weak acid environment. Table 1[1] provides examples of this phenomenon. The break- down of these metal cyanides by continuously refluxing for one hour with a pH buffer at 4.5, agrees with the wet chemistry methods for W.A.D. cyanides.[2] When determining the amount of free cyanide, the free cyanide should be detected separately and subtracted from the W.A.D. cyanide value obtained. The formation of free cyanide, due to the dissociation of the metal cyanide complexes, produces a degree of danger. This is the reason for the W.A.D. cyanide content in a solution to be considered a good indication of the toxicology of the cyanides present.

NAME	FORMULA	DISSOCIATION CONSTANT
Tricyanocuprate	$[Cu(CN)_3]^{-2}$	5.0×10^{-28}
Tetracyanonickelate	$[Ni(CN)_4]^{-2}$	1.0×10^{-22}
Dicyanosilverate	$[Ag(CN)_2]^{-1}$	1.0×10^{-21}
Tetracyanocadminate	$[Cd(CN)_4]^{-2}$	1.4×10^{-17}
Tetracyanozincate	$[Zn(CN)_4]^{-2}$	1.3×10^{-17}

Table 1 Weak acid discernable metal cyanide complexes, formulas and dissociation constants.

1.1.4 Moderately strong cyanide complexes

The dissociation constants of the moderately strong cyanide complexes are higher than that of the W.A.D. metal cyanides. A few of these metal cyanide complexes are listed in Table 2 [1]. These metal cyanides are stable in the absence of light. To test for these cyanides, dissociation has to be achieved by lowering the pH of the solution to 1 after a suitable reflux time and then analysing the quantity of free cyanide produced.

NAME	**FORMULA**	**DISSOCIATION CONSTANT**
Hexacyanoferrate(III) or Ferricyanide	$[Fe(CN)_6]^{-3}$	1.0×10^{-52}
Hexacyanoferrate(II) or Ferricyanide	$[Fe(CN)_6]^{-4}$	1.0×10^{-47}
Tetracyanomercurate(I)	$[Hg(CN)_4]^{-2}$	4.0×10^{-42}

Table 2 Strong cyanide complexes, formulas and dissociation constants

1.1.5 Toxicity of cyanide

Cyanide is a highly poisonous substance, which can be lethal to humans even in small quantities. A lethal dosage for a human can range between 50 and 200 mg. By definition a toxicant is a chemical, physical or biological agent which acts upon a living organism producing an undesirable harmful effect. The level of toxicity measured is dependent upon the organism affected, and the dosage and form of the toxicant. Cyanide is high on the list of environmentally unfriendly substances. Just as the chemistry of cyanide is complex so to is the understanding of its toxicity.[3]

The gaseous form of cyanide, hydrogen cyanide, which occurs at a low pH will be rapidly absorbed by an organism by means of ingestion or inhalation. The primary enzyme affected, cytochrome oxidase, which is contained within cells of the body and which is essential for the utilisation of oxygen. The central nervous system of higher animals has the greatest oxygen requirements, thus, an inactivation of the enzyme will lead to asphyxiation and tissue death. The decrease in oxygen will lead to the failure of all vital function and ultimately the death of the organism. All processes utilising cyanide will therefore be maintained at a high pH, preferably in excess of 10.

1.2 Cyanide in industry

1.2.1 Cyanidation process in the gold industry

Cyanide is used extensively in the mining industry for the extraction of gold and silver from slurries. Although other noncyanide lixiviants have been investigated, cyanidation remains the preferred method, the reason largely attributed to economics[4].

The reversible reaction by which gold is extracted from its ore can be described by the Elsner's equation:

$$\mathbf{4Au + 8NaCN + O_2 + 2H_2O \Leftrightarrow 4NaAu(CN)_2 + 4NaOH}$$

The cyanide ion can form metal complexes with copper, nickel, mercury, zinc, iron and lead. The partial consumption of cyanide within the gold extraction process stems from the unusual chemistry of cyanide when forming a complex in solution. Hence, the partial consumption creates cyanide contamination of the wastewater.

1.2.2 Gold dissolution

The gold dissolution process can be described by two equations, which forms hydrogen peroxide as an intermediate[4]:

$$\mathbf{2Au + 4NaCN + O_2 + 2H_2O \Leftrightarrow 2NaAu(CN)_2 + 2NaOH + H_2O_2}$$

$$\mathbf{2Au + 4NaCN + 2H_2O \Leftrightarrow 2NaAu(CN)_2 + 2NaOH}$$

The overall equation is the above mentioned Elsner equation.

Weak cyanide solutions can be used, since gold and cyanide form a strong and stable complex. Silver is leached similarly to gold, but the complex formed is weaker than that of the gold cyanide complex. Hence, to create the similar effect a longer contact time and / or a stronger cyanide solution is needed for the dissolution of silver. Gold can dissolve twice as fast as silver, but to create the same conditions as for gold, a 10-fold cyanide level is needed to be used for the equivalent silver dissolution. The increase in formation of metal cyanide and cyanide concentrations also increases the cost of treatment.

1.2.3 Gold recovery from solution

Cyanide is used as a depressant in the flotation[4] of base metal sulphide ores. During the flotation process, metal cyanides are formed (e.g. copper and iron). These complexes are removed by cyanide, although less cyanide is used as in the equivalent removal of gold from ore.

1.3 The environmental impact of cyanide

1.3.1 Effluent treatment of mineral processing plant

Several different effluent streams may be produced at a mineral processing plant[4]. These effluent streams may also exhibit different characteristics, thus resulting in different treatments. However, for this survey, we take a more general approach. Tailing ponds are most commonly used for run-off from mill sites, which contain cyanide in the effluent. Another method used is the dumping of cyanide in plant tailings and waste streams. The risk of this method is minimised by plant management policy to reduce the impact on the environment and to reduce cost. Unfortunately, free cyanide and cyanide complexes report to the tailings of mineral processing plants. Another factor to consider is seasonal changes which will affect the concentrations of the effluent. Table 3[5] is a good estimation of concentrations that can be expected in the effluent of mineral processing plants.

PARAMETER	RANGE OF CONCENTRATIONS (mg/l)
Arsenic	< 0.02 -10.0
Cadmium	< 0.005 - 0.02
Chromium	< 0.02 - 0.1
Copper	0.1 - 400.0
Iron	0.50 - 40.0
Lead	< 0.01 - 0.1
Manganese	0.1 - 20.0
Mercury	< 0.0001 - 0.05
Nickel	0.02 - 10.0
Selenium	< 0.02 - 6.0
Silver	< 0.005 - 2.0
Zinc	0.05 - 100.0
Total cyanide	0.5 - 1000.0
Weak acid dissociable(WAD) cyanide	0.5 - 650.0
Free cyanide	< 0.01 - 200.0
Ammonia-N	< 0.1 - 50.0
Thiocyanate	< 1.0 - 2000.0
pH	2.0 - 11.5
Hardness (as ppm $CaCO_3$)	200 - 1500
Sulphate	5 - 20000
Temperature (in degC)	0 - 35

Table 3 Chemical composition of barren decant

The cyanide concentrations listed in Table 3 can reach as much as 1000ppm, while copper, nickel, zinc and iron are the most prevalent transition metals. The transition metals that are present will tend to form metal cyanide complexes. These complexes are termed "Weak Acid Dissociable Cyanides". These complexes will form:

$$[Cu(CN)_2]^{-1}, [Cu(CN)_3]^{-2}, [Cu(CN)_4]^{-3}, [Ni(CN)_6]^{-2}, [Zn(CN)_4]^{-2}$$

The copper presented above will be in the cuprous form.

Cyanide complexes which bond more strongly are termed "Moderately strong cyanide complexes". Iron tends to form a more strongly bonded complex with cyanide. These complexes will form:

$$[Fe(CN)_6]^{-4}, [Fe(CN)_6]^{-3}$$

The iron complexes formed above have a valence of two and three respectively.

1.3.2 Degradation mechanisms

Cyanide has the ability to form numerous metal complexes. This results in a range of solubilities and unstableness of some of the complexes formed. In turn this will lead to free cyanide being released from decomposition of the complexes.

Within the environment there are mainly eight [6, 7 & 8] degradation mechanisms:

- **Degradation (chelation) : the metal cyanide compounds that are formed by means of chelation or complexation with transition metals are less toxic than free cyanide.**
- **Precipitation of cyanide complex : the iron cyanide complex forms insoluble salts with copper, nickel and silver.**
- **Adsorption : the attenuation of cyanide in soil.**
- **Oxidation to cyanate : strong oxidisers convert cyanide to cyanate.**
- **Volatilisation : the formation of HCN gas from cyanide and water.**

- **Biodegradation : aerobic condition converts the cyanide salts to nitrates.**
- **Formation of thiocyanate : the sulphur in the environment reacts with the free cyanide to form thiocyanate.**
- **Saponification / hydrolysis of HCN : the hydrolysis of HCN to form formic acid or ammonium formate as the pH drops within the system.**

1.3.2.1 Natural attenuation

Natural degradation is the most economical method for the destruction of cyanide especially if tailing impoundment already exists. Systematic decomposition of cyanide in tailing ponds occurs when left exposed to natural elements[10]. The main mechanism that occurs in ponds is volatilisation of HCN. The natural uptake of carbon dioxide from the air and low pH rainwater, effectively lowers the pH of the pond. The lowering of the pH causes a change in the CN^-/ HCN concentrations, which consequently increases the HCN concentration. This then causes volatilisation.

Variables affecting cyanide decomposition:

- **pH**
- **Temperature**
- **UV irradiation**
- **Aeration**
- **Initial cyanide concentration**
- **Metal content**
- **Surface area / depth ratio**

The most significant effect on the volatilisation rate of free cyanide is temperature and aeration. [9]

Advantages of natural degradation of cyanide.

- **Low capital cost.**
- **Minimising formation of toxic by-products during degradation process.**
- **Versatility and simplicity.**

Moderately strong cyanide complexes that are formed with iron tends to be resistant to natural attenuation. These "strong complexes" can, after being temporarily exposed to an oxidising agent, decompose, releasing dangerous free cyanide into the environment.

1.3.2.2 Alkaline chlorination

This is the most widely used cyanide destruction process. The process[11, 4] involves the destruction of free and W.A.D. forms of cyanide under alkaline conditions.

The first stage sees the administering of chlorine as a solution or as a solid form. The destruction of cyanide produces cyanogen chloride (CNCl), which is hydrolysed to cyanate (CNO) in alkaline conditions. Chloride can also be introduced in the gaseous form:

$$\mathrm{Na(CN) + Cl_2 \Rightarrow (CN)Cl + NaCl}$$

At the second stage hydrolysis of the cyanogen chloride takes place to form cyanate.

$$\mathrm{(CN)Cl + 2NaOH \Rightarrow NaCNO + NaCl + H_2O}$$

At the last stage hydrolysis of cyanate produces, ammonia and carbonate.

$$\mathrm{2NaCNO + 4H_2O \Rightarrow (NH_4)_2CO_3 + Na_2CO_3}$$

Only free cyanide and weak metal cyanide complexes can be sufficiently removed by alkaline chlorination. To effectively remove more stable metal cyanide compounds an addition of ultra violet light and / or an increase in temperature is necessary. This limits the effectiveness of the process on cyanide waste waters, which have a low iron content. [11, 4]

1.3.2.3 Copper catalysed hydrogen peroxide process

DuPont patented this process[10] in 1974, which involves contacting the waste solution with a 41% solution of hydrogen peroxide. The 41% solution contained a little amount of formaldehyde and copper. A similar process was developed, which also used a hydrogen peroxide solution, but with a few parts per million of copper sulphate. Both processes involved the hydrogen peroxide oxidising the cyanide in the W.A.D. metal cyanide complexes and free cyanide, in the presence of copper to form cyanate. The W.A.D. metal cyanides, which are oxidised, will release the metals and form a hydroxide precipitation.

Cyanide oxidation to cyanate:

$$\mathbf{CN^- + H_2O_2 \Rightarrow OCN^- + H_2O \ \ (copper)}$$

Oxidation of W.A.D. cyanide complexes:

$$\mathbf{M(CN)_4^{-2} + 4H_2O + 2OH^- \Rightarrow M(OH)_2 (\downarrow) + 4OCN^- + 4H_2O}$$

where M represents cadmium, copper, nickel or zinc.
The following reactions is that of the iron cyanides and cyanate.

$$\mathbf{2Cu^{2+} + Fe(CN)_6^{-4} \Rightarrow Cu_2Fe(CN)_6 (\downarrow)}$$

$$\mathbf{OCN^- + 2H_2O \Rightarrow CO_3^{-2} + NH_4^+}$$

The process described above are used extensively in industry and yields acceptable environmental cyanide standards in the effluent. [10]

The advantages of this process:

- **Simplicity.**
- **Low capital cost.**
- **Extensive amount of knowledge, supported by Dupont and Degussa.**

The disadvantages of this process:

- **High reagent costs, i.e. copper sulphate and hydrogen peroxide.**
- **The cyanide is destroyed, but not recovered.**
- **The precipitated metals, i.e. ammonia and thiocyanate needs further treatment to meet environmental standards.**

1.3.2.4 Sulphur dioxide / air cyanide destruction process(INCO process)

This process[12] converts W.A.D. cyanide to cyanate by means of sulphur dioxide and oxygen mixtures. This is achieved in the presence of elevated copper concentrations and in a controlled pH environment.

INCO process:

$$\mathbf{CN^- + SO_2 + O_2 + H_2O \Rightarrow CNO^- + H_2SO_4} \qquad \textbf{(excessive copper)}$$

By means of a reduction process, the iron complexed cyanides are reduced to the ferrous state and precipitated as insoluble metal ferrocyanide salt. The general formula for the ferrocyanide salts are $M_2Fe(CN)_6$, where M can be copper, nickel or zinc.

The reduction reaction:

$$2Fe^{3+} + SO_2 + 2H_2O \Rightarrow 2Fe^{2+} + 4H^+ + SO_4^{-2}$$

or

$$2Fe(CN)_6^{-3} + SO_2 + 2H_2O \Rightarrow 2Fe(CN)_6^{-4} + 4H^+ + SO_4^{-2}$$

The precipitaion reaction:

$$2M^{2+} + Fe(CN)_6^{-4} + H_2O \Rightarrow M_2Fe(CN)_6 . H_2O \ (\downarrow)$$

The thiocyanide that is formed can be removed only after the cyanide is removed. This process requires greater retention time and reagent usage. The sulphuric acid which is formed is neutralized by lime or caustic. [12]

The advantages of this process:

- **Good results obtained by treating pulps, clarified barren and decant solutions.**
- **The excellent technical support from INCO personnel.**
- **The effective removal of cyanide and heavy precipitated metals.**

The disadvantages of this process:

- **The reagent cost.**
- **The non-retrievability of cyanide.**
- **The large production of gypsum.**
- **The royalty payments to INCO for their patent of the process.**

1.3.2.5 Biological treatment of cyanide wastes

High concentrations of free cyanide can be treated by means of biological processes[13]. Currently they have also been used in the treatment of mining effluents containing metal cyanides. The biological treatment of cyanide tailings removes all cyanides, including W.A.D. and stable metal cyanides.

The removal of cyanides and metal cyanides is made possible by a combination of oxidation and sorption into the biofilm. The ammonia that is present gets converted to nitrate by means of the nitrification process. The cyanide breakdown is made possible by various species of organisms, which is identified as Pseudomonas. The general form of the equation, which is responsible for the oxidative breakdown of cyanide is:

$$M_xCN_y + H_2O + \tfrac{1}{2}O_2 \Rightarrow M\text{ - biofilm} + HCO_3 + NH_3$$

where M represents iron, copper, nickel or zinc

$$2SCN^{-} + 4H_2O + 5O_2 \Rightarrow 2SO_4^{-2} + 2HCO_3^{-} + NH_3$$

The second step converts ammonia to nitrate by means of nitrification.

$$2NH_4^{+} + 3O_2 \Rightarrow 2NO_2^{-} + 4H^{+} + 2H_2O$$

$$2NO_2^{-} + O_2 \Rightarrow 2NO_3^{-}$$

The advantages of this process:

- **Simplicity of design.**
- **Environmental friendly process.**
- **Low cost of reagent.**

The disadvantages of process:

- **High capital cost.**
- **Lack of application in industry.**
- **Cyanide recovery non-existent.**

Biological processes are adversely affected by dramatic changes in temperature.[13]

1.4 Ion exchange resins

1.4.1 Chemical and physical properties

The organic ion exchange resins[18] are one of the most significant classes of resins. The matrix of these resins consists of a macromolecular three dimensional network of hydrocarbon chains. These matrices carry anion or cation groups. The introduction of divinylbenzene, a cross linking agent, makes the resin insoluble. The resin is a single macromolecule with carbon-carbon bonds that makes the resin insoluble in any solvent.

The structure of resins will determine the chemical, thermal and mechanical stability of the ion exchange resin. The structure on the other hand will depend on the degree of crosslinking of the matrix and the nature and number of fixed ionic groups. The mesh width of the matrix, which is dependant on the degree of crosslinking, will determine the swelling ability of the resin and the mobility of counter ions in the resin. The rate of ion exchange is dependant on the latter.

Highly crosslinked resins have mesh widths of only a few Angstrom, while with very weak crosslinked resins, mesh widths can exceed 100 Angstrom. Resins which are highly crosslinked are more resistant to mechanical breakdown and attrition.

Chemical and thermal degradation of the matrix by means of oxidation and loss of ionic groups can cause the resin to deteriorate. Commercial resin are very stable in solvents, except when strong oxidising and reducing agents are present. These resins are also normally stable at temperatures up to 100°C, except strong base anion resins that deteriorate at temperatures above 60°C.

Ion exchange equilibrium is determined by the chemical nature of the fixed ionic groups. These groups can either be an acid or base with varying strength. Ionisation of weak acid groups (i.e. $-COO^-$) occur at high pH whereas will combine with H^+ ions to form an undissociated -COOH at low pH. Strong acid groups such as $-SO_3$

will remain ionised at low temperatures, while weak base groups (i.e. $-NH_3$) will lose a proton to form $-NH_2$. Strong base groups (i.e. $-N^+(CH_3)_3$) remain ionised at high pH.

The fixed ionic groups determine which ions the resin will associate with, since the fixed groups will tend to prefer ion pairs or complexes with which it willl associate. Resins with fixed sulphonic acid groups will tend to associate with Ag^+ ions. Carboxylic acid groups have a larger affinity for alkaline earth cations while chelating groups attract heavy metal ions.[18]

1.4.2 Preparation

Ion exchange resins are normally copolymers prepared[18] from vinyl polymers, the technique used being polymerisation. The monomers are mixed and a benzoyl peroxide is added as a polymerisation catalyst. The mixture is then agitated in a aqueous solution at temperatures between 85°C and 100°C to assist with polymerisation.

During mixing small droplets will form and remain in suspension. Stabilisers in the aqueous solution prevents agglomeration of the droplets. The suspension stabiliser, viscosity of solution and agitation determines the size of the droplets. The end product is in the form of uniform spherical beads.

The structure of the resin is heterogeneous in nature, as long as solvents are used which expand the resin. These resins are normally called macroporous or macroreticular resin. The structure of the latter resin entails fixed large pores, presenting a sponge like matrix, which imparts optimum resistance to mechanical and osmotic shock.

1.5 Mechanism of ion exchange

The chemical reaction[18] between an electrolyte in solution and an insoluble electrolyte with which the solution is contacted are mainly responsible for ion exchange. Ion exchange is purely a diffusion phenomenon, which can be categorised by the following processes:

- **Diffusion of ions from bulk of liquid to external surface of exchanger particle.**
- **Diffusion of ions inward through the solid to the site of exchange.**
- **Exchange of the ions.**
- **Outward diffusion of released ions to the surface of the solid.**
- **Diffusion of released ions from the surface of the solid to the bulk of the liquid.**

The exchanging ions are cationic or anionic in nature and the exchange of ions can be determined by other processes namely chelation or complex formation.

1.5.1 Anion exchange

Strong base anion resins are used to remove anions such as $Cu(CN)_4^{-2}$ and $Zn(CN)_4^{-2}$. The functional groups of the strong base resins are normally an ammonium group possessing a permanent positive charge. The anion exchange reaction can be represented by the following equation for zinc cyanide, where the symbol |- denotes the inert backbone and X^- denotes a monovalent anion such as OH^-:

$$|\text{-}N^+R_3X^- + Zn(CN)_4^{2-} \Rightarrow |\text{-}N^+R_3Zn(CN)_4^{-2} + 2\,X^-$$

The regeneration process can be performed by shifting the equilibrium to the left. This is accomplished by increasing the concentration of X^-. The regenration process of weak base resins can be done by adjusting the pH, while regeneration of strong base resins are dependant on the affinity of the metal cyanides for the strong base resins. [18]

This phenomenon explains why the equilibrium loading of heavy metals, such as copper, nickel and zinc in two of South African mines are more readily adsorbed than gold and silver[19].

The metal cyanide anion can displace the counter ion associated with a positively charged group and therefore become attached to the strong base resin by the formation of an ion pair. The main advantage of strong base resins is that the reaction is not dependant on pH when adsorption is considered.

1.5.2 Cation exchange

Positively charged[18] ions penetrate the structure of the resin and interchange with another positively charged ion connected to the fixed ionic group. Cation resins can be categorised in two groups:

- **Strong acid exchange resin.**
- **Weak acid exchange resin.**

The functional groups of strong acid exchange resins are usually from sulphuric acid. The low pK_a of a strong acid is analogous to the degree of ionisation, which permits the hydrogen to be dissociated and able for exchange over a wide pH range. The cation exchange resin reaction can be represented by the following reaction:

$$\text{R-SO}_3^-\text{H}^+ + \text{Cu}^{2+} \Leftrightarrow \text{R-SO}_3^-\,\text{Cu}^{2+} + 2\,\text{H}^+$$

The functional groups of weak acid exchange resins originate from weak acids, commonly carboxylic or phenolic groups. These resins are only useful in a very narrow pH range.

1.5.3 Ion exchange with chelation

Chelateion exchangers have a high selectivity, which makes it ideal for the recovery of valuable metals. The affinity of a particular metal ion to a certain chelating ion exchanger depends on the chelating group. This selectivity makes it a very important agent in the treatment of waste water. These ion exchangers are normally co-ordinating co-polymers with covalent side bonds which forms co-ordinated bonds with most toxic metals. The co-ordination type interaction causes the chelating type of exchangers to be very selective towards commonly used metals such as Zn^{2+}, Cu^{2+}

and Ni^{2+} over competing alkaline (Na^{+}, K^{+}) and alkaline earth (Ca^{2+}, Mg^{2+}) metal cations[20].

The chelating ion exchangers subsist of chelating agents, namely iminodiacetic. The chelating agents are introduced into the matrix of a styrene-divinylbenzene polymer. The chelating ion exchangers have two properties which distinguishes it from normal ion exchange resins:

- **The high selectivity.**
- **Bond strength.**

The high selectivity depends mainly on the chelating group and not the size of the ion, charge or physical properties. These properties mentioned above normally determine the preferences of ordinary resins.

The bond strength in ordinary ion exchange resins are in the range of 2 - 3 Kcal/mole, while it ranges between 15 - 25 Kcal/mole for chelating resins. This is evidence that the electrostatic strength[21] is much higher in chelating resins than in ordinary resins.

1.6 Chemical processes for the recovery of cyanide

1.6.1 Acidification, volatilisation and re-adsorption

When cyanide waters are acidified, HCN is formed, which then volatilises as a gas assisted by heating or air sparging. The gas is then re-absorbed in an alkaline medium i.e. caustic or milk of lime spray. [5]

The acidification reaction:

$$\mathbf{Ca(CN)_2 + H_2SO_4 \Rightarrow 2HCN + CaSO_4}$$

and for metal cyanides:

$$M(CN)_2 + H_2SO_4 \Rightarrow 2HCN + M^{2+}\,SO_4^{-2}$$

The volatilisation of free cyanide:

$$HCN / H_2O \Rightarrow HCN / Air$$

There are many factors influencing the rate and extent of HCN removal from solution through air stripping:

- **The pH of the solution.**
- **Type of cyanide.**
- **Concentration of cyanide.**
- **Temperature of solution.**
- **Pressure maintained with in recovery system.**
- **Air to liquid ratio.**
- **Mechanical dispersion equipment.**
- **Viscosity of solution.**

The absorption reaction:

$$HCN + NaOH / \tfrac{1}{2}\,Ca(OH)_2 \Rightarrow NaCN / \tfrac{1}{2}\,Ca(CN)_2 + H_2O$$

Precipitation and re - neutralisation as hydroxide:

$$M^{2+} + 2OH \Rightarrow M(OH)_2$$

Precipitation of iron complexes:

$$Na_4Fe(CN)_6 + 2CuSO_4 \Rightarrow Cu_2Fe(CN)_6 + 2Na_2SO_4$$

The advantages of this process:

- **Efficiency in recovering of W.A.D. cyanide complexes and free cyanide for re-use.**
- **Low cost of reagent consumption.**
- **Diversity of input variable fluctuations and able to process slurries and decant waters.**

The disadvantages of process:

- **Possible hazards associated with hydrocyanic gas.**
- **High capital outlay.**
- **Inability to remove metal cyanides.**

1.6.2 Recovery of cyanides using ion exchange resins

Ion exchange resins are widely used for the recovery of cyanide and cyanide complexes from clarified / unclarified solutions, mainly in the plating and galvanising industry. Some of these processes are described in the following sections.

The advantages of using ion exchange resins is the ability of the resins to remove small concentrations of cyanide quickly and also to recover cyanide, without toxic intermediaries e.g. cyanate and thiocyanate.

1.6.2.1 Carlson process (pat. 1982)

The Carlson process[14] is primarily used to remove toxic metals and cyanide from waste water, especially the effluent of plating baths. The contaminated liquid is passed upwardly through three separate layers of resin. The amount of the individual layers of resin used will be dictated by the nature and quantitative character of the toxic materials to be removed.

The three resins that are contacted with the feed solution are:

- **Strong base anion exchange resin.**
- **Weak acid cation exchange resin.**
- **Strong acid cation exchange resin.**

The first (strong base resin (Type 1)), with quaternary ammonium functional groups:

$$\mathbf{R - N^+ - (CH)_3}$$

or

$$\mathbf{R - N^+ - (CH_2 - CH_3)_3}$$

The second (weak acid resin (carboxylic type)):

$$\mathbf{R - COO^-}$$

The third (strong acid resin) is the standard sulfonic type.

$$\mathbf{R - SO_3^-}$$

The regeneration of the acid takes place in two phases. The first phase uses a strong acid solution (i.e. hydrochloric acid) to convert the cation resins into the hydrogen form and the strong base resin into the chloride form. The second phase uses a caustic solution, which is passed through a portion of the bed. This converts the strong base resin to the hydroxyl form and the weak acid resin to the sodium form. This procedure does not affect the strong acid resin. [14]

1.6.2.2 Witteck development

This invention recovers free cyanide[15] and complex heavy metal cyanides from gold mill effluent. A weak or strong anion exchange resin with a macroporous structure in the sulphate form can be used. The effluent passes through the bed of resin, causing metal cyanide complexes i.e. zinc, copper and iron to be readily absorbed, while the free cyanide passes through the bed. The product will contain some metal complexes and free cyanide in solution, but can be re-used in the further leaching of ores. The process can be optimised by alternating the resin beds between the loading and regeneration stages, with the limits of resin loading being determined by monitoring for breakthrough.

Passing sulphuric acid upwards through the bed of resin, displaces the metal cyanide complexes and returns the resin to the sulphate form. The regenerated effluent is then fed into a liquid-gas contacter, where air assists in the volatilisation of the hydrocyanic gas. The hydrocyanic gas is then passed through a scrubber, which absorbs the HCN into solution.

Spiking the regenerant solution with an oxidant such as hydrogen peroxide, potassium peroxide, sodium peroxide or ozone causes the controlled oxidation of the metal ion of the metal cyanide complex, which is absorbed under controlled oxidation conditions. The process can be optimised by introducing an oxidant at a rate sufficient to maintain a redox potential of +500mV in the regenerant solution. [15]

1.6.2.3 The GM - IX process

This process[16] uses an ion exchange resin in conjunction with a gas membrane to selectively recover cyanide from spent regenerant solution. This process is used for the recovery of cyanide from a solution, where the cyanide has formed a complex with zinc. In industry, the recovery process is used in the recovery of cyanide from effluent from steel and iron manufacturing, photographic bleaching and metal plating and finishing industries.

The waste-water solution contains anionic zinc cyanide and free cyanide, which will be readily adsorbed onto a strong base resin that will be in the sulphate form. This will produce an effluent free of zinc cyanide complexes and free cyanide. Regeneration takes place by means of circulating a dilute solution of sulphuric acid through the bed of resin over a long period of time, due to the slow kinetics of desorption.

Hydrocyanic acid is formed during desorption, the removal of the acid is accomplished by passing it over a gas permeable membrane, which has a solution of caustic soda circulating on the opposite side. The hydrocyanic gas passes through the membrane and will be absorbed by the caustic soda, which will completely remove the acid. The free cyanide that is adsorbed in the caustic circuit can be re-used as a sodium cyanide solution.

1.6.2.4 The Coltinari process

The Coltinari process[17] removes cyanide metal complexes by means of a weak base anion resin. The free cyanide is allowed to pass through the bed and can be re-used in the process or sold as a by-product.

Metal salts can be used to form metal complexes in the feed solution to the resin. When adsorption onto the resin is complete, the cyanide complexes are eluted by means of a milk- of lime solution. The elution process can be optimised by recycling the eluting fluid through a bed of solid calcium hydroxide so as to maintain the eluting fluid in calcium hydroxide saturation.

This process causes a high concentration of cyanide to form in the eluate. The eluate is then subjected to acidification / volatilisation process. The acidification is done with sulphuric acid. The product of acidification / volatilisation, hydrocyanic gas, will be effectively removed by means of heating and air-sparging.

1.7 Ion exchange in dilute heavy metal solutions

The first process to use ion exchange for the recovery of metals, was the recovery of copper from waste liquors in the cuprammonium rayon and brass industry, silver from photographic film manufacturing wastes and chromium from electroplating wastes. The first large scale plant recovered the metal uranium from leached solutions.

A large amount of research was conducted in this field opening the door to other possibilities in the recovery of metals from leach liquors. The exchange process is especially useful in the treatment of solutions containing heavy metals[22] in the range of 10 ppm or less.

There are a few parameters, which will have an effect on the adsorption of heavy metals on ion exchange resins:

- **The effect of pH.**
- **Temperature.**
- **Agitation.**
- **The presence of competing ions.**

Diaz and Mijangos [23], applied the ion exchange process to industrial wastewater, which included metals, such as copper, nickel and zinc. Chelating resins were used due to its selective properties. Good loading was achieved on the resin, but the exchange process was dependent on pH. It was also shown that the copper retention was most efficient at low pH values.

Shallcross[24] proved the selective behaviour of strong acid cation exchange resins by showing the resins infinity for divalent alkali-earth metal ions over monovalent alkali ions.

1.8 Significance of the literature review

- **Many processes have been developed and tested for cyanide recovery.**
- **Many of these processes lack economic viability or are not affective.**
- **The effect of competing complexes in the ion exchange pores are not well documented.**
- **Iron and copper cyanide are present in relatively large quantities in mining effluent, hence the selection of these species for this study.**

CHAPTER 2

MASS TRANSFER KINETICS AND EQUILIBRIUM LOADING

2.1 Kinetic parameters

The diffusional properties, which takes place in the adsorption process can be divided into two mechanisms:

- **Interdiffusion of counter ions in the adherent films.**
- **Interdiffusion of counter ions within the resin itself (intraparticle diffusion).**

The rate of ion exchange will be controlled by the slower of the two processes[18].

2.1.1 External film diffusion

The film diffusion mass transfer model assumes that the overall exchange phenomenon is controlled by the liquid -phase mass transfer resistance to ionic interdiffusion in the stationary liquid film around the exchanger particle[25].

Film diffusion is favoured by factors which will increase the rate of interdiffusion in the beads and reduce the rate in the films. Film diffusion of this type will be characterized in systems with high concentrations of ion exchangers, low degree of crosslinking and small particle size and dilute solutions with inefficient agitation[18]. The flux equation for mass transfer in the liquid boundary layer can normally be described by a linear driving force[26],

$$n_1 = k_f (C - C_s)$$

where k_f is the external film mass transfer coefficient.

2.1.2 Intraparticle diffusion

There are many chemical reactions taking place during a ion exchange process.

Yoshida[27], proved that chelating ion exchange reactions may be rate controlling for very small particle sizes, a radius less than 10^{-4} m.

Normally particle diffusion control can be seen in larger particle sizes. The chelation reaction does influence the uptake rates, since it bonds with the ions whose diffusion depends on ion exchange[18]. The reaction of ions in solution are normally fast, except the complexing of some trivalent transition-metal ions. When looking at this phenomenon it can be calculated that reaction-retarded diffusion control will be more likely than reaction control.

2.2 Material balance equations

This model represents the accumulation of adsorbate in the macropores of the resin and was applied to the anion exchange resin.

2.2.1 Batch stirred tank reactor

The structure and properties of the resin beads determines the rate at which ion exchange takes place. It may be assumed that film diffusion is rate controlling in the initial stages of a batch adsorption experiment. Diffusion through the liquid film can be described by Fick's first law:

$$n = -D\frac{dC}{dr}$$

Assuming spherical geometry and integrating Fick's first law equation over the thickness of the film leads to:

$$n = k_f\left(C - C_s\right)$$

where,

$$k_f = \frac{D}{\alpha}$$

When describing the flux of adsorbate through the differential element of the spherical adsorbent particle, Fick's equation becomes:

$$n = D\rho_R \frac{d\underset{\sim}{Q}}{dr}$$

When performing a mass balance over a different element for spherical beads with a radical thickness Δr yields:

Accumulation in macropores = mass flow into macropores at (r + Δr) - mass flow in
macropores at r

$$4\pi r^2 \rho_R \frac{d\underset{\sim}{Q}}{dt} = D\rho_R \frac{d}{dr}\left[r^2 \frac{d\underset{\sim}{Q}}{dr}\right]4\pi$$

The mass balance equation can be simplified into the following partial differential equation:

$$\frac{d\underset{\sim}{Q}}{dt} = D\frac{d^2Q}{dr^2} + \frac{2D}{r}\frac{d\underset{\sim}{Q}}{dr}$$

This differential equation represents the material balance for the macropores.

The following equation is the mass balance over the batch reactor:

$$-V\frac{dC}{dt} = nA$$

The surface area of the resin beads can be described by the following :

$$A = \frac{6M}{\rho_R dp}$$

The combination of Fick's first law and the two above mentioned equations leads to the liquid-phase material balance equation:

$$\frac{dC}{dt} = \frac{6k_f M}{\rho_R dpV}(C_s - C)$$

When assuming accumulation of metals at the external surface of the adsorbent, the following equation can be written:

$$\frac{dQ}{dr} = \frac{k_f}{\alpha D}(C - C_s)$$

2.2.2 Numerical solution

2.2.2.1 Batch stirred tank reactor

The parabolic partial differential equation can be solved by substituting finite divided differences for the partial derivatives[6].

2.3 Estimation of kinetic parameters

2.3.1 External mass transfer coefficient

In this chapter relevant assumptions have to be made for external film transfer in a batch reactor[28]:

- **The resin particles are equivalent spheres.**
- **The transport of metal ions and complexes into the pores of the resin can be described by a surface diffusion mechanism.**
- **Intraparticle diffusion is negligible during the initial stages of ion exchange.**
- **Accumulation of metal ions and complexes in the liquid phase within the pores of the resin is negligible.**
- **The ion exchange reaction occurs instantaneously so that the equilibrium exists at the solid-liquid interface.**
- **Isothermal conditions occur during ion exchange.**

The external transfer coefficient has to be estimated to provide an input into the model. The initial stages of adsorption are dominated by film transfer and a linear concentration gradient from the bulk liquid to the resin particle. The assumption that the adsorbate concentration at the particle surface C_s is negligible in the early stages compared to the bulk liquid concentration C is made.

This means that the liquid phase material balance equation,

$$\frac{dC}{dt} = \frac{6k_f M}{\rho_R dpV}(C_s - C)$$

will simplify to:

$$\frac{dC}{dt} = \frac{6k_f M}{\rho_R dpV} C$$

Integrating the above mentioned equation results in:

$$ln\left[\frac{C_0}{C}\right] = \frac{6k_f M}{\rho_R dpV} t \qquad t \to 0$$

The determination of the slope can be calculated by plotting ln Co / C vs time of the adsorption results over a short period of time:

$$SLOPE = \frac{k_f 6M}{\rho dpV}$$

Thus, the rate of adsorption (k_f) can be calculated by the above mentioned equation:

$$\frac{slope\rho\, dpV}{6M} = k_f = rate(m/s)$$

2.4 Ion exchange isotherms

The concentration ratios of the competing counter- ion species in the ion - exchanger and in the solution during equilibrium are different. The ion exchanger normally prefers one species over the other. This phenomenon results in the species being distributed differently between the aqueous solution and the ion exchange resin[18].

2.4.1 Single solute isotherms

By using equilibrium isotherms the distribution of the heavy metals between the ion exchanger and aqueous solution can be quantitatively explained.

The Freundlich:

$$Q_e = AC_e^n$$

The Langmuir:

$$Q_e = \frac{AC_e}{1 + BC_e}$$

When solving the Freundlich isotherm we plot $\ln Q_e$ vs $\ln C_e$, by using this method we linearise the Freundlich equation to the following form:

ln q = ln A + n ln C , where

ln A = y-intercept and

n = slope of Q_e vs C_e

When solving the Langmuir equation we plot $1/Q_e$ vs $1/C_e$, by using this method we linearise the Langmuir equation to the following form:

$$\frac{1}{Q_e} = \frac{1}{AC_e} + \frac{B}{A}$$

where,

$1/A$ = slope of $1/Q_e$ vs $1/C_e$ and

B/A = y-intercept

2.4.2 Multi - solute isotherms

If the Freundlich isotherm describes the loading of each individual species the following may be used for a two component system[9]:

$$Q_{e.1} = A_1 C_{e.1} \left[C_{e.1} + B_{1-2} C_{e.2}\right]^{n1-1}$$

for component one, while the isotherm for component two is:

$$Q_{e.2} = A_2\ C_{e.2} \left[C_{e.2} + B_{2-1} C_{e.1}\right]^{n2-1}$$

The following multi-component Langmuir equation can also be used for two component systems:

$$Q_e = \frac{AC_e}{1 + B_{1-2}C_e}$$

The above mentioned multi - component Freundlich equations can be written in the following linear form:

$$f(C_{e,1}) = \left[\frac{A_1 C_{e,1}}{Q_{e,1}}\right]^{\frac{1}{1-n1}} - C_{e,1} = B_{1-2}C_{e,2}$$

for component 1, while the isotherm for component 2 is:

$$f(C_{e,2}) = \left[\frac{A_2 C_{e,2}}{Q_{e,2}}\right]^{\frac{1}{1-n2}} - C_{e,2} = B_{2-1}C_{e,1}$$

When $f(C_{e.1})$ or $f(C_{e.2})$ is plotted against $C_{e.1}$ or $C_{e.2}$ respectively, the competition coefficients B_{12} or B_{21} can be obtained by the slopes of the regression lines. These equations can only be solved if the species one and two both follow the Freundlich isotherm in a single solute solution.

The Langmuir equation can also be used for multi - component sytems:

$$Q_{e,1} = \frac{A_1 C_{e,1}}{1 + B_{1-2}C_{e,2}}$$

and

$$Q_{e,2} = \frac{A_2 C_{e.2}}{1 + B_{2-1} C_{e,1}}$$

These multi - component equations can be written in the following linear form:

$$\frac{1}{Q_{e.1}} = \frac{1}{A_1 C_{e.1}} + \frac{B_{1-2} C_{e,2}}{A_1 C_{e.1}}$$

for component 1, while the linear form for component 2 is:

$$\frac{1}{Q_{e.2}} = \frac{1}{A_2 C_{e,2}} + \frac{B_{2-1} C_{e.1}}{A_2 C_{e.2}}$$

These equations can be solved by plotting $1/Q_{e.1}$ and $1/Q_{e,2}$ against $C_{e2}/A_1C_{e.1}$ and $C_{e.1}/A_2C_{e.2}$ respectively, the competition coefficients B_{12} and B_{21} can be obtained by the slopes of the regression lines. These equations can only be solved if the species one and two both follow the Langmuir isotherm in a single solute solution.

CHAPTER 3

EXPERIMENTAL

This chapter describes the experimental and analytical techniques that were used to conduct the work contained in this thesis.

3.1 Experimental components

The experiments were performed with four different types of strong base anion exchange resins. The adsorbates used were potassium cyanide, copper(I)cyanide and potassium hexacyanoferrate(III). The CuCN is an insoluble precipitate, which had to be dissolved in excess potassium cyanide. The Amberlite product sheet reports the following properties for the four different anion exchange resins:

3.1.1 Amberlite IRA402Cl

The Amberlite IRA402Cl is a strongly basic anion exchange resin, with a clear gel structure. The main use of this resin is the treatment of electroplating waste and the isolation of anionic metal complexes.

Matrix	Styrene divinylbenzene copolymer
Functional groups	$-N^+(CH_3)_3$
Ionic form	Cloride
Capacity	>1.30 eq/L
Specific gravity	1.063 to 1.093

3.1.2 Amberlite IRA458Cl

The Amberlite IRA458Cl is an acrylic gel type strongly basic anion exchange resin. The main use of this resin is the adsorption of organic molecules present in many water supplies.

Matrix	Crosslinked acrylic gel structure
Functional groups	$-N^+R_3$
Ionic form	Cloride
Capacity	>1.25 eq/L
Specific gravity	1.06 to 1.1

3.1.3 Amberlite IRA900Cl

The Amberlite IRA900Cl is an macroreticular polystyrene type strong base anion exchange resin containing ammonium groups. The main use of this resin is the removal of large size soluble organic molecules.

Matrix	Styrene divinylbenzene copolymer
Functional groups	$-N^+(CH_3)_3$
Ionic form	Cloride
Capacity	>1.0 eq/L
Specific gravity	1.050 to 1.080

3.1.4 Amberlite IRA958Cl

The Amberlite IRA958Cl is a macroreticular strongly basic anion exchange resin exhibiting quaternary ammonium functionality in a crosslinked acrylic polymer matrix. The main use of this resin is the removal of large organic molecules and the removal of colour bodies from cane sugar syrups.

It can also be used in the purification of various chemical and pharmaceutical products.

Matrix	Crosslinked acrylic macroeticular structure
Functional groups	Quaternary ammonium
Ionic form	Cloride
Capacity	>1.8 eq/L
Specific gravity	1.05 to 1.08

3.2 Preparation and pre-treatment

Each resin was washed with three bed volumes of distilled water. After washing the resins, six bed volumes of sodium hydroxide were used to replace the chloride ionic form with a hydroxide. The resins were then washed again with three bed volumes of distilled water.

The ion exchange experiments commenced by the addition of 1 ml of resin in the hydroxide form to the reactor, as well as 5 ml of a 3 M sodium hydroxide solution to keep the pH at 12. Eight grab samples were taken at increasing time intervals to determine the solute decay.

3.3 Experimental apparatus

All experiments were performed in a perspex reactor of diameter 10 cm and height 15 cm. These reactors also contain three evenly spaced baffles. The solutions were agitated by a perforated flat blade impeller of width 6 cm and height 5 cm. The solution volume was one litre and a constant stirring speed of 200 rpm was maintained.

3.4 Analytical methods

The metal concentrations were determined by the use of a Varian Techtron AA-1275 atomic absorption spectrophotometer, with an air - acetylene flame. The results indicates the wt % (mass basis) of metal loaded onto the resin. The free cyanide concentrations were measured by means of a cyanide ion selective electrode which consisted of a built in reference electrode (combination electrode). The electrode is used to measure the cyanide ions present in the aqueous solution. The Blanc Correction and Calibration Method was used to measure the low levels of cyanide present in the solution.

3.5 Ion exchange test-work

The ion exchange adsorption experiments involved the removal of potassium cyanide, iron and copper cyanide complexes in batch experiments with the above mentioned resins. The amount of resin used was determined by means of the "tap method" and was approximately 1ml, except for the experiments done with potassium cyanide, in which case it was 5ml. The amount of resin used was sufficient to adsorb two thirds of the metal cyanides present. To ensure that the reaction kinetics of the different resins were comparable, attention was given to the geometric configuration and agitation power input per unit volume to ensure they were identical and thus comparable.

3.5.1 Metal cyanide complex adsorption tests

To conduct these tests a 1000 ppm stock solution was made up for copper and iron respectively from potassium hexacyanoferrate(III) and copper(I)cyanide. Each resin was contacted with iron and copper separately. One resin, IRA900Cl, was then chosen to be contacted by copper and iron simultaneously.

3.5.2 Free cyanide ion exchange tests

These tests were performed with a stock solution of 1000 ppm CN^-, which was made up from potassium cyanide. Each resin was contacted with different concentrations of free cyanide.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Parameter estimation

A program was specifically designed to calculate the mass transfer coefficient, single component and multi-component isotherms. This was done by using a linear regression model. Linear regression fits a line to a series of points that indicate past values of one independent value (time) and one dependent value (concentration). The slope of the trend line is found by the equation mentioned below. The Y (concentration) and X (time) are the values of the dependent variable and the independent variable respectively. The regression equations used in the computer program is as follows.

$$b = \frac{n\sum XY - \sum X \sum Y}{n\sum X^2 - \left(\sum X\right)^2}$$

The point where the trend line crosses the vertical axis can be found by the following equation:

$$a = \overline{Y} - b\overline{X}$$

The program also calculates the coefficient of determination. This tells us how closely a group of points coincides with a straight line. This number quantifies for the sample data the percentage of variation in the dependent variable that is explained by the regression line. The coefficient of determination (r^2) can be calculated from equation:

$$r^2 = \frac{a\sum Y + b\sum XY - n\overline{Y}^2}{\sum Y^2 - n\overline{Y}^2}$$

4.2 Mass transfer kinetics

The program was originally developed to evaluate k_f and single component isotherms, but was extended to incorporate multi-component equilibria. The reason is explained in section 4.3.2.

It has been found that the kinetics of ion exchange is relatively fast and that equilibrium conditions were attained in a relatively short period of time (Figure 1- 5).

As stated in Chapter 3, all experiments were conducted under constant operating conditions and values obtained for the external mass transfer coefficient could be compared directly.

The calculated k_f values are summarised in Table 5. From Table 5 it becomes apparent that the kinetics of ion exchange favours copper cyanide when IRA900Cl and IRA458Cl is used as adsorbates and is higher for iron cyanide in the other two cases. From the multi-component experiments conducted with IRA900Cl the superior kinetics of copper cyanide is highlighted. Furthermore, IRA900Cl and IRA402Cl shows superior kinetics of ion exchange to the other resins used.

4.3 Equilibrium parameters

4.3.1 Single component isotherms

It has been found that both the Freundlich and Langmuir isotherms explained all single solute ion exchange adequately. This is graphically illustrated in Figures 6 - 11. For ease of explanation, the Freundlich isotherm was selected to describe equilibrium conditions.

The equilibium constants, which were calculated by the computer program are tabulated in Table 4. The constant A, which is a measure of the magnitude of equilibrium loading at lower equilibrium concentrations, has superior values for copper and iron cyanide as compared to that obtained for free cyanide in single solute systems. This is ascribed to the multi - valent nature of the complexes. This clearly indicates that copper and iron cyanide can be recovered more easily at low solution concentrations. The A values obtained in complex removal for IRA900Cl and IRA402Cl was in general higher than that obtained for the other two resins tested. This is attributed to the tri - methyl ammonium functional group, which are more attracted to the multi - valent cyanide complexes. Furthermore, the magnitude of A in cases of copper cyanide recovery exceeds that obtained for iron cyanide except where IRA958Cl was used as adsorbent.

The larger values of n obtained in cases where free cyanide was the adsorbate shows the dependency of this process on the solution concentration. The relatively small values in cases where the metal cyanide complexes were recovered, again shows the relatively small dependency on the level of solution concentration and that these species can be recovered to relatively low concentrations.

The above parameter phenomenon is possibly best explained by example:
If the IRA402Cl resin is contacted with free cyanide, iron cyanide and copper cyanide and the equilibrium solution concentrations are 100 ppm in all cases, equilibrium loading will be as follows:

$q_{e.CN}$: 186 mg/l
$q_{e.Fe}$: 34 mg/l
$q_{e.Cu}$: 46 mg/l

Should the equilibrium solution concentration be reduced to 5 ppm the loadings will be as follows:

$q_{e.CN}$: 1.2 mg/l
$q_{e.Fe}$: 14.8 mg/l
$q_{e.Cu}$: 16.7 mg/l

Due to the toxic nature of cyanide, even in small concentrations, an effective removal process will depend on a low level of cyanide in the effluent stream. Ion exchange resin thus seems to be effective in complex removal, but not where free cyanide is present.

Due to the fact that the IRA900Cl resin performed strongly from a kinetic point of view and proved to posses good equilibrium loading capacities, it was selected for the tests to be performed in a multi-component system.

4.3.2 Multi-component isotherms

It was found that the multi-component Freundlich isotherm best explained two-component complex equilibrium loading as compared to the Langmuir type isotherm. Although the multi-component Freundlich isotherm provided a good 'fit' to the experimental data, a unique solution was not found. The values obtained for the parameters A, B and n were found to vary substantially depending on the mathematical method used. The graphical procedure as explained in Chapter 3 did not provide an accurate prediction. The 'solver' approach in an Excel spreadsheet was then followed which provided an accurate prediction. These results were reported in a puplished paper (See Appendix D). However, this technique resulted in large values of A and small values for n1-1 and n2-1. Therefore, it was decided to expand the 'Pascal' program to incorporate multi-component equilibria. The result obtained was found to be more realistic. These are listed in Table 4. Furthermore, B_{21} should theoretically be the inverse of B_{12}, which is clearly not the case. This is a further indication that the isotherm developed, purely serves as a empirical correlation.

It is interesting to note that the two component Freundlich isotherm explained the equilibrium loading of copper and iron cyanide well in the three component experiments. This indicates that free cyanide had little effect on metal cyanide recovery and that competition for active sites exists mainly between the complexes. Metal cyanide complexes will thus be recovered preferentially to free cyanide. This may be seen as a positive phenomenon in that cyanide complexes are generally more stable than free cyanide, resulting in these species being more harmful to the environment.

As is the case with single solute experiments, relatively large A values were obtained, indicating that copper and iron cyanide can be removed at low concentrations in multi-component systems.

		Single component systems				**Multi - component systems**				
Resin	**Species**	**Freundlich isotherm constants**		**Langmuir isotherm constants**		**Freundlich isotherm constants**			**Langmuir isotherm constants**	
		A	**n**	**A**	**B**	**A**	**B**	**n**	**A**	**B**
IRA402Cl	free cyanide	0.085	1.67	0.149	-0.026					
	Fe cyanide	9.40	0.28	5.216	-0.028					
	Cu cyanide	9.69	0.34	8.60	0.247					
IRA458Cl	free cyanide	0.99	0.72	0.882	0.059					
	Fe cyanide	6.46	0.24	0.416	0.387					
	Cu cyanide	8.47	0.27	7.220	0.288					
IRA900Cl	free cyanide	0.387	1.09	0.495	0.001					
	Fe cyanide	6.143	0.23	5.442	0.387	6.95	0.06	0.05	17.15	-0.3
	Cu cyanide	10.39	0.32	9.145	0.255	8.31	0.01	0.2	11.76	0.5
IRA958Cl	free cyanide	1.283	0.61	1.079	0.079					
	Fe cyanide	7.334	0.22	12.82	0.92					
	Cu cyanide	5.847	0.32	5.102	0.268					

Table 4 **Multi and single component constants**

RESIN	SPECIES	[INITIAL]($mg.l^{-1}$) Single adsorbate solution	[INITIAL]($mg.l^{-1}$) Multi-component solution	k_f ($m.s^{-1}$) [x 10^5]
IRA900Cl	Fe cyanide	18.82		3.45
	Cu cyanide	25.07		3.68
	Fe cyanide		17.65	2.72
	Cu cyanide		19.55	3.72
IRA958Cl	Fe cyanide	18.34		3.54
	Cu cyanide	21.05		2.15
IRA402Cl	Fe cyanide	19.5		3.70
	Cu cyanide	20.06		3.40
IRA458Cl	Fe cyanide	19.25		2.60
	Cu cyanide	19.52		3.30

Table 5 Mass transfer coefficient

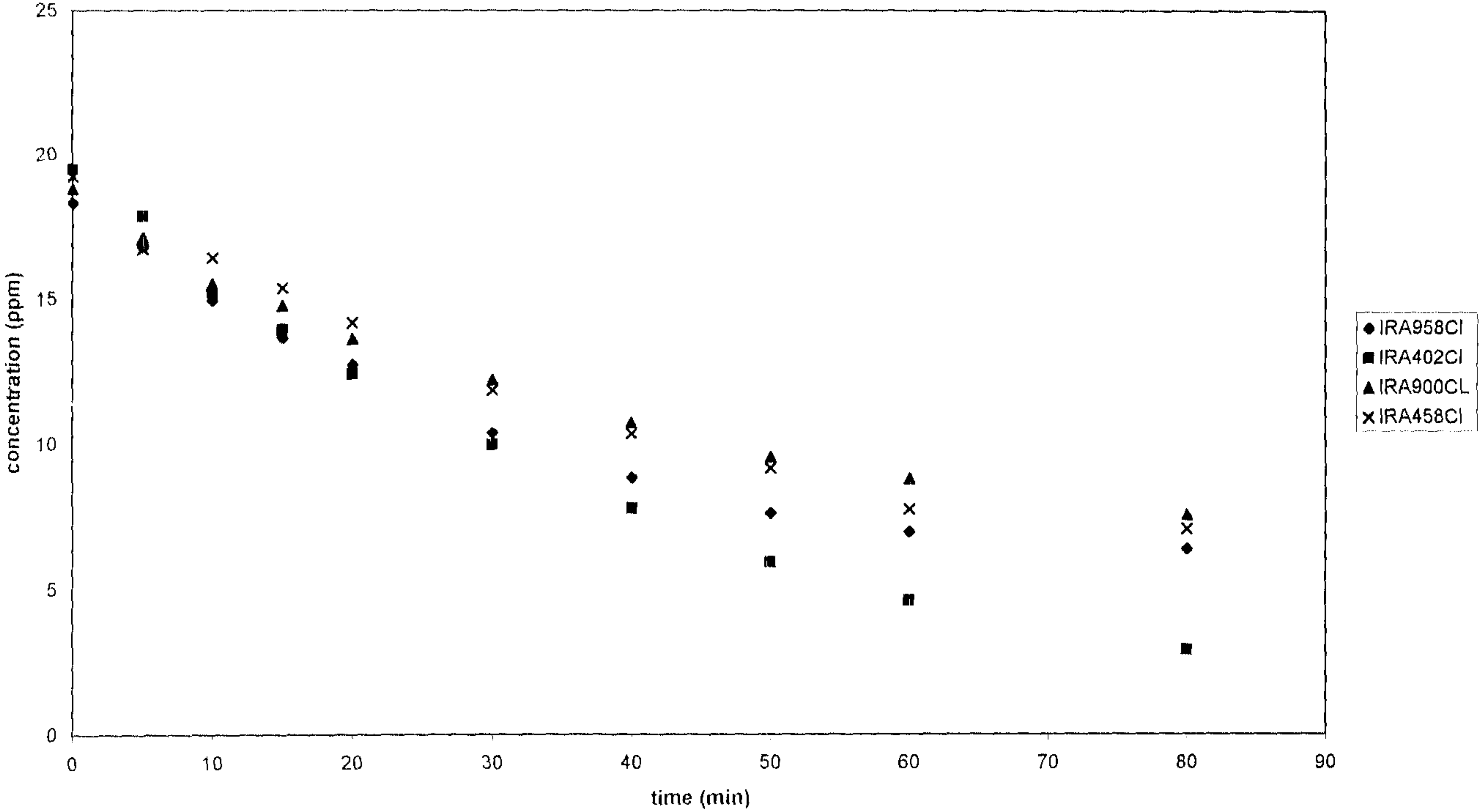


Figure 1 Adsorption of potassium hexacyanoferrate(III) onto four different strong base anion exchange resins

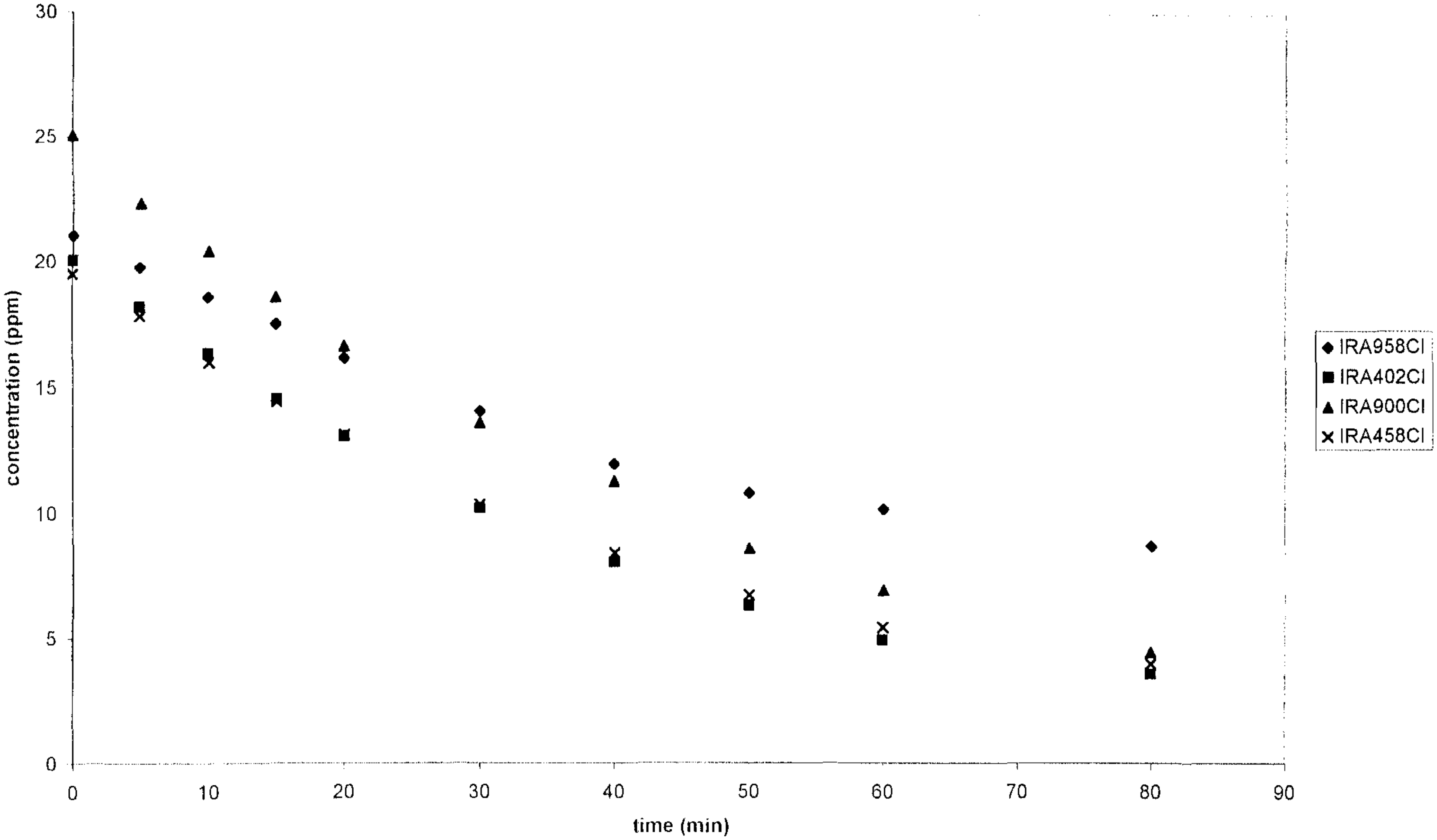


Figure 2 Adsorption of copper(III)cyanide onto four different strong base anion exchange resins

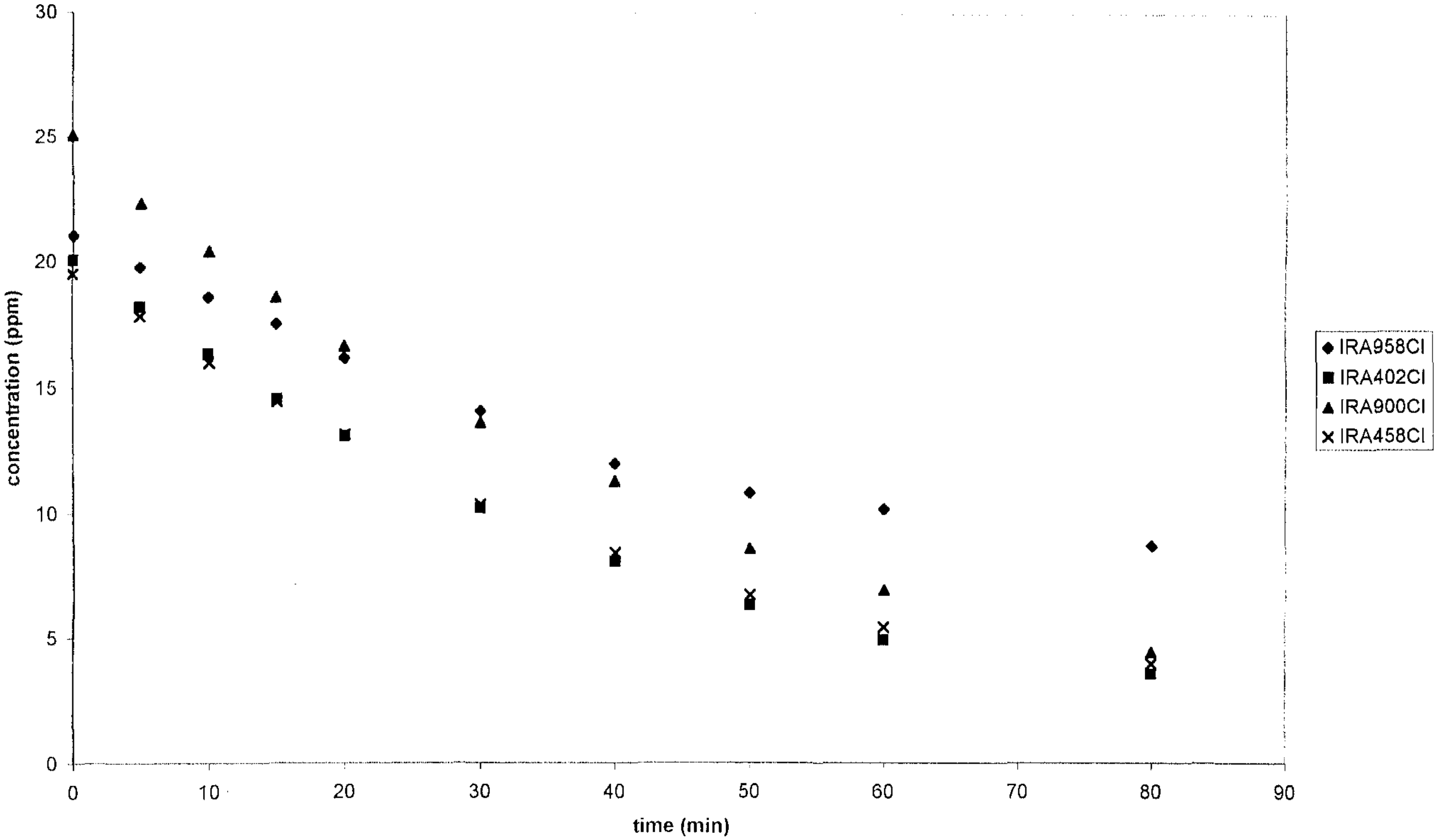


Figure 2 Adsorption of copper(III)cyanide onto four different strong base anion exchange resins

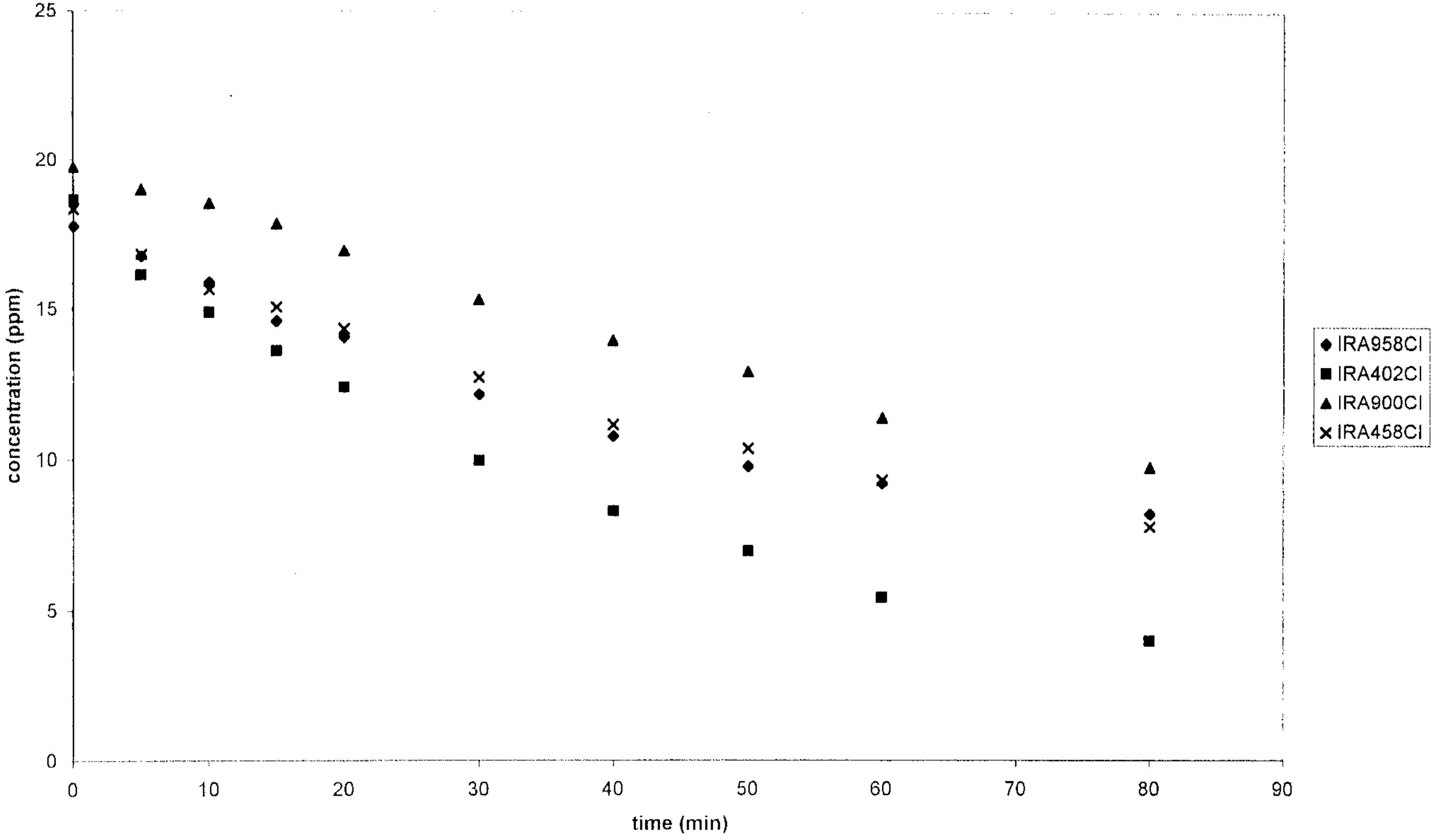


Figure 3 Adsorption of potassium hexacyanoferrate(III) and potassium cyanide(10 ppm) onto four different strong base anion exchange resins

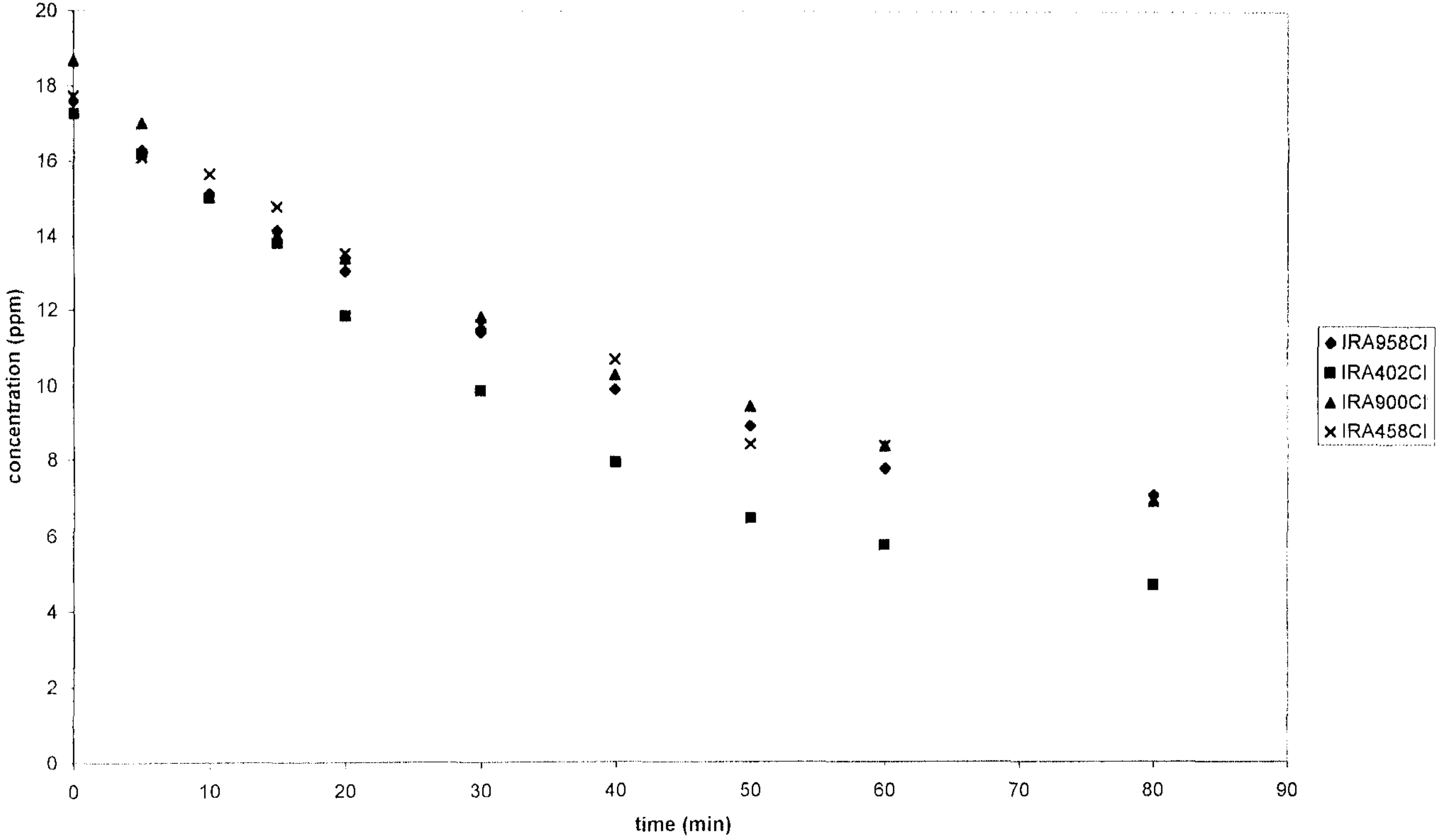


Figure 4 Adsorption of potassium hexacyanoferrate(III) and potassium cyanide(20 ppm) onto four different strong base anion exchange resins

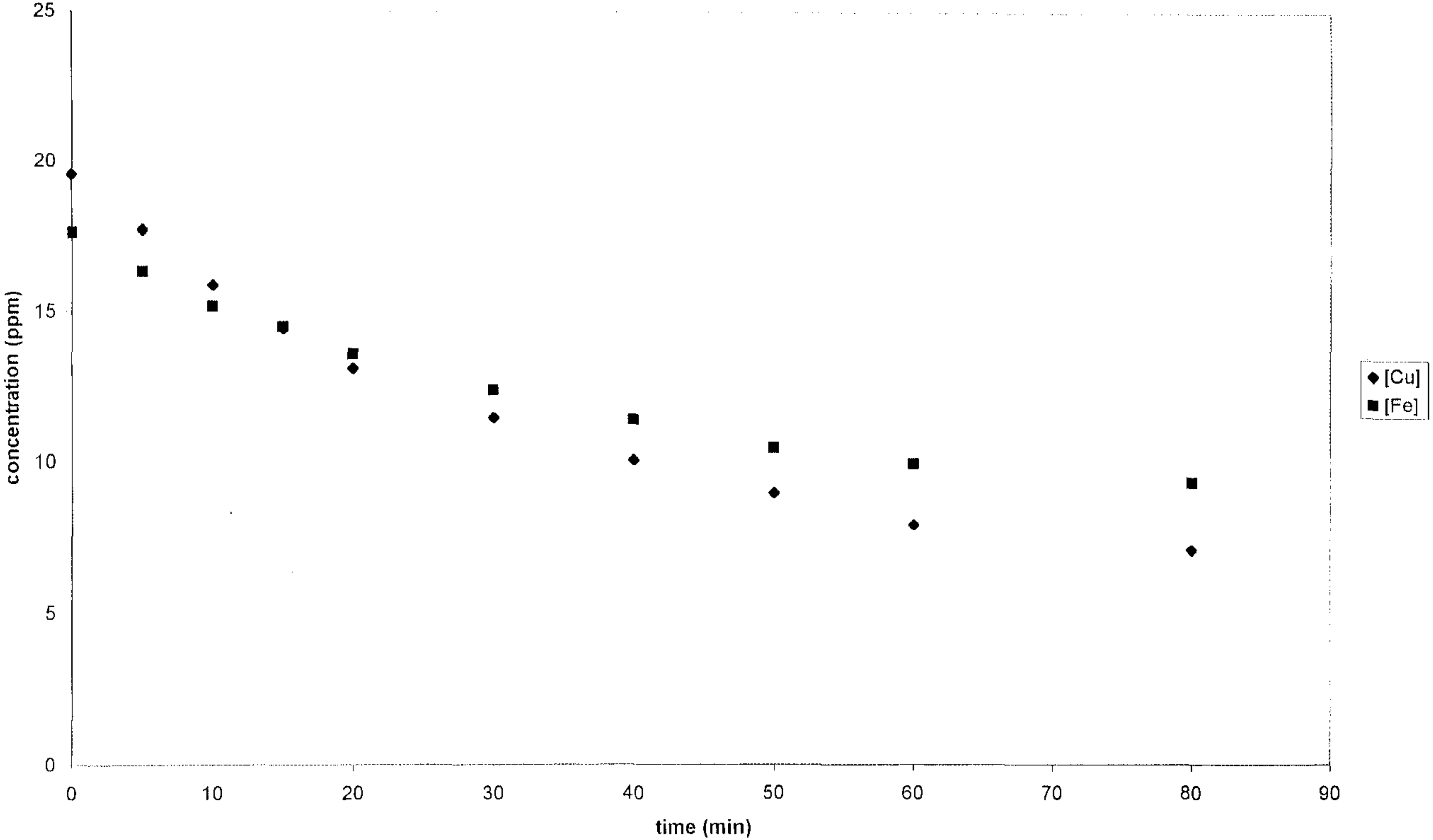


Figure 5 Adsorption of copper and iron cyanide complexes onto IRA900Cl

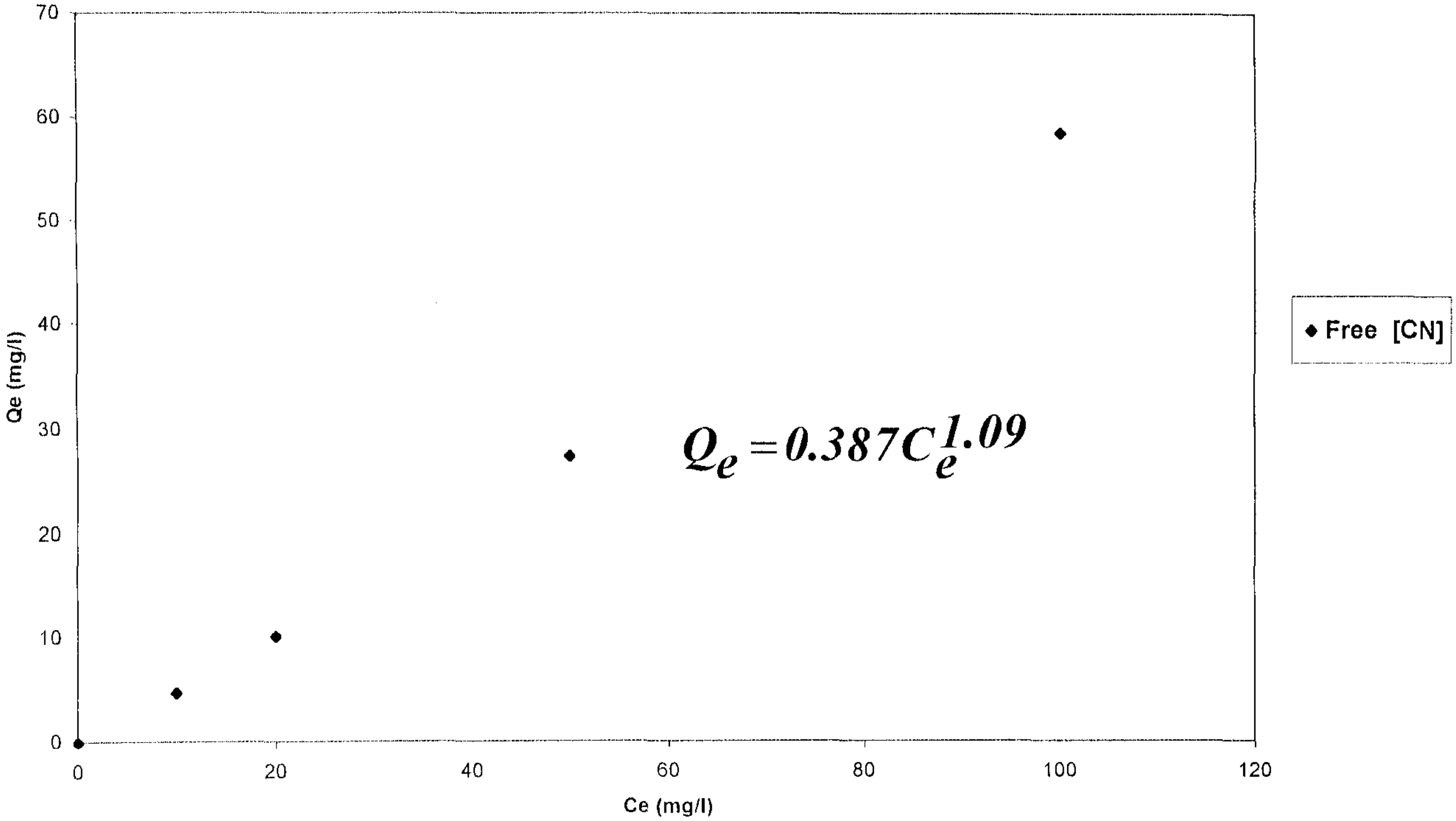


Figure 6 Adsorption of free cyanide onto Amberlite IRA900Cl

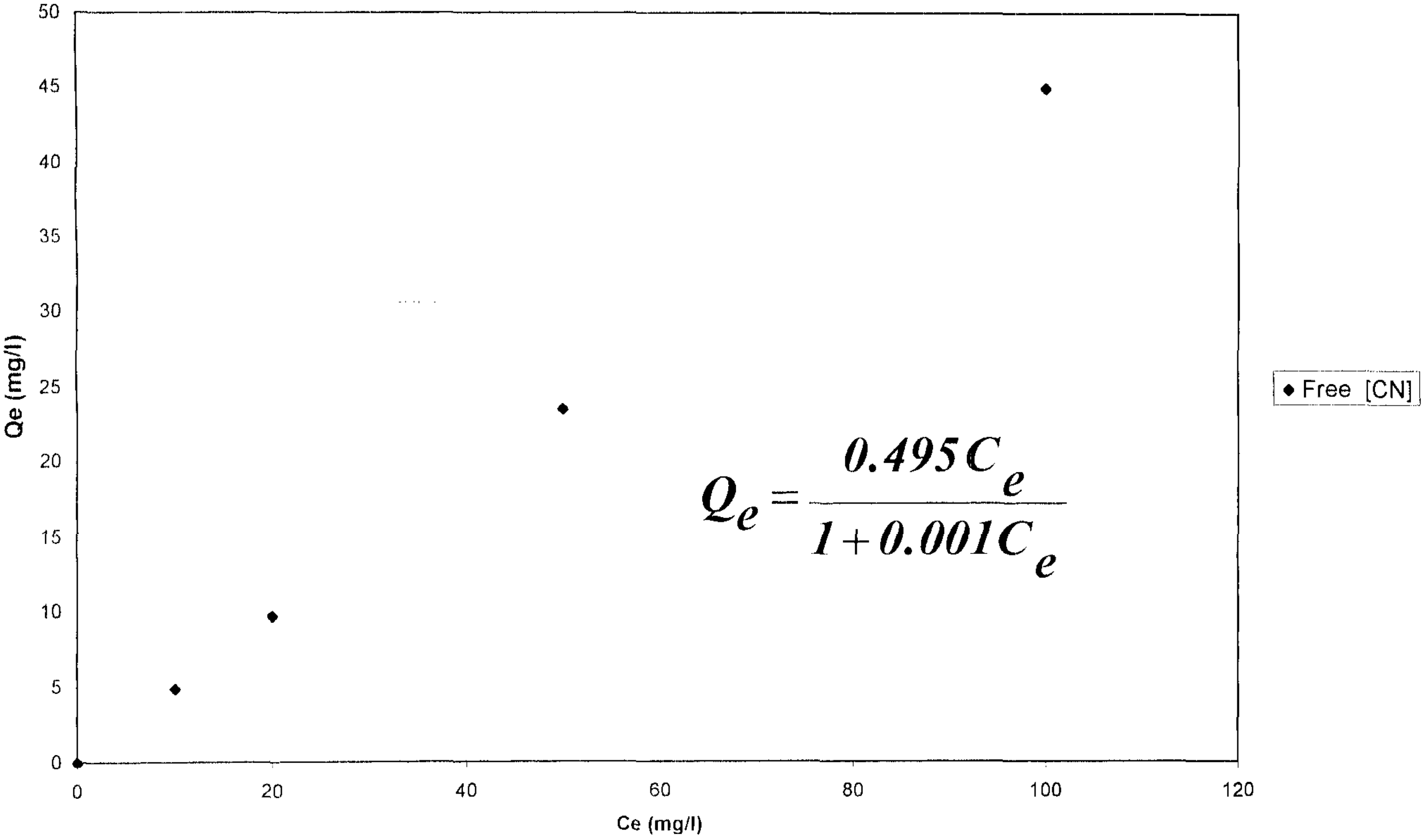


Figure 7 Adsorption of free cyanide onto Amberlite IRA900Cl

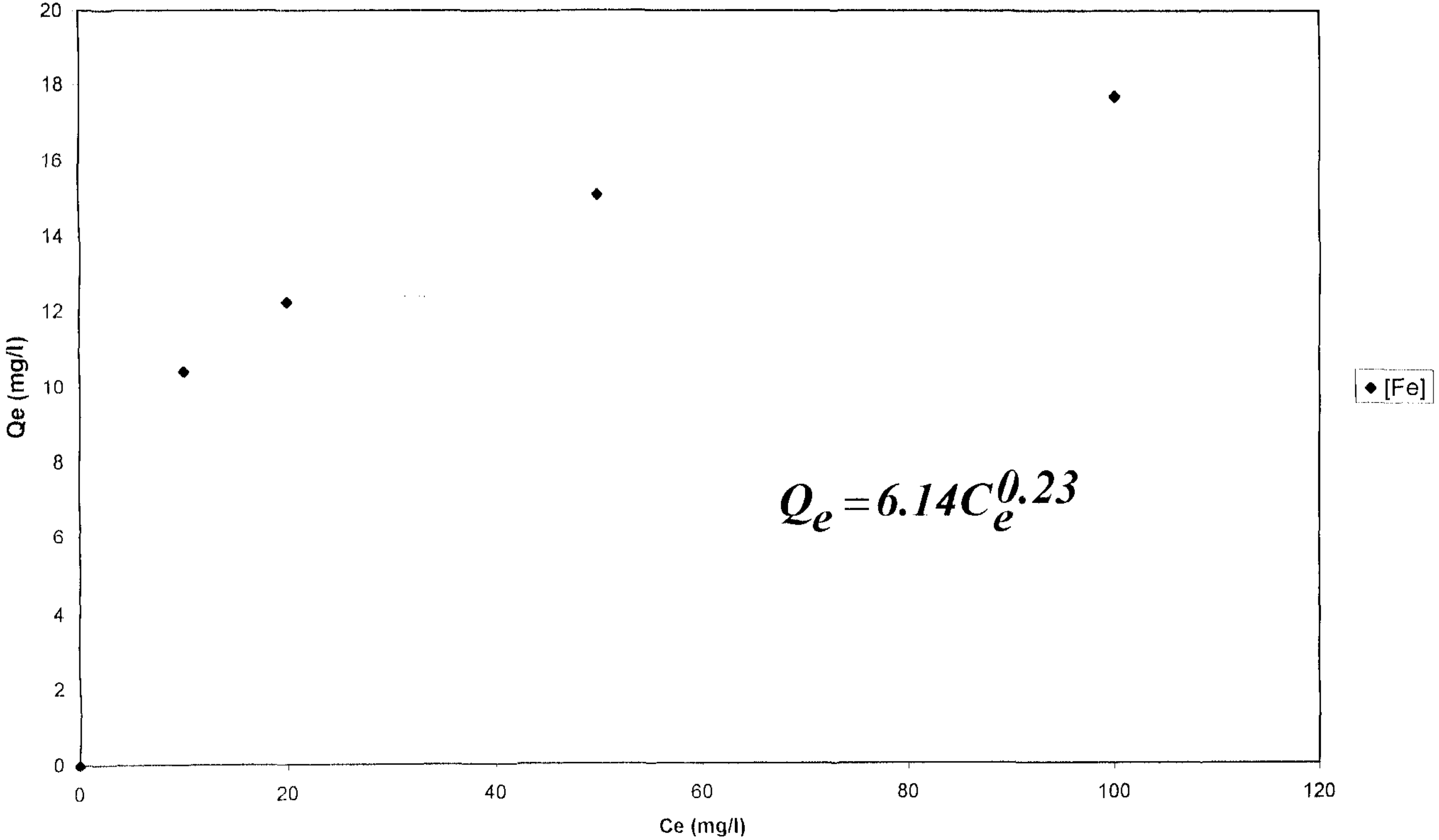
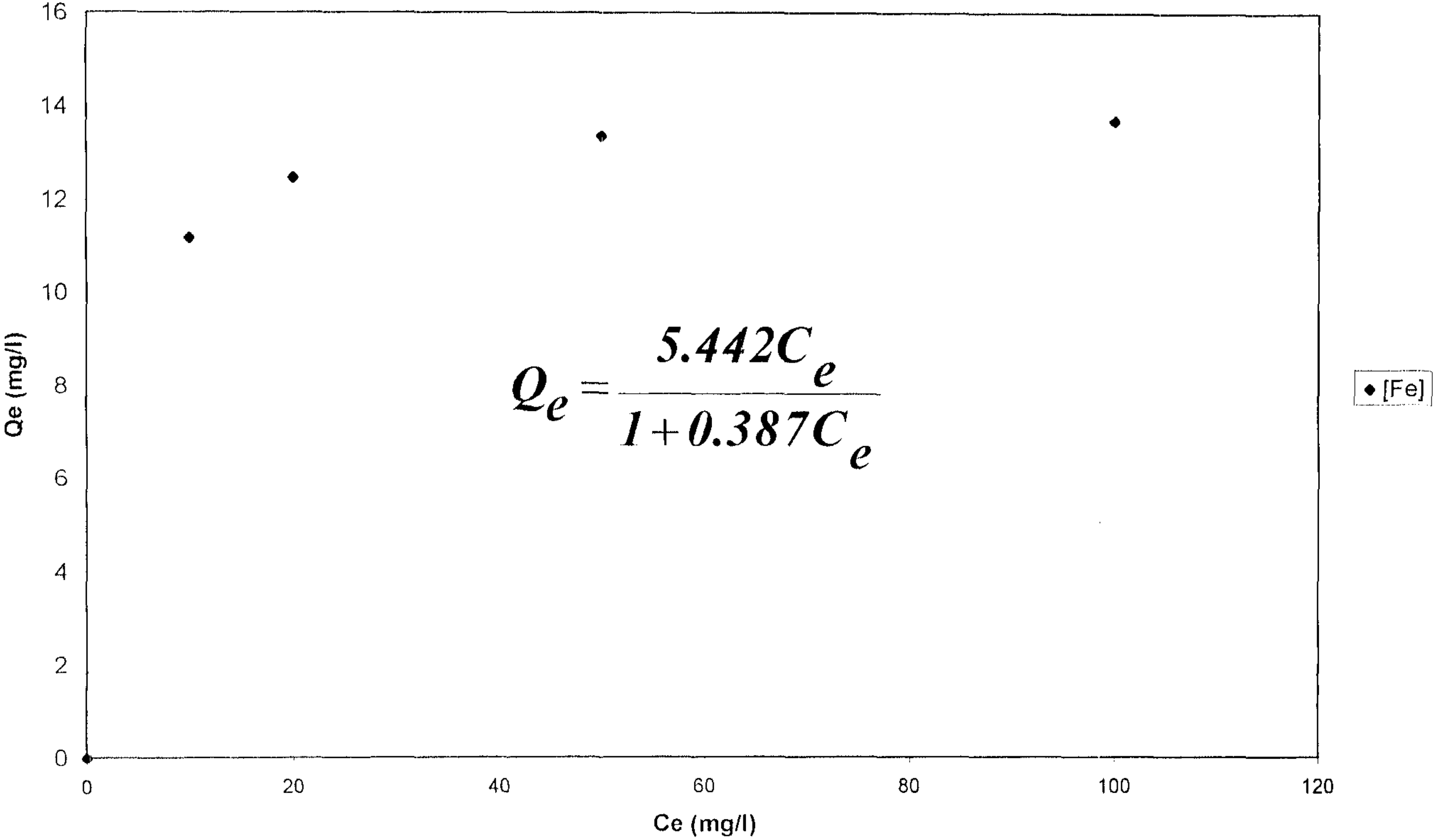


Figure 8 Adsorption of metal cyanide complex onto Amberlite IRA900Cl



$$Q_e = \frac{5.442C_e}{1+0.387C_e}$$

Figure 9 Adsorption of metal cyanide complex onto Amberlite IRA900Cl

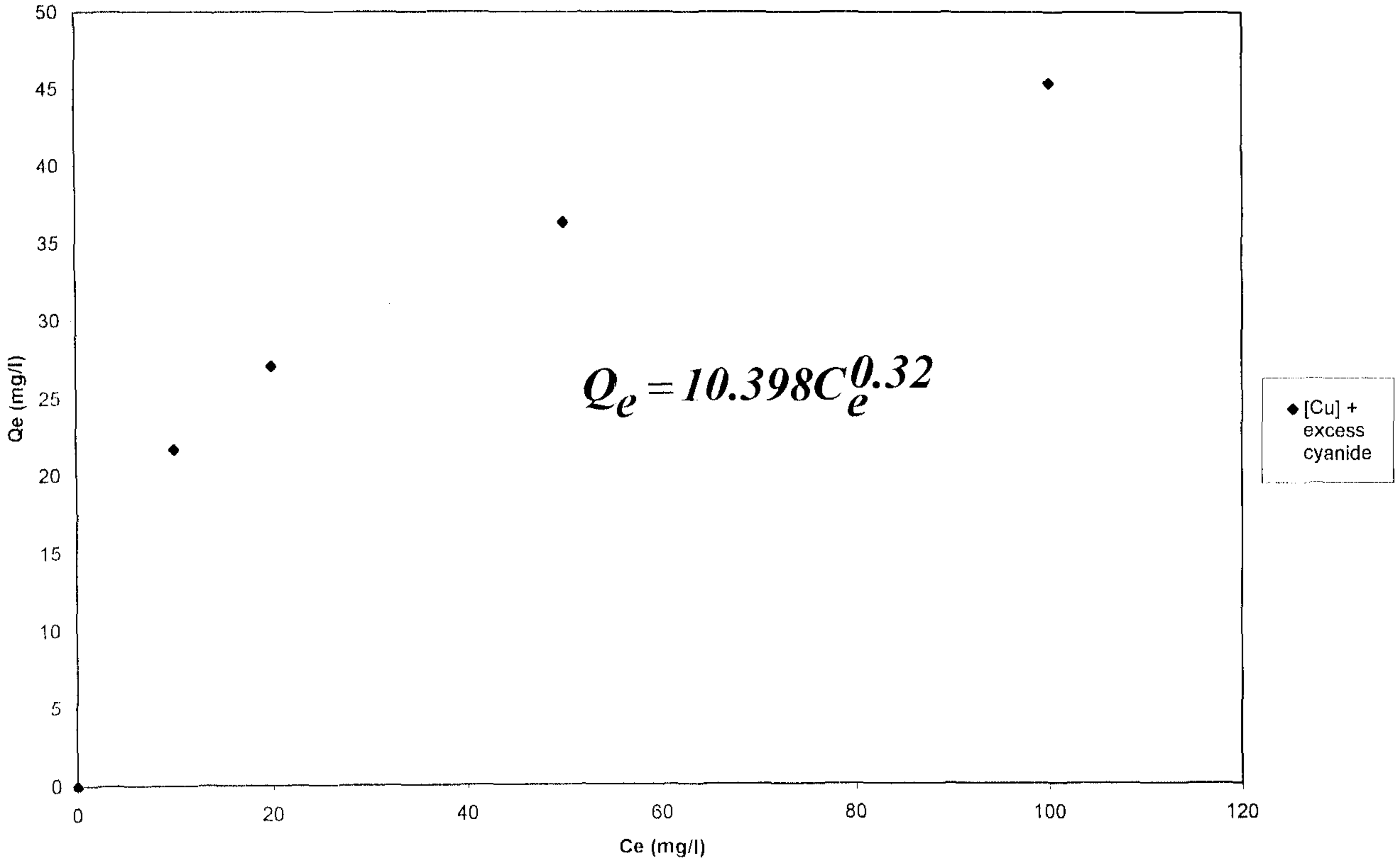


Figure 10 Adsorption of metal cyanide complex and excess cyanide onto Amberlite IRA900Cl

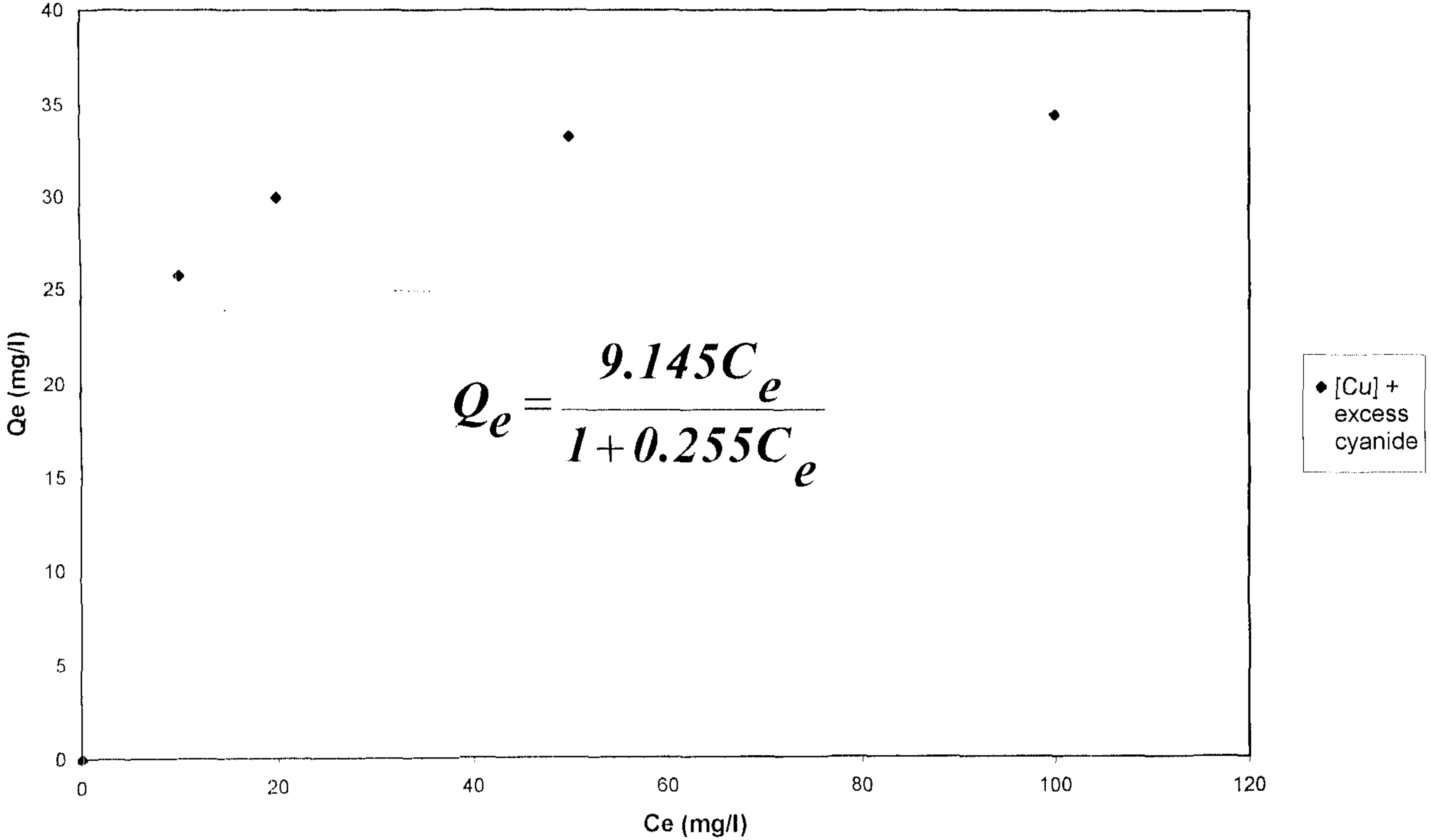


Figure 11 Adsorption of metal cyanide and excess cyanide onto Amberlite IRA900Cl

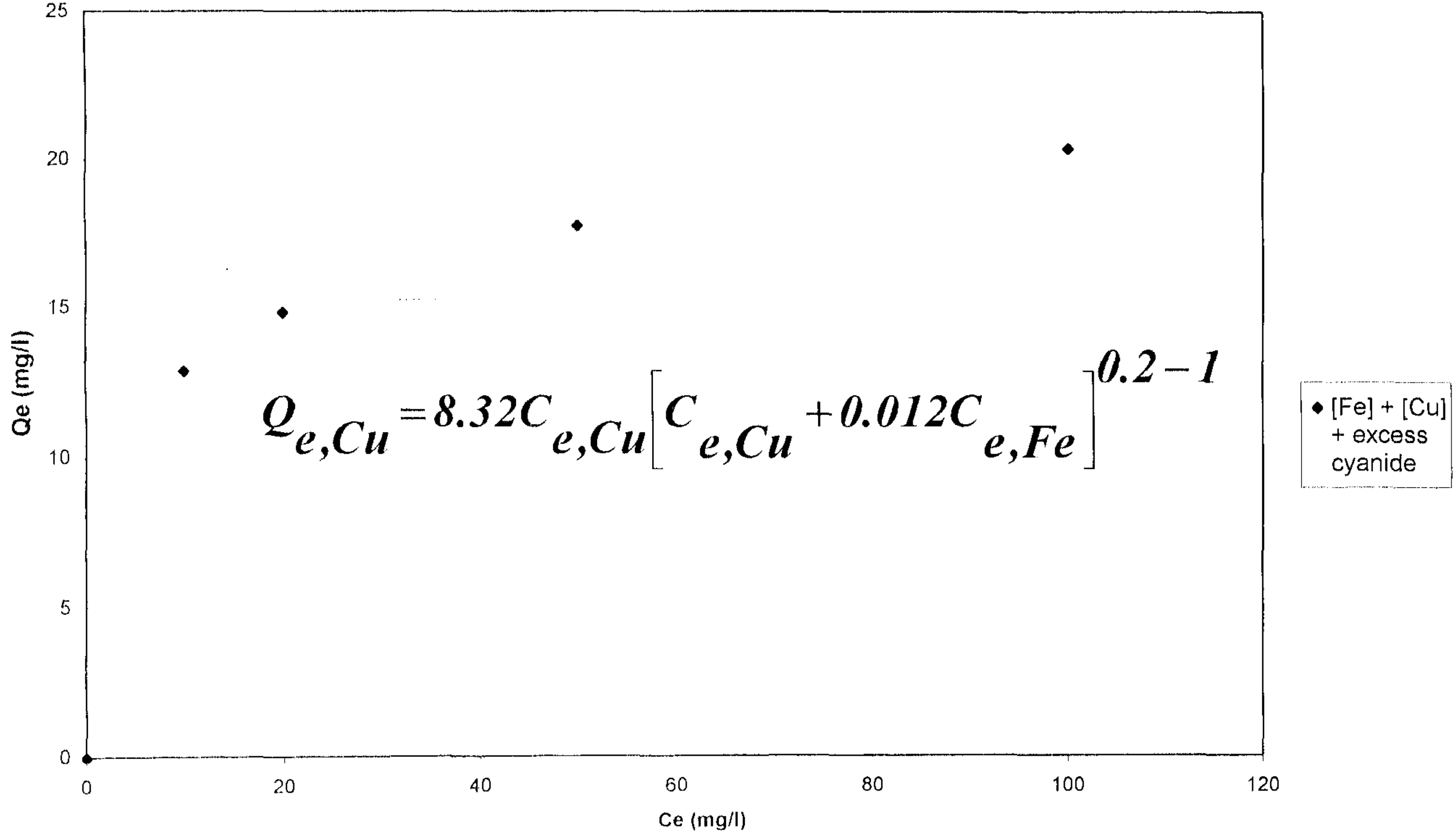


Figure 12 Adsorption of metal cyanides and excess cyanide onto Amberlite IRA900Cl

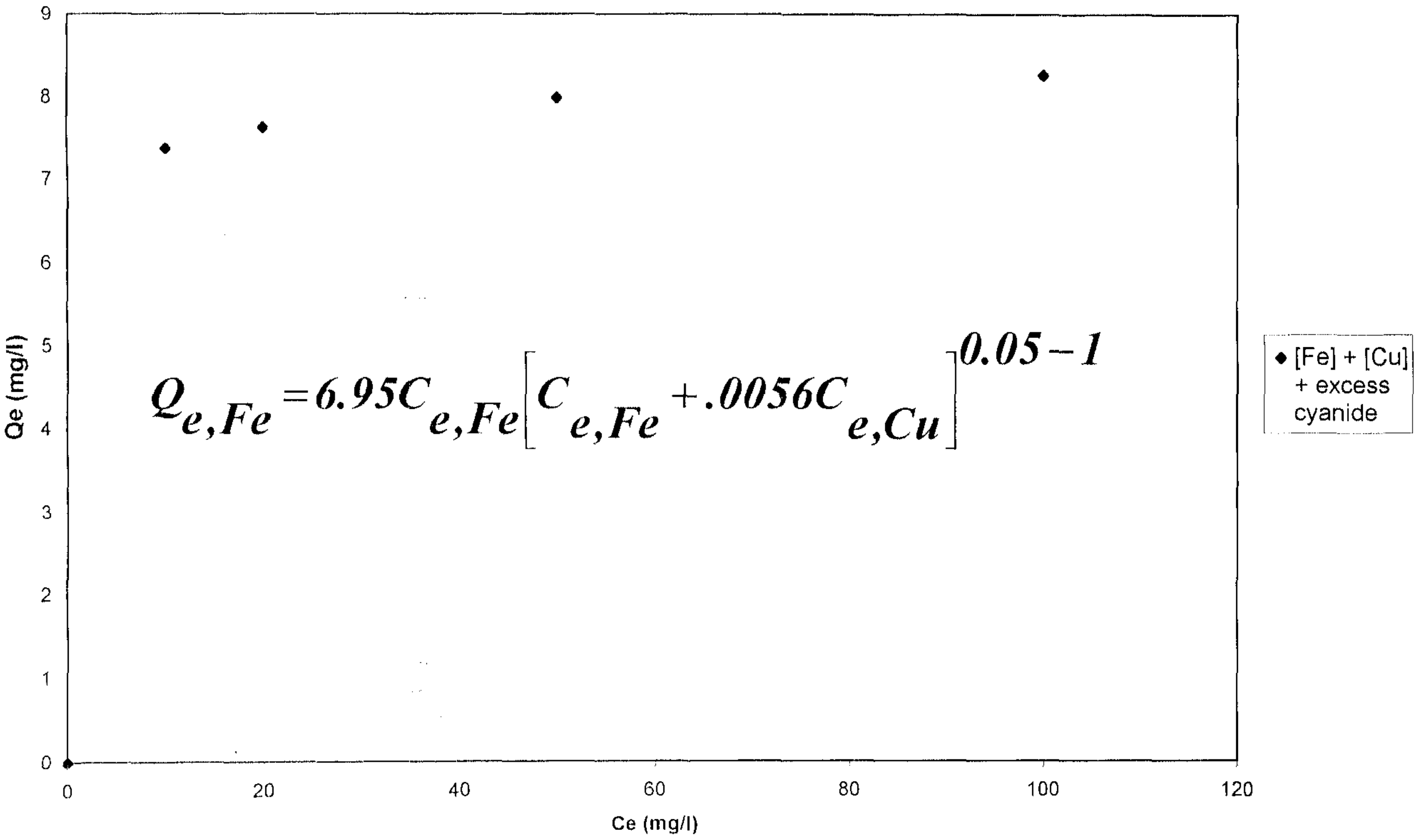


Figure 13 Adsorption of metal cyanides and excess cyanide onto Amberlite IRA900Cl

CONCLUSIONS AND FUTURE WORK

The aim of this study was to evaluate the interaction of the four resins with heavy metal cyanides and free cyanide solutions. Amberlite resins IRA900Cl and IRA402Cl posses superior loading capabilities as compared to IRA458Cl and IRA958Cl.

The kinetics of ion exchange was rapid with equilibrium reached in a short time. Equilibrium conditions were well explained by the Freundlich isotherms in both single and multi-component systems. Furthermore, metal cyanide complexes can be recovered to lower solution concentrations as compared to free cyanide. Also, free cyanide had little effect on the equilibrium loading of copper and iron cyanide in the multi-component systems tested.

Further work should include the recovery of the species in a column configuration. Also, the regeneration of the resin should be evaluated by both conventional methods and in an acidic medium.

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NOMENCLATURE

A	Constant
a	Constant
B	Constant
C	Solution concentration [mg.l^{-1}]
C_e	Equilibrium solution concentration[mg.l^{-1}]
C_o	Initial solution concentration[mg.l^{-1}]
d	Resin particle diameter [m]
D	Surface diffusivity (m^2/s)
k_f	Mass transfer parameter [m.s^{-1}]
M	Mass of resin [kg]
n	Constant
Q	Equilibrium loading [mg.g^{-1}]
t	Time [s]
V	Volume [m^3]
ρ	Density [kg.m^{-3}]
$\overline{X}$	Arithmetic mean of independent value
X	Values of independent variable
Y	Actual values of dependent variable
n	Number of data points
$\overline{Y}$	Arithmetic mean of dependent variable

Greek letters

α	Phase conversion factor (m^3 of resin / m^3 of wet settled resin)
ρ	Apparent density (g / m^3)

APPENDIX A

RAW DATA OF EXPERIMENTAL WORK

Experiment no.1

Equilibrium adsorption of free cyanide on Amberlite IRA900Cl

Volume of solution = 1.0 L

Volume of resin = 10 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
7.8	5.2	2.6
20	14	6
78	48	30
106	78	28
200	108	108

Experiment no.2

Equilibrium adsorption of iron cyanide and free cyanide on Amberlite IRA900Cl.

Volume of solution = 1.0 L
Volume of resin = 5 ml
Stirring speed = 200 rpm
pH of solution = 12.00

C_0 (mg/l)	C_0 (mg/l) Free cyanide	C_e (mg/l)	q_e (mg/l)
10.33	20	2.68	7.65
19.76	10	9.8	9.96
36.3	20	28.58	7.72
9.15	10	2.70	6.45
18.67	20	6.96	11.71

Experiment no.3

Equilibrium adsorption of iron cyanide on Amberlite IRA900Cl.

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
9.84	2.72	7.12
18.82	7.6	11.22
39.03	26.89	12.14

Experiment no.4

Equilibrium adsorption of copper cyanide on Amberlite IRA900Cl

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
10.7	1.39	9.31
25.07	4.47	20.60
36.29	11.37	24.92
64.62	29.47	35.15
91.45	61.03	30.42

Experiment no.5

Equilibrium adsorption of iron, copper and free cyanide on Amberlite IRA900Cl.

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l) Copper cyanide	C_0 (mg/l) Iron cyanide	q_e (mg/l) Copper cyanide	q_e (mg/l) Iron cyanide
11.5	9.98	9.47	7.08
19.55	17.65	12.44	8.29
41.01	38.04	15.58	7.94

Experiment no.6

Equilibrium adsorption of free cyanide on Amberlite IRA958Cl

Volume of solution = 1.0 L

Volume of resin = 10 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
2.2	1.1	1.1
9.7	6.5	3.2
19	8.9	10.10
54	42	12
63	52	11

Experiment no.7

Equilibrium adsorption of iron cyanide and free cyanide on Amberlite IRA958Cl.

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_0 (mg/l) Free cyanide	C_e (mg/l)	q_e (mg/l)
9.59	20	3.27	6
17.9	10	8.27	9.63
36.82	20	24.56	12.26
9.92	10	4.86	5.06
19.93	20	9.48	10.45

Experiment no.8

Equilibrium adsorption of iron cyanide on Amberlite IRA958Cl.

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
8.70	1.25	7.45
18.34	6.43	11.91
38.04	25.73	12.31

Experiment no.9

Equilibrium adsorption of copper cyanide on Amberlite IRA958Cl

Volume of solution = 1.0 L
Volume of resin = 5 ml
Stirring speed = 200 rpm
pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
11.63	2.96	8.67
21.05	8.74	12.31
37.91	25.72	12.19
61.04	40.86	20.18
100.78	74.58	26.20

Experiment no.10

Equilibrium adsorption of free cyanide on Amberlite IRA458Cl

Volume of solution = 1.0 L

Volume of resin = 10 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
10	7.1	3.9
19	14	5
120	74	46
120	70	50
130	112	18

Experiment no.11

Equilibrium adsorption of iron cyanide and free cyanide on Amberlite IRA458Cl.

Volume of solution = 1.0 L
Volume of resin = 5 ml
Stirring speed = 200 rpm
pH of solution = 12.00

C_0 (mg/l)	C_0 (mg/l) Free cyanide	C_e (mg/l)	q_e (mg/l)
10.32	20	2.01	8.31
18.38	10	7.82	10.56
38.84	20	26.03	12.81
11.38	10	3.93	7.45
17.74	20	7.01	10.73

<u>Experiment no.12</u>

Equilibrium adsorption of iron cyanide on Amberlite IRA458Cl.

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
8.67	1.82	6.85
19.25	7.1	12.15
39.01	27.73	11.28

Experiment no.13

Equilibrium adsorption of copper cyanide on Amberlite IRA458Cl

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
10.35	1.87	8.48
19.52	4.01	15.51
37.25	18.63	18.62
60.59	40.17	20.42
97.65	69.93	27.72

Experiment no.14

Equilibrium adsorption of free cyanide on Amberlite IRA402Cl

Volume of solution = 1.0 L

Volume of resin = 10 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
9.2	7.7	1.5
20	13	7
26	14.2	11.8
136	52	84
158	78	80

Experiment no.15

Equilibrium adsorption of iron cyanide and free cyanide on Amberlite IRA402Cl.

Volume of solution = 1.0 L
Volume of resin = 5 ml
Stirring speed = 200 rpm
pH of solution = 12.00

C_0 (mg/l)	C_0 (mg/l) Free cyanide	C_e (mg/l)	q_e (mg/l)
10.23	20	2.95	7.28
18.66	10	4.01	14.65
36.24	20	19.04	17.20
10.02	10	3.61	6.41
17.27	20	4.69	12.58

Experiment no.16

Equilibrium adsorption of iron cyanide on Amberlite IRA402Cl.

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
10.41	1.61	8.8
19.6	2.93	16.67
37.51	17.11	20.4

Experiment no.17

Equilibrium adsorption of copper cyanide on Amberlite IRA402Cl

Volume of solution = 1.0 L

Volume of resin = 5 ml

Stirring speed = 200 rpm

pH of solution = 12.00

C_0 (mg/l)	C_e (mg/l)	q_e (mg/l)
10.57	1.43	9.14
20.06	3.57	16.49
34.72	9.97	24.75
61.04	26.89	34.15
82.53	50.21	32.32

APPENDIX B

AMBERLITE DATA PRODUCT SHEETS

ROHM AND HAAS

ION EXCHANGE RESINS

PRODUCT DATA SHEET

AMBERLITE IRA458 Cl

Industrial Grade Acrylic Strong Base Anion Exchange Resin

AMBERLITE IRA458 Cl is an acrylic gel type strongly basic anion exchange resin, with unique chemical and physical properties. It combines high operating capacity and low silica leakage values.
The acrylic structure of AMBERLITE IRA458 Cl allows for effective adsorption during the service run and good desorption during regeneration of the naturally occurring organic molecules present in many water supplies.

PROPERTIES

Matrix	Crosslinked acrylic gel structure
Functional groups	$-N^+R_3$
Physical form	Transparent white beads
Ionic form as shipped	Chloride
Total exchange capacity [1]	≥ 1.25 eq/L (Cl^- form)
Moisture holding capacity [1]	57 to 64 % (Cl^- form)
Specific gravity	1.06 to 1.10 (Cl^- form)
Shipping weight	720 g/L
Particle size	
Uniformity coefficient	≤ 1.90
Harmonic mean size	600 - 900 µm
Fine contents [1]	< 0.300 mm : 2.0 % max
Coarse beads	> 1.180 mm : 20 % max
Maximum reversible swelling	$Cl^- \rightarrow OH^-$: 20 %

[1] Contractual value
Test methods are available on request.

SUGGESTED OPERATING CONDITIONS (Water Treatment)

Maximum operating temperature	35°C
Minimum bed depth	700 mm
Service flow rate	5 to 40 BV*/h
Regenerant	NaOH
Flow rate	2 to 8 BV/h
Concentration	2 to 4 %
Level	50 to 150 g/L
Minimum contact time	30 minutes
Slow rinse	2 BV at regeneration flow rate
Fast rinse	4 to 8 BV at service flow rate

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

AMBERLITE IRA458 Cl is designed to be used in co-flow regeneration units. It is recommended as the working anion exchange resin, or in combination with AMBERLITE IRA96 for demineralisation of water having up to 30 % silica when low caustic regenerant consumption and good resistance to organic fouling are primarily required. AMBERLITE IRA 458 Cl is also used for the decolourisation of sugar juices.

PERFORMANCE

The engineering data sheet EDS 0273 A provide information to calculate the operating capacity and silica leakage of AMBERLITE IRA458 Cl used in water treatment.

HYDRAULIC CHARACTERISTICS (Water Treatment)

AMBERLITE IRA458 Cl gives a pressure drop of about 14 kPa/m bed depth per 10 m/h at 15°C.
A backwash flow rate of 7 m/h gives a bed expansion of about 70 % at 15°C.
Pressure drop data are valid at the start of the service run with a clear water and a correctly classified bed.

LIMITS OF USE

Rohm and Haas manufactures special resins for food processing and potable water applications. As governmental regulations vary from country to country, it is recommended that potential users seek advice from their Amberlite representative in order to determine the best resin choice and optimum operating conditions.

In Europe, all our products are produced in ISO 9002 certified manufacturing facilities.

CAUTION

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

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ION EXCHANGE RESINS

PRODUCT DATA SHEET

AMBERLITE IRA958 Cl

Industrial Grade Strong Base Anion Exchange Resin

AMBERLITE IRA958 Cl is a macroreticular strongly basic anion exchange resin exhibiting quaternary ammonium functionality in a crosslinked acrylic polymer matrix. The high porosity of its macroreticular structure allows more complete removal of large organic molecules and provides excellent resistance to physical breakdown by attrition and osmotic shock. The acrylic composition of the matrix contributes to excellent desorption of organics during regeneration. AMBERLITE IRA958 Cl is particularly useful as an organic scavenger for the adsorption of natural organic matter from surface water. Placed ahead of an ion exchange deionisation system, AMBERLITE IRA958 Cl helps prevent organic fouling of the working anion exchange resins of the plant. AMBERLITE IRA958 Cl is also used in sugar juice decolourisation to remove colour bodies from cane sugar syrups and in purification of various chemical and pharmaceutical products.

AMBERLITE IRA958 Cl complies with the FDA 21 CFR 173.25 regulation : all that is required at the time of commissioning is to perform a full regeneration cycle followed by a rinse with at least 10 bedvolumes of water.

PROPERTIES

Matrix	Crosslinked acrylic macroreticular structure
Functional groups	Quaternary ammonium
Physical form	White opaque beads
Ionic form as shipped	Chloride
Total exchange capacity [1]	$\geq$ 0.8 eq/L (Cl^- form)
Moisture holding capacity [1]	66 to 72 % (Cl^- form)
Specific gravity	1.05 to 1.08 (Cl^- form)
Shipping weight	720 g/L
Particle size	
Uniformity coefficient	$\leq$ 1.8
Harmonic mean size	630 to 850 µm
Fine contents [1]	< 0.355 mm : 1.0 % max
Coarse beads	> 1.180 mm : 5.0 % max

[1] Contractual value

Test methods are available on request.

SUGGESTED OPERATING CONDITIONS (Scavenger)

Maximum operating temperature	80°C (Cl^-)	
Minimum bed depth	600 mm	
Service flow rate	8 to 40 BV*/h	
Regenerant	NaOH 2 % +	NaCl 10 %
Flow rate (BV/h)	2 to 6	2 to 6
Level (g/L)	6 to 40	160 to 300
Minimum contact time	30 minutes	
Slow rinse	5 to 10 BV	
Fast rinse	Same as regenerant for first bed displacement, then same as service flow rate	

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

SUGGESTED OPERATING CONDITIONS (Sugar)

Service	2 to 4 BV*/h
Sweetening off	2.5 BV/h at 60°C with softened or demineralised water
Backwash	7 to 8 m/h at 60°C with softened or demineralised water
Regenerant	NaCl
Level	150 to 250 g/L
Concentration	10 % at 60°C
Rinse requirement	5 to 10 BV
Sweetening on	2.5 BV/h dilute syrup

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

PERFORMANCE (Scavenger)

Based on previous experience in industrial installations and laboratory studies, an average capacity for organics of 10 to 40 g (as $KMnO_4$) per litre of resin can be expected.

This value should be considered as an approximate indication and it is recommended that some column tests be undertaken on site in order to determine the operating capacity of AMBERLITE IRA958 Cl for a particular water.

HYDRAULIC CHARACTERISTICS (Water treatment)

AMBERLITE IRA958 Cl gives a pressure drop of about 13 kPa/m bed depth per 10 m/h at 15°C.
A backwash flow rate of 6 m/h gives a bed expansion of about 65 % at 15°C.
Pressure drop data are valid at the start of the service run with a clear water and a correctly classified bed.

LIMITS OF USE

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

In Europe, all our products are produced in ISO 9002 certified manufacturing facilities.

CAUTION

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

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ION EXCHANGE RESINS

PRODUCT DATA SHEET

AMBERLITE IRA900 Cl

Industrial Strong Base Anion Exchange Resin

AMBERLITE IRA900 Cl is a macroreticular polystyrene type 1 strong base anion exchange resin containing quaternary ammonium groups. This allows complete removal of all anions, including weakly dissociated ones like silica. The macroreticular structure embodies fixed large pores, presenting a sponge-like matrix. This feature combined with the strong basicity permits the removal of large size soluble organic molecules. In addition the macroreticular structure imparts superior resistance to mechanical and osmotic shock.

PROPERTIES

Matrix	Styrene divinylbenzene copolymer
Functional groups	$-N^+(CH_3)_3$
Physical form	Ivory beads
Ionic form as shipped	Chloride
Total exchange capacity [1]	$\geq$ 1.0 eq/L (Cl^- form)
Moisture holding capacity [1]	58 to 64 % (Cl^- form)
Specific gravity	1.050 to 1.080 (Cl^- form)
Shipping weight	700 g/L
Particle size	
Uniformity coefficient	$\leq$ 1.80
Harmonic mean size	650 - 820 µm
Fine contents [1]	< 0.300 mm : 0.5 % max
Coarse beads	> 1.180 mm : 3.0 % max
Maximum reversible swelling	$Cl^- \rightarrow OH^-$: about 25 %
Chemical resistance	Insoluble in dilute solutions of acids or bases and common solvents

[1] *Contractual value*
Test methods are available on request.

SUGGESTED OPERATING CONDITIONS (Water Treatment)

Minimum bed depth	700 mm
Service flow rate	up to 120 BV*/h
Regenerant	NaOH
Flow rate	2 to 8 BV/h
Concentration	2 to 4 %
Level	50 to 150 g/L
Minimum contact time	30 minutes
Slow rinse	2 BV at regeneration flow rate
Fast rinse	4 to 8 BV at service flow rate

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

APPLICATIONS

AMBERLITE IRA900 Cl is the ideal choice in all cases where the highest quality of deionised water is desired. Due to its excellent mechanical strength and good kinetics, it is particularly recommended for applications such as condensate polishing where the resin can be operated at flow rates up to 120 BV/h or 120 m/h. AMBERLITE IRA900 Cl can be used as an organic scavenger placed in front of a deionization system. Working in the chloride form, it removes the more harmful organic substances from the raw water, protecting subsequent anion exchange resins from possible irreversible organic fouling.

AMBERLITE IRA900 Cl is also suitable for colour removal from sugar syrups.

PERFORMANCE

The engineering data sheet EDS 0258 A provide information to calculate the operating capacity and silica leakage of AMBERLITE IRA900 Cl used in water treatment.

LIMITS OF USE

Rohm and Haas manufactures special resins for food processing and potable water applications. As governmental regulations vary from country to country, it is recommended that potential users seek advice from their Amberlite representative in order to determine the best resin choice and optimum operating conditions.

HYDRAULIC CHARACTERISTICS (Water Treatment)

Figure 1 shows the bed expansion of AMBERLITE IRA900 Cl, as a function of backwash flow rate and water temperature. Figure 2 shows the pressure drop data for AMBERLITE IRA900 Cl, as a function of service flow rate and water temperature. Pressure drop data are valid at the start of the service run with a clear water and a correctly classified bed.

Figure 1 : **BED EXPANSION**

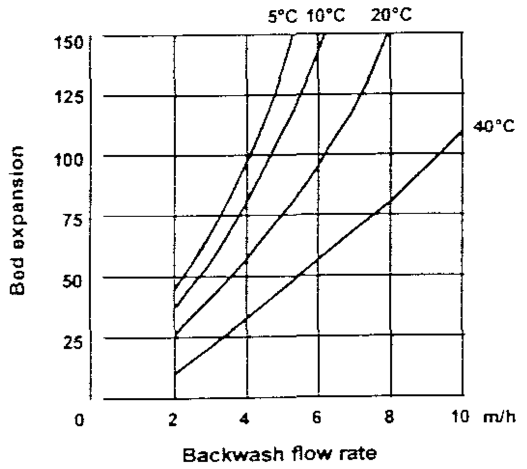
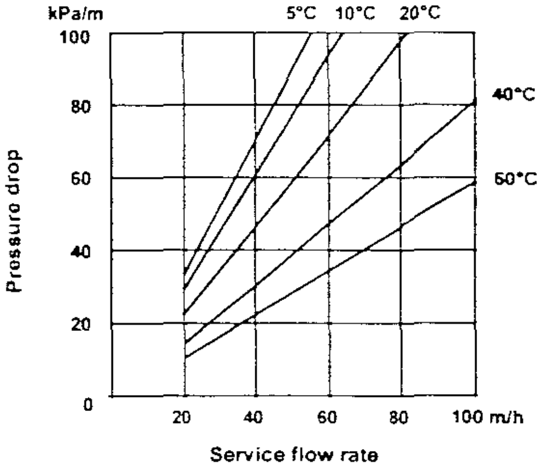


Figure 2 : **PRESSURE DROP**



In Europe, all our products are produced in ISO 9002 certified manufacturing facilities.

CAUTION

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

ROHM AND HAAS ION EXCHANGE RESINS

PRODUCT DATA SHEET

AMBERLITE IRA402 Cl

Industrial Grade Strongly Basic Anion Exchanger

AMBERLITE IRA402 Cl is a premium grade strongly basic anion exchange resin of the type 1, with a clear gel structure. It is based on crosslinked polystyrene and has a very high bead integrity, good regeneration efficiency and excellent rinse performance. It is used in co-flow regeneration and conventional counterflow systems with downflow loading and upflow regeneration with air or water holddown. Combined with a strong acid cation exchanger, AMBERLITE IRA402 Cl reduces both strong and weak acid concentrations to extremely low levels. Its main use is therefore water demineralisation. Other fields of application include the treatment of electroplating waste and the isolation of anionic metal complexes.

PROPERTIES

Matrix	Styrene divinylbenzene copolymer
Functional groups	$-N^+(CH_3)_3$
Physical form	Pale yellow translucent beads
Ionic form as shipped	Chloride
Total exchange capacity [1]	$\geq$ 1.30 eq/L (Cl^- form)
Moisture holding capacity [1]	49 to 55 % (Cl^- form)
Specific gravity	1.063 to 1.093 (Cl^- form)
Shipping weight	670 g/L
Particle size	
Uniformity coefficient	$\leq$ 1.6
Harmonic mean size	600 - 750 µm
Fine contents [1]	< 0.300 mm : 1.0 % max
Coarse beads	> 1.180 mm : 5.0 % max
Maximum reversible swelling	$Cl^- \rightarrow OH^-$: 30 %

[1] *Contractual value*

Test methods are available on request.

SUGGESTED OPERATING CONDITIONS

Maximum operating temperature	60°C
Minimum bed depth	700 mm
Service flow rate	5 to 40 BV*/h
Regenerant	NaOH
Flow rate	2 to 8 BV/h
Concentration	2 to 4 %
Level	60 to 150 g/L
Minimum contact time	30 minutes
Slow rinse	2 BV at regeneration flow rate
Fast rinse	4 to 8 BV at service flow rate

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

AMBERLITE IRA402 Cl gives a pressure drop of about 13 kPa/m bed depth per 10 m/h at 15°C.
A backwash flow rate of 6.5 m/h gives a bed expansion of about 70 % at 15°C.
Pressure drop data are valid at the start of the service run with a clear water and a correctly classified bed.

LIMITS OF USE

AMBERLITE IRA402 Cl is suitable for industrial uses. For all other specific applications such as pharmaceutical, food processing or potable water applications, it is recommended that all potential users seek advice from Rohm and Haas in order to determine the best resin choice and optimum operating conditions.

In Europe, all our products are produced in ISO 9002 certified manufacturing facilities.

CAUTION

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

APPENDIX C

The following software, written in Pascal calculates the mass transfer coefficient, single component Freundlich and Langmuir isotherms. The software can also be utilised to calculate the multi - component Freundlich and Langmuir isotherms. The software stores the different values for the variables in arrays and then calculates the different components by means of procedures.

```
program thesis;

type
arraytype=array[1..1000] of real;

var
array1,array2,array3:arraytype;
C,calc,value:integer;
sumx,sumy,density,volume,
diameter,mass,conc1,conc2,time2,conc3,time3,yval1,yval2,yval3,
ysqr,xsqr,xy,xmean,ymean,number,gradient,ycut:real;

{Prompts and stores amount of experiments and concentrations}
procedure experiments (var valuex,valuey:arraytype;var value:integer);

var C:integer;

begin
write ('Enter the amount of experiments done:');
readln (value);
writeln;
for C:=1 to value do
begin
write ('Enter the initial concentration(mol/dm^3) for each experiment:');
readln (valuex[C]);
end;
writeln;
for C:=1 to value do
begin
write ('Enter the equilibrium concentration(mol/dm^3) for each experiment:');
readln (valuey[C]);
end;
writeln;
end;

{Prompts and stores equilibrium concentrations}
procedure experiments1 (var valuez:arraytype;value:integer);

var
C:integer;

begin
for C:=1 to value do
begin
write ('Enter the equilibrium concentration(mol/dm^3) for the other element in
solution:');
readln (valuez[C]);
end;
end;

{Calculates and displays the Freundlich isotherm}
procedure freundlichcalculation (var valuex,valuey:arraytype;value:integer);

var
C:integer;
sumofx,sumofy,sumofxsqr,sumofysqr,sumofxy,averagex,averagey,b,a,sqrr,constant:re
al;

begin
for C:=1 to value do
begin
```

```
sumofx:=sumofx+ln(valuey[C]);
sumofy:=sumofy+ln(valuex[C]-valuey[C]);
sumofxsqr:=sumofxsqr+sqr(ln(valuey[C]));
sumofysqr:=sumofysqr+ sqr(ln(valuex[C]-valuey[C]));
sumofxy:=sumofxy+ln(valuey[C])*ln(valuex[C]-valuey[C]);
end;

averagex:=sumofx/value;
averagey:=sumofy/value;
b:=(value*sumofxy-sumofx*sumofy)/(value*sumofxsqr-sqr(sumofx));
a:=averagey-b*averagex;
sqrr:=(a*sumofy+b*sumofxy-value*sqr(averagey))/(sumofysqr-value*sqr(averagey));
constant:=exp(a);
writeln;
writeln ('The Freundlich isotherm: Qe=',constant:6:3,'Ce^',b:4:2);
writeln;
writeln ('The coefficient of determination(R^2):',sqrr:6:3);
end;

{Calculates and displays the multi-component Freundlich isotherm}
procedure multifreundlich (var array1,array2,array3:arraytype;value:integer);

var
C:integer;
sumofx,sumofy,sumofxsqr,sumofysqr,sumofxy,averagex,averagey,b,a,sqrr1,constant,s
umofx1,sumofy1,sumofxsqr1,sumofysqr1,sumofxy1,b1,n:real;

begin
for C:=1 to value do
begin
sumofx:=sumofx+ln(array2[C]);
sumofy:=sumofy+ln(array1[C]-array2[C]);
sumofxsqr:=sumofxsqr+sqr(ln(array2[C]));
sumofysqr:=sumofysqr+ sqr(ln(array1[C]-array2[C]));
sumofxy:=sumofxy+ln(array2[C])*ln(array1[C]-array2[C]);
end;

averagex:=sumofx/value;
averagey:=sumofy/value;
b:=(value*sumofxy-sumofx*sumofy)/(value*sumofxsqr-sqr(sumofx));
a:=averagey-b*averagex;
sqrr1:=(a*sumofy+b*sumofxy-value*sqr(averagey))/(sumofysqr-value*sqr(averagey));
constant:=exp(a);

for C:=1 to value do
begin
sumofx1:=sumofx1+array3[C];
sumofy1:=sumofy1+((((constant*array2[C])/(array1[C]-array2[C]))**(1/(1-b)))-
array2[C]);
sumofxsqr1:=sumofxsqr1+sqr(array3[C]);
sumofysqr1:=sumofysqr1+sqr((((constant*array2[C])/(array1[C]-array2[C]))**(1/(1-
b)))-array2[C]);
sumofxy1:=sumofxy1+(array3[C]*((((constant*array2[C])/(array1[C]-
array2[C]))**(1/(1-b)))-array2[C]));
end;
b1:=(value*sumofxy1-sumofx1*sumofy1)/(value*sumofxsqr1-sqr(sumofx1));
n:=b-1;
writeln ('The Multi component Freundlich equation
is:Qe=',constant:4:2,'Ce1(Ce1+',b1:6:3,'Ce2)^',n:6:3);
end;
```

```
{Calculates and displays the Langmuir isotherm}
procedure langcalculation (var valuex,valuey:arraytype;value:integer);

□
var C:integer;
□
var
□
sumofx,sumofy,sumofxsqr,sumofysqr,sumofxy,averagex,averagey,b,a,sqrr,constant,co
nstantb:real;

begin
for C:=1 to value do
begin
sumofx:=sumofx+1/(valuey[C]);
sumofy:=sumofy+1/(valuex[C]-valuey[C]);
sumofxsqr:=sumofxsqr+sqr(1/(valuey[C]));
sumofysqr:=sumofysqr+ sqr(1/(valuex[C]-valuey[C]));
sumofxy:=sumofxy+1/(valuey[C])*1/(valuex[C]-valuey[C]);
end;

averagex:=sumofx/value;
averagey:=sumofy/value;
b:=(value*sumofxy-sumofx*sumofy)/(value*sumofxsqr-sqr(sumofx));
a:=averagey-b*averagex;
sqrr:=(a*sumofy+b*sumofxy-value*sqr(averagey))/(sumofysqr-value*sqr(averagey));
constant:=1/(b);
constantb:=constant*a;
writeln ('The Langmuir isotherm:
Qe=(',constant:6:3,'Ce)/(1+',constantb:6:3,'Ce)');
writeln;
writeln ('The coefficient of determination(R^2):',sqrr:6:3);
end;

{Calculates and displays the multi-component Langmuir isotherm}
procedure multilangmuir (var valuex,valuey,valuez:arraytype;value:integer);

var
C:integer;
sumofx,sumofy,sumofxsqr,sumofysqr,sumofxy,averagex,averagey,b,a,sqrr,constant,co
nstantb,sumofx1,sumofy1,sumofxsqr1,sumofysqr1,sumofxy1,b1:real;

begin
for C:=1 to value do
begin
sumofx:=sumofx+1/(valuey[C]);
sumofy:=sumofy+1/(valuex[C]-valuey[C]);
sumofxsqr:=sumofxsqr+sqr(1/(valuey[C]));
sumofysqr:=sumofysqr+ sqr(1/(valuex[C]-valuey[C]));
sumofxy:=sumofxy+1/(valuey[C])*1/(valuex[C]-valuey[C]);
end;

averagex:=sumofx/value;
averagey:=sumofy/value;
b:=(value*sumofxy-sumofx*sumofy)/(value*sumofxsqr-sqr(sumofx));
a:=averagey-b*averagex;
sqrr:=(a*sumofy+b*sumofxy-value*sqr(averagey))/(sumofysqr-value*sqr(averagey));
constant:=1/(b);
constantb:=constant*a;
```

```
for C:=1 to value do
begin
sumofx1:=sumofx1+1/(valuex[C]-valuey[C]);
sumofy1:=sumofy1+valuez[C]/(constant*valuey[C]);
sumofxsqr1:=sumofxsqr1+sqr((1/(valuex[C]-valuey[C])));
sumofysqr1:=sumofysqr1+sqr((valuez[C]/(constant*valuey[C])));
sumofxy1:=sumofxy1+(1/(valuex[C]-valuey[C])*(valuez[C]/(constant*valuey[C])));
b1:=(value*sumofxy1-sumofx1*sumofy1)/(value*sumofxsqr1-sqr(sumofx1));
end;
writeln ('The multi component Langmuir
equation=',constant:6:3,'Ce1/(1+',b1:6:3,'Ce2)');
end;

{Prompts and extracts values for calculating mass transfer coefficient}
procedure masstransfer (var v1,v2,v3,v4,v5,v6,v7,v8,v9,v10,v11,v12:real);

const
v13=0;
begin
write ('Enter the density of the resin (kg/m^3):');
readln (v1);
writeln;
write ('Enter the volume of the reactor (m^3):');
readln (v2);
writeln;
write ('Enter the particle diameter (m):');
readln (v3);
writeln;
write ('Enter the mass of resin (kg):');
readln (v4);
writeln;
write ('Enter the initial concentration (ppm):');
readln (v5);
v10:=ln(v5/v5);
writeln ('Enter the time (s):',v13:2);
writeln;
write ('Enter the concentration of the second sample (ppm):');
readln (v6);
v11:=ln(v5/v6);
write ('Enter the time elapsed before the second sample (s):');
readln (v7);
writeln;
write ('Enter the concentration of the third sample (ppm):');
readln (v8);
v12:=ln(v5/v8);
write ('Enter the time elapsed  before the third sample (s):');
readln (v9);
end;

{Calculates masstransfer coefficient}
procedure massstats(var v14,v15,v16,v17,v18,v19,v20,v7,v9,v10,v11,v12:real);

const
v13=0;
number=3;

begin
v14:=v13+v7+v9;
v15:=v10+v11+v12;
v16:=Sqr(v10)+Sqr(v11)+Sqr(v12);
v17:=Sqr(v13)+Sqr(v7)+Sqr(v9);
```

```
v18:=v13*v10+v7*v11+v9*v12;
v19:=(v13+v7+v9)/number;
v20:=(v10+v11+v12)/number;
end;

procedure masstrendline (var b,v21,v22,v23,v24:real);

const
number=3;

begin
b:=(number*v21-v22*v23)/(number*v24-Sqr(v22));
end;

{Displays mass transfer coefficient}
□
function masstransfercoefficient (var b,v1,v2,v3,v4:real):real;

begin
masstransfercoefficient:=(b*v1*v2*v3)/(6*v4);
end;


begin
while calc<>0 do
begin
writeln;
writeln ('     ****************************************************');
writeln ('     *ENTER EQUIVALENT NUMBER FOR SPECIFIC CALCULATION, *');
writeln ('     *TO END CALCULATION ENTER (0).                     *');
writeln ('     ****************************************************');
writeln;
writeln ('1:Mass transfer calculation.');
writeln ('2:Freundlich isotherm calculation.');
writeln ('3:Langmuir isotherm calculation.');
writeln ('4:Freundlich multi component isotherm calculation.');
writeln ('5:Langmuir multi component isotherm calculation.');
writeln;
write ('Enter equivalent number:');
readln (calc);

if calc=1 then
begin
masstransfer
(density,volume,diameter,mass,conc1,conc2,time2,conc3,time3,yval1,yval2,yval3);
massstats(sumx,sumy,ysqr,xsqr,xy,xmean,ymean,time2,time3,yval1,yval2,yval3);
masstrendline (gradient,xy,sumx,sumy,xsqr);
writeln;
writeln ('The mass transfer
coefficient(kf):',masstransfercoefficient(gradient,density,volume,diameter,mass)
:10:8,'m/s');
end;


if calc=2 then
begin
experiments (array1,array2,value);
freundlichcalculation (array1,array2,value);
end;

if calc=3 then
```

```
begin
experiments (array1,array2,value);
langcalculation (array1,array2,value);
end;

if calc=4 then
begin
experiments (array1,array2,value);
experiments1 (array3,value);
multifreundlich (array1,array2,array3,value);
end;

if calc=5 then
begin
experiments (array1,array2,value);
experiments1 (array3,value);
multilangmuir (array1,array2,array3,value);
end;
end;
end.
```

APPENDIX D

PUBLISHED ARTICLE

WASTE TREATMENT AND ENVIRONMENTAL IMPACT IN THE MINING INDUSTRY
(M.A. Sánchez, F. Vergara and S.H. Castro. Eds.) University of Concepción.

THE RECOVERY OF CYANIDE BY ION EXCHANGE RESIN

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ABSTRACT

Cyanide is used extensively in the mining industry to leach gold and silver from their ores. This results in free cyanide and various other cyanide complexes reporting to the effluent streams of these operations. In this study the removal of these species from solution by means of ion exchange resins was investigated. Equilibrium conditions, kinetic parameters and the competitive exchange nature of the process was evaluated. From the results obtained it has been found that ion exchange resin could be used effectively to recover free cyanide and certain cyanide complexes from solution. Furthermore, it is believed that the cyanide could effectively be recovered and re-used in the process facilitating a decrease in operating costs and having a positive effect on the environment.

INTRODUCTION

Cyanide, in the form of calcium or sodium cyanide, is used extensively to leach gold and silver in the mining industry. Furthermore, due to equilibrium constraints and kinetic considerations, cyanide is added in excess to that required theoretically, resulting in free cyanide and cyanide complexes reporting to effluent streams (Stanley, 1987). In view of the fact that cyanide is highly toxic and fatal in small dosages, authorities have been forced to tighten plant discharge regulations. Thus gold producers have been made aware of the necessity to reduce the levels of these toxic species in plant discharge.

Although various methods exist whereby free cyanide may be destroyed, the cost effective recovery of these species have not been achieved on large scale in the mining sector (Lawr, 1929; McNamara, 1987; Avedesian et al., 1983). Moreover, certain cyanide complexes are highly stable and difficult to destroy (Smith and Mudder 1991).

The first phase of this study concentrates on the effective removal of free cyanide and certain cyanide complexes by various ion exchange resins. The second section, which falls outside the scope of this paper, deals with the recovery of the cyanide by means of an acidic stripping agent, evolving HCN gas, which is then recycled to the leaching stage.

THEORY

External Mass Transfer

When making the relevant assumptions, an expression for external film transfer in a batch reactor may be found (Van Deventer, 1984):

- The adsorbent particals are equivelant spheres
- Intraparticle diffusion is negligible during the initial stages of ion exchange
- Isothermal conditions during ion exchange
- Equilibrium exists at the solid-liquid interface

THEN:

$$k_f = \frac{\ln\left(\frac{C_0}{C_t}\right)}{t} \quad \frac{\rho dV}{6M}$$

Equilibrium

Single adsorbate equilibrium loading is frequently described by the Freudlich isotherm (Morris and Weber, 1962):

$$\underset{\sim}{Q}_e = AC_e^n$$

Provided the Freudlich isotherm describes the equilibrium loading of each individual species, the following may be used for a two component system (Sheindorf et al.,1981).

$$\underset{\sim}{Q}_{e,1} = a_1 C_{e,1}\left[C_{e,1} + B_{12} C_{e,2}\right]^{n1-1}$$

Furthermore, for multi-component equilibria, empirical correlations such as the Fritz and Schluender isotherm have been proposed (Fritz and Schluender, 1974).

EXPERIMENTAL

All experiments were conducted in a 1 liter baffled tank reactor using mechanical agitation at constant stirring speed. Also, experiments were conducted at a constant pH of 12 to eliminate HCN formation. Four different resins were evaluated and will be named A. B. C. and D to protect supplier interest. A volume of 1 ml resin, measured by the "tap method" was used an all experiments. Free cyanide, copper and nickel cyanide was recovered from solution and the recovery efficiency determined by mass balance by monitoring the solution concentration decay by means of an atomic absorption spectophotometer.

RESULTS AND DISCUSSION

Due to the limited length of the article it was decided to only list the results obtained when using the ion exchange resin that showed the most promising results in the cyanide recovery experiments. This resin will be named resin A.

EQUILIBRIUM PARAMETERS

It was found that the single component Freundlich isotherm best explained single adsorbate equilibrium conditions for the set of tests performed :

$$CN \quad : \quad Q_e = 0.39\, C_e^{1.1}$$

$$Fe\ Cyanide \quad : \quad Q_e = 6.0\, C_e^{0.23}$$

$$Cu\ Cyanide \quad : \quad Q_e = 10.4\, C_e^{0.32}$$

By inspection it becomes clear that the single solute recovery of copper cyanide is superior to that of iron cyanide recovery at low and high concentrations. Furthermore, the equilibrium values of free cyanide removal is superior at higher concentrations but inferior at lower equilibrium solution concentrations. These results were consistent to that obtained when the other ion exchange resins were used as exchange agents. These results are graphically shown in Figure 1.

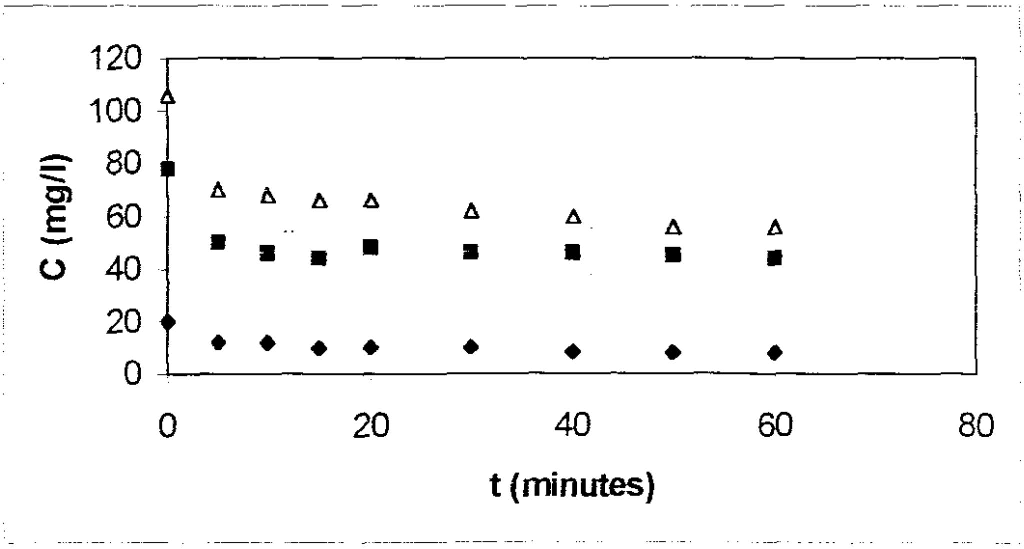

Figure I: Equilibrium loading of free cyanide and ion- and copper cyanide complexes

When copper- and iron cyanide were removed from an excess free cyanide solution, it was found that the effect of free cyanide could be ignored and that a two-component Freundlich-type isotherm described the competitive nature of the process adequately. Thus, free cyanide influence was minimal and it was not necessary to revert to the use of multi-component isotherms such as the Fritz and Schuendler isotherm. The following was obtained by using numeric techniques :

$$Q_{e.Cu} = 16.8\, C_{e.Cu}\left[C_{e.Cu} + 1.1C_{e.Fe}\right]^{0.2-1}$$

$$Q_{e.Fe} = 23.5\, C_{e.Fe}\left[C_{e.Fe} + 3.6C_{e.Cu}\right]^{0.06-1}$$

By analysing the above relationships it becomes clear that copper cyanide ion exchange has a much larger influence on iron cyanide exchange in the multi-component solution than the reverse. This is clear from the relatively large difference in the values of the competing factors, B_{12} and B_{21}. This result is consistent with results obtained by using any of the other ion exchange resins used.

Kinetic Parameters

Kinetics of ion exchange in all experiments conducted were found to be relatively fast. This is graphically illustrated for free cyanide recovery in Figure 2 where it becomes clear that equilibrium conditions are attained rapidly.

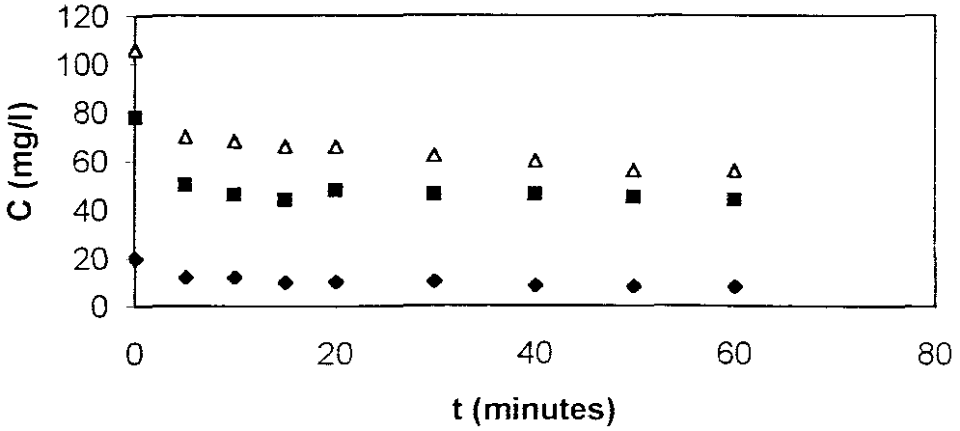

Figure ii: Solution decay of free cyanide

The mass transfer parameter, kf, obtained in various Copper- and Iron cyanide solutions are tabulated below. By closer investigation it becomes clear that the kinetics of Copper cyanide recovery is superior to that of Iron cyanide removal. This result is consistent with results obtained using resins B, C and D.

Table I: Mass transfer parameters for ion- and copper cyanide complexes

SPECIES	[INITIAL] mg.l^{-1}) Single adsorbate solution	[INITIAL] (mg.l^{-1}) Multi-component solution	k_f (m.s^{-1}) [x 10^5)
Fe cyanide	9.8		3.3
Cu cyanide	10.7		5.0
Fe cyanide	39.0		1.7
Cu cyanide	36.3		2.5
Fe cyanide		40.1	1.5
Cu cyanide		40.3	1.9

CONCLUSIONS AND FUTURE WORK

It has been found that free cyanide and copper- and iron cyanide complexes could be recovered from solution effectively in a batch configuration and that single solution ion exchange equilibria are well explained by the Freundlich isotherm. Furthermore, the kinetics of ion exchange is relatively fast with equilibrium attained within a short period of time. Copper cyanide complexes was found to have a larger equilibrium loading and higher mass transfer kinetics when compared to iron cyanide complexes over the whole range of ion exchange resins applied.

Future work will include the investigation of the regeneration process and effective recycling of the cyanide to the leaching stage.

Nomenclature

A	Constant
a	Constant
B	Constant
C	Solution concentration [mg.l^{-1}]
d	Resin particle diameter [m]
k_f	Mass transfer parameter [m.s^{-1}]
M	Mass of resin [kg]
n	Constant
Q	Equilibrium loading [mg.g^{-1}]
t	Time [s]
V	Volume [m^3]
ρ	Density [kg.m^{-3}]

e	Equilibrium