INVESTIGATION OF SOLVENT-EXTRACTION OPTIONS FOR ZINC RECOVERY FROM HIGH CHLORIDE SOLUTIONS FOR THE ANGLO RESEARCH ZINC PROCESS

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Declaration

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Abstract

Anglo Research (AR), a division of Anglo Operations Limited, is developing a chloride-based processing route for the recovery of zinc from sulfide ores. The Anglo Research Zinc (tARZn) process incorporates a chloride leach. Solvent extraction (SX) is being considered as a potential leach liquor purification option for the process. It is envisaged that the pregnant leach solution (PLS) will be sent to SX after which zinc will be recovered as plate metal and chlorine gas generated from an electrowinning step.

In this study, the critical experimental and solution parameters that affect extraction and stripping were investigated. Based on preliminary test work and a review of the literature, an anionic extractant (Alamine 336) and two neutral extractants (CYANEX 923 and tri-*n*-butylphosphate (TBP)) were chosen for further investigation for use in a chloride-based SX process. An important factor used to select these extractants was the nature of the extractable zinc species in the aqueous feed. The tetra-chloro zinc complex ($ZnCl_4^{2-}$) was identified as the dominant species in solution at the leach liquor compositions expected from the tARZn process. The tetra-chloro zinc complex can be extracted by the anionic extractant through an anion-exchange process. The neutral extractants are able to extract the tetra-chloro complex as a neutral species (H_2ZnCl_4) through a solvation process. To allow for a direct comparison of the performance of the extractants, it was envisioned that all extractants would be used at a concentration of 1 *M* in solution with a diluent (Shellsol A150). However this was not possible with Alamine 336 as at concentrations greater than 0.3 *M* it became too viscous and impractical to work with. The other two extractants were used at concentrations of 1 *M*. Synthetic solutions (with no impurities) were used in the study instead of leach liquors from leaching experiments so as to allow for easier solution analysis of the factors influencing extraction.

The study into the effects of the various solution parameters has shown that the extraction curves exhibit a maximum as a function of both zinc and chloride concentrations. The acid concentration ranges investigated were very narrow and at the high end of the range investigated by other authors in literature. The trend observed was one of decreasing extraction with increasing acid strength. Maximum zinc extraction was observed at around 1.0 *M* zinc in the feed and at a range of 1.8 to 4.7 *M* chloride in the feed. The tARZn leach solution, expected to be the feed solution to SX, has a solution composition of 1.0 *M* zinc, 5.2 *M* chloride and an acid concentration of 2.8 *M*. This feed solution composition is seen to fall within the range of feed zinc and chloride concentrations that would offer favourable and maximum zinc extraction. The acid concentration is believed to be on the high side such that it possibly would have a detrimental effect on the extraction.

Investigations to determine the stoichiometry of the extraction reaction and the nature of the extracted complex by the slope analysis method did not yield conclusive results. The results obtained using this method suggested stoichiometric factors of 1 for Alamine 336 and 2 for both CYANEX 923 and TBP, respectively. However, the molar ratio of extractant to zinc in the organic phase (at maximum zinc loading) obtained in the investigations of the various solution parameters suggest that the extraction reactions have stoichiometric factors of 2 for Alamine 336, possibly 2 to 3 for CYANEX 923 and possibly 6 to 9 for TBP. The investigation into the experimental and solution parameters that affect zinc extraction showed that CYANEX 923 is the best extractant of the three studied for this application. The highest loading capacity of 0.47 *M* zinc was obtained using CYANEX 923, compared with 0.17 *M* using Alamine 336 and 0.12 *M* using TBP.

Stripping was investigated using two strip liquors: distilled water and a 1 *M* sodium chloride (NaCl) solution. Stripping test work performed on Alamine 336 showed that stable emulsions were formed in the organic phase at the pH values investigated of 6, 7 and 8. Stripping of CYANEX 923 using distilled water was poor with a low loaded strip liquor concentration of 0.05 *M* zinc obtained. Stripping of CYANEX 923 with a 1 *M* sodium chloride solution was worse than with water. It was shown that TBP could be successfully stripped using both distilled water and a 1 *M* sodium chloride solution as strip liquors. Stripping efficiencies of up to 99% were obtained for both strip liquors with loaded strip liquors containing 0.73 and 0.62 *M* zinc for the distilled water and 1 *M* sodium chloride solution, respectively.

It has been shown that SX can be used to recover zinc from chloride solutions. TBP was chosen as the most suitable extractant for use in an SX step for the tARZn process. The main factor in selecting TBP over the other two extractants was the ease of stripping using distilled water. Although the extraction performances of the other two extractants were markedly better than TBP, their main disadvantages were that no suitable strip liquor was identified in this study.

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1.0 INTRODUCTION

Zinc metal is an important commodity in the global economy and is fourth in terms of world metal production by tonnage. The end use of zinc is mostly in the building and construction industry with other major end users being the automotive and household appliances industries. Initial zinc consumption mainly goes into corrosion protection by the process of galvanising (47%). It is also used to make brass (copper-zinc alloy) and bronze (primarily a copper-tin alloy) which account for 19% of the consumption, 14% is used for zinc alloys (for die-casting industries) and 9% for chemicals (British Geological Survey, 2008).

1.1 Primary Zinc Production

Current primary zinc production is dominated by the roast-leach-electrowinning (RLE) process. According to the Metals Economics Group (2009), global mine zinc refined production reached 11.7 million metric tons in 2008. It is estimated that up to 80% of the refined zinc production was *via* the RLE process. The RLE process uses zinc sulfide concentrate as feed stock which is first roasted to produce a zinc oxide calcine along with zinc ferrite and other minor phases. The calcine is then dissolved in a dilute sulfuric acid solution. The resulting zinc sulfate solution is then purified to remove metal impurities by processes of:

- pH adjustment, using calcine or basic salts of zinc as a base,
- cementation with zinc metal (in powder form together with activators such as copper, arsenic or antimony) to remove cobalt and nickel,
- and, if required, gypsum purification.

The purified solution is then electrowon to produce special high grade (SHG) zinc cathodes (99.995% minimum purity as prescribed by the London Metals Exchange) for melting and casting as final product (slabs and plates normally referred to as ingots).

One of the complexities of the RLE process is the link between zinc production and the sulfuric acid by-product. The sulfuric acid (or alternate sulfur chemicals) by-product is a result of the sulfur dioxide produced during roasting which has to be treated for environmental reasons. The residues produced by the RLE process are usually voluminous and require impounding which further increases the producer’s risk exposure to environmental liability. This has led to the development of a number of alternative processes for the treatment of zinc ores and concentrates. According to Pelser (2005), the following processes have been developed to treat zinc concentrates:

- Dynatec Zinc Pressure Leach Process,
- Union Minière Direct Leach Process,
- Outokumpu Concentrate Leach Process,
- MIM Albion Process,
- MIM Bioleaching Process (Biozinc).

Apart from the MIM bioleaching process where sulfur is rejected as gypsum, all of the processes are direct leaching methods whereby sulfur is rejected as elemental sulfur during leaching (Pelser, 2005).

The Dynatec process is the most mature of these processes, having been commercially operated at Hudson Bay Mining and Smelting Company in Canada, and can be seen as proven technology. All the other processes are at atmospheric conditions and are marked by slow leaching kinetics. The Union Minière and Outokumpu processes have been developed as cost-effective methods of expanding existing RLE circuits without the production of additional sulfuric acid. The MIM Albion process relies on ultra-fine milling to improve the leaching kinetics while the MIM bioleaching process employs bacteria for the oxidative leaching of zinc sulfide. All of the atmospheric processes have been developed to provide a low capital cost alternative to pressure leaching.

In addition to the direct leaching of high grade zinc concentrates, the treatment of complex bulk concentrates, low grade ores, and oxide ores continues to attract interest. Approaches that have been considered for the treatment of these ores include:

- Low or medium temperature pressure leaching followed by conventional purification/ electrowinning or by solvent extraction (SX)/ electrowinning,
- Heap or stirred tank bioleaching with zinc SX/ electrowinning after iron removal,
- Co-processing of zinc sulfides and zinc oxides for acid balance and control,
- Chloride processing (INTEC Zinc Process).

The Modified Zincex process has been employed at Skorpion Zinc in Namibia. This process was developed by Técnicas Reunidas (TR) as an adaptation of their Zincex process originally developed to extract zinc from impure chloride leach solutions. In the Skorpion flow sheet, the oxidised silicate minerals are leached using sulfuric acid. The solution is then purified by pH adjustment (to remove iron, aluminium and silica) followed by zinc recovery using SX which rejects impurities that are deleterious to electrowinning and upgrades the dilute leach liquor from 30 g/l Zn to an advance electrolyte of greater than 90 g/l Zn which is suitable for electrowinning. According to Cole and Sole (2002), the use of SX enables the entire process stream to be treated for the selective recovery of zinc using a single SX circuit. This means that the impurity-removal operations are small, treating only a bleed stream of the main circuit, rather than the entire process stream as in traditional flow sheets (Cole and Sole, 2002).

1.2 Secondary Zinc Production

Due to growing environmental concerns, many governments have made it obligatory to treat effluents and flue dusts to stipulated limits before being discharged into the environment. This has resulted in development of recycle plants to recover zinc from secondary sources. The main sources of zinc recycling are illustrated in Figure 1-1. Brass scrap and galvanising residue account for almost 70% of the recycled zinc.

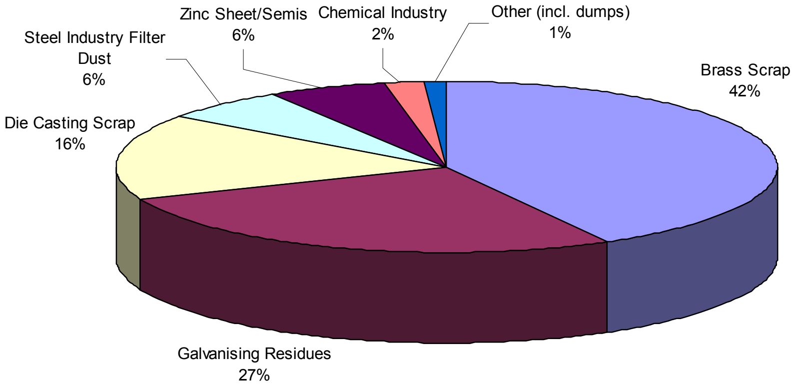


Figure 1-1 Main sources for zinc recycling (International Zinc Association, 2004).

Pyrometallurgical processes have been implemented for the treatment of secondary sources but these are limited in efficiency due to the strict requirement of a constant feed composition which is not always possible with secondary or recycled resources. Their economic viability also depends on a high production capacity. A number of hydrometallurgical processes have been developed as alternatives and implemented to overcome these constraints. TR has been at the forefront of developing processes to treat secondary sources of zinc. TR's Zincex technology was implemented in 1975 by Metalquímica del Nervion (MQN), Spain, for the recovery of zinc from secondary sources such as pyrite (Nogueira *et al*., 1979; Nogueira *et al*., 1980). The plant situated in Bilboa, Spain, produced 8000 t/a of zinc having a purity of 99.99%. The Quimigal plant, situated in Barreiro, Portugal, also used the Zincex process to treat secondary zinc (Nogueira *et al.*, 1982). Built in 1980, the plant had a design capacity of 11 500 t/a zinc. Both of these plants have now closed.

1.3 Solvent Extraction in Zinc Processing

Base metals such as copper, nickel and cobalt have benefited from the incorporation of SX processes in their flow sheets. This has led to higher production capacities at reduced capital and operating costs. SX has not yet achieved the same impact in processing of primary zinc sources. In contrast, zinc SX is well established in the refining of other base metals, employed mainly as a technique of eliminating zinc as an impurity. However, in recent times, the focus has changed to recovering the zinc as a by-product. One of the main obstacles in process development for zinc processing is the stringent electrolyte specifications required in the electrowinning process to produce SHG zinc. This is due to the fact that elements such as copper, cobalt and nickel have an adverse effect in the electrowinning performance of a zinc cell house. The successful implementation of SX at Skorpion Zinc, as the first plant to use SX for the recovery of zinc from a primary source, has shown the potential benefits SX could have on zinc processing (Cole and Sole, 2002).

Developments in SX for zinc processing have focused on delivering a sulfate-based zinc electrolyte to allow the conventional electrowinning of SHG zinc. Although there have been developments of improved and new organic extractants, coupled with the development of new materials of construction that can handle the corrosive nature of chloride solutions, there is still no commercial process that uses a zinc chloride SX process for the production of zinc. However, it is expected that the development of these processes is expected to grow in importance with the development of chlorine and hydrochloric acid leaching processes.

Several processes working in a chloride medium have been proposed in the past and tested up to pilot-plant scale. The most prominent of these are the Zincex and Zinclor processes, both developed by TR. A lot of research and development work has gone into extracting zinc from secondary sources and recycling of zinc. The removal and recycling of zinc from these sources is seen as a key environmental issue. A number of the proposed processes have incorporated SX as a means of recovering zinc in an environmentally friendly manner.

1.4 Scope of this Study

Anglo Research (AR), a division of Anglo Operations Limited, is developing a chloride-based processing route for the recovery of zinc from sulfide ores. The Anglo Research Zinc (tARZn) process incorporates a chloride leach. The pregnant leach solution (PLS) is sent to SX after which zinc is recovered as plate metal and chlorine gas is generated from electrowinning. A bleed stream is taken off for impurity removal. A simple block diagram of the process is given in Figure 1-2.

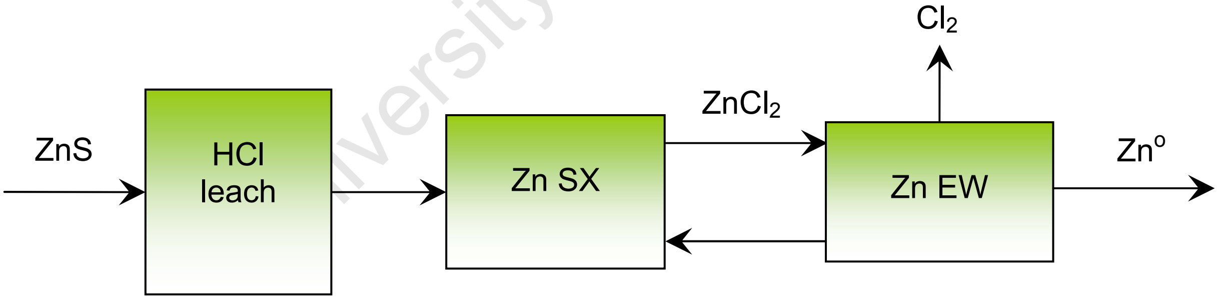


Figure 1-2 Simplified flow diagram of the core of the Anglo Research Zinc process.

One of the current objectives of the project, to further assist in the development of the tARZn process, is to achieve confidence and knowledge levels required for the design of a project-specific piloting exercise. To achieve this objective, it is necessary to investigate leach liquor purification options for the tARZn process. One of the unit operations being considered for the tARZn process is SX.

The purpose of this study is to develop an SX system suitable for the recovery of zinc from high-chloride leach liquors in the tARZn process. It is currently envisaged that zinc electrowinning will be conducted in a chloride-based electrolyte and therefore it is desirable that the SX step generate the required electrolyte solution. To achieve this goal, the study will focus on the following parameters:

- Selection of a suitable extractant that offers selective and quantitative extraction of zinc from chloride solutions,
- Investigate the effect of zinc, chloride, acid and ferrous concentrations on zinc extraction,
- Investigate the stoichiometry of the extraction reaction and determine the nature of the extracted complex,
- Identify an appropriate strip liquor and optimise the stripping characteristics.

From the above-mentioned areas of focus, the aim is to identify the critical experimental and solution parameters that affect the extraction and stripping characteristics. This work will determine the suitability of SX as a purification step in the development of the tARZn process.

To simplify the investigation and to allow for ease of analysis of the various parameters being investigated, it was decided to conduct all test work using synthetic solutions instead of using actual leach solutions generated from leaching experiments. The synthetic solutions are of a similar composition to the leach solutions generated in the leaching experiments.

2.0 LITERATURE REVIEW

Although chloride routes for the treatment of sulfides have been known for over a century, few of them have been commercialised due to the associated corrosion problems (Cole and Sole, 2002). There have been several processes proposed that incorporate SX as the purification step before proceeding to electrowinning. Técnicas Reunidas have been at the forefront of developing these processes with their Zincex and Zinclor processes.

Several studies have been carried out on the use of SX to selectively extract and separate zinc from chloride solutions using different extractants. Most of the reported work in literature has focused on extracting zinc from secondary sources such as spent pickling solutions from hot-dip galvanising plants. The removal of zinc from these solutions is seen as a key environmental issue. Hot-dip galvanising is a process used to provide a metallic coating of zinc onto various types of steel. This is done in order to improve their corrosion resistance. Prior to the coating, the surfaces are pickled using hydrochloric acid (HCl) solutions to remove rust and clean the surface. In some instances, pickling solutions are used to remove poor zinc coatings. Legislation places a limit on the allowable zinc and chloride levels in waste water and these solutions have to be further treated before being discharged. The Ruthner process is the traditional route that has been used to treat the spent pickling solutions. This is a pyrohydrolysis process which involves the evaporation of HCl and the formation of granules of iron oxides at temperatures of up to 800°C (Regel *et al.*, 2001). This process is seen as environmentally unfriendly and limited to solutions containing less than 0.5 g/l zinc. Some plants have used lime to precipitate zinc and iron hydroxides but, in this case, special sealed landfills are required for the disposal of the toxic elements contained to prevent them from penetrating the soil and ground water (Grzeszczyk and Regel-Rosocka, 2007). SX is seen as a possible solution to develop an environmentally friendly process to recover zinc from the pickling solutions.

The review of literature has highlighted the important and critical findings reported from the various studies. Particular focus was given to findings that can be used in assisting the development of an SX process for the tARZn process. The work reported in literature shows a particular attention to the recovery of zinc from secondary sources, such as spent pickling solutions from hot-dip galvanising plants, with very little work reported on the primary processing of zinc from ores or concentrates. Nevertheless, the work reported in literature, though limited in terms of reporting on stripping data and process development, provides valuable information on the challenges faced in using SX to recover zinc from chloride solutions.

2.1 Aqueous Speciation and Choice of Extractants

An important consideration to take into account in SX is the nature of the extractable metal species in the aqueous feed. This plays an important role in selecting the appropriate extractant to be used. A review by Jha *et al*. (2002) on the extraction of zinc from complex chloride solutions concluded that zinc could be extracted using acidic (cationic), basic (anionic), solvating, or a mixture of these extractants. A suitable organic solvent composition could be used to selectively extract and separate zinc from solution depending on the concentration, acidity and constituents present in the aqueous feed solutions (Jha *et al*., 2002). Some of the factors that influence these observations are discussed in the following sections.

2.1.1 Aqueous speciation

Figure 2-1 shows the speciation diagram for zinc at different chloride concentrations. The diagram was calculated using the stability constant data from Ruaya and Seward (1986). These stability constant data was determined from solutions containing 0.1 *M* zinc. At chloride concentrations below 1 *M*, the dominant species are $ZnCl_2$ and $ZnCl^+$. At a concentration of 1 *M* Cl^-, the main species are $ZnCl_4^{2-}$, $ZnCl_2$, and $ZnCl^+$. At chloride concentrations of greater than 1.5 *M*, the $ZnCl_4^{2-}$ species dominates.

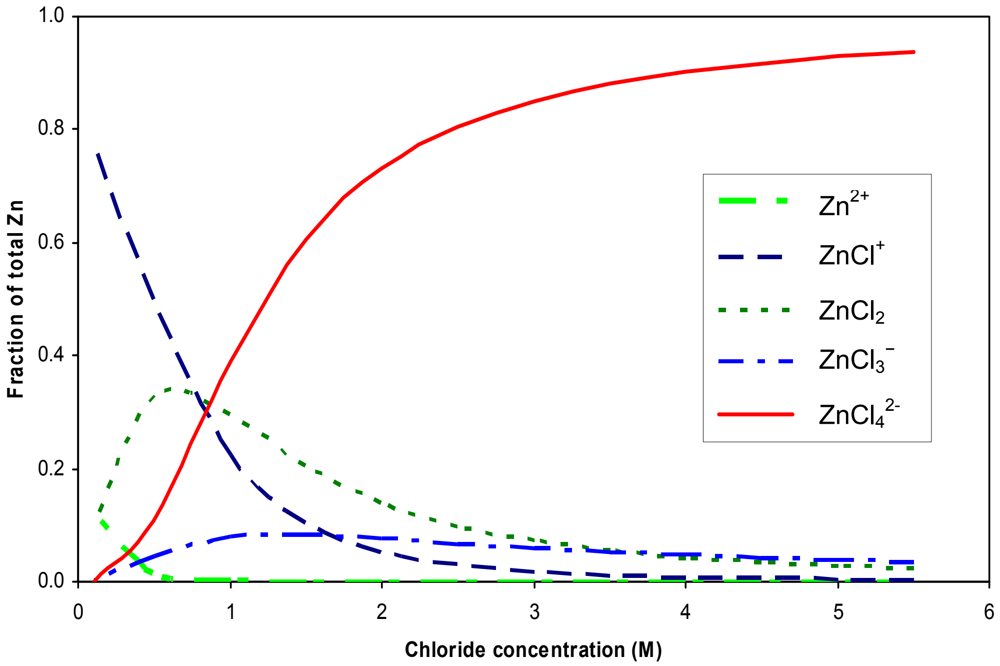


Figure 2-1 Speciation of zinc in chloride solutions at 100ºC in a solution matrix containing 0.1 M zinc (based on data from Ruaya and Seward, 1986).

Samaniego *et al*. (2006) summarised the distribution of zinc(II) chloro-complexes in aqueous solutions reported in the literature as reproduced in Table 2-1. The solution compositions presented in Table 2-1 were based on spent pickling solutions, mostly from hot-dip galvanising plants in Poland. It is evident from the data that the predominant zinc species at various chloride and acidity (HCl) concentrations, in the solutions investigated in the literature, was identified as the $ZnCl_4^{2-}$ species. The data also indicates that various combinations of zinc, chloride and acid concentration will yield different dominant zinc species. The work done by Miesiac and Szymanowski (2004) shows that at a lower chloride concentration (at the same zinc and acid concentration), the $ZnCl_4^{2-}$ species decreased from over 90% to approximately 50%. The amount of $ZnCl_3^-$ species increased from less than 10% to over 30%. It can be deduced from the data that lower chloride concentrations will favour the formation of the $ZnCl_3^-$ species (and the other species $ZnCl_2$ and $ZnCl^+$). The data from the work done by Mishonov *et al*. (2001) shows that an increase in the zinc concentration resulted in a decrease in the amount of $ZnCl_4^{2-}$ (from 90% to less than 80%) when compared to the data from Regel *et al*. (2001). This was accompanied by an increase in the amount of $ZnCl_3^-$ species.

Table 2-1 Distribution of zinc(II) chloro-complexes in acidic solutions (from Samaniego et al. (2006)).

Reference	**Feed (*M*)**			**Distribution (%)**			
	Zn	**Cl^-**	**HCl**	**$ZnCl_4^{2-}$**	**$ZnCl_3^-$**	**$ZnCl_2$**	**$ZnCl^+$**
Regel *et al*., 2001	0.1	5	0.6 - 3.6	90	-	-	-
Mishonov *et al*., 2004	0.9	5.2	0.5 - 2.3	78	11	6	5
Cierpiszewski *et al*., 2002	0.0076	5		92	7	-	-
Niemczewska *et al*., 2004	0.3	5		92	8	-	-
Miesiac and Szymanowski, 2004	0.076	5	2.5	94	6	-	-
	0.076	3.4	2.5	54	34	10	2
	0.305	5	2.5	92	8	-	-
	0.305	3.8	2.5	49	36	0.12	3

The data in Table 2.1 highlights the fact that various concentrations of zinc, chloride and acidity will result in differing dominant zinc species. Although in most instances the $ZnCl_4^{2-}$ species is dominant, it is evident that in conditions where the molar ratio of zinc to chloride is less than the stoichiometric minimum of 4, then other zinc species become significant. Therefore the solution compositions are a major factor on the extraction of zinc and more specifically, the molar ratio of zinc to chloride is likely to influence the nature of the extractable species.

From the preliminary investigations conducted by Sole and Mathenjwa (2008) on leach liquors produced from the tARZn process, containing approximately 1 *M* Zn, 5.2 *M* Cl^- and 2.8 *M* HCl, zinc was identified to occur in solutions in multiple speciation states, both neutral and anionic. "The obvious choice for extractants would therefore be anionic-exchange extractants, neutral oxygen-donor extractants, and combinations thereof to purify and concentrate the zinc" (Sole and Mathenjwa, 2008).

Sole and Baloyi (2007) reported speciation diagrams for the main impurities expected in the tARZn leach liquors - ferric (Fe(III)), copper (Cu), lead (Pb) and manganese (Mn) - based on the data of Ringbom (1963). Figure 2-2 shows the speciation diagrams for these impurities as given by Sole and Baloyi (2007). It is evident from Figures 2-1 and 2-2 that, in the range of chloride concentrations of 4 to 6 *M*, zinc forms the most stable anionic complexes. Pb and Mn also complex with chloride to a high degree, indicating that these impurities might be co-extracted. The other metals exist predominantly as cationic or neutral species under these conditions. The obvious immediate choice of extractant would therefore be an anion exchanger.

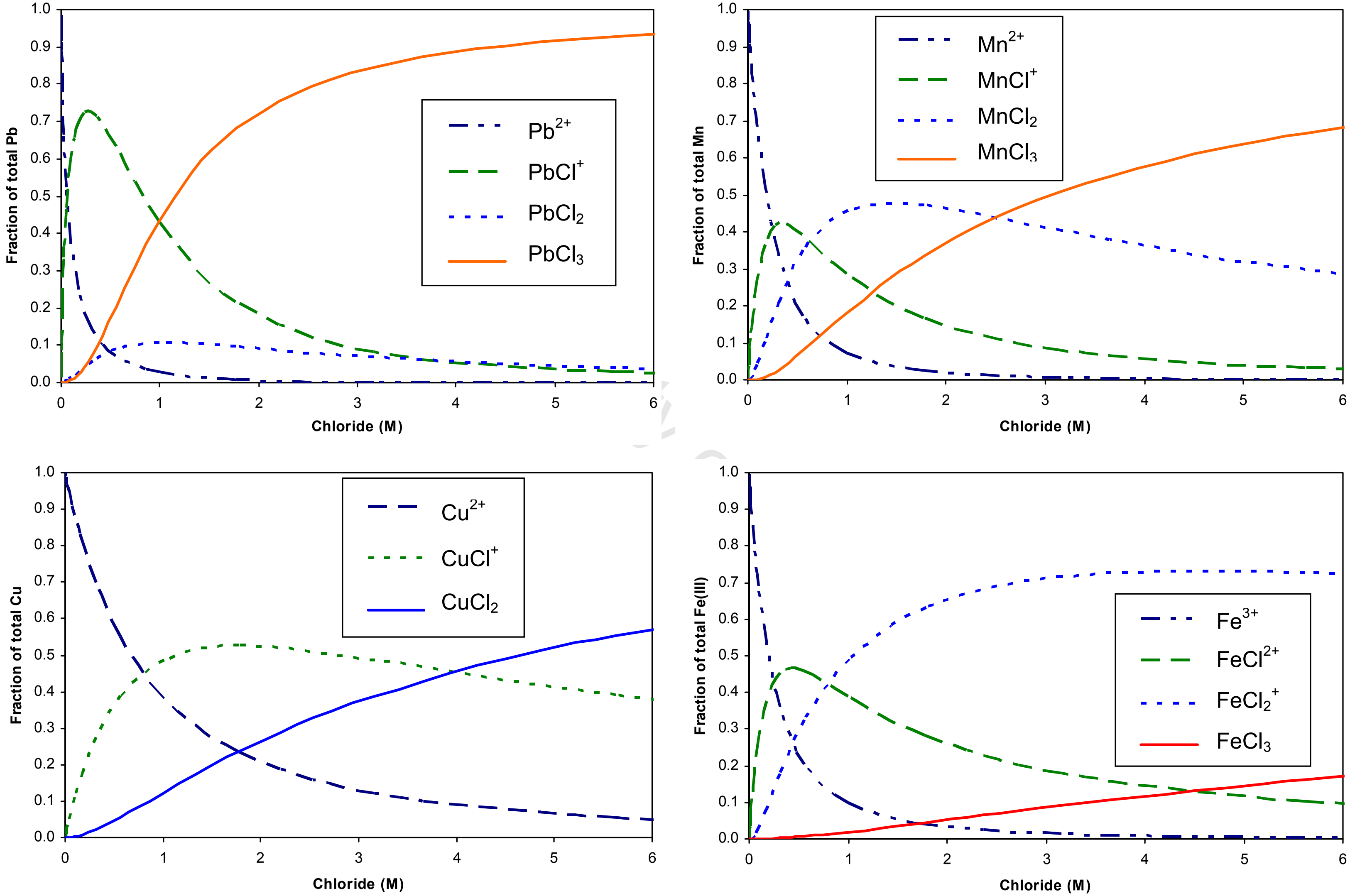


Figure 2-2 Speciation of Fe(III), Cu, Pb and Mn in chloride media, calculated from the data of Ringbom (1963) (from Sole and Baloyi (2007)).

2.1.2 Anionic extractants

According to Ritcey and Ashbrook (1984), anionic (basic) extractants are limited to amines and quaternary ammonium halides in commercial SX processing. The effectiveness of amines as extractants is largely dependent on the ability of the metal ions to form anionic complexes in the aqueous phase which can then be extracted by amines in an anion-exchange process (Ritcey and Ashbrook, 1984). The extraction reaction involving tertiary amine extractants (represented as R_3N) is given by equation 2-1.

$$ZnCl_4^{2-}\ (aq) + 2\ R_3NH^+Cl^-\ (org) \leftrightarrow (R_3NH)_2ZnCl_4\ (org) + 2\ Cl^-\ (aq) \qquad \textit{Eq. 2-1}$$

The amine requires protonation by acid before it can be used as an anion exchanger by equation 2-2, indicated for HCl in this case:

$$R_3N\ (org) + HCl\ (aq) \leftrightarrow R_3NH^+Cl^-\ (org) \qquad \textit{Eq. 2-2}$$

The extent of the exchange indicated in equation 2-1 is a function of the relative affinity of the two anions for the organic cation and the relative solvation energy of the anions by the aqueous phase.

Quaternary amines (represented as R_4NX) are characterized by a permanent positive charge, where the counter ion (X) is generally (but not necessarily) the chloride (Cl^-) species. The extraction reaction is as given in equation 2-3.

$$ZnCl_4^{2-}\ (aq) + 2\ R_4N^+Cl^-\ (org) \leftrightarrow (R_4N)_2ZnCl_4\ (org) + 2\ Cl^-\ (aq) \qquad \textit{Eq. 2-3}$$

Because of the permanent positive charge of the quaternary amine, it can extract anions over a wider pH range than the corresponding tertiary amines.

Regel-Rosocka *et al*. (2003) proposed that the extraction reaction could also be due to the mechanism of adduction of the neutral metal complexes as given in equation 2-4.

$$n\ HX + MX\ (aq) + n\ R_3N\ (org) \leftrightarrow (R_3NH)_nMX_{m+n}\ (org) \qquad \textit{Eq. 2-4}$$

It was suggested that the reaction above is most likely if the amines have not been pre-protonated before extraction (Regel-Rosocka *et al*., 2003).

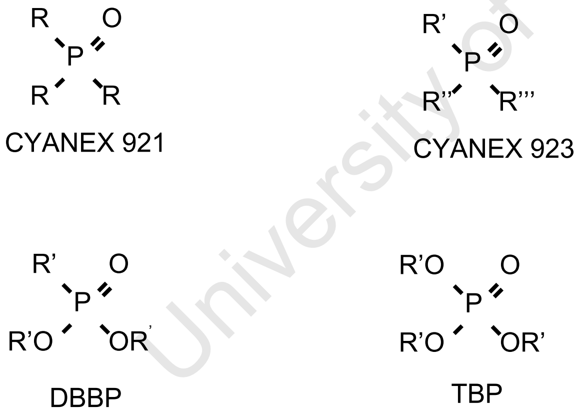
2.1.3 Neutral extractants

The reaction systems for these extractants are based on the solvation of neutral inorganic molecules or complexes by electron donor-containing extractants (Ritcey and Ashbrook, 1984). The oxygen of the phosphoryl group is responsible for the coordination bond formed with the metal. By means of this solvation, the solubility of inorganic species in the organic phase is increased. The reaction is given in equation 2-5.

$Zn^{2+} + n\ Cl^{-} + m\ L \leftrightarrow ZnCl_nL_m$ *Eq. 2-5*

Commercially available neutral extractants include CYANEX 921, CYANEX 923, dibutylbutyl-phosphonate (DBBP) and tri-*n*-butylphosphate (TBP), the basic structures of which are shown in Figure 2-3.

CYANEX 921 is tri-*n*-octylphosphine oxide (TOPO), while CYANEX 923 is a related phosphine oxide where the alkyl chains are a range of carbon chain lengths. The advantage of CYANEX 923 is that it is a liquid at room temperature, whereas CYANEX 921 occurs as a waxy solid. DBBP and TBP are analogues of the phosphine oxides. TBP, which is a tri-ester of phosphoric acid, consists mainly of OR groups while CYANEX 921 consists of R groups. The difference in the groups affects the extractive properties of the extractants. The OR group is electron withdrawing and the R groups are electron releasing and thus the R groups enhance the ability of the phosphoryl oxygen to coordinate to a metal (Ritcey and Ashbrook, 1984). It is therefore generalised that as the carbon-phosphorous bond number increases, the coordination ability increases (Ritcey and Ashbrook, 1984).



CYANEX 921

CYANEX 923

DBBP

TBP

Figure 2-3 General structures of some commercially available neutral extractants.

Samaniego *et al*. (2006) cited the following reactions in their study of the chemical equilibrium of the extraction of zinc(II) from a high acidic medium using TBP as an extractant. Stripping was carried out using service water based on spent pickling solutions.

$H_2ZnCl_4\ (aq) + 2\ TBP \leftrightarrow H_2ZnCl_4.2TBP\ (org)$ *Eq. 2-6*

$HZnCl_3\ (aq) + 3\ TBP \leftrightarrow HZnCl_3.3TBP\ (org)$ *Eq. 2-7*

$ZnCl_2\ (aq) + 2\ TBP \leftrightarrow ZnCl_2.2TBP\ (org)$ *Eq. 2-8*

It was suggested that reaction 2-6 is favoured for aqueous feed solutions of high acidity and it is enhanced by increasing acidity and chloride concentration. Reaction 2-7 was said to be significant at HCl concentrations of 0.8 to 2.7 *M* and it is shifted to the right with increasing acidity. It was suggested that reaction 2-6 dominates for concentrations of HCl and chloride below 0.8 and 1 *M*, respectively. It is important to note that the work was done using model dilute solutions, thus the trends given are general guidelines only.

2.2 Zinc Chloride Solvent-Extraction Processes

The hydrometallurgical processing of ores, concentrates and secondary sources in chloride media has potential due to the better leaching characteristics of chlorine and acid (Jha *et al*., 2002). Coupled with the development of better materials of construction that have improved the capability to handle the corrosive and volatile nature of this media, zinc recovery in chloride media is currently of great interest. Organic solvents are also being developed to selectively extract the desired metal species using SX processes. The studies on recovering zinc from spent pickling solutions focus on the selection of a suitable extractant with little information on stripping or on process development.

Currently there are no known plants that use a zinc chloride SX process for the production of zinc. A number of chloride-based SX routes have been proposed in the past, but few have been commercialised. Some of the proposed processes are discussed in the following sections.

2.2.1 Zincex and Modified Zincex Processes

Técnicas Reunidas developed technology that was used for the extraction of zinc from impure chloride leach solutions to produce an advance electrolyte suitable for conventional zinc electrowinning from a sulfate media. The Zincex process involves a two-stage SX operation. In the first SX stage, zinc chloride ($ZnCl_4^{2-}$) was extracted from a feed solution (50 – 60 g/l Zn) at 45 – 50ºC using a secondary amine, Amberlite LA-2.

$$2\ R_2NH_2Cl + ZnCl_4^{2-} \rightarrow (R_2NH_2)_2ZnCl_4 + 2\ Cl^- \qquad \textit{Eq. 2-9}$$

Species such as copper, cadmium, and iron that form anionic chloride complexes are also extracted, although selectivity from arsenic, nickel, cobalt, and lead was achieved. It was noted that the redox potential of the feed liquor must be less than 300 mV in order to obtain some selectivity from iron. After washing to remove entrained aqueous feed, the loaded solvent was stripped with water to give a zinc electrolyte containing 50 – 60 g/l Zn.

$$(R_2NH_2)_2ZnCl_4 + H_2O \rightarrow 2\ R_2NH_2Cl + Zn^{2+} + 2\ Cl^- \qquad \textit{Eq. 2-10}$$

In the second SX stage, zinc was extracted from the first-stage loaded strip liquor using di(2-ethylhexyl)phosphoric acid (D2EHPA) which was then washed with dilute acid to remove any entrained chloride ions and stripped into a sulfate-based spent electrolyte. The second SX circuit was selective for zinc over copper and cadmium, producing an advance electrolyte containing ~90 g/l Zn, 0.02 g/l Fe, and < 0.001 g/l Cu, Cd, Co, and As. Conventional electrowinning of zinc from sulfate media is possible and it was claimed that zinc cathode of 99.99% purity was achieved. This technology was implemented in 1975 by Metalquímica del Nervion (MQN), Spain, for the recovery of zinc from secondary sources such as pyrite (Nogueira *et al*., 1979; Nogueira *et al*., 1980). The plant, situated in Bilboa, Spain, produced 8000 t/a of zinc having a purity of 99.99%.

The Quimigal plant, situated in Barreiro, Portugal, also used the Zincex process to treat secondary zinc (Nogueira *et al.*, 1982). Built in 1980, the plant had a design capacity of 11 500 t/a zinc. Both of these plants have now closed.

In the Modified Zincex Process, only the second SX stage is included in the flow sheet. D2EHPA is used as the extractant, and the process treats sulfate liquors only. This process has been commercialised at the Skorpion Zinc plant in Namibia and is also planned to be implemented at the Dowa zinc refinery in Akita, Japan.

2.2.2 Zinclor Process

This process involves ferric chloride leaching of zinc concentrates followed by SX and electrowinning. Nogueira and Cosmen (1983) investigated di-*n*-pentylpentylphosphonate (DPPP) as an extractant for the Zinclor process. The extraction is proposed to take place *via* the solvation of $ZnCl_2$ as in reaction 2-11.

$$ZnCl_2 + 2\ DPPP \rightarrow ZnCl_2.2DPPP \qquad \textit{Eq. 2-11}$$

The distribution coefficients were shown to increase with increasing DPPP concentration (up to 1.6 *M*) and with increasing chloride concentration (up to 2.0 *M*, added as NaCl to the aqueous phase). Under the extremes of these conditions tested, organic-phase zinc loadings of up to 24 g/l were measured.

Stripping of the loaded organic phase is carried out with hot brine solution, giving a purified electrolyte of ~65 g/l Zn as $ZnCl_2$. It is also possible to strip using water. In practice, it was envisaged that stripping would be accomplished using spent electrolyte, which would have a composition of 30 g/l Zn and a sodium chloride (NaCl) concentration of 120 to 240 g/l. In the proposed flow sheet the spent catholyte would be sent to a SX step called the catholyte depletion section to remove the residual $ZnCl_2$ (Nogueira *et al*., 1983). In this section the spent catholyte is contacted counter-currently in several stages with the barren organic from the stripping section. The $ZnCl_2$ is almost completely extracted, resulting in an organic extract which is relatively low in $ZnCl_2$ which is sent to the extraction section. The aqueous raffinate from this section is an almost zinc-free NaCl solution which is pumped to the anodic compartment of the cell in electrowinning as the anolyte feed. The chloride ions are oxidised to chlorine gas on a dimensionally stable anode (DSA). The loaded strip liquor would be treated by electrowinning to produce zinc cathode and regenerate chlorine gas for recycle to leaching (Nogueira and Cosmen, 1983). It was reported that in the pilot-plant run at TR's Research Centre in

Madrid (results obtained for the period March to May 1983), the SX process consisted of two extraction stages, four stages for catholyte depletion and nine stages for stripping (Nogueira *et al*., 1983). The organic solution used was 50% DBBP in kerosene with DBBP being used instead of the proposed DPPP extractant because it is a commercially available reagent. The extraction and catholyte depletion stages were operated at ambient temperature of 18 to 25°C while the stripping section was operated at 50 to 60°C (Nogueira *et al*., 1983).

2.2.3 CENIM-LNETI Process

The CENIM-LNETI process proposed the use of concentrated ammonium chloride solutions to leach the non-ferrous metals (Zn, Cu, Pb, *etc*.) from bulk concentrates (Amer *et al*., 1995). In the CENIM-LNETI flow sheet, the extraction of zinc precedes the extraction of copper. Zinc extraction by SX would use D2EHPA modified with isodecanol. Due to the co-extraction of other minor metals to some extent, it was necessary to purify the organic phase by scrubbing the impurities from the loaded organic in two stages using a zinc chloride solution. The removal of chloride contamination from the organic phase is achieved by three washing stages before stripping the zinc from the loaded organic phase with spent electrolyte in three stages. The ammonia is fixed as metal amine complexes and provides the necessary neutralisation capacity for the acid released during the extraction of the metal ions. A great advantage of the process is the absence of iron in the leach liquors due to the high pH values (pH 6 to 7) used for leaching.

2.2.4 Recovery of zinc from spent pickling solutions

Lin (1993) studied the extraction reaction of zinc with DBBP in chloride solutions and identified the stoichiometric factors of each reactant and product. Escaid 110 (Exxon Co., Houston), an aliphatic hydrocarbon, was used as the diluent. In the studies of the effect of pH on zinc extraction, it was found that the extraction of zinc is independent of aqueous pH. The independence indicates that the mechanism of extraction is solvation. By using the slope analysis method it was determined that for the system of dilute zinc chloride solution, two moles of DBBP reacted with one mole of zinc. A series of tests was conducted to saturate the DBBP with zinc, with the initial concentration of DBBP at 1.87 *M*, the chloride concentration maintained at 7 *M* and the zinc in the aqueous feed varied from 0.0079 M to 2.76 *M*. A plot of the molar ratios of total DBBP to zinc in the organic phase at equilibrium against the concentration of zinc in the aqueous feed showed that the molar ratio of total DBBP to zinc in the organic phase decreased to 2 when the zinc concentration in the aqueous feed increased to 2.33 *M* and remained constant for higher aqueous feed concentrations of zinc. Additional tests were conducted with an initial DBBP concentration of 0.6 *M*. A similar curve was obtained with the molar ratio of total DBBP to zinc in the organic phase at equilibrium reaching a value of 2 at a zinc concentration in the aqueous feed of 0.71 *M* with the ratio remaining constant at 2 with further increases in the aqueous feed zinc concentration. The stoichiometric factor of the chloride ions in the extraction reaction was investigated by varying the chloride concentration from 1 to 3.5 *M*. Due to the fact that the amount of zinc extracted was negligible compared to the amount of DBBP (working with dilute solutions), the activity of free DBBP was considered to be constant. Activities of water and chloride ions under varying chloride concentrations were determined using a combination of published data and a number of assumptions. From this it was determined that the two moles of chloride ions and four moles of water were involved in the reaction per mole of zinc extracted.

Alguacil *et al*. (1999) studied the extraction of Zn(II) from chloride solutions using DBBP in Exxsol D100 in work similar to that done by Lin (1993). The solutions contained less than 10 g/l Zn(II) and a high chloride concentration of 7 *M* without any addition of acid. The predominant species was assumed to be $ZnCl_2$. They reported the distribution coefficient of zinc to be independent of equilibrium pH, thus suggesting a solvation extraction system. By slope analysis they determined the stoichiometric ratio of Zn to DBBP in the loaded organic to be 1:2. They also reported the stoichiometric factor of water to be 4 and indicated that two chloride ions were involved for each metal extracted. The findings of Alguacil *et al.* (1999) are in agreement with the work done earlier by Lin (1993) who reported similar findings in a study investigating extraction of zinc chloride with DBBP in Escaid 110. The extraction reaction proposed for DBBP is given in equation 2-12. The effect of other metals on zinc extraction efficiency was not taken into account in these studies.

$$Zn^{2+}(aq) + 2\ Cl^{-}(aq) + 2\ DBBP + 4\ H_2O \leftrightarrow ZnCl_2 2DBBP 4H_2O\ (org) \qquad \textit{Eq. 2-12}$$

Kirschling *et al*. (2001) studied the recovery of Zn(II) with TBP and CYANEX 923 from model HCl solutions. It was reported that Zn(II) can be recovered from HCl solutions with TBP both in extraction and membrane processes. It was also concluded that CYANEX 923 was too strong an extractant to achieve effective stripping. Stripping efficiency of CYANEX 923 was below 20% even when hot water was used in three consecutive strips.

Regel *et al*. (2001) investigated the recovery of Zn(II) from HCl spent pickling solutions using various extractants. The following reagents were used in the study: TBP, CYANEX 921, CYANEX 923, CYANEX 302 (bis(2,2,4-trimethylpentyl)monothiophosphinic acid) and Alamine 336. A low aromatic kerosene was used as the diluent. The aim of the work was to select a suitable reagent to recover Zn(II) from spent pickling solutions. Their work showed that the extraction improved with increasing extractant concentration and hydrochloric acid (up to 3.2 *M* HCl) for the solvating extractants. Extraction with CYANEX 923 was better than with CYANEX 921 for Zn(II) but there was negligible difference in their extraction abilities for Fe(III). In comparison to TBP, the CYANEX reagents extracted significantly more Zn(II) and Fe(III). It was reported that CYANEX 302 was relatively inactive. The study using Alamine 336 showed that both Zn(II) and Fe(III) were quantitatively extracted by the basic extractant from the hydrochloric acid solutions when used at appropriate molar excess, reported to be 7.2 and 2.4 mol/mol for Zn(II) and Fe(III), respectively.

Their next set of studies used aqueous feed containing 3.2 and 0.58 *M* HCl, 5 *M* Cl^-, 5 or 0.5 g/l Zn(II) and high amounts of ferrous (Fe(II)) at 50 g/l or Fe(III) at 30 g/l. TBP was used in undiluted form and CYANEX 923 and Alamine 336 as 1.44 *M* solutions in kerosene. The CYANEX 923 and Alamine 336 completely extracted the Zn(II) with negligible interference from the Fe(II). No precipitation was observed but it was found that the organic phase became more viscous with loading. It was also observed that the Alamine 336 extracted a significant amount of HCl. For the Alamine 336, precipitation of iron hydroxides was observed and poor phase separation occurred when the feed contained 0.58 *M* HCl. Although the CYANEX 923 also co-extracted some HCl, this did not lead to any precipitation or formation of third phases. Extraction of Zn(II) with TBP was above 90% with negligible interference from the Fe(II). Fe(III) was strongly extracted by the three extractants, with the extraction by CYANEX 923 amounting to 97 − 98% and Alamine 336 yielded between 92 and 100%. Higher extractions of Fe(III) were observed for the lower concentrations of hydrochloric acid. It was reported that for the strong extractants (CYANEX 923 and Alamine 336), the effect of HCl concentration on the extraction of Fe(III) was small. The extraction of Fe(III) did not lead to a decrease in the extraction of Zn(II) for Alamine 336 but a small decrease was observed for the CYANEX 923. The TBP showed a significant decrease in Zn(II) extraction, which was even higher with an aqueous feed containing 3.2 *M* HCl. The observation that iron ions were still extracted (20 to 30% for CYANEX 923 and Alamine 336 but low for TBP) when the feed contained only Fe(II) led to the deduction that there was possible oxidation of ferrous to ferric ions during the extraction process. It was deduced that trace amounts of undesired metal ions such as cobalt and nickel, which act as oxidation catalysts, could have been introduced during the synthesis processes for the extractants.

In the stripping work it was found that Zn(II) could easily be stripped from TBP by using water. The presence of iron did not disturb the process although three stages were needed to achieve greater than 95% efficiency for both Zn(II) and Fe(III). Stripping of Zn(II) from CYANEX 923 and Alamine 336 using cold and hot water, 1 *M* HCl or 1 *M* NaOH was not successful. The highest stripping efficiency that could be achieved for CYANEX 923 was when using 3 *M* NaOH and only 60% stripping was obtained. However, such a solution could not be used in the presence of iron as it resulted in precipitation of iron hydroxides in a colloidal form and the phases could not be separated. Stripping isotherms were determined by carrying out three successive stages of stripping using fresh water each time for the loaded TBP. It was observed from the stripping test work for TBP that stripping of Zn(II) was low in the first stage and higher in the second and third stages. The reason for the different stripping isotherms obtained was explained as being mainly due to the stripping of HCl in the first stage with the extracted complex changing from $H_2ZnCl_4.2L$ to $ZnCl_2.3L$, with L representing the solvating extractant. The liberation of the HCl resulted in a weaker complex and thus the Zn(II) stripping increased. TBP was thus chosen as the most suitable extractant as it could transfer zinc from the aqueous feed to the stripping solution with the best compromise between strong extraction ability and ease of stripping.

In work conducted to remove Zn(II) from spent hydrochloric acid solutions from zinc hot galvanizing plants, Cierpiszewski *et al.* (2002) reported that Alamine 336 and Aliquat 336 induced the oxidation of iron(II) to iron(III) and thus the co-extraction of iron was enhanced.

Regel-Rosocka *et al*. (2003) reviewed the extraction of Zn(II) in the presence of Fe(II) and Fe(III) with various basic and solvating reagents. They used various computing methods to determine the speciation of their model solutions consisting of Zn(II), Fe(II) and Fe(III) which they used to motivate the use of neutral and basic extractants for the recovery of Zn(II) from chloride solutions. They also indicated that the composition of the extracted complex can change in the counter-current process due to a change of chloride and HCl acid concentrations in the aqueous phase. It was suggested that when amines are used for Zn(II) extraction, the most probable mechanism is the adduction of a neutral metal complex. If the amine has been pre-protonated then the extraction mechanism is similar to that for the quaternary ammonium salts with an anion-exchange mechanism. It was implied that the stripping of zinc should be possible by changing pH, by using ammonia solutions for stripping from tertiary amines or by the use of excess chlorides in the case of quaternary salts. They cautioned that the adjustment of pH must take into account the possibility of the precipitation of iron, especially Fe(III) hydroxides. They recommended TBP as the best compromise which permitted both effective extraction of the zinc and stripping with water.

In later work, Regel-Rosocka *et al.* (2005) investigated DBBP (Rhodia, USA) as an extractant using Exxsol D 220/230 (ExxonMobil Chemical, Germany) as a diluent. A comparison between DBBP and TBP was made. Their work aimed to obtain more data on using DBBP as an extractant at Zn(II) concentrations of greater than 10 g/l. They also quantified the transfer of water to the organic phase and the effect of iron on Zn(II) extraction. Extraction isotherms from feed solution compositions of 0.1 to 50 g/l Zn(II), 0.58 *M* HCl and 5 *M* Cl^- indicated good extraction for both diluted and undiluted DBBP. The higher extraction capability of DBBP compared to TBP was demonstrated by the higher loading capacity of 60% volume DBBP compared to 80% TBP. This observation is consistent with theory as discussed earlier, with DBBP having more C-P bonds compared to TBP. The disadvantage is the higher solubility of DBBP in water due to the higher polarity of the phosphoryl group in the phosphonate molecule. A significant amount of water was transferred: about 6 and 9% volume in 80 and 100% volume DBBP, respectively. This was reported to increase up to 7 and 11% in 80 and 100% volume DBBP, respectively, on stripping with water. However in successive stripping steps, this did not change, suggesting that the organic phase had become saturated with water. It was suggested that addition of kerosene increases the hydrophobicity of DBBP without significant reduction of its extraction power.

The authors proposed the extracted species of zinc to be $ZnCl_4^{2-}$ with the complex formed with DBBP to be $H_2ZnCl_4.2DBBP$. Extraction of chloride ions observed in the 0.6 *M* HCl system corresponded to an amount of chloride calculated from HCl and Zn(II) transferred to the organic phase, assuming the extraction of $ZnCl_4^{2-}$. It was only in the case of a high initial Zn(II) concentration of 50 g/l that the determined amount was not consistent with that calculated. It was suggested that in this case the extracted species was $ZnCl_2$.

Fe(II) transfer to the organic phase was found to be higher than that for TBP although this had negligible effect on zinc extraction. Fe(II) extraction was found to increase significantly (over 40%) with an increase of organic-to-aqueous (O:A) volumetric phase ratio. High transfer of water to the organic phase was also observed. It was suggested that extraction of Fe(II) to the organic phase occurs by transport of metal cations in the water pool of reverse micelles as in the case of TBP (Regel-Rosocka and Szymanowski, 2005). Thus it was concluded that 80% volume DBBP could be used to selectively extract zinc from solutions containing Fe(II) in the following stages: extraction at an O:A phase ratio of

5:1 to recover 100% zinc and only 3.5% Fe(II), scrubbing with a small amount of water at an A:O phase ratio of 1:5 to remove Fe(II), followed by stripping with water at an O:A phase ratio of 1:1 to recover Zn(II).

Grzeszczyk and Regel-Rosocka (2007) studied the extraction of Zn(II), Fe(II) and Fe(III) from DBBP. A low aromatic kerosene, Exxsol D220/230, was used as the diluent in the experiments. They reported that a comparison of Zn(II) extraction isotherms of DPPB and TBP showed that extraction efficiency was higher for DBBP than for TBP. This is consistent with theory that the extraction effectiveness of neutral organophosphorus compounds depends on the polarity of the P-O bond and increases with the increasing number of C-P bonds. The higher hydrophilicity of DBBP compared to TBP was identified as the main disadvantage but this could be overcome by the addition of more diluent (kerosene in this case) which had the effect of increasing the hydrophobicity of DBBP without significant reduction in its extraction power. The investigators also observed co-extraction of hydrochloric acid which decreased with the following order of the accompanying metal ions: Zn(II) > Fe(II) > Fe(III) for 100 and 80% DBBP. The data provided evidence for the high capacity of DBBP to form complexes with HCl. Their findings showed the extracted species to be $ZnCl_2$ and $ZnCl_4^{2-}$ which is consistent with previously reported findings by other authors (Samaniego *et al*., 2006). The results calculated by the slope analysis method showed that for solution compositions of up to 20 g/l Zn, 1.8% (0.58 *M*) HCl and 5 *M* Cl^-, the predominant extracted species is $ZnCl_4^{2-}$ and for higher Zn(II) content in the feed $ZnCl_2$ is transferred to the organic phase. Stripping was carried out three times consecutively using fresh water each time. The stripping efficiency increased significantly in the second stage. This was explained by the co-extraction of HCl to the organic phase which is then preferentially stripped in the first stage with up to 0.35 *M* and 0.1 *M* HCl stripped in the first and second stages of stripping, respectively. After removal of the HCl, stripping of Zn was more effective in the successive two stages. It was also pointed out that DBBP was less corrosive towards steel and plastic compared to TBP.

2.3 Summary

From the review conducted it is noted that there are currently no known plants that use a zinc chloride SX process for the production of zinc. A number of processes have been proposed in the past, with the most prominent being the Zincex and Zinclor processes, both developed by Técnicas Reunidas. The Zincex process is a two-stage SX process that uses a secondary amine, Amberlite LA-2, to recover zinc as the zinc tetra-chloro species ($ZnCl_4^{2-}$) in the first stage. In the second SX stage zinc is extracted from the first stage loaded liquor using D2EHPA which is then washed with dilute acid to remove any entrained chloride ions, and stripped into a sulfate-based spent electrolyte. This process allows for conventional electrowinning of zinc from a sulfate medium. In the Zinclor process it was proposed to use DPPP to recover zinc as the neutral species $ZnCl_2$ and the loaded organic would be stripped using hot brine solution to produce a purified electrolyte of ~65 g/l Zn. In pilot-plant trials 50% DBBP in kerosene was used instead of DPPP as it is a commercially available reagent. The extraction was done in two stages while stripping was done using water in nine stages at temperatures of 50 to 60°C.

Studies into the recovery of zinc from spent pickling solutions from hot-dip galvanising plants have involved the evaluation of various extractants for zinc extraction from chloride solutions. Investigations to select a suitable extractant have involved the study of basic (anionic) extractants, Alamine 336 and Aliquat 336, and neutral extractants, such as CYANEX 921, CYANEX 923, TBP and DBBP. Although the studied anionic extractants could quantitatively extract zinc, they were eliminated as feasible extractants due to poor phase separation and the precipitation of iron hydroxides. This problem occurred when HCl acid was introduced into the model solutions.

From the review of the literature, it would seem the most appropriate extractants for investigation would be TBP and DBBP as they can efficiently extract zinc from chloride solutions and can be easily stripped using water. CYANEX 923 seems to be too strong an extractant to achieve effective stripping. Alamine 336 also appears to form strong emulsions that affect phase separation. The presence of Fe(II) had negligible effect on the extraction of zinc for TBP, DBBP and CYANEX 923 although co-extraction of Fe(II) was observed. Since there is also significant transfer of water into the organic phases for TBP and DBBP it was postulated that extraction of Fe(II) to the organic phase occurs by transport of metal cations in the water pool of reverse micelles. It was suggested that Fe(II) could be removed by scrubbing with water. The presence of Fe(III) has a negative effect on zinc extraction for the three extractants and is strongly extracted. It was advised that Fe(III) ion should be reduced to Fe(II) before extraction. Observations that Fe(II) was strongly extracted in some cases led to the deduction that there was possible oxidation of ferrous to ferric ions during the extraction process. TBP and DBBP could be effectively stripped using three stages of fresh water. Stripping was carried out three times consecutively using fresh water each time. The stripping efficiency increased significantly in the second stage. This was explained by the co-extraction of HCl to the organic phase which is then preferentially stripped in the first stage. This would suggest that there is a limit to the amount of HCl acid that can be tolerated in the feed solution to extraction.

3.0 EXPERIMENTAL METHODS

3.1 Reagents

3.1.1 Aqueous phase

Synthetic solutions of similar composition to that obtained from the tARZn process leach experiments were made up using analytical grade (AR) chemical reagents supplied by Associated Chemical Enterprises (ACE). The product data sheets for the various regents used to make the synthetic solutions are provided in Appendix A. For this study synthetic solutions of composition 66.7 g/l (1.0 *M*) Zn, 184 g/l (5.2 *M*) Cl, and 2.8 g/l (2.8 *M*) H^+) were taken as representative of the leach liquor that would be used as feed to the SX circuit based on the average final solution composition used by Sole and Mathenjwa (2008) in their preliminary investigations.

3.1.2 Organic phase

From the preliminary investigation, results indicated that the most suitable extractants were Alamine 336 (supplied by Cognis, Ireland) and CYANEX 923 (Cytec, Canada). Tri-butyl phosphate (TBP, supplied by Bayer, Germany) was also used for the investigation as literature cited it as the most suitable extractant. Organic phases were made up in the aromatic diluent Shellsol A150 (Shell Chemicals, South Africa). The aromatic diluent was preferred to aliphatic diluents due to its better solvation characteristics. Alamine 336 is a tertiary amine organic phase that requires protonation before being used for the extraction experiments. The protonation process ensures that the tertiary amine is in the acidic form which enables it to act as an anion exchanger. This was done by contacting the Alamine 336 at an O:A phase ratio of unity with 6 *M* HCl. CYANEX 923 and TBP were used as received. The data sheets for the organic reagents are also provided in Appendix A.

3.2 Extraction Experiments

Synthetic aqueous solutions for each set of experiments were made in batches of 250 ml. For each extraction experiment, 50 ml of the aqueous solution was used and the remaining 100 ml of solution was either used for repeat experiments, if required, or submitted as the feed sample for analysis. The CYANEX 923 and TBP organic phases were used at concentrations of 1 *M* which corresponded to 39.5% and 27.2% v/v, respectively, in Shellsol A150. Alamine 336 was used at a volume concentration of 14.8% v/v which corresponds to 0.3 *M*. This represents the maximum concentration that could be used for this extractant since at higher concentrations the organic phase becomes too viscous and impractical to handle. The extractant concentrations were chosen to be 1 *M* (with the exception of Alamine 336) to allow for simple and comparable analysis of the effect of the various parameters investigated in this study on a molar basis. The reasons for the chosen conditions are further explained in Section 3.6.

Extraction isotherms were measured by contacting the different aqueous phase solutions at O:A volumetric phase ratios of 1. Contact was carried out using magnetic stirring for 15 minutes at room temperature. On completion of the contact, the phases were allowed to separate in separating funnels. Each sample of the aqueous phase was analysed for Zn, Fe, Cl, Na and H^+. Each of the organic phase samples was analysed for Zn, Fe and Na. The operating procedures for the experimental work are provided in Appendix B.

3.2.1 The effect of feed zinc concentration on extraction

These sets of experiments were designed to saturate the extractants with zinc. This would allow the maximum loading capacity of the extractants to be determined as well as the molar ratio of zinc extracted in the organic phase to extractant. From this molar ratio it should be possible to deduce the number of extractant molecules involved in the extraction process.

A series of extraction experiments was carried out at various starting zinc concentrations. Table 3-1 gives the range of zinc concentrations used for the study. The solution composition used was 5.2 *M* (184 g/l) Cl^- and 2.8 *M* (2.8 g/l) H^+. The zinc concentration was varied using AR zinc chloride ($ZnCl_2$) and/or zinc nitrate hexahydrate ($ZnNO_3.6H_2O$) supplied by ACE. Hydrochloric acid (32% AR grade) was added to give the required acid concentration.

Table 3-1 Initial zinc concentrations for the extraction experiments to determine the effect of initial zinc concentration on extraction.

Test labels	**Zinc concentration**	
	(*M*)	**(g/l)**
Z1	0.01	0.5
Z2	0.02	1.0
Z3	0.04	2.5
Z4	0.08	5.0
Z5	0.15	10.0
Z6	0.30	19.6
Z7	0.50	32.7
Z8	0.80	52.3
Z9	1.00	65.4
Z10	1.50	98.1
Z11	2.00	130.8
Z12	2.50	163.5
Z13	2.75	179.8

To prepare solutions that have a lower zinc concentration than the base case solution, zinc chloride was used to adjust the zinc concentration to the desired level and hydrochloric acid was added to the specified acid concentration of 2.8 *M*. Sodium chloride was added to give the specified total chloride concentration of 5.2 *M*. To prepare solutions that have a higher zinc concentration than the base case solution, zinc chloride and hydrochloric acid were added to achieve the specified concentrations of 2.8

M H^+ and 5.2 *M* Cl^-. Zinc nitrate was added to make up the additional zinc required for the experiments. Zinc nitrate was chosen as a suitable reagent as it completely dissociates in solution and the nitrate ions are not expected to interfere or compete for ligands in the extraction reaction. The test labels for all experiments as well as the amount of reagents used to make up the synthetic solutions are provided in Appendix C.

3.2.2 Study of the effect of feed chloride concentration on extraction

To study the effect of chloride concentration in the feed solution on the extraction of zinc, a series of extraction experiments were conducted at various starting chloride concentrations. The synthetic solutions consisted of 1 *M* (66.7 g/l) Zn and 2.8 *M* (2.8 g/l) H^+. The chloride concentration was adjusted using sodium chloride (NaCl). Table 3-2 presents the various chloride levels that were investigated in the study.

Table 3-2 Initial chloride concentrations for the extraction experiments to study the effect of chloride concentration on zinc extraction.

Test labels	**Chloride concentration**	
	(*M*)	**(g/l)**
CL1	0.1	3.5
CL2	0.2	7.1
CL3	0.5	17.7
CL4	1.0	35.5
CL5	2.0	70.9
CL6	3.0	106.4
CL7	4.0	141.8
CL8	5.0	177.3
CL9	6.0	212.7
CL10	6.2	220.0

To prepare solutions that have chloride concentrations of 0.1 *M* to 2.0 *M*, zinc nitrate was added to achieve the specified zinc concentration of 1.0 *M.* Nitric acid was added to give the specified acid concentration of 2.8 *M*. Sodium chloride was used to adjust the chloride concentration to the desired levels. For the 3.0 *M* and 4.0 *M* solutions, zinc chloride was added to achieve the specified zinc concentration of 1.0 *M.* Nitric acid was added to give the specified acid concentration of 2.8 *M* and sodium chloride was used to adjust the chloride concentration to the desired levels. To prepare solutions of chloride concentration 5.0 *M* to 6.21 *M*, zinc chloride was added to achieve the specified zinc concentration of 1.0 *M* and hydrochloric acid was added to achieve the specified acid concentration of 2.8 *M*. Sodium chloride was used to adjust the chloride concentration to the desired levels. As discussed previously, zinc nitrate and nitric acid were chosen as suitable reagents as they completely dissociate in solution and the nitrate ions are not expected to interfere or compete for ligands in the extraction reaction.

3.2.3 The effect of acidity (pH) on extraction

To study the effect of acid concentration or pH of the feed solution on the extraction of zinc, synthetic solutions consisting of 1 *M* (66.7 g/l) Zn and 5.2 *M* (184 g/l) Cl^- were made. The acid concentration was adjusted using nitric acid (HNO_3). The various acid concentrations investigated in the study are provided in Table 3-3. The pH for the feed aqueous solutions and the equilibrium pH were taken upon completion of the extraction tests.

Table 3-3 Initial acid concentrations used to study the effect of acidity on zinc extraction.

Test labels	**Acid concentration**
	(g/l)
H1	0.25
H2	0.50
H3	1.00
H4	2.00
H5	3.00
H6	4.00

To prepare solutions at varying acid concentrations, zinc chloride was added to achieve the specified zinc concentration of 1.0 *M*. Sodium chloride was added to give the required concentration of 5.2 *M* total chloride. Nitric acid was used to adjust the acid concentration to the required levels for each experiment.

3.2.4 Investigation of the reaction stoichiometry and nature of the extracted complex

In order to determine the stoichiometry of the reaction and the nature of the extracted complex, a series of tests was conducted where the concentration of the extractants was varied. From the data obtained in this study, the slope analysis method was used to determine the number of extractant molecules involved in the extraction process. The slope analysis method is further explained in Section 3.7. Table 3-4 gives the various concentrations investigated for all three extractants studied in this work. A synthetic solution consisting of 1 *M* (66.7 g/l) Zn, 2.8 *M* (2.8 g/l) H^+ and 5.2 *M* (184 g/l) Cl^- was used for all the experiments.

Table 3-4 Extractant concentrations investigated to determine the reaction stoichiometry and nature of the extracted complex.

Alamine 336		**CYANEX 923**		**TBP**	
Concentration	**Volume**	**Concentration**	**Volume**	**Concentration**	**Volume**
(*M*)	**(%)**	**(*M*)**	**(%)**	**(*M*)**	**(%)**
0.02	1	0.3	10	0.3	8.2
0.04	2	0.6	25	0.6	16.3
0.1	5	1	39.5	1	27.2
0.2	10	1.5	59	1.5	40.5
0.3	15	2	79	2	54.5
		2.5	100	2.5	68.1
				3	81.7
				3.7	100

3.2.5 Investigation of the effect of iron(II) on extraction

A series of experiments was done to determine the effect of iron(II) in the feed solution on the extraction of zinc. Synthetic solutions consisting of 1 *M* (66.7 g/l) Zn, 2.8 *M* (2.8 g/l) H^+ and 5.2 *M* (184 g/l) Cl^- were made and AR grade ferrous chloride ($FeCl_2$) (supplied by Sigma, Germany) was used to adjust the iron(II) concentration. The various iron(II) concentrations investigated in the study are given in Table 3-5.

Table 3-5 Initial iron(II) concentrations for the extraction experiments to study the effect of iron(II) concentration.

Test Labels	**Fe(II) concentration**	
	(M)	**(g/l)**
F1	0.01	0.4
F2	0.02	0.9
F3	0.05	2.8
F4	0.08	4.3
F5	0.1	5.6

3.3 Stripping Experiments

The loaded organic used for the stripping tests was prepared as follows. A synthetic leach liquor consisting of 66.7 g/l (1.0 *M*) Zn, 184 g/l (5.2 *M*) Cl, and 2.8 g/l (2.8 *M*) was contacted with the organic extractants at an O:A ratio of 1:2. Contact was carried out using magnetic stirring for 15 minutes at room temperature. On completion of contact, the phases were allowed to separate and the aqueous phase was discarded. The remaining organic phase was again contacted with fresh synthetic leach liquor at an O:A ratio of 1:2, stirred for 15 minutes and then allowed to separate. The aqueous phase was discarded and the organic phase was then termed the loaded organic. The loaded organic was analysed as the head sample for the completion of the mass balance. All the stripping test work was carried out using this loaded organic.

For the CYANEX 923 and TBP stripping experiments, the following O:A ratios were used to produce the stripping isotherms: 0.1, 0.25, 0.5, 1, 2, 5 and 10. Two potential strip liquors were investigated: deionised water and a 1 *M* sodium chloride (NaCl) solution. The stripping of Alamine 336 was investigated at pH values of 6, 7 and 8. A 10 *M* sodium hydroxide (NaOH) solution was used to maintain a constant pH. The high concentration of sodium hydroxide was used to ensure that as little amount of solution as possible was added to alter the pH so that a phase ratio of unity was maintained. The operating procedures for the stripping work are provided in Appendix B.

3.4 Analytical Methods

The aqueous and organic analyses were carried out by de Bruyn Spectroscopic Solutions (Midrand, South Africa) by inductively coupled plasma optical emission spectroscopy (ICP-OES). Both aqueous and organic phases were analysed directly, using matrix-matched standards for calibration. The aqueous phase solutions were analysed for Zn, Fe, Cl and Na, while the organic phases were analysed for Zn, Fe and Na. Analysis for acid concentration in the aqueous phase was done by titration using the Metrohm 794 Basic Titrino, 776 Dosimats autotitrator using 0.1 *M* sodium hydroxide (NaOH) solution in the Acid Laboratory of the Anglo Research Technology department.

3.5 Mass Balance Calculations

The metal balances for Zn and Na were calculated as the mass ratio of the outgoing mass to the incoming mass. The outgoing mass is contained in the organic and aqueous phases after contacting and separation. The incoming mass is represented by the feed solutions (synthetic PLS) and the fresh organic phase. It was assumed that no significant volume changes occur after equilibrium and that enough time had been allowed for complete phase separation to occur. The chloride and proton concentrations could not be measured directly in the organic phase so these data were calculated by difference between the content in the feed and that in the aqueous phase after contact with the organic. Tests that yielded mass balances that deviated by more than 10% were flagged as being inaccurate but were not excluded from the reporting.

Metal extraction was calculated as the mass of zinc in the organic phase divided by the mass of zinc in the feed solution. Metal extraction could also be calculated as the mass ratio of the difference of metal in the feed and the raffinate aqueous solutions to the mass in the feed solution. If a mass balance is obtained then both these calculations should give similar results.

3.6 Analysis Using the Distribution Coefficient (D)

The distribution coefficient, D, is defined as the ratio of the total metal concentration in the organic phase to the total metal concentration in the aqueous phase. The distribution coefficient was calculated for Zn and Na for all the experiments. The distribution coefficient for Na was used as a check to ensure that Na was not interfering with the extraction process. For the other elements of interest it was not always possible to calculate the value of D as these elements were not directly measured in the organic phase and their values had to be calculated by mass balance of the system.

The distribution coefficient is a measure of how well a solvent will extract a metal. As defined it has no units and is not a constant. Factors that affect the distribution coefficient include:

- Phase ratio (O:A);
- Extractant concentration;
- Temperature;
- pH;
- Metal complexation in the aqueous and organic phases;
- Metal concentration in the aqueous phase.

Taking into account the above-mentioned factors, it can be inferred that the value of D by itself has no real meaning. Thus the conditions under which the results are obtained are important in making an analysis of how good an extraction system is. Ritcey and Ashbrook (1984) strongly emphasise that values of D are unique to a particular system and that comparison of different systems should only be done when the experimental conditions are identical for each system. Values of D alone cannot be used as a measure of the efficiency of the extraction system and therefore it is advised that considerable caution should be exercised when making comparisons of systems. Ritcey and Ashbrook (1984) however point out that despite these restrictions, the distribution coefficient, or log D, is the most widely used parameter in SX studies together with the loading capacity of the extractant.

In the studies described in Section 3.2, the impact of the factors described above was mitigated as follows:

- An O:A phase ratio of 1 was used for all the extraction experiments.
- The extractant concentration used was 1 *M* for Cyanex 923 and TBP. Alamine 336 was used at 0.3 *M* as this represents the highest concentration that can be practically used. At higher concentrations, the viscosity of the organic phase becomes a significant factor on the practical use of this extractant. The extractant concentration was only varied for the studies on the effect of extractant concentration.
- All experiments were conducted at room temperature.
- The starting pH of the aqueous feed solutions was the same except for the study of the effect of pH.
- Metal concentrations were kept constant except in the study of the impact of zinc concentration.
- Chloride concentration was also kept constant except in the study of the effect of chloride concentration. The chloride is important as it is responsible for complexation with the zinc in the aqueous solution.

Further to this, the feed solution for each condition investigated per study was prepared in bulk and used for all three systems to eliminate the possibility of variation of concentration that might occur if that for each experiment had been prepared separately.

3.7 Extraction Reaction and Mechanism

In this study it is expected that the tetra-chloro zinc species ($ZnCl_4^{2-}$) will be the main anionic species in the aqueous solution. This is based on the fact that the aqueous phase composition of the solutions to be tested are of high ionic strength (high zinc, chloride and acidity concentrations) which tends to favour the formation of the tetra-chloro species (see Section 2.1.1). Extraction for the neutral extractants (CYANEX 923 and TBP) is then expected to proceed according to the reaction given in equation 3-1 (Grzeszczyk and Regel-Rosocka, 2007).

$$2\,H^+_{aq} + ZnCl^{2-}_{4,aq} + n\,L_{org} \leftrightarrow H_2ZnCl_4 \cdot nL_{org} \qquad \textit{Eq. 3-1}$$

The equilibrium constant for reaction 3-1 can be written as follows:

$$K_{ext} = \frac{[H_2ZnCl_4 \cdot nL_{org}]}{[H^+]^2_{aq}[ZnCl_4^{2-}]_{aq}[L_{org}]^n} \qquad \textit{Eq. 3-2}$$

The stability constant for the $ZnCl_4^{2-}$ species is given by equation 3-3:

$$\beta_4 = \frac{[ZnCl_4^{2-}]_{aq}}{[Zn^{2+}][Cl^-]^4} \qquad \textit{Eq. 3-3}$$

This can be re-written to give:

$$[ZnCl_4^{2-}]_{aq} = \beta_4[Zn^{2+}]_{aq}[Cl^-]^4_{aq} \qquad \textit{Eq. 3-4}$$

The total zinc concentration, $[Zn]_{aq,t}$, is given by the sum of concentrations of all zinc forms in the aqueous phase as shown by equation 3-5.

$$[Zn]_{aq,t} = [Zn^{2+}] + [ZnCl^+] + [ZnCl_2] + [ZnCl_3^-] + [ZnCl_4^{2-}] \qquad \textit{Eq. 3-5}$$

By taking into account the stability constants of the individual complexes, equation 3-5 can be rewritten as equation 3-6.

$$[Zn]_{aq,t} = [Zn^{2+}]_{aq}\left(1 + \sum_{i=1}^{4} \beta_i [Cl^-]^i_{aq}\right) \qquad \textit{Eq. 3-6}$$

By substituting equation 3-4 into equation 3-2 the equilibrium constant is re-written as follows:

$$K_{ext} = \frac{[H_2ZnCl_4 \cdot nL_{org}]}{[H^+]^2_{aq}\beta_4[Zn^{2+}]_{aq}[Cl^-]^4_{aq}[L_{org}]^n} \qquad \textit{Eq. 3-7}$$

By rearranging equation 3-5 to get an expression for [Zn^{2+}] and substituting it into equation 3-7, equation 3-8 is obtained:

$$K_{ext} = \frac{[H_2ZnCl_4 \cdot nL_{org}]}{\dfrac{[H^+]_{aq}^2 \beta_4 [Zn]_{aq,t} [Cl^-]_{aq}^4 [L_{org}]^n}{\left(1+\sum_{i=1}^{4} \beta_i [Cl^-]_{aq}^i\right)}} \qquad \textit{Eq. 3-8}$$

Equation 3-8 can further be simplified to obtain equation 3-9.

$$K_{ext} \frac{\beta_4 [Cl^-]_{aq}^4 [H^+]_{aq}^2}{\left(1+\sum_{i=1}^{4} \beta_i [Cl^-]_{aq}^i\right)} = \frac{[H_2ZnCl_4 \cdot nL_{org}]}{[Zn]_{aq,t} [L_{org}]^n} \qquad \textit{Eq. 3-9}$$

The distribution coefficient is defined as

$$D = \frac{[H_2ZnCl_4 \cdot nL_{org}]}{[Zn]_{aq,t}} \qquad \textit{Eq. 3-10}$$

Substitution of equation 3-10 into equation 3-9 gives

$$K_{ext} \frac{\beta_4 [Cl^-]^4 [H^+]_{aq}^2}{\left(1+\sum_{i=1}^{4} \beta_i [Cl^-]_{aq}^i\right)} = \frac{D}{[L_{org}]^n} \qquad \textit{Eq. 3-11}$$

Taking logarithm gives:

$$\log K_{ext} + \log \frac{\beta_4}{\left(1+\sum_{i=1}^{4} \beta_i [Cl^-]_{aq}^i\right)} + 4\log[Cl^-]_{aq} + 2\log[H^+] = \log D - n\log[L_{org}] \qquad \textit{Eq. 3-12}$$

Introducing a constant K:

$$K = K_{ext} [Cl^-]^4 [H^+]^2 \frac{\beta_4}{\left(1+\sum_{i=1}^{4} \beta_i [Cl^-]_{aq}^i\right)} \qquad \textit{Eq. 3-13}$$

Using the constant K allows the equation 3-12 to be simplified to equation 3-14.

$$\log D = \log K + n\log[L_{org}] \qquad \textit{Eq. 3-14}$$

Equation 3-14 is a linear equation from which the slope, n, can be determined by plotting logD against log[L_{org}]. This value of n corresponds to the number of extractant molecules involved in the extraction process. This value can be determined experimentally by varying the extractant concentration at constant pH and chloride concentration. Similarly, the number of protons involved in the extraction process can be determined from a plot of pH versus logD at constant extractant and chloride concentrations. The number of chloride ions can also be determined by a plot of logCl^- versus logD at constant pH and extractant concentration. The various plots discussed represent the slope analysis method which is generally used to determine the stoichiometry of the extraction reaction. It can also be deduced from equation 3-12 that increasing the chloride concentration and pH (decreasing proton concentration) should result in an increase of the distribution coefficient and thus zinc extraction should increase.

In deriving equation 3-14, the species concentrations have been used which assume an activity coefficient of unity. This assumption is, strictly speaking, only valid for ideal solutions (dilute solutions). The equation might not be valid for solutions with high ionic strength. However, it is hoped that the equation can be used to give an indication of the nature of the extracted complexes though it might not give the linearity that is observed for dilute solutions. An appropriate approach would be to derive the equation using activity coefficients as the general case. Activity coefficients would then be required for the chloride and protons in these solutions. Activity coefficient data are not readily available for high ionic strength solutions such as the ones being investigated. The Debye-Huckel theory can be used to calculate activity coefficients but that still would not yield accurate results. The activity coefficient would only provide an indication of the deviation from unit activity coefficient. The Pitzer model would probably give better results but an attempt to use this approach in this study would result in work that would move beyond the scope of this project.

The extraction reaction for the anionic extractant, Alamine 336, is expected to be according the reaction given by equation 3-15. This reaction shows that acid concentration (pH) should not be a significant factor in the extraction of zinc. Also it should be evident that if the amine was protonated using hydrochloric acid, then increasing chloride concentration will result in the reverse reaction being favoured resulting in lower zinc extraction.

$$ZnCl^{2-}_{4,aq} + 2\,R_3NH^+Cl^-{}_{org} \leftrightarrow R_3NH^+ZnCl_{4,org} + 2\,Cl^-_{aq} \qquad \textit{Eq. 3-15}$$

4.0 RESULTS

The detailed results for all the experimental work are given in Appendix C. Included in the results are the raw chemical analyses, the mass balance and extraction calculations. Other calculated parameters such as the distribution coefficient, average accountabilities of the metals, standard deviations and molar ratios of various elements are included as well.

4.1 Zinc Extraction at Various Initial Metal Concentrations

Figure 4-1 gives a plot of the distribution coefficient as a function of the aqueous feed zinc concentration. The distribution coefficients for CYANEX 923 and Alamine 336 are an order of magnitude higher than for TBP. This is consistent with the work reported by Kirschling *et al*. (2001). These authors further suggested that undiluted or highly concentrated TBP must be used to obtain a high level of extraction. Isotherms produced from their work showed that the concentration of TBP must be at least 80% and zinc concentration in the feed must be below 20 g/l.

It can be seen from Figure 4-1 that the feed zinc concentration has a pronounced effect on the distribution coefficients for the Alamine 336 and CYANEX 923. The distribution coefficient initially increases up to initial zinc concentrations of 0.08 and 0.15 *M* for Alamine 336 and CYANEX 923, respectively, and then decreases. The effect of zinc concentration on the distribution coefficient for TBP is not as noticeable as for the other two extractants. It shows a linear decrease of an order of magnitude throughout the range of concentrations investigated. These results are in line with expectations as it was anticipated that with increasing feed zinc concentration the zinc extracted will increase until the extractants become saturated with zinc at their maximum loading capacity. Therefore the zinc in the organic phase should remain constant while that in the aqueous phase will increase, resulting in a decrease of the value of the distribution coefficient.

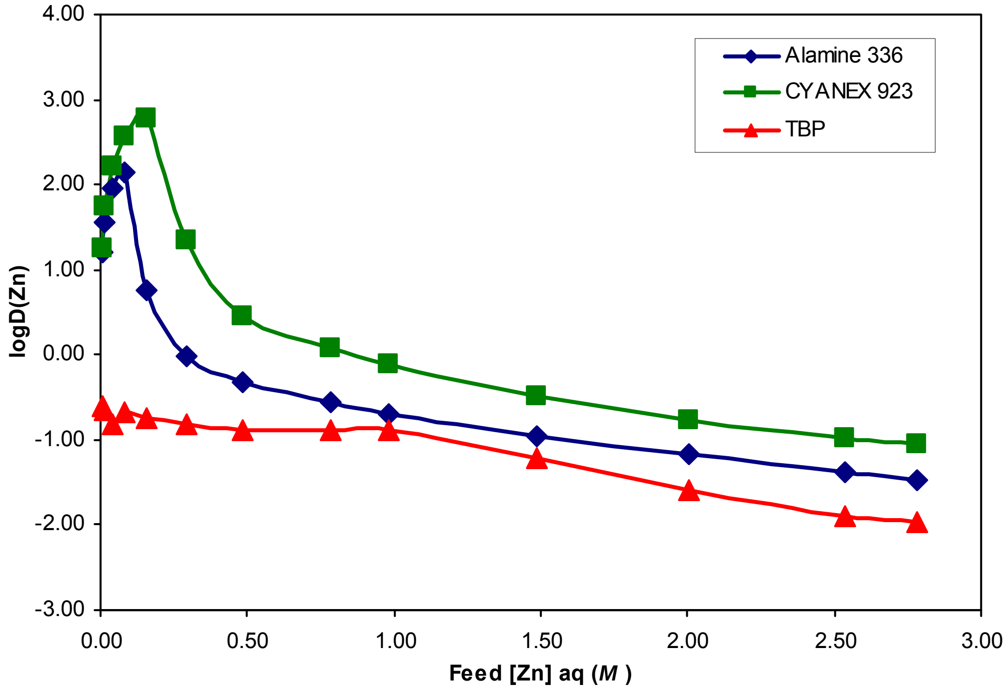


Figure 4-1 Effect of zinc concentration in the aqueous feed on the distribution coefficient for zinc.

Aqueous phase:	5.2 *M* Cl^- and 2.8 *M* H^+ at varying zinc concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

Figure 4-2 is a graphical representation of the effect of the zinc concentration in the aqueous feed on the molar ratio of the total extractant to zinc in the organic phase. For Alamine 336 and CYANEX 923, the molar ratio of total extractant to zinc in the organic phase decreased to approximately 2 when the zinc concentration increased to between 0.49 and 0.78 *M*, respectively. Contrary to what is reported in literature (Lin, 1993; Alguacil *et al*., 1999), the molar ratio increases as the zinc concentration increases above 1.5 *M*. For Alamine 336, the molar ratio increased to 3 at a zinc concentration of 2 *M*. The ratio for CYANEX 923 increased to 3 at a zinc concentration of 1.5 *M* and reached a ratio of 4 at 2.5 *M* zinc. For TBP, the molar ratio of total extractant to zinc decreased to 9 at 1 *M* zinc and then increased again to 30 at higher zinc concentrations. The molar ratio of total extractant to zinc is expected to reach a minimum value and to remain constant at that value with increasing zinc concentration in the feed as the extractants will be saturated with zinc and no additional metal can be extracted.

The molar ratio values of extractant to zinc of 2 obtained for the Alamine 336 system at initial feed zinc concentrations of between 0.15 and 1.5 *M* correspond to a stoichiometric factor of 2. Therefore it is most likely that the anionic species extracted by the Alamine 336 are the zinc tetra-chloro or tri-chloro species ($ZnCl_4^{2-}$ or $ZnCl_3^-$) or a mixture of both species. For CYANEX 923 the molar ratio is 2 at feed zinc concentrations of between 0.8 and 1.0 *M* and increases thereafter to values of 3 and 4. This supports the extraction of the neutral species H_2ZnCl_4 and $HZnCl_3$ as put forward by Samaniego *et al.* (2006) by two molecules of the neutral extractants, with further suggestions that they are the more likely species to be extracted at HCl acid concentrations greater than 0.8 *M*. The suggested species were from model dilute solutions and thus are applicable only as trends. For TBP the molar ratio of 9 does not conform to the expected extractable species as reported in literature. Suggestions have been made about the possibility of the extraction of the poly-nuclear zinc species of the form $Zn_2Cl_6^{2-}$ which can occur in high chloride media (Alves *et al.*, 2008), however data are not readily available for this species and it is not clear how many extractant molecules would be needed to extract this species.

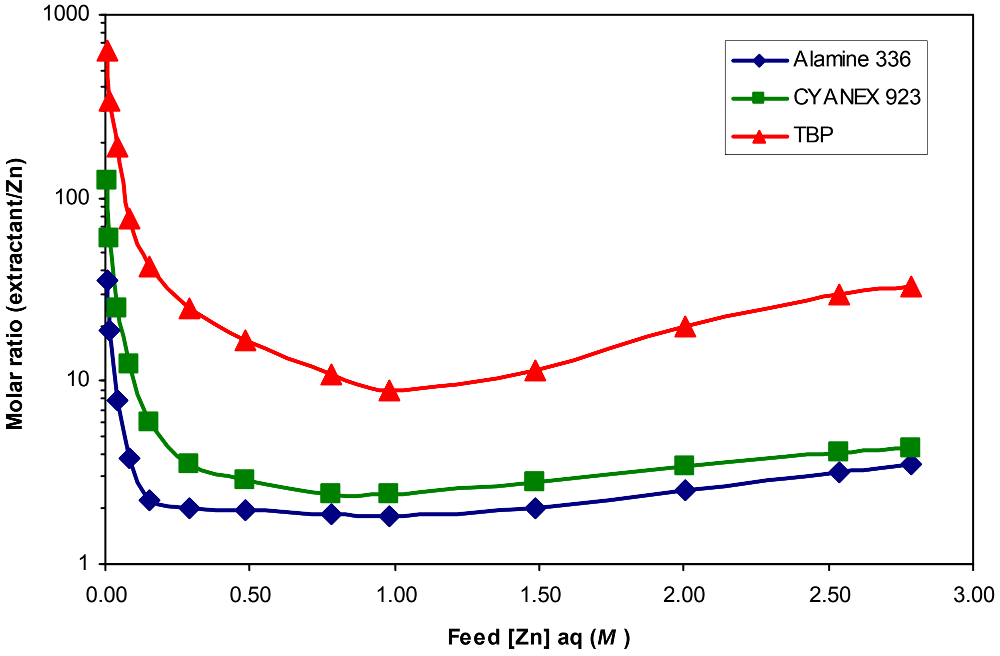


Figure 4-2 Effect of zinc concentration in the aqueous feed on the molar ratio of extractant to zinc in the organic phase.

Aqueous phase:	5.2 *M* Cl^- and 2.8 *M* H^+ at varying zinc concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

It has been observed that the molar ratio shows an increasing trend at feed zinc concentrations of between 1.5 and 2.75 *M*. This would indicate that lower loading is achieved at these higher zinc concentrations, as confirmed by Figure 4-3 which illustrates the zinc extracted in the organic phase at various feed zinc concentrations. Figure 4-3 confirms the higher loading achieved by CYANEX 923 compared to TBP which is as expected from literature: TBP, which is a tri-ester of phosphoric acid, consists mainly of OR groups that are electron withdrawing and CYANEX 923 consists mainly of electron-releasing R groups that enhance the ability of the phosphoryl oxygen to coordinate to a metal. The decrease in zinc concentration in the organic phase at high feed zinc concentrations is not expected as explained before. The zinc extracted is expected to reach a maximum loading and remain constant for all three extractants.

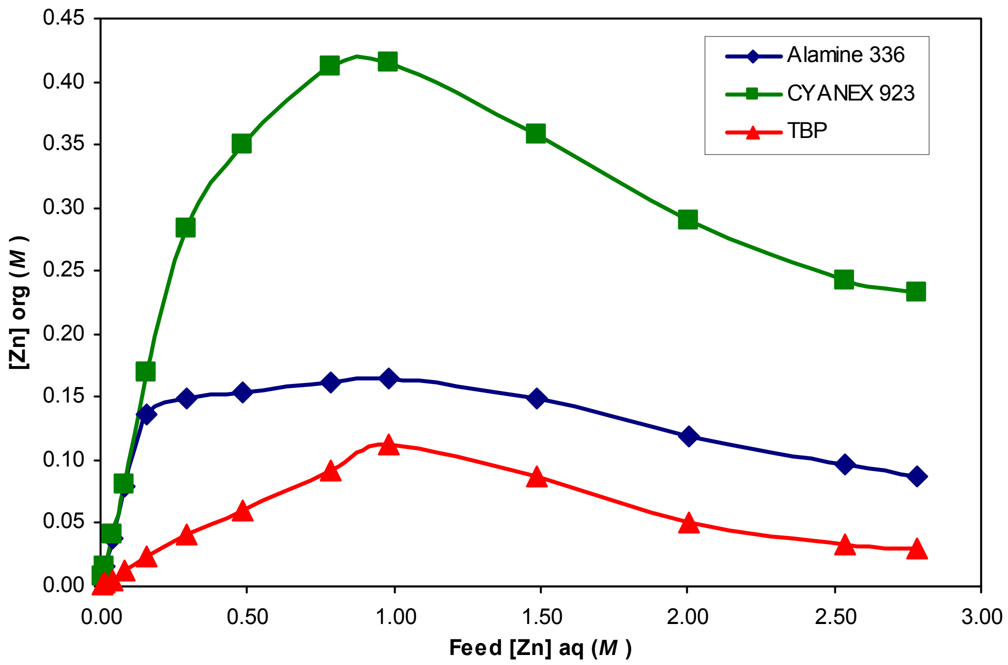


Figure 4-3 Effect of zinc concentration in the aqueous feed on the zinc extracted in the organic phase.

Aqueous phase: 5.2 *M* Cl^- and 2.8 *M* H^+ at varying zinc concentration.
Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions: Phase ratio of 1; room temperature.

Given that the initial acidity of the feed solution is high, 2.8 *M* H^+, it is not expected that the extraction of zinc decreased as a result of metal hydrolysis due to an increased pH for the anionic extractant, Alamine 336. Metal hydrolysis is not expected to be a factor for the other two extractants either, as they are neutral extractants and their extraction mechanism is not primarily dependent on pH but rather on factors such as metal anionic complexes, chloride and extractant concentrations in the aqueous phase. Figure 4-4 shows that the equilibrium aqueous acid (H^+) concentration does not vary significantly with increasing feed zinc concentration for Alamine 336. Therefore pH is thus not considered to have an influence in the decreased extraction of zinc for the Alamine 336 system.

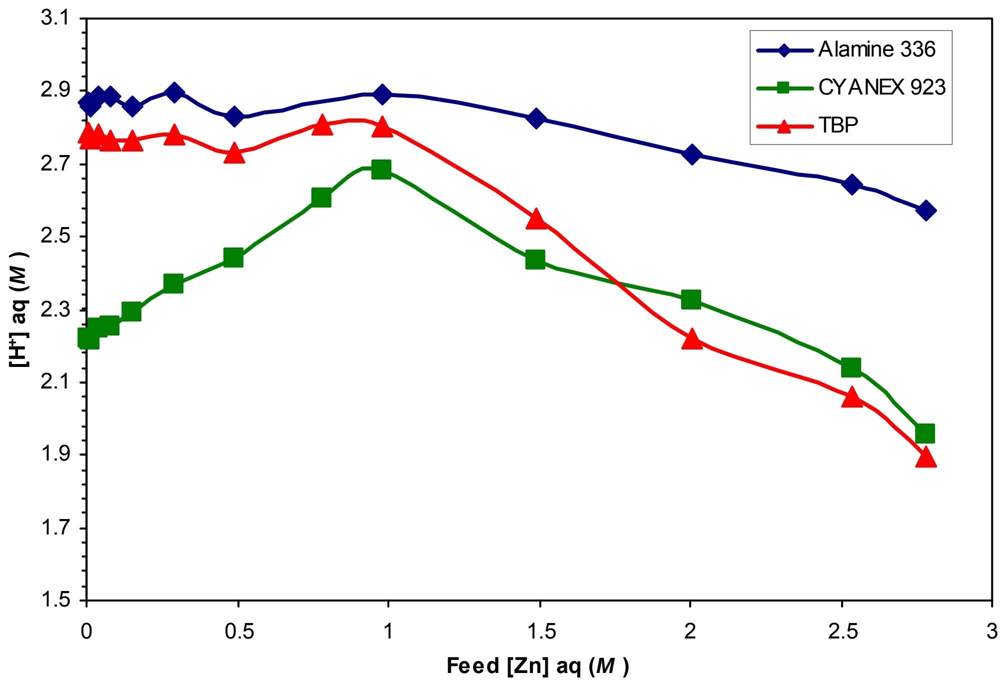


Figure 4-4 Effect of zinc concentration in the aqueous feed on the equilibrium proton concentration in the aqueous phase.

Aqueous phase: 5.2 *M* Cl^- and 2.8 *M* H^+ at varying zinc concentration.
Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions: Phase ratio of 1; room temperature.

For CYANEX 923, the equilibrium aqueous acid concentration initially increased, corresponding with increasing metal extraction up to an initial feed zinc concentration of 1 *M*. This trend is not expected as CYANEX 923 is a neutral extractant and acidity should not be a primary factor. If the acidity was a factor its concentration would be expected to decrease in the aqueous raffinate due to its co-extraction together with zinc as the species H_2ZnCl_4. At zinc concentrations greater than 1.0 *M* the equilibrium aqueous acid concentration decreased, corresponding with the decrease in metal extraction. This would suggest that at this point the extraction of H^+ as hydrochloric (HCl) acid seems to be favoured as has been reported by some authors in literature (Grzeszczyk and Regel-Rosocka, 2007).

The equilibrium aqueous acid concentration for the TBP system initially remained constant but then decreased, also corresponding with decreasing zinc extraction, suggesting that extraction of acid as HCl acid could be occurring. A look at the corresponding graph for the equilibrium aqueous chloride concentration (Figure 4-5) shows that, for all three extractants, the chloride concentration decreased, corresponding to increasing metal extraction. The chloride concentration then seemed to reach a lower equilibrium value and then started to increase with decreasing metal extraction. This could be possibly be explained by the fact that metal extraction of zinc accounts for four chloride ions as the extractable species is expected to be the tetra-chloro complex ($ZnCl_4^{2-}$) for Alamine 336 and as the H_2ZnCl_4 species for the other two extractants. With the decreased zinc extraction at the higher feed zinc concentrations, less chloride is co-extracted even with the possibility of acid extraction and thus the chloride concentration in the aqueous phase should remain constant or slightly increase from the lower equilibrium values (at maximum loading levels of zinc).

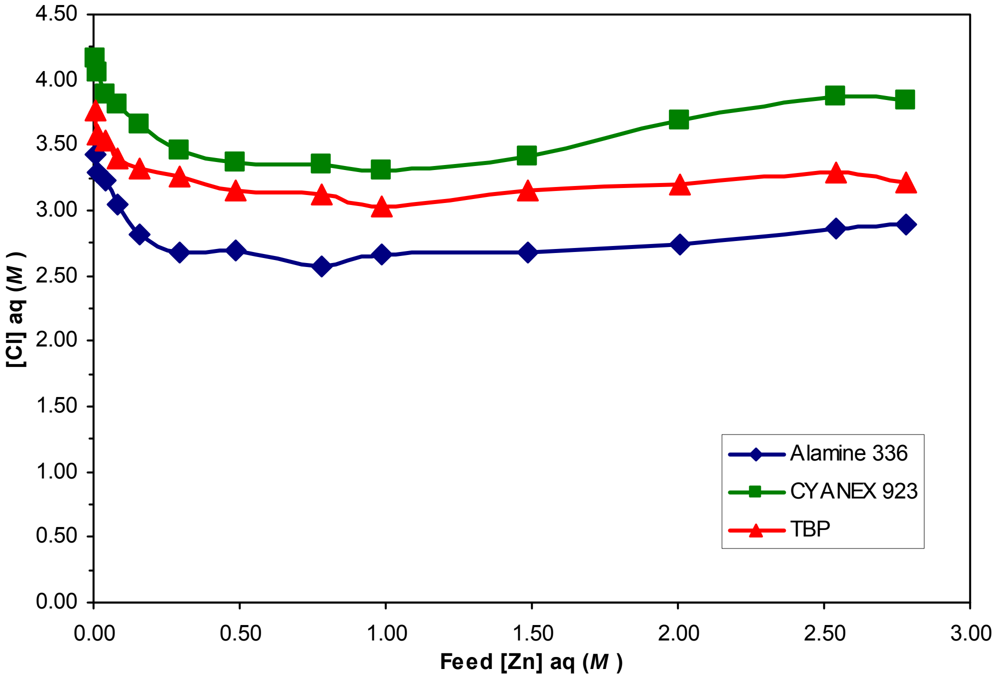


Figure 4-5 Effect of zinc concentration in the aqueous feed on the equilibrium chloride concentration in the aqueous phase.

Aqueous phase:	5.2 *M* Cl^- and 2.8 *M* H^+ at varying zinc concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of; room temperature.

4.2 Zinc Extraction at Various Initial Chloride Concentrations

It is expected that with increasing chloride concentration the speciation of zinc in solution should favour the formation of the tetra-chloro complex of zinc ($ZnCl_4^{2-}$) which is suitable for extraction by all three extractants being studied. Figure 4-6 shows the effect of chloride concentration in the aqueous feed on the distribution coefficient for zinc. As expected, increasing chloride concentration has a positive effect on the distribution coefficient up until 1.83 *M* chloride for all three extractants. The distribution coefficient decreases to a minimum then again shows an increasing trend. Due to the consistency of the minima displayed by the results for all three extractants, it is believed that this is not due to experimental error but a real effect. The results are in agreement with equation 3-12 which shows that an increase in chloride concentration should have a positive effect on zinc extraction.

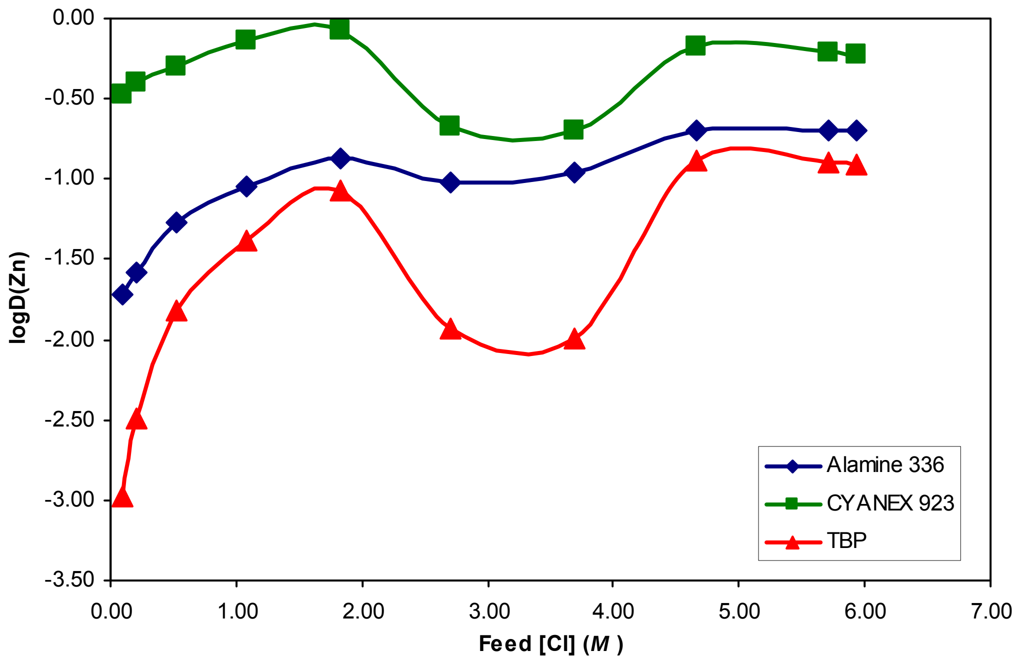


Figure 4-6 Effect of chloride concentration in the aqueous feed on the distribution coefficient for zinc.

Aqueous phase: 1.0 *M* Zn and 2.8 *M* H^+ at varying chloride concentration.

Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.

Conditions: Phase ratio of 1; room temperature.

The effect of chloride concentration on the molar ratio of extractant to zinc in the organic phase is shown in Figure 4-7. The molar ratio of extractant to zinc decreases for all three extractants as the feed solution becomes progressively saturated with chloride. As noted before, there is as unexplained increase that occurs between 2.0 and 5.0 *M* chloride concentrations. The ratio for TBP is an order of magnitude higher than for the other extractants. This effect was also observed in the experiments of varying feed zinc concentration. The molar ratio decreases to 9 for TBP, 3 for CYANEX 923 and 2 for Alamine 336. These results compare well with those reported in the study of the effect of feed zinc concentration where ratios of 2 to 4 were reported for CYANEX 923, 2 to 3 for Alamine 336 and 9 to 33 for TBP at maximum loading capacities. Although it is possible that the extractants were not completely saturated with zinc in these experiments, the results as presented in Figure 4-3 (which shows the effect of feed zinc concentration on zinc loading in the organic phase) do indicate that the maximum loading capacity should be achieved at a zinc concentration 1.0 *M* feed zinc for all three extractants.

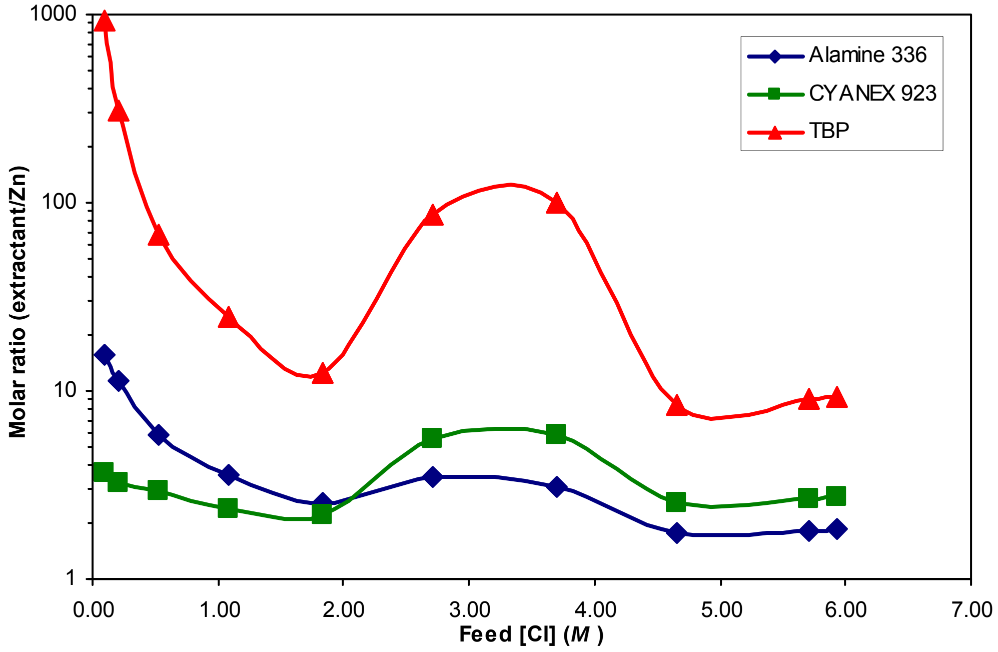


Figure 4-7 Effect of chloride concentration in the aqueous feed on the molar ratio of extractant to zinc in the organic phase.

Aqueous phase:	1.0 *M* Zn and 2.8 *M* H^+ at varying chloride concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

The effect of chloride concentration on zinc extraction for the three extractants is shown in Figure 4-8. Similar observations are made as seen before in the experiments investigating the effect of feed zinc concentration (Section 4.1) that the highest loading is obtained with CYANEX 923 followed by Alamine 336 and then TBP. The maximum loading capacities obtained of 0.46, 0.15 and 0.12 *M* zinc for CYANEX 923, Alamine 336 and TBP, respectively, agree with those reported in the previous study on the effect of feed zinc concentration. The increasing trend in zinc extraction from low to high chloride levels in the aqueous feed supports the speciation diagram (Ruaya and Seward, 1986) and work reported by other authors (Lin, 1993 and Alguacil *et al*., 1999). It is believed that the amount of zinc in the form of the tetra-chloro species in the solution increases with increasing chloride concentration and this is the species suitable for extraction by the extractants.

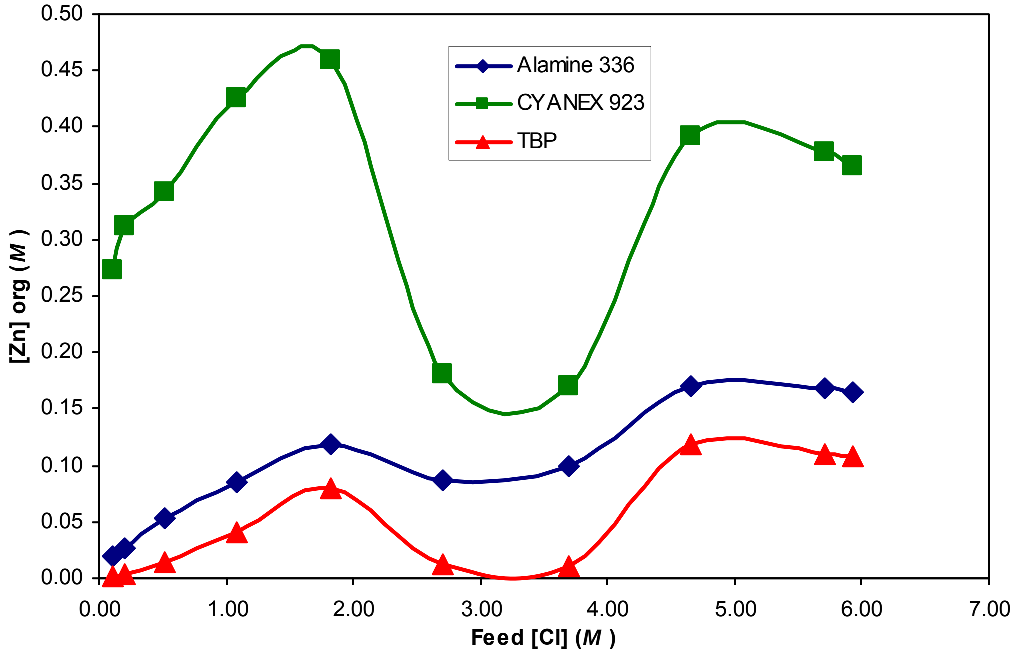


Figure 4-8 Effect of chloride concentration in the aqueous feed on zinc extracted in the organic phase.

Aqueous phase: 1.0 *M* Zn and 2.8 *M* H^+ at varying chloride concentration.
Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions: Phase ratio of 1; temperature.

Figure 4-9 shows the effect of increasing chloride concentration on the equilibrium acid concentration. It should be noted that although it was desired to maintain a constant acidity level in the feed for all the experiments, this was not achieved. The variable acid concentrations could possibly be attributed to analytical error as previous experience has shown that errors do arise when performing acid titrations in solutions with high chloride concentrations. The acid concentration in the feed solutions varied from 1.44 *M* to 2.90 *M* as can be found in Appendix C. It is not known if this variation could have had a major impact on the results obtained. The effect of acidity is reported in Section 4.3.

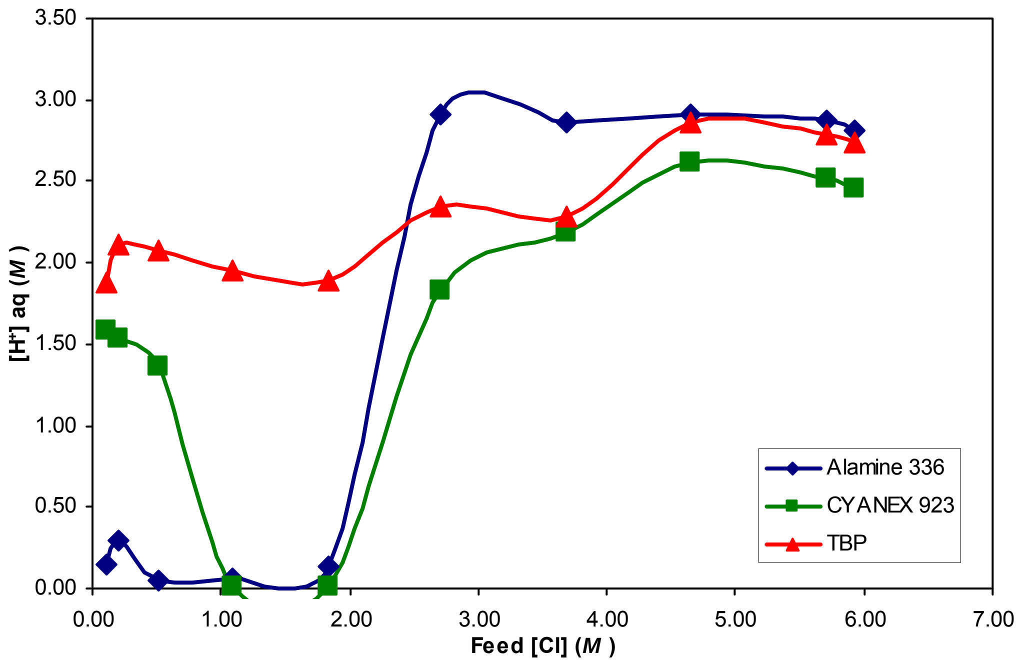


Figure 4-9 Effect of chloride concentration in the aqueous feed on equilibrium acid concentration in the aqueous phase.

Aqueous phase: 1.0 *M* Zn and 2.8 *M* H^+ at varying chloride concentration.
Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions: Phase ratio of 1; room temperature.

4.3 Effect of pH on Zinc Extraction

The distribution coefficient for the Alamine 336 system decreases with increasing acid concentration as illustrated in Figure 4-10, ranging from 0.09 at high acid concentration to 0.18 at low acid concentrations. Results for Alamine 336 are not consistent with the reaction given by equation 15 which shows that protons should not have a significant effect on the extraction of zinc. According to Ritcey and Ashbrook (1984), the extraction of metals by amines from hydrochloric acid solutions exhibits a maximum in the extraction curve. The decrease in extraction after a certain acid concentration was explained as probably due to the preferential extraction of acid, with the suggested species being HCl_2^-.

The distribution coefficient for CYANEX 923 decreases up to 10 times with increasing acid concentration. The distribution coefficient for TBP shows a significant decrease with increasing acid concentration. It should be noted that very low pH values were used for this investigation compared to literature where the pH was varied between 1 and 5. According to the reaction given by equation 3-12 it is expected that lower pH values (increased protons) should result in the increase of zinc extraction for the neutral extractants. The opposite effect is observed in this study.

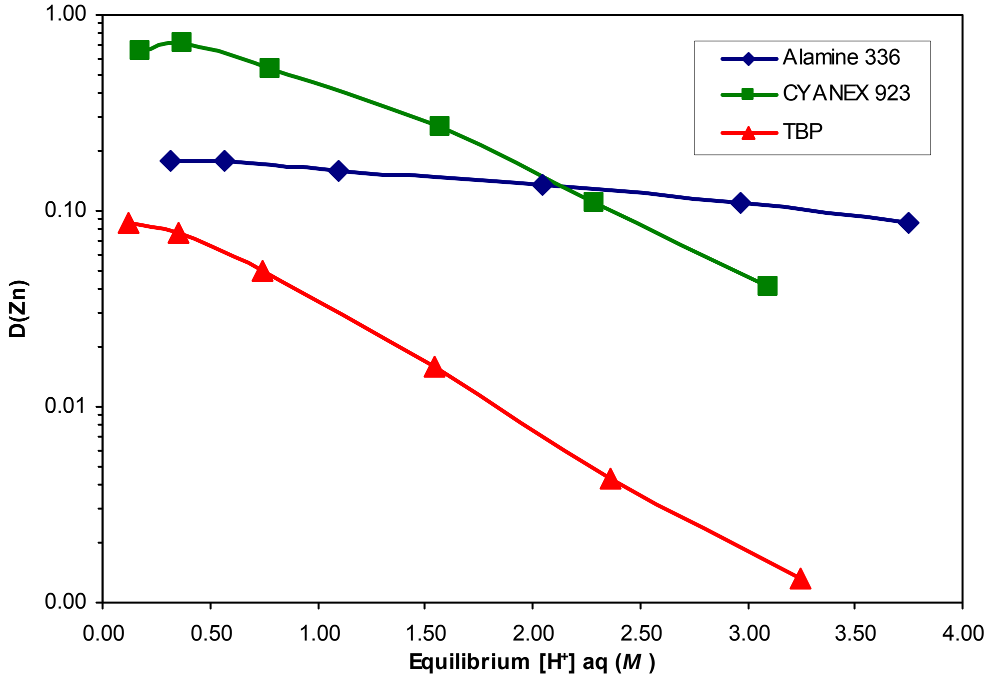


Figure 4-10 The effect of acid concentration on the distribution coefficient for zinc.

Aqueous phase:	1.0 *M* Zn and 5.2 *M* Cl^- at varying acid concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

The effect of increasing acidity on the molar ratio of extractant to zinc is shown in Figure 4-11. Increasing acidity has little (less significant) effect on the molar ratio for the Alamine 336 system which is consistent with the reaction given by equation 3-15. The molar ratio for CYANEX 923 increases from a value of 2 at low acid concentration to 26 at high concentration (the ratio decreases with increasing pH). A similar trend is observed for TBP with the ratio increasing from a value of around 13 to 769. The high ratios that are obtained at high acid concentrations are probably due to the fact that lower amounts of zinc are extracted and therefore inflate the values of the ratios calculated. No meaningful observations can be made with reference to the number of extractant molecules involved in the extraction process at these acid levels except to say that the loading capacity seems to be drastically lowered at the high acid concentrations. The lowered loading capacity would be undesirable for a commercial process thus the high acid levels (low pH) are not desirable operating conditions for the tARZn extraction process.

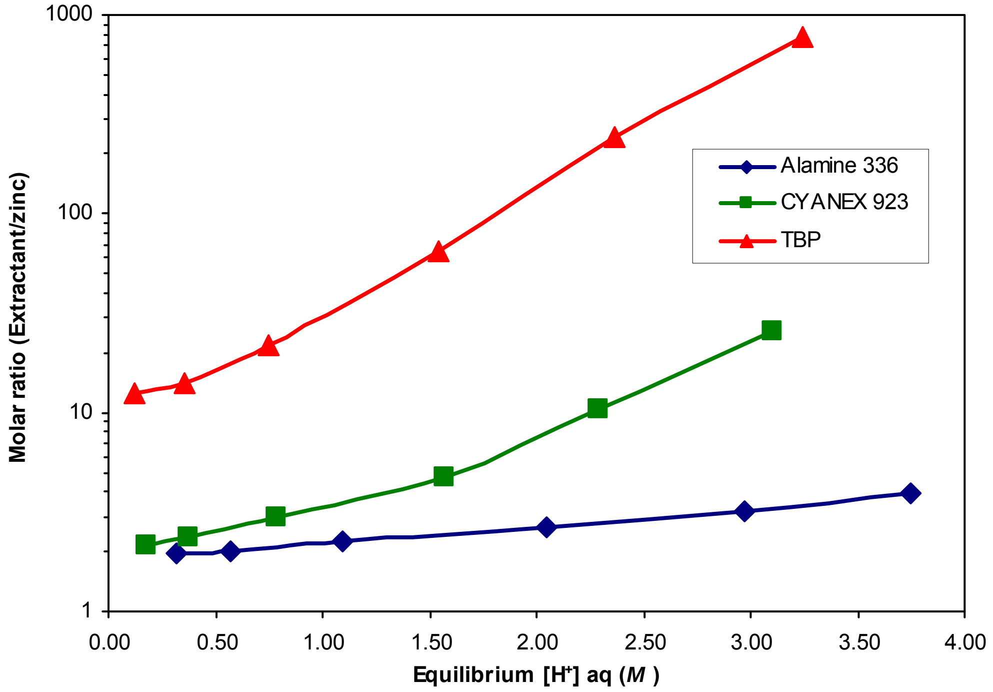


Figure 4-11 Effect of acid concentration on the molar ratio of extractant to zinc.

Aqueous phase:	1.0 *M* Zn and 5.2 *M* Cl^- at varying acid concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

Figure 4-12 confirms the observation that increasing acidity did have an impact on the zinc extracted by the Alamine 336 system. The zinc extracted by the organic phase decreased from 0.15 *M* to 0.08 *M* with increasing acidity. Increasing acidity results in a decrease in the amount of zinc extracted by the CYANEX 923 and TBP systems (Figure 4-12). The decreasing extraction could be due to the increased extraction of hydrochloric (HCl) acid. According to Ritcey and Ashbrook (1984), the effect of acid concentration on extraction by TBP is similar to that with amines where the metal extraction increases with increasing acid up to a certain point, after which the extraction then decreases due to the preferential extraction of acid. This trend is not readily observed in these studies since the work was carried out over a narrow range and at high acidity (low pH values). However the trend of increasing extraction with decreasing acidity (increasing pH) is observed for all extractants.

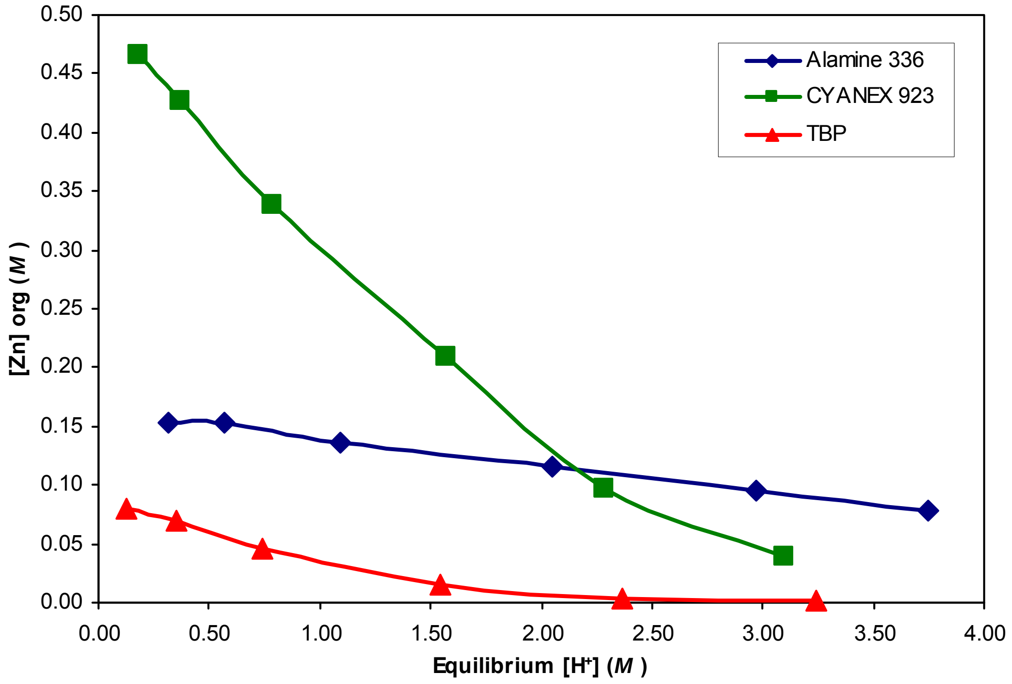


Figure 4-12 Effect of acid concentration on zinc extraction.

Aqueous phase:	1.0 *M* Zn and 5.2 *M* Cl^- at varying acid concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

Figure 4-13 shows the effect of increasing acidity on the equilibrium chloride concentration in the aqueous phase. It is observed that the chloride concentration decreased sharply with increasing acidity in the acidity range of 0 to 0.5 *M* H^+ for all three extractants. Thereafter, the decrease in chloride concentration is less pronounced. The sharp decrease in the equilibrium chloride concentration corresponds to the initial high zinc ($ZnCl_4^{2-}$ or H_2ZnCl_4) extractions observed at the lower acidity levels. The extraction of zinc then rapidly decreased with increasing acidity and thus the aqueous equilibrium chloride concentration shows a less pronounced decrease.

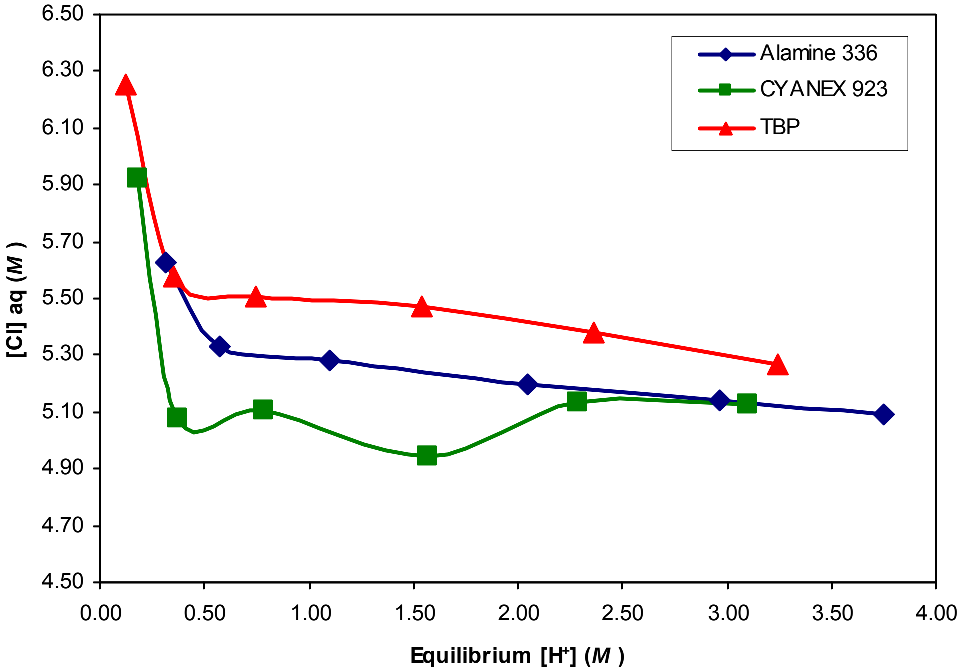


Figure 4-13 Effect of acid concentration on equilibrium chloride concentration in the aqueous phase.

Aqueous phase:	1.0 *M* Zn and 5.2 *M* Cl^- at varying acid concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

4.4 Effect of Extractant Concentration on Zinc Extraction (Extraction Reaction Stoichiometry)

Figure 4-14 shows the plot of $\log D_{Zn}$ versus log[extractant] for all three extractants. As expected, the zinc extraction increases with increasing extractant concentration for all three extractants. However for CYANEX 923 the maximum loading seems to occur at extractant concentrations of between 1.5 to 2.0 *M* and not at the undiluted form of the extractant (100% CYANEX 923 at 2.53 *M*). It is expected that a plot of $\log D_{Zn}$ versus log[extractant] would be linear, with the slope corresponding to the number of extractant molecules (slope analysis method). It has been shown in the previous study (Section 4.3) that the extraction of zinc using Alamine 336 is not significantly affected by the acid concentration whereas extraction with TBP is affected to some extent and for CYANEX 923 zinc extraction is significantly impacted.

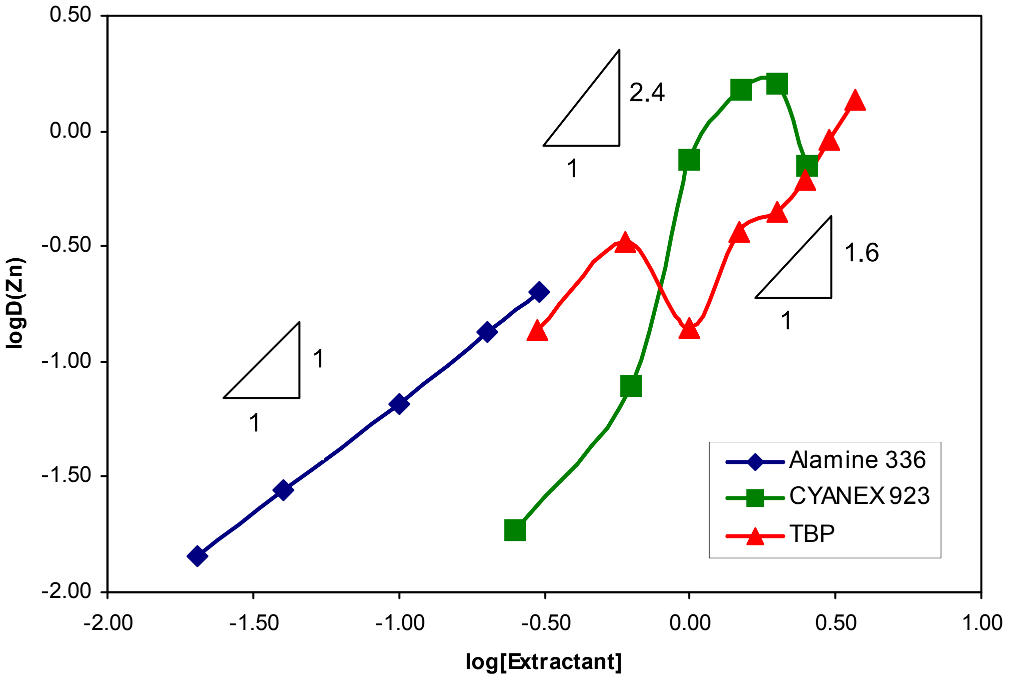


Figure 4-14 Effect of extractant concentration on the zinc distribution coefficient.

Aqueous phase:	1.0 *M* Zn, 5.2 *M* Cl^- and 2.8 *M* H^+.
Organic phase:	Varying extractant concentrations.
Conditions:	Phase ratio of 1; room temperature.

A slope of approximately 1 (0.98) was obtained for the Alamine 336 system. The graph for TBP is not linear as shown, however the mass balances for the first two experimental points were out of the allowable limit (112 and 128%, respectively). Thus if these two points are omitted from the plot then a better plot is obtained with a slope of 1.6. Similarly with CYANEX 923, the plot is not linear. Even though the mass balances for the first two experimental points were beyond the allowable limit, the plot with the two points omitted is still not linear. A slope of 2.4 is obtained when the last data point is omitted.

The assumptions and applicability of the slope analysis technique to the solutions investigated in this work has already been discussed in section 3.7. The slope analysis technique is generally applied in investigations using dilute solutions such that the amount of zinc and chloride extracted are much smaller than the initial concentration of extractant. Therefore, the concentration of free extractant at equilibrium can be considered to be equal to the initial concentration. In this study, the synthetic PLS solution used contains high concentrations zinc, acid and chloride and it is therefore unlikely that the free extractant concentration at equilibrium can be considered to be equal to the initial extractant concentration. In fact, it is quite likely that the extractants are saturated with zinc, especially at lower extractant concentrations, meaning there is little or no free extractant after equilibrium.

Since the slope analysis technique did not yield conclusive results, it was decided to further investigate the nature of the extracted complex using the available data. It was thought that by using the same analogy of plotting the molar ratio of the total extractant to chloride and protons in the organic phase, as previously done for zinc (Figure 4-1, Figure 4-7 and Figure 4-11), more information could be obtained about the nature of the extracted complexes. Examples of these graphs are given in Figure 4-15, which illustrates the effect of the zinc concentration in aqueous feed on the molar ratio of the total extractant to chloride in the organic phase, and Figure 4-16, which illustrates the effect of increasing acidity on the molar ratio of total extractant to proton in the organic phase. The remainder of the graphs plotted for the molar ratio of total extractant to chloride and protons for the various solution parameters investigated (studies of the effect of zinc, chloride, proton and extractant concentration on zinc extraction) are provided in Appendix D.

The approach followed was that to determine the nature of the extracted complex for the neutral extractants, interaction of the three elements (H, Zn and Cl) had to be taken into account. It was thought that this interaction of the three elements yielded complexes which could be represented as $H_xZn_yCl_z$. By calculating the molar ratio of total extractant to these elements, the values of x, y and z could be determined. The results obtained from the graphs were also inconclusive and did not provide further information on the nature of the extracted complexes. The graphs do however confirm that there is interaction of the three elements and that the extracted species/complexes vary with changing solution conditions.

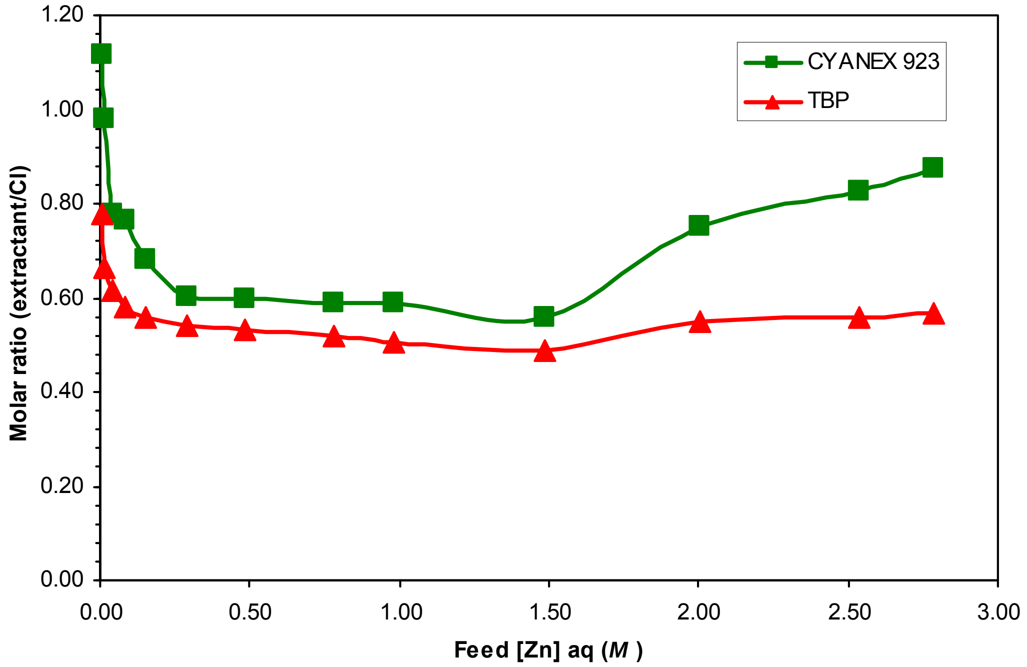


Figure 4-15 Effect of zinc concentration in the aqueous feed on the molar ratio of extractant to chloride in the organic phase.

Aqueous phase: 5.2 *M* Cl^- and 2.8 *M* H^+ at varying zinc concentration.
Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions: Phase ratio of 1; room temperature.

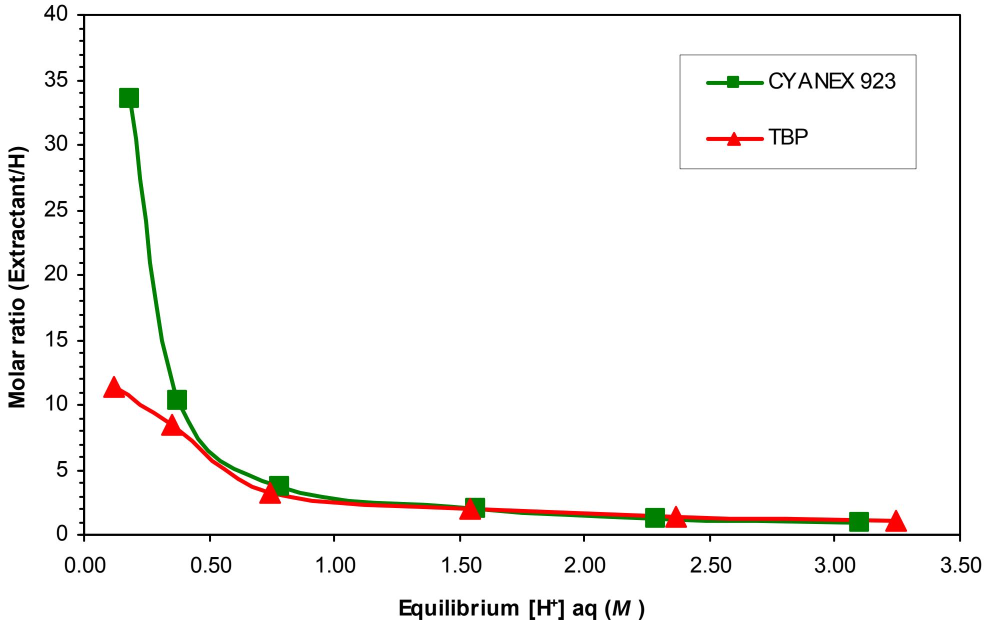


Figure 4-16 Effect of acid concentration on the molar ratio of extractant to proton in the organic phase.

Aqueous phase: 1.0 *M* Zn and 5.2 *M* Cl^- at varying chloride concentration.
Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions: Phase ratio of 1; room temperature.

4.5 Effect of Iron Concentration on Zinc Extraction

Figure 4-17 shows that the presence of iron(II) does not affect the extraction of zinc at iron(II) concentrations ranging from 0.01 *M* to 0.1 *M* for all three extractants. In Figure 4-18 it is seen that zinc loads to similar levels as seen in previous studies of 0.4 *M*, 0.2 *M* and 0.11 *M* for CYANEX 923, Alamine 336 and TBP, respectively. It is shown in Figure 4-19 that the distribution coefficient of iron(II) decreases with increasing iron(II) concentration.

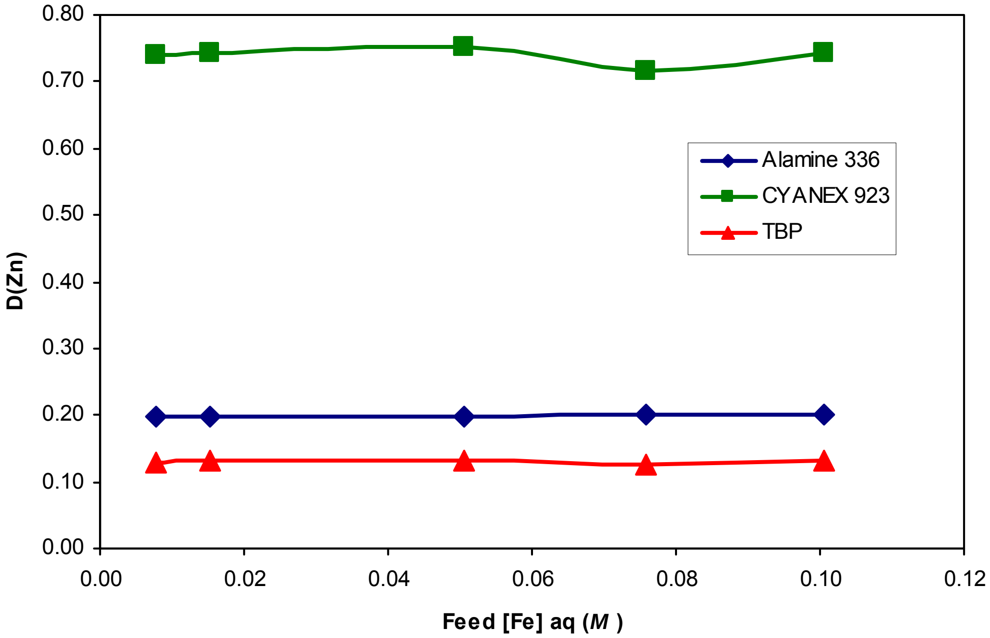


Figure 4-17 Effect of iron(II) concentration on zinc extraction.

Aqueous phase: 1.0 *M* Zn, 5.2 *M* Cl^- and 2.8 *M* H^+.

Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.

Conditions: Phase ratio of 1; room temperature.

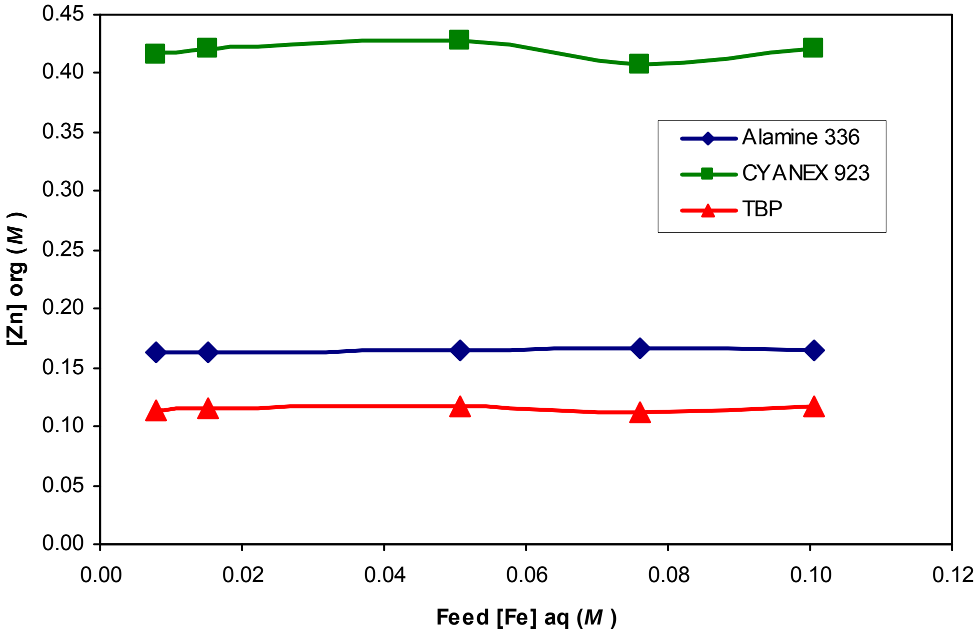


Figure 4-18 Effect of iron(II) concentration in the feed solution on zinc extraction.

Aqueous phase: 1.0 *M* Zn, 5.2 *M* Cl^- and 2.8 *M* H^+.

Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.

Conditions: Phase ratio of 1; room temperature.

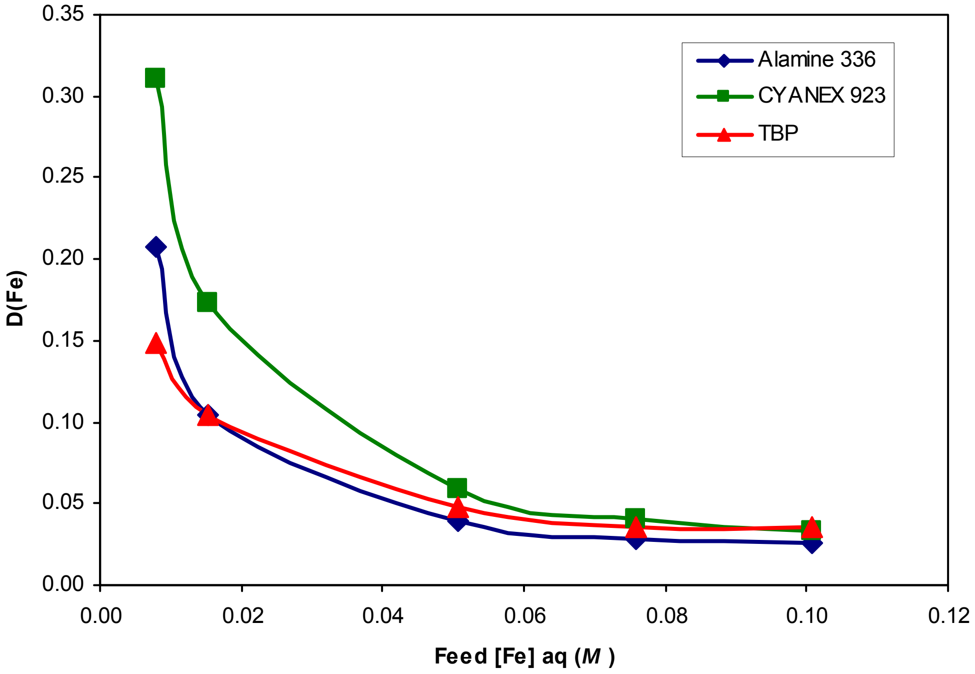


Figure 4-19 Effect of iron(II) concentration in the feed solution on the distribution coefficient for iron.

Aqueous phase: 1.0 *M* Zn, 5.2 *M* Cl^- and 2.8 *M* H^+.
Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions: Phase ratio of 1; room temperature.

The selectivity factor for zinc over iron(II) is defined as β_{Fe}^{Zn} = D_{Zn}/D_{Fe}. This value only gives an indication of whether the two metals can be separated. The values of the selectivity factors obtained from this study are tabulated in Table 4-1. It is evident that CYANEX 923 has the greatest selectivity factor followed by Alamine 336 and then TBP. The selectivity factor shows an increasing trend with increasing feed iron(II) concentration. This shows that separation of zinc from iron(II) should not pose a significant challenge. Regel-Rosocka *et al*. (2003) observed that the worst selectivities for zinc over iron(III) and iron(II) were obtained for the strongest solvating reagent which is CYANEX 923. However it is observed that CYANEX 923 had the better selectivity in these experiments.

Table 4-1 The effect of iron(II) concentration on the selectivity coefficient for the extraction of zinc over iron(II).

Iron(II) concentration	**Selectivity factor (D_{Zn}/D_{Fe})**		
(*M*)	**Alamine 336**	**CYANEX 923**	**TBP**
0.01	1	2	1
0.02	2	4	1
0.05	5	13	3
0.08	7	18	4
0.1	8	23	4

The effect of iron(II) on the molar ratio of extractant to zinc in the organic phase is tabulated in Table 4-2. The molar ratios remain constant over the range of iron(II) concentrations investigated. The molar ratio constants are 2 for Alamine 336 and CYANEX 923; and 9 for TBP. These correspond well with the values reported in all the other previous studies in this work.

Table 4-2 The effect of iron(II) concentration on the molar ratio of extractant to zinc in the organic phase.

Iron(II) concentration	**Molar Ratio (extractant/Zn)**		
(*M*)	**Alamine 336**	**CYANEX 923**	**TBP**
0.01	2	2	9
0.02	2	2	9
0.05	2	2	9
0.08	2	2	9
0.1	2	2	9

4.6 Stripping

Stripping is essentially the reverse reaction to extraction. Consequently this implies that stripping is limited to the ability to reverse the extraction reactions as given in equations 3-1 and 3-15 by employing conditions which shift the equilibrium to the left. The extraction reaction for anionic extractants, as given by equation 3-15, implies that increasing the chloride concentration would shift the equilibrium to the left and result in stripping of zinc from the organic phase. It should also be possible to achieve stripping by introducing a more strongly extracted anion than the tetra-chloro zinc complex ($ZnCl_4^{2-}$).

Another important factor to consider is the stability of the extracted metal organic complex. The greater the stability constants of the extracted complexes then the greater the likelihood that it will be difficult to disassociate them. According to Ritcey and Ashbrook (1984), for extractions systems where high salt or acid concentrations are required for metal extraction, such as anionic extractants and neutral extractants, stripping with water usually does result in shifting the equilibrium to the left.

4.6.1 Stripping with water

Table 4-3 gives the zinc loading in the loaded organic phases that were used for the stripping test work. pH dependence test work was done for the Alamine 336 system in order to obtain an optimal stripping pH range. Three pH values (pH 6, 7 and 8) were chosen for this work. It was, however, found that stable emulsions were formed in the organic phase at the chosen pH values. Figure 4-20 shows the solutions in the separating funnel after phase separation. The solutions were allowed to stand overnight and there was no change observed. It is evident that water is not suitable for the stripping of this extractant.

Table 4-3 Zinc concentration in the loaded organic phases used for the stripping test work.

Extractant	**Organic concentration (*M*)**	**Zinc concentration (*M*)**
Alamine 336	1.0	0.18
CYANEX 923	1.0	0.42
TBP	0.3	0.12

Figure 4-20 Photographs showing the stable emulsions formed in the organic phases in separating funnels from the pH dependence test work for Alamine 336. Stripping was conducted at pH values 6, 7 and 8.

Stripping isotherms for CYANEX 923 and TBP using distilled water are given in Figures 4-21 and 4-22, respectively. It is observed from the isotherm that stripping of zinc from the CYANEX 923 system is poor and the concentration of zinc in the loaded strip liquor is almost negligible. The highest zinc concentration achieved in the loaded strip liquor was 0.05 *M* (3.5 g/l). The zinc concentration in the organic phase decreased from 0.42 *M* to 0.18 *M* (27.4 g/l to 11.7 g/l).

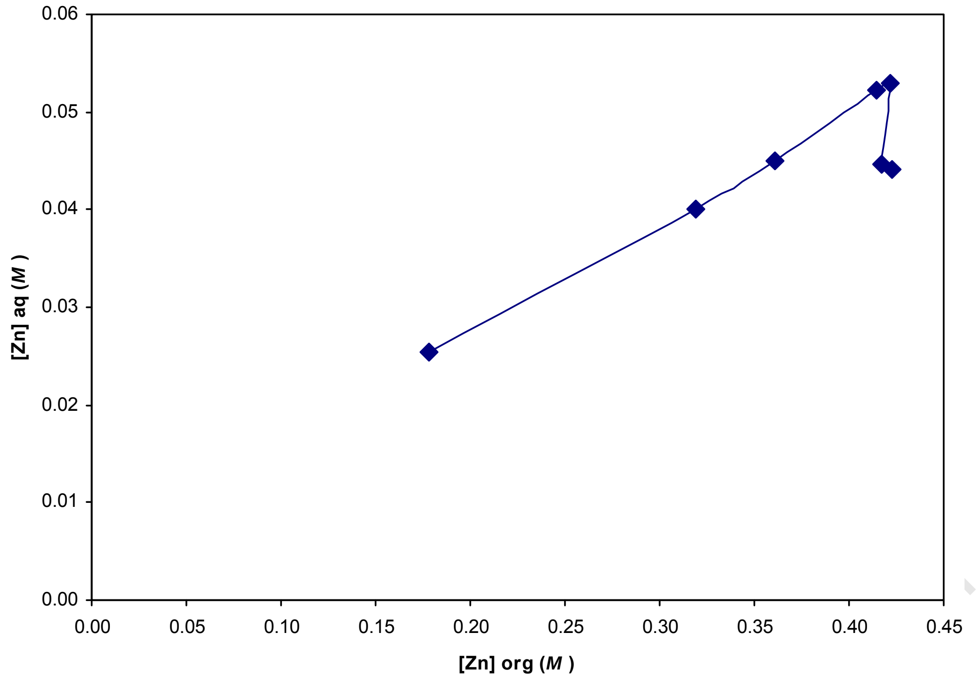


Figure 4-21 Stripping isotherm for CYANEX 923 using distilled water as strip liquor.

Aqueous phase:	Distilled water.
Organic phase:	CYANEX 923 loaded to 0.42 *M* Zn.
Conditions:	Room temperature.

The stripping isotherm for TBP shows that zinc can be successfully stripped from the organic phase into the strip liquor with a strip efficiency of up to 99% achievable. The stripping isotherm is demonstrably steep, suggesting that the stripping can be achieved in a few strip stages. Strip liquors with a zinc concentration of up to 0.73 *M* (48.1 g/l) can be generated from TBP using distilled water.

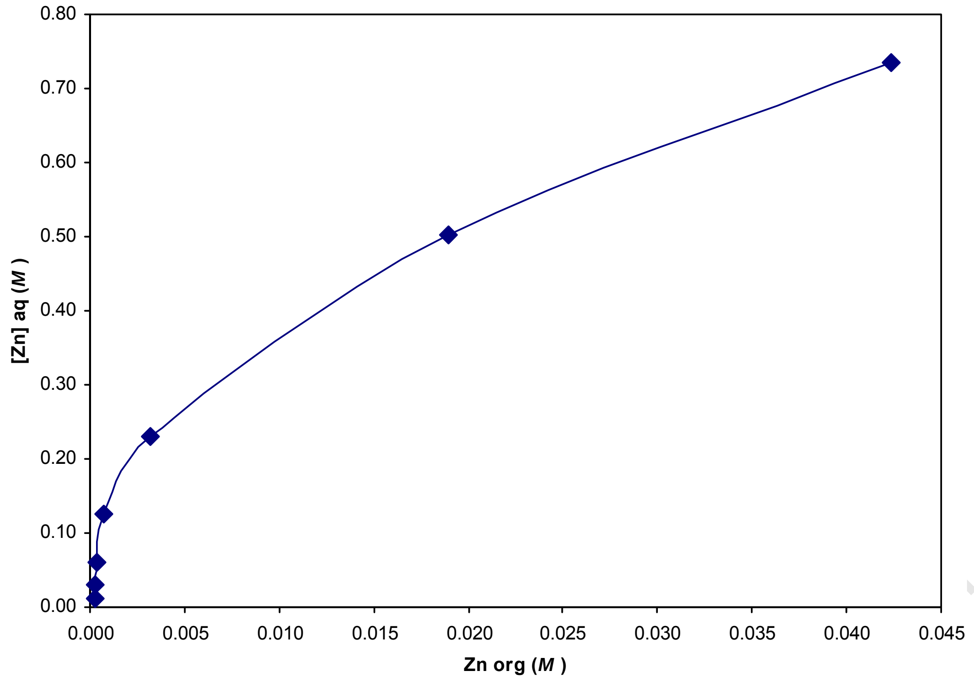


Figure 4-22 Stripping isotherm for TBP using distilled water as strip liquor.

Aqueous phase:	Distilled water.
Organic phase:	TBP loaded to 0.12 *M* Zn.
Conditions:	Room temperature.

4.6.2 Stripping with sodium chloride

Stripping isotherms for CYANEX 923 and TBP using a strip liquor of 1 *M* sodium chloride are given in Figures 4-23 and 4-24, respectively. Stripping of zinc from the CYANEX 923 system is poor and the concentration of zinc in the loaded strip liquor is almost negligible. The isotherm shows that zinc can not be successfully stripped from the CYANEX 923 organic phase. The shape of the isotherm does suggest that there might be two different species of zinc that are stripped off, with one being more easily recovered.

The stripping isotherm for TBP shows that zinc can be successfully stripped from the organic phase into the strip liquor with a strip efficiency of up to 99% achievable using a 1 *M* sodium chloride solution. The stripping isotherm is demonstrably steep, suggesting that the stripping can be achieved in a few number of strip stages. Strip liquors with a zinc concentration of up to 0.62 *M* (40.4 g/l) can be generated from TBP using the 1 *M* sodium chloride solution. The zinc concentration in this sodium chloride strip liquor is 0.1 *M* lower than that obtained with distilled water. In practice it is normally desired to achieve a high zinc loading in the loaded strip liquor, therefore water would be preferred as it gives the higher zinc concentration.

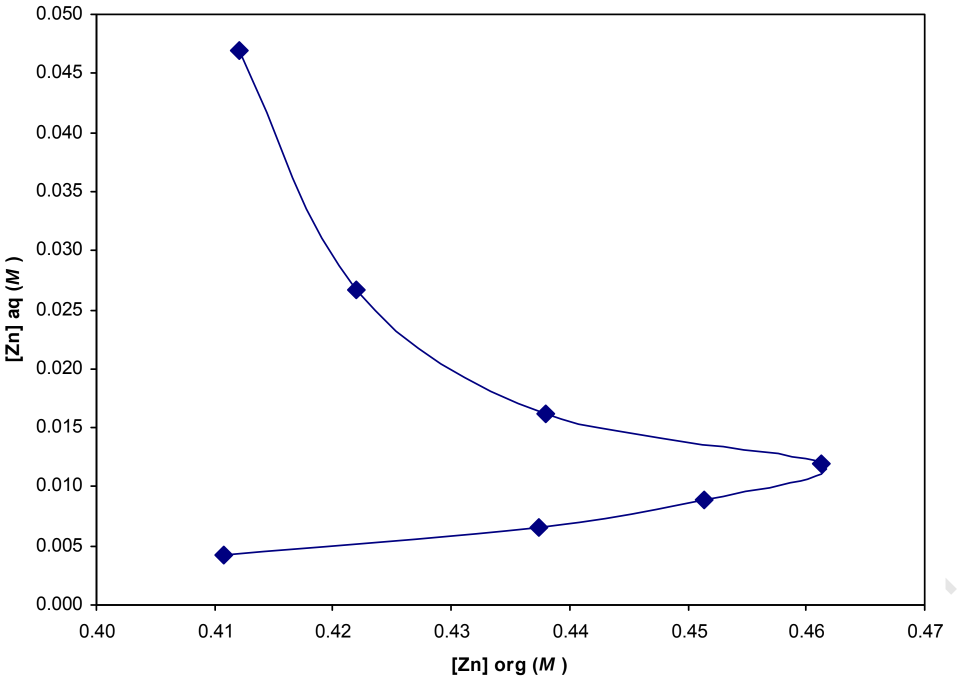


Figure 4-23 Stripping isotherm for CYANEX 923 using 1 M sodium chloride as strip liquor.

Aqueous phase:	1 *M* NaCl.
Organic phase:	CYANEX 923 loaded to 0.42 *M* Zn.
Conditions:	Room temperature.

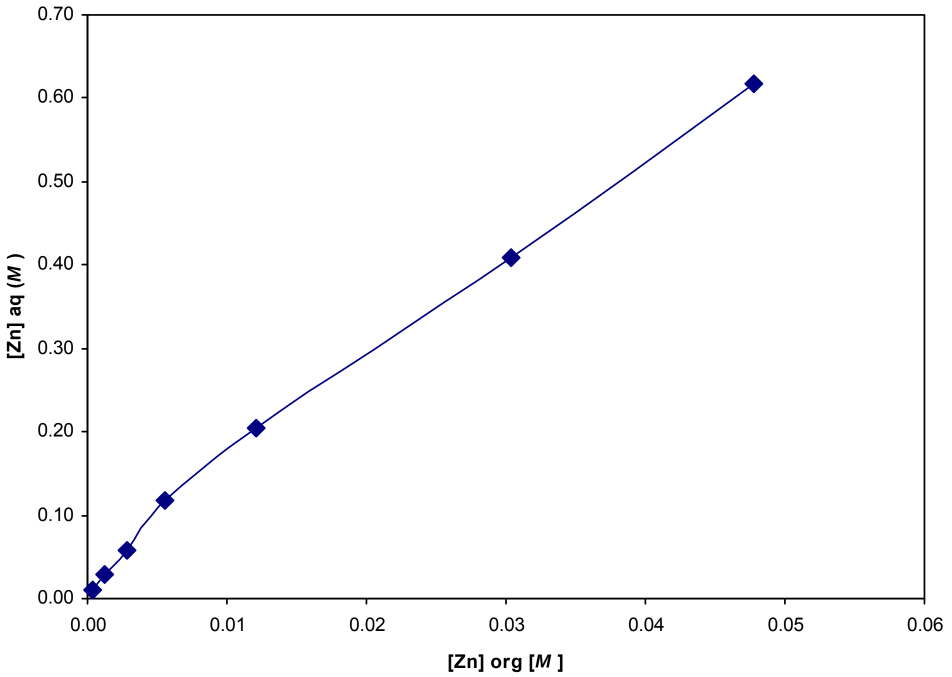


Figure 4-24 Stripping isotherm for TBP using 1 M sodium chloride solution as strip liquor.

Aqueous phase:	1 *M* NaCl.
Organic phase:	TBP loaded to 0.12 *M* Zn.
Conditions:	Room temperature.

5.0 DISCUSSION

Three extractants were evaluated for their suitability to extract zinc from chloride solutions for the tARZn process. The three extractants chosen for evaluation were Alamine 336, CYANEX 923 and TBP. These extractants were chosen based on preliminary investigations and supported by work done by various other authors as reported in literature. A review of the literature revealed that the anionic tetra-chloro ($ZnCl_4^{2-}$) and tri-chloro zinc ($ZnCl_3^-$) complexes were likely to be the dominant form of zinc in solution at the compositions to be found in the leach solutions for the tARZn process. However, it is also evident from the literature that different concentrations of zinc, chloride and acid result in different dominant species of zinc ($ZnCl_4^{2-}$, $ZnCl_3^-$, $ZnCl_2$ or $ZnCl^+$). Anionic extractants should therefore be suitable to offer quantitative zinc extraction. It is also readily accepted that neutral extractants are also able to extract the anionic ($ZnCl_4^{2-}$ and $ZnCl_3^-$) complexes as neutral complexes of the form H_2ZnCl_4 or $HZnCl_3$. From the preliminary test work conducted on various extractants it was found that Alamine 336 and CYANEX 923 offered the best extraction. TBP was also investigated in this work as it was highly recommended to be the most suitable extractant by various authors in literature.

In the investigation of the effect of aqueous feed zinc concentration on zinc extraction it was observed that zinc extraction increased up to a maximum and then decreased at concentrations greater than 1.0 *M*. This result is as expected since the extractants will reach their maximum loading capacities after which no more zinc can be extracted. The unexpected result was the observation that the zinc concentration in the organic phase decreased at zinc concentrations higher than 1.0 *M* (Figure 4-3). It was expected that the zinc concentration in the organic phase would remain constant with higher zinc concentrations in the aqueous feed, assuming that the zinc complex formed with the extractant is more stable than those of any other species in solution. At zinc concentrations lower than 1.0 *M*, the chloride and proton concentrations are higher than the zinc concentration in solution. The implication of this is that there is excess chloride (relative to zinc) available in solution such that the formation of the various expected species ($ZnCl_4^{2-}$, $ZnCl_3^-$, $ZnCl_2$ or $ZnCl^+$) should not be stoichiometrically limited. The neutral extractants are able to offer quantitative extraction of zinc species such as $ZnCl_2$, $HZnCl_3$ and H_2ZnCl_4. Correspondingly, the species involved in the extraction reaction by the anionic extractant would be $ZnCl_4^{2-}$ and $ZnCl_3^-$.

Zinc concentrations greater than 1.3 *M* give a molar ratio of zinc to chloride in solution that is less than the stoichiometric minimum of 4 required to favour the formation of the $ZnCl_4^{2-}$ complex in the tARZn leach solutions. Analogously, at zinc concentrations greater than 1.73 *M* the molar ratio of zinc to chloride in solution is less than the stoichiometric minimum of 3 required to favour the formation of the $ZnCl_3^-$ complex. At a zinc concentration of 2.6 *M* the molar ratio of zinc to chloride is 1 to 2 which stoichiometrically favours the formation of $ZnCl_2$. Although the dominant species of zinc are expected to change with the increasing zinc concentration, it is expected that any three of these expected species ($ZnCl_4^{2-}$, $ZnCl_3^-$ and $ZnCl_2$) should be extracted by the neutral extractants. The anionic extractant is expected to be able to extract the $ZnCl_4^{2-}$ and $ZnCl_3^-$ species.

At zinc concentrations greater than 1.0 *M*, the excess zinc in solution may favour the formation of species such as the hexachlorodizincate species of zinc ($Zn_2Cl_6^{2-}$). Alves *et al*. (2008) suggested that such a species may occur in high chloride media. Although there are no data available concerning the hexachlorodizincate species of zinc, its larger structure would be expected to make it more difficult to extract compared to the smaller tetra-chloro zinc species. This could possibly explain the decrease in extraction observed at higher than 1.0 *M* zinc concentration if these species were present.

The investigation into the effect of feed chloride concentration on zinc extraction revealed that zinc extraction increased with an increase of chloride concentration from 0.1 *M* to 2 *M*. In this range the chloride concentration is lower than the zinc concentration and there is also a high concentration of protons. The molar ratio of zinc to chloride in the range of 0.1 *M* to 1.0 *M* is not stoichiometrically favourable for any of the expected species. The speciation diagram (Figure 2-1) suggests that the dominant species in the range 0 to 1.0 *M* chloride should be $ZnCl_2$ and $ZnCl^+$, however this was for 0.1 *M* zinc. Since quantitative zinc extraction was observed, it is likely that the zinc species involved in the extraction reaction is $ZnCl_2$ for the neutral extractants. The species involved in the extraction reaction for the anionic extractant is likely to be a mixture of $ZnCl_4^{2-}$ and $ZnCl_3^-$.

Zinc extraction decreased at chloride concentrations between 2 *M* and 4 *M*. The decrease observed is uncharacteristic as it is expected that at this range the molar ratio of zinc to chloride stoichiometrically favours the existence of $ZnCl_2$ (at 2 *M* chloride), $ZnCl_3^-$ (at 3 *M* chloride) and $ZnCl_3^-$ (at 4 *M* chloride) complexes. These species are expected to be extracted by all three extractants. However, the chloride concentration reaches an equivalent concentration to the proton concentration of 2.8 *M* in this range. The decrease in zinc extraction observed may be due to preferential extraction of HCl in this range as all three extractants are well known as acid extractants (Sarangi *et al*., 2006).

The zinc extraction increased at chloride concentrations greater 4 *M*. A chloride concentration of 4 *M* represents the minimum required stoichiometrically to coordinate with 1.0 *M* zinc concentration. This therefore suggests that the $ZnCl_4^{2-}$ species may become dominant and is preferentially extracted from the aqueous solution.

The investigation into the effect of acid concentration on zinc extraction showed that extraction decreased with increasing acid concentration (low pH values). It is also observed that the acid concentration of 2.8 *M*, expected to be the level in the feed of the tARZn leach solution, falls within a range of acid concentrations which generally result in lower extraction of zinc. Co-extraction of HCl is expected as has been reported by Sarangi *et al*. (2006). In their work they investigated the recovery of HCl using Alamine 336, Aliquat 336, TBP and CYANEX 923 from solutions containing 5.09 *M* HCl. They reported that the acid was extracted by all four extractants and, with the exception of Alamine 336, could be easily stripped with water. The extraction of HCl was found to occur in the following order: Alamine 336 > CYANEX 923 > Aliquat 336 > TBP. For all the extractants studied they reported that the species extracted into the organic phase was associated with one mole of extractant.

It was found that the presence of iron(II) in solution did not affect the extraction of zinc at iron(II) concentrations ranging from 0.01 to 0.1 *M*. Co-extraction of iron(II) was observed but the distribution coefficient for iron(II) decreased with increasing iron(II) concentration in the feed. CYANEX 923 had the greatest selectivity factor for zinc over iron(II) followed by Alamine 336 and then TBP. It was observed that the selectivity factor showed an increasing trend with increasing feed iron(II) concentration. It is therefore expected that higher iron(II) concentrations should not have a detrimental effect on zinc extraction although more iron(II) will be co-extracted. The expected iron concentration in the tARZn process is 0.24 *M* as iron(II) and negligible amounts of iron(III).

The study into the effects of the various solution parameters has shown that the extraction curves exhibit a maximum as a function of both zinc and chloride concentrations. The range of acid concentrations investigated were very narrow and at the high end of the range. Thus the trend observed was one of decreasing extraction with increasing acid strength. Maximum zinc extraction is observed at around 1.0 *M* zinc in the feed and at a 2.0 *M* chloride in the feed. The tARZn leach solution, expected to be the feed solution to SX, has a solution composition of 1.0 *M* zinc, 5.2 *M* chloride and an acid concentration of 2.8 *M*. This feed solution composition is seen to fall within the range of feed zinc and chloride concentrations that would offer favourable and maximum zinc extraction. The acid concentration is believed to be on the high side, such that it possibly would have a detrimental effect on the extraction achievable.

Investigations to determine the stoichiometry of the extraction reaction and the nature of the extracted complex did not yield conclusive results. Experimental results from test work where the extractant concentration was varied at constant aqueous solution composition did not yield the expected linear plots when the logarithm of the extractant concentration was plotted against the logarithm of the distribution coefficient for zinc. Taking into account these observations the slopes obtained which would correspond to the number of extractant molecules involved in the extraction process are; 0.98 for Alamine 336, 2.4 for CYANEX 923 and 1.6 for TBP. Thus this suggests that the stoichiometric factors in the extraction reactions are 1 for Alamine 336 and 2 for both CYANEX 923 and TBP. The results for Alamine 336 are unexpected as according to the reaction given in equation 3-15 the extractant should have a stoichiometric factor of 2 in the extraction reaction.

The calculations of the molar ratio of extractant to zinc in the organic phase (at maximum zinc loading) obtained in the investigations of the various solution parameters are given in Table 5-1. The results show greater consistency and agreement. The molar ratio of extractant to zinc suggests that the extraction reactions have stoichiometric factors of 2 for Alamine 336, possibly 2 to 3 for CYANEX 923 and possibly 6 to 9 for TBP.

Table 5-1 The maximum zinc loading and the molar ratio of extractant to zinc obtained in the studies of the effect of the various solution parameters.

Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* all in Shellsol A150 (except for extractant concentration investigation).

Conditions: Phase ratio of 1 at room temperature.

Parameter investigated	**Maximum zinc loading (*M*)**			**Molar ratio (extractant:zinc)**		
	Alamine 336	**CYANEX 923**	**TBP**	**Alamine 336**	**CYANEX 923**	**TBP**
Zinc	0.16	0.42	0.11	2	2	9
Chloride	0.17	0.46	0.12	2	2	8
Acidity	0.15	0.47	0.08	2	2	13
Extractant	0.17	0.60*	0.57*	2	3	6
Iron(II)	0.17	0.43	0.12	2	2	9

*These were obtained using the pure form of the extractants (undiluted) and thus greater loading is to be expected.

The results from the investigations into the experimental and solution parameters that affect zinc extraction have shown that CYANEX 923 is the best extractant of the three studied in terms of extraction performance. It gave the highest loading of zinc at 0.47 *M* with a probable stoichiometric factor of 2 in the extraction process. Alamine 336 was the next best performing extractant with a loading capacity of 0.17 *M* zinc and a stoichiometric factor of 2. TBP was the worst performing extractant of the three as it loaded zinc up to a concentration of 0.12 *M* with the extraction process having a stoichiometric factor of up to 6 or 9.

It is generally expected that the lower the molar ratio of extractant to metal in the extractable species, the greater will be the loading capacity of the extractant. The results follow this trend, with the loading capacity decreasing according to the order: CYANEX 923 > Alamine 336 > TBP. The molar ratios of extractant to zinc increase in a similar order: CYANEX 923 < Alamine 336 < TBP. The maximum loading values reported from the extraction work appear to be credible as the loaded organic used for the stripping work (generated by contacting the organic twice at an A:O phase ratio of 2) also yielded similar results of 0.18 *M*, 0.42 *M* and 0.12 *M* for Alamine 336, CYANEX 923 and TBP, respectively.

A comparison of the extraction efficiency of the three extractants based on zinc extracted per mole of extractant shows that Alamine 336 is the best of the three extractants (Table 5.2). The extraction performance of Alamine 336 on a molar basis is seen to be slightly superior to that of CYANEX 923. Despite the fact that Alamine 336 is the superior extractant in terms of extraction efficiency, on a molar basis (*M* zinc extracted per M extractant), one factor that weighs against its practical application is the observed increase in viscosity at extractant concentrations of greater than 0.3 *M*. This increased viscosity could result in the formation of stable emulsions and the associated handling issues in practical application in industry.

Table 5-2 Comparison of the extraction performance of the three extractants on a molar basis (M Zn extracted per M extractant) in the studies of the effect of the various solution parameters.

Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* all in Shellsol A150 (except for extractant concentration investigation).

Conditions: Phase ratio of 1 at room temperature.

	Zinc loading per mole of extractant (M Zn/M extractant)		
Parameter investigated	**Alamine 336**	**CYANEX 923**	**TBP**
Zinc	0.54	0.42	0.11
Chloride	0.56	0.46	0.12
Acidity	0.51	0.47	0.08
Extractant	0.55	0.60	0.57
Iron(II)	0.55	0.43	0.12

The loading capacities of the three extractants can be improved by using higher concentrations of the extractant or even the pure form of the extractants (undiluted in diluent) as shown in Table 5-3. The data shown in Table 5-3 further emphasises the fact that it is possible to obtain quantitative extraction of zinc using all three extractants.

Table 5-3 The effect of extractant concentration on the loading of zinc into the organic phase.

Aqueous phase: 1.0 *M* Zn, 5.2 *M* Cl^- and 2.8 *M* H^+.

Conditions: Phase ratio of 1 at room temperature.

Alamine 336		**CYANEX 923**		**TBP**	
Volume	**Zinc Extracted**	**Volume**	**Zinc Extracted**	**Volume**	**Zinc Extracted**
(%)	**(*M*)**	**(%)**	**(*M*)**	**(%)**	**(*M*)**
1	0.01	10	0.02	8.2	0.14
2	0.03	25	0.06	16.3	0.31
5	0.06	39.5	0.43	27.2	0.13
10	0.12	59	0.60	40.5	0.28
15	0.17	79	0.60	54.5	0.32
		100	0.40	68	0.39
				82	0.48
				100	0.57

Table 5-4 gives a comparison of the extraction efficiency of the three extractants on a molar basis of zinc extracted per mole of extractant. Alamine 336 shows superior extraction efficiency on a molar basis when compared to the other three extractants. The data in Table 5-4 also suggests that all three extractants are more effective at extracting zinc, on a molar basis, at lower extractant concentrations. The extraction of zinc per mole of extractant is observed to decrease at extractant concentrations greater than 5%, 39.5% and 16.3% for Alamine 336, CYANEX 923 and TBP, respectively. However, low extractant concentrations also result in lower loading of zinc in the organic phase (Table 5-3) which is not desirable in practice.

Table 5-4 Comparison of the effect of extractant concentration on the loading of zinc on a molar basis (M Zn extracted per M extractant).

Aqueous phase: 1.0 *M* Zn, 5.2 *M* Cl^- and 2.8 *M* H^+.
Conditions: Phase ratio of 1 at room temperature.

Alamine 336		**CYANEX 923**		**TBP**	
Volume (%)	**Extraction (*M* Zn / *M* L_{org})**	**Volume (%)**	**Extraction (*M* Zn / *M* L_{org})**	**Volume (%)**	**Extraction (*M* Zn / *M* L_{org})**
1	0.69	10	0.06	8.2	0.45
2	0.66	25	0.09	16.3	0.52
5	0.60	39.5	0.43	27.2	0.13
10	0.58	59	0.40	40.5	0.19
15	0.55	79	0.30	54.5	0.16
		100	0.16	68	0.16
				82	0.16
				100	0.16

Stripping test work performed on Alamine 336 showed that stable emulsions formed in the organic phase at the pH values investigated of 6, 7 and 8. Thus the optimal conditions for stripping of Alamine 336 were not determined. Stripping of CYANEX 923 using distilled water was poor with a low loaded strip liquor concentration of 0.05 *M* zinc obtained. Stripping of CYANEX 923 with a 1 *M* sodium chloride solution as a strip liquor was worse than with water. It was shown that TBP could be successfully stripped using both distilled water and a 1 *M* sodium chloride solution as a strip liquor. Stripping efficiencies of up to 99% were obtained for both strip liquors with loaded strip liquors containing 0.73 and 0.62 *M* zinc for the distilled water and 1 *M* sodium chloride solution, respectively.

It is evident from the work conducted that the extraction reaction is complex. This is most likely due to speciation in the aqueous solution. Different concentrations of zinc, chloride and acid in the feed will result in different dominant zinc species. For the neutral extractants (CYANEX 923 and TBP) it is expected that three zinc species ($ZnCl_2$, $HZnCl_3$ and H_2ZnCl_4) are most likely involved in the extraction process. It is further expected that co-extraction of HCl is likely to occur. The species involved in the extraction reaction for Alamine 336 (anionic extractant) are most likely to be $ZnCl_4^{2-}$ or $ZnCl_3^-$. It has also been suggested that hydrochloric acid could also be extracted as the species HCl_2^-. This species is most likely to occur in solutions of high ionic strength. This multiple speciation in the aqueous solution makes it difficult to easily identify the nature of the extracted complex. An added complexity is the possibility that a change or shift of species occurs due to the shifting of equilibrium as the extraction reaction proceeds.

Further evidence of the multiple speciation involved in the extraction reaction is presented in the discontinuity observed in the stripping isotherms for CYANEX 923 (Figure 4-21 and 4-23). The shape of the stripping isotherm observed in Figure 4-23 suggests that two different species are extracted. The one species is more easily stripped into the aqueous phase.

This study has shown that the leach liquors of the tARZn process can be purified using SX as a purification step. Of the three extractants studied, CYANEX 923 was found to give the best extraction performance (loading of zinc). Although Alamine 336 was found to be a slightly more effective extractant, on a molar basis (zinc extracted per mole of extractant), the lower loading of zinc achieved is unlikely to be attractive in practice. Due to CYANEX 923 being a strong extractant no suitable strip liquor was identified. It is desirable to use a strip liquor which would be readily available within the tARZn process. This would limit the potential strip liquors to either de-ionised water, a solution of sodium chloride or a solution of HCl or a mixture containing some sodium chloride and HCl. Stripping of TBP was achieved using water and, although it had lower extraction qualities than both CYANEX 923 and Alamine 336, it was therefore chosen as the best compromise. Alamine 336 could not be stripped using either water or the sodium chloride solution.

The solution parameters investigated indicated that the leach solutions of the tARZn process are suitable for purification by SX. The concentrations of zinc, chloride and acid have a significant impact on the aqueous speciation and the nature of the extractable complex formed. These solution parameters are seen as key in the purification by SX. Therefore solution concentrations to be fed into SX will have to be tightly controlled to maintain a favourable speciation in solution for extraction. The expected acidity of the leach liquors is in a range that is characterised by poor extraction by all three extractants and more thought will have to be given on how the acidity can be lowered to promote extraction. Co-extraction of HCl is also very likely under these conditions and its impact on the stripping has not been verified.

One parameter that has not been addressed in this study, and that could have an impact on the co-extraction and carryover of impurities, is the deportment of water. It is accepted that neutral extractants are likely to carry over significant amounts of water, due to their solvating nature, which can have a significant impact on the water balance of the process. Kuhar *et al*. (2009) reported that the extractant organic phases contained approximately 0.2%, 2.6% and 2.2% coordinated water for Alamine 336, CYANEX 923 and TBP, respectively. The Karl Fischer titration method was used to determine the amount of coordinated water in the organic phase.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The results presented in this study have shown that SX is a suitable purification step for the leach solutions of the tARZn process. The concentrations of zinc, chloride and the acidity were found to have a significant impact on the extraction process of all three extractants. Iron(II) did not have an impact on the extraction of zinc. Based on the results obtained in this study it is concluded that TBP is the most suitable commercially available extractant to use in an SX process for the tARZn process. It has been shown that it offers a compromise in acceptable quantitative extraction of zinc from chloride solutions and it can be stripped using distilled water.

Although CYANEX 923 was identified as the most suitable extractant based on the extraction process, it was shown not to be feasible as no suitable strip liquor was identified in this study. Alamine 336 was found to be the most efficient extractant on a molar basis (M zinc extracted per mole of extractant). However, Alamine 336 was not selected as the optimal pH for stripping was not identified and stable emulsions were formed at the investigated pH range of 6 to 8.

The loading capacity of TBP can be improved by using a higher concentration of extractant or in its pure (undiluted) form. At higher concentration the TBP is expected to load up to 0.57 *M* zinc which is comparable to the loading of 0.60 *M* zinc for CYANEX 923, also obtained at higher extractant concentration.

Although this work has shown that it is possible to use SX as a purification step for the tARZn process, it is recommended that further work be carried out. It is therefore necessary to continue with extraction test work to further optimise the use of TBP as an extractant. The optimisation test work should initially focus on determining an optimal aqueous feed acid concentration for extraction and optimising the strip liquor to be used. Further work should also be conducted to address the impact of impurities on the process. Once these issues have been investigated it should then be possible to develop extraction and stripping McCabe-Thiele diagrams to allow for the design of a piloting circuit.

It is also recommended that further efforts be made into determining the optimal pH for stripping for the Alamine 336 extractant as it showed that, despite being used at a lower concentration than the other two extractants, it was able to achieve quantitative zinc extraction. The effect of temperature on the stripping of Alamine 336 should also be investigated as it is well known that higher temperatures could help improve the stripping characteristics of the extractant. Similarly for CYANEX 923, it is recommended that more effort be put in to find alternative strip liquors, or the use of other methods such as precipitation to remove the loaded metal from the organic phase, as it has been shown that it has good extraction qualities. There is also scope to investigate if there are any synergistic benefits to be had by using a mixture of any of these extractants.

Further work is also required to further develop the understanding of the stoichiometry of the extracted species as the nature of the extractable species affects the loading capacity as well as how easily it is stripped. The presences of polymeric forms of an extractant will also affect the loading capacity of the extractant. Since the lower utilisation of the loading capacity of the extractant can be an economic issue it is recommended that techniques such as vapour pressure osmometry be also pursued to determine the molecular mass of extractants and extracted complexes to establish if polymerisation does occur during the extraction process.

There are limited speciation data readily available for the high ionic strength solutions being investigated for this work and for the tARZn process. To get more accurate data for activity coefficients needed to compute some of the calculations, simplified models using the Debye-Huckel theory will not be sufficient. It might therefore be necessary to approach this deficiency by using the Pitzer model to get more accurate data which will assist in developing a better understanding of the speciation in tARZn solutions. A combination of accurate speciation data and careful judicious mass balances of the three elements (H, Zn and Cl) might shed a lot more light on the interaction of various H-Zn-Cl complexes. This should give an indication of the overall position of the equilibrium between H-Cl-Zn complexes in solution with various H-Zn-Cl-L complexes in the organic phase.

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APPENDIX A

REAGENT DATA SHEETS

A. APPENDIX A: REAGENTS DATA SHEETS

The data sheets for the reagents used in the experiments are provided in the appendix in alphabetical order as follows:

- Alamine 336
- CYANEX 923
- Ferrous chloride
- Hydrochloric acid
- Nitric acid
- Shellsol A150
- Sodium chloride
- Tributylphosphate (TBP)
- Zinc chloride
- Zinc nitrate

1. Chemical product and company identification

Product name:
ALAMINE 336
CAS:
68814-95-9

Supplier
Cognis Corporation
5051 Estecreek Drive
Cincinnati, OH 45232-1446
Phone: +1 (866) 910-0598
Fax-no.: +1 (513) 482-3576

Emergency Information Chemtrec:
+1-800-424-9300

2. Composition / information on ingredients

General chemical description:
Tri C8-10 Alkyl Amines

COMPONENT:	CAS-No.	CONCENTRATION (Wt. %):
Tri-C8-10-alkyl amines	68814-95-9	100

3. Hazards identification

EMERGENCY OVERVIEW

Warning
Causes skin and eye irritation.
May be harmful if swallowed.
May be harmful to aquatic life.

Delivery state:
liquid

State:
liquid

Odor:
amine-like

Color(s):
light yellow

Routes of entry:
Skin contact

Potential Health Acute Effects:

Inhalation:
Prolonged or excessive inhalation may cause respiratory tract irritation.

Skin contact:
Causes skin irritation.

Eye contact:
Causes eye irritation.

Ingestion:
May be harmful if swallowed.

Potential Chronic Health Effects:
None known

4. First aid measures

After inhalation:
Move to fresh air.
If adverse health effects develop seek medical attention.

After skin contact:
Rinse with plenty of water.
Remove contaminated clothes.
Get medical attention.

After eye contact:
Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes.
Get medical attention.

After ingestion:
Give one to several glasses of water to drink and refer to medical personnel or take direction from either a physician or a poison control center.

5. Fire fighting measures

Flash point:
335 °F (335 °F)
ASTM D 92-97; QP1363.2; Flash and Fire Points by Cleveland Open

Flammable/Explosive limits:

Lower limits:
Not determined.

Upper limits:
Not determined.

Suitable extinguishing media:
Water Spray
Foam.
Carbon dioxide.
Dry Chemical

Unusual fire or explosion hazards:
Water may spread fire (product floats on water).

Additional fire fighting advice:
Use water only as a blanket.

6. Accidental release measures

Environmental precautions:
Collect rinsate for disposal.

Process for cleaning and take-up:
Pick up spilled material and containerize for recovery or disposal.
Using adequate protective equipment, add dry material to absorb spill (if large spill, first dike to contain).
Flush area with dilute (5%) acetic acid.

7. Handling and storage

Handling:

Handling advice:
No particular measures required.

8. Exposure controls / personal protection

Indication for system design:
Ensure adequate ventilation.

Personal protection measures:

Respiratory protection:
Not applicable with adequate ventilation.

Hand protection:
Protective gloves made of plastic.
Protective gloves made of rubber.

Eye protection:
Wear tight fitting goggles.

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9. Physical and chemical properties

General description:

Delivery state:	liquid
State:	liquid
Odor:	amine-like
Color(s):	light yellow

Designation	Value	Method
Density	0.800 g/cm3	
Solubility in Water	Negligible (< 0.1 %)	no information
Analysis of Volatile matter	0 %	no information
Analysis of Volatile organic components	0 %	no information

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10. Stability and reactivity

Stability:

Conditions to avoid:
None known

Dangerous decomposition products:
None if used for intended purpose.

Decomposition advices:
No decomposition if used according to specifications.

Reactivity:

Materials to avoid:
None known

Hazardous polymerization:
Will not occur

11. Toxicological information

Acute oral toxicity:
LD50 > 2000 mg/kg body weight (analogy)
LD50 > 5000 mg/kg body weight (Experiment)

Skin irritation:
irritating (analogy)
irritating (Experiment)

Eye irritation:
irritating (analogy)

In vitro mutagenicity:
not mutagenic (analogy)

12. Ecological information

Acute fish toxicity:
LC50 > 1 - <= 10 mg product/l. (analogy)

Acute bacterial toxicity:
EC0 > 1 - <= 10 mg product/l. (analogy)

Ultimate biodegradation:
Good biodegradability. All organic substances contained in the product achieve > 60% BOD/COD or CO2 liberation, or > 70% DOC reduction in tests for ease of degradability. Threshold values for 'readily degradable' (e.g. to OECD method 301) are reached.

13. Disposal considerations

Waste disposal of product:
Dispose of in an approved landfill in accordance with federal, state / provincial and local regulations.
This product, if disposed as shipped, is not a hazardous waste as specified in 40 CFR 261.

14. Transport information

U.S. Department of Transportation Ground (49 CFR):

Proper shipping name:	Environmentally hazardous substances, liquid, n.o.s. (trialkylamine C8-C10)
Hazard class or division:	9
Danger Labels:	9
Identification number:	UN 3082
Packing group:	III
Marine pollutant:	None
ERG/EMS:	171
RQ:	None

International Air Transportation (ICAO/IATA):

Proper shipping name:	Environmentally hazardous substance, liquid n.o.s. (trialkylamine C8-C10)
Hazard class or division:	9
Danger Labels:	9
Identification number:	UN 3082
Packing group:	III
RQ:	None

Water Transportation (IMO/IMDG):

Proper shipping name:	ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S. (trialkylamine C8-C10)
Hazard class or division:	9
Danger Labels:	9
Identification number:	UN 3082
Packing group:	III
Marine pollutant:	None
ERG/EMS:	F-A;S-F
RQ:	None

The transport information provided represents the regulatory transport classification of the product without consideration to packaging, quantity, or modal restrictions and exceptions. It is the user's responsibility to determine the appropriate packaging and modal requirements and/or limitations for the product quantity being shipped.

15. Regulatory information

TSCA Inventory Status:	This product and/or all of its components are either included on or exempt from the TSCA Inventory of Chemical Substances.
SARA 311/312 Hazard Categories:	Immediate Health
TSCA 12(b) Components:	none

SARA 313 Toxic Chemicals: none

SARA 302 Extremely Hazardous Substances: none

CERCLA Hazardous Chemicals: none

California Proposition 65: No California Proposition 65 listed chemicals are known to be present.

16. Other information

NFPA Rating (US)	Value
Health	2
Fire	1
Reactivity	0
Special Hazard	

HMIS Rating (US)	Value
Health	2
Flammability	1
Reactivity	0

All information, recommendations, and suggestions appearing herein concerning our product are based upon tests and data believed to be reliable. However, it is the user's responsibility to determine the safety, toxicity, and suitability for his own use of the product described herein. Since the actual use by others is beyond our control, no guarantee, express or implied, is being made as to the effects of such use, the results obtained, or the safety and toxicity of the product nor is their any assumed liability arising out of use, by others, of the product referred to herein. The information herein is not to be construed as absolutely complete since additional information may be necessary or desirable when particular or exceptional conditions or circumstances exist or because of applicable laws or government regulations.

CYTEC

CYANEX® 923 Extractant

Solvent Extraction Reagent

- Recovery of uranium from wet process phosphoric acid
- Cesium recovery
- Recovery of rhenium
- Acetic acid recovery from effluent streams
- Phenol extraction

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ANALYTICAL METHODS

CYANEX® 923 extractant is a liquid phosphine oxide which has potential applications in the solvent extraction recovery of both organic and inorganic solutes from aqueous solution, e.g. carboxylic acids from effluent streams and the removal of arsenic impurities from copper electrolytes.

The major advantage of CYANEX 923 extractant over similar extraction reagents, e.g. TOPO (trioctylphosphine oxide), is that it is completely miscible with all common hydrocarbon diluents even at low ambient temperatures. The major benefit of high solubility lies in the ability to prepare concentrated, stable solvents which can recover solutes (e.g. acetic acid) that are normally only weakly extracted by this type of reagent.

Composition

CYANEX 923 extractant is a mixture of four trialkylphosphine oxides as follows:

$R_3P(O)$ $R_2R'P(O)$ $RR'_2P(O)$ $R'_3P(0)$
Where R = $[CH_3(CH_2)_7]$ - normal octyl
R'= $[CH_3(CH_2)_7]$ - normal hexyl

Average Molecular Weight = 348 (approximately)

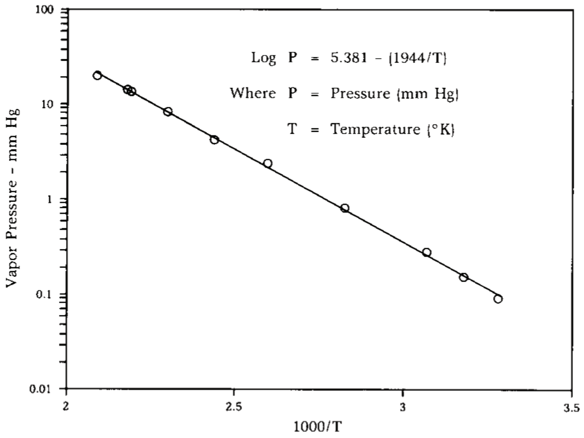
Typical Properties

Trialkylphosphine oxides : 93%
Appearance : Colorless mobile liquid
Specific Gravity : 0.88 at 25°C
Freezing Point : -5 to 0°C
Viscosity : 40.0 centipoise at 25°C
: 13.7 centipoise at 50°C
Flashpoint : 182°C
(Closed Cup Setaflash)
Autoignition Temperature : 281°C
Vapor Pressure* : 0.09 mm. Hg at 31°C
Boiling Point : 310°C at 50 mm Hg
Solubility in Water : > 10 mg/1
CYANEX 923 extractant : 8 w/o

Surface Tension	@ 25°C	9.0 dynes/cm
	@ 100°C	7.5 dynes/cm
	@ 150°C	5.2 dynes/cm
Viscosity Kinematic	@ 25°C	51.6 cSt
	@ 50°C	18.9 cSt
	@ 100°C	4.2 cSt
Specific Heat	@ 25°C	0.45 cal/gm/°C
	@ 50°C	0.47 cal/gm/°C
	@ 100°C	0.51 Cal/gm/°C
Thermal Conductivity	@ 25°C	0.000302 cal/cm/sec/°C
	@ 120°C	0.000288 cal/cm/sec/°C
	@ 200°C	0.000274 cal/cm/sec/°C

** Shown as function of temperature in Figure 1*

FIG. 1 — EFFECT OF TEMPERATURE ON VAPOR PRESSURE



Suitability of Construction Materials

Samples of the following plastics and rubbers (in the form of tubing) were immersed for 200 hours at 50°C in glass vessels containing CYANEX 923 extractant.

The results are summarized below:

Material	Remarks
Butyl Rubber	Unsuitable. Rapid swelling and softening.
Teflon Fluorocarbon Film*	Suitable. No detectable effect.
Polypropylene	Suitable. No detectable effect.
Natural & Black Latex Rubber	Unsuitable. Complete dissolution in less than 192 hours.
PVC (Laboratory Grade)	Short-term suitability. Loss of plasticity in less than 192 hours.
PVC (Solvent Grade)	Suitable. Only a slight increase in dimension observed.
Red Gum Rubber	Unsuitable: Rapid swelling and softening.
Viton Fluoroelastometer*	Suitable. No detectable effect.
Silicone	Unsuitable. Disintegrated after 56 hours.

Samples of the following metals in the form of coupons (approximate dimensions 50 mm x 20 mm. x 3 mm) were immersed for 1000 hours at 50°C in glass vessels containing CYANEX 923 extractant. The following observations were made.

Metal	Remarks
Mild Steel	No detectable corrosion.
Stainless Steel (316)	No detectable corrosion.
Stainless Steel (304)	No detectable corrosion.
Aluminum	No detectable corrosion.

**Product of E.L DuPont* de Nemours & Co.

ORGANIC SOLUTES

Carboxylic Acid Recovery

Processes in petrochemical plants, wood pulping mills, and other chemical facilities often generate aqueous effluent streams containing carboxylic acids; particularly acetic acid. Typically, these acids are present in concentrations between 1 and 50 g/l.

A solvent extraction plant to recover acetic acid from an effluent stream has been operated successfully by Lenzing A.G. in Austria since 1983. Briefly, the process involves extracting acetic acid with a solvent containing TOPO and stripping the loaded solvent by distillation.

The advantage of using CYANEX 923 extractant in this application, as opposed to TOPO, lies in the ability to prepare a concentrated, low freezing point solvent.

This leads to lower staging requirements in extraction and virtually eliminates the problem of plant freeze-up during periods when the ambient temperature is low.

The potential for CYANEX 923 extractant in this application is illustrated by the acetic acid extraction isotherms shown in Figure 2. The isotherms were plotted from the data in Table 1.

FIG. 2 — ACETIC ACID EXTRACTION ISOTHERMS

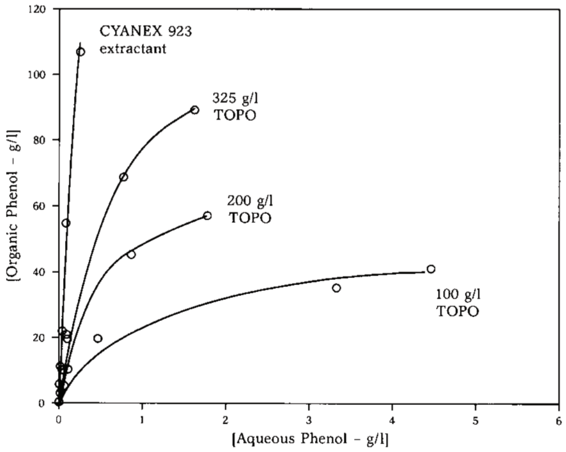


TABLE 1
Acetic Acid Recovery

Solvents : CYANEX 923 extractant undiluted) 150 g/l and 400 g/L TOPO in DPA diluent*
Aqueous : 10 g/l acetic acid (approx.)
Temperature : 50°C
Contact Time : 5 minutes

Equilibrium Acetic Acid Concentration (g/l)

	150 g/l TOPO		400 g/l TOPO		CYANEX 923 extractant	
A/O	Org.	Aq.	Org.	Aq.	Org.	Aq.
10	-	-	-	-	27.7	6.84
5	-	-	-	-	22.0	5.22
2	5.60	7.20	8.40	5.80	13.0	3.11
1	5.30	4.70	7.50	2.50	7.87	1.74
0.5	3.43	3.15	4.48	1.05	4.41	0.80
0.2	1.77	1.15	1.92	0.40	-	-
0.1	0.95	0.55	9.95	0.20	-	-

* *DPA,a high boiling (330-379oC) diphenylalkene diluent, is a product of Conoco Chemicals Co. (a division of Conoco).*

Phenol Recovery

Phenols, like carboxylic acids, are a common component of many aqueous effluents, e.g. waste streams produced during coal liquefaction, coal gasification (steel manufacture), and in the petrochemical industry.

Again, the potential benefit of recovering phenol by solvent extraction with CYANEX 923 extractant is the ability to construct plants with minimal staging requirements. Since phenol is strongly extracted by phosphine oxides, the advantages of CYANEX 923 extractant vs. TOPO are less marked than in the case of the more weakly extracted acetic acid. The major factor in choosing between the two in phenol systems will obviously depend upon the concentration of phenol in the effluent.

Phenol extractions isotherms are shown in Figure 3 and were plotted using the batch, shake-out data given in Table 2. Composition of the aqueous solution was chosen to approximate a real effluent. As with carboxylic acids, stripping is achieved by distillation.

Estimates indicate significant savings in capital and operating costs vs. the conventional Phenosolvan process.

FIG. 3 — PHENOL EXTRACTION ISOTHERMS

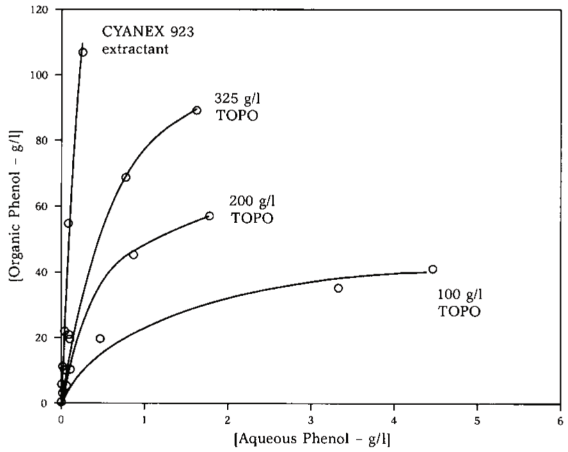


TABLE 2
Phenol Recovery

Solvents : CYANEX 923 extractant (undiluted) 100, 200 and 325 g/l TOPO in Nalkylene 500 diluent*
Aqueous : 10 g/l phenol (approx.) and 30 g/l Na_2SO_4. Initial pH = 5 (approx.)
Temperature : 50°C
Contact Time : 5 minutes

Equilibrium Phenol Concentration (g/1)

	100 g/l		200 g/l		325 g/l		CYANEX 923 extractant	
A/O	Org.	Aq.	Org.	Aq.	Org.	Aq.	Org.	Aq.
10	-	-	-	-	88.8	1.65	107.2	0.28
7	40.0	4.48	56.6	1.79	68.2	0.79	-	-
5	34.3	3.34	45.0	0.87	-	-	54.6	0.089
2	19.4	0.47	19.6	0.10	20.9	0.08	21.0	0.028
1	10.1	0.10	9.84	0.04	10.5	0.04	11.0	0.013
0.5	5.07	0.05	4.93	0.02	5.25	0.03	5.50	0.005
0.25	2.54	0.02	2.46	0.01	2.63	0.02	2.75	0.002**

* *Nalkylene 500, a linear alkyl benzene di7uent, is a product of Conoco Chemicals Co. (a division of Conoco.)*
***Detection limit of the analytical method.*

Ethanol Extraction

CYANEX 923 extractant exhibits a separation factor in ethanol/water solutions near the maximum useful limit for recovery from continuous fermentation broths, typically containing 5% ethanol. Higher values do not further reduce extractor size or energy required in the downstream distillation. This is illustrated in Figure 4 where separation factors for CYANEX 923 extractant and for other candidate extractants are shown in relation to the upper and lower limits. Extraction coefficients, and their effect on extractor size, are also plotted in Figure 4. The coefficient for CYANEX 923 extractant is well into the flat part of the curve. This excess capacity can be exchanged for increased separation factor, if needed, by dilution with inert diluents.

The principle advantage of CYANEX 923 extractant lies in its very low solubility in water. This obviates or minimizes extra processing of raffinate that would be required by more soluble extractants. The solubilities in water of CYANEX 923 extractant and of other candidate ethanol extractants are compared in Table 3.

FIG. 4 — ETHANOL EXTRACTION

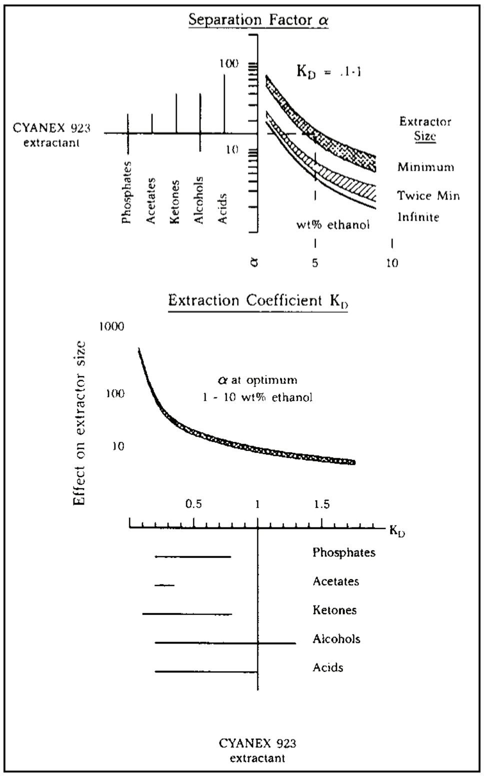


TABLE 3
Solubility in Water, WT%

	Exptl(1)	UNIFAC(4)
CYANEX 923 extractant	0.001(2)	
Phosphates		
Tri-n-Butyl	0.042(3)	
Acetates		
n-Butyl	0.64	
i-Butyl	0.85	
Ketones		
Methyl Isobutyl	1.9	
Diisobutyl	0.083	
Isophorone		0.19
Alcohols		
3-Phenyl-l-Propanol		0.15
2-Ethyl-l-Butanol		0.88
3-Methyl-3-Pentanol	4.3	
4-Methyl-2-Pentanol	1.6	
3-Ethyl-3-Pentanol	1.7	
2,4-Dimethyl-3-Pentanol	0.7	
1-Octanol	0.051	
2,2-Dimethyl-3-Octanol		0.017
3,7-Dimethyl-3-Octanol		0.017
1-Nonanol	0.013	
1-Decanol	0.0037	
4-Decanol		0.016
1-Dodecanol	0.00023	
1-Tridecanol		0.00072
Acids		
2-Ethyl-4-Methyl Pentanoic		0.24
n-Hexanoic	1.1	
2-Ethyl Hexanoic		0.24
n-Octanoic		0.24
Neodecanoic		0.032

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(1) J.M. Sorenson and W. Arlt, "Liquid-Liquid Equilibrium Data Collection," DECHEMA, Vol. V, Part 1 (1979)

(2) This work

(3) W.N. Schulz and J.P. Navratil, "Science and Technology of Tributyl Phosphate," CRC Press (1982)

(4) A. Fredenslund, et. al., "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," AICHE Journal *21, No. 6, (1975), pp. 1086-1099.*

INORGANIC SOLUTES

Impurity Removal from Copper Electrolytes

Briefly, the advantages of removing arsenic, antimony and bismuth impurities from copper electrolytes by solvent extraction rather than conventional processes consist of improvements in current efficiency, the quality of electrolytic copper, and in the productivity of the tankhouse. Minimizing the formation of arsine gas is also an important consideration.

Data on the extraction of arsenic, antimony and bismuth from a synthetic, nickeliferous copper electrolyte are given in Table 4. The corresponding arsenic and antimony extraction isotherms are shown in Figure 5. McCabe-Thiele interpolations indicated a reduction in the electrolyte arsenic concentration from 6 g/1 to 1 g/l in two theoretical stages at O/A = 4. Under these conditions, the data indicated quantitative extraction of bismuth, 30-40% extraction of the antimony and a solvent loaded to 10-20 g/l H_2SO_4. High selectivity against copper and nickel extraction was observed. Copper loading in the solvents varied from 3 to 5 mg/1 while no nickel extraction was observed.

Scrubbing sulfuric acid from the loaded solvent was readily achieved with water. The data in Table 5 and Figure 6 implied essentially quantitative removal in 3 theoretical stages at O/A=8 to produce a scrub liquor containing 130 g/l H_2SO_4 for recycle. The feasibility of a selective metal/acid scrub was also indicated.

Water proved to be an effective strip feed at a lower O/A ratio as shown by the data in Table 6 and the arsenic stripping isotherm plotted in Figure 7

Interpolations from the isotherm showed complete arsenic stripping in 5 stages at O/A = 2. Quantitative antimony stripping was estimated under these conditions while approximately 0.07 g/l bismuth remained loaded on the solvent.

Solubility losses of the extractant in this system varied from 1 mg/l in the electrolyte to 10 mg/l in the strip liquor.

TABLE 4
Arsenic, Antimony and Bismuth Extraction Isotherms

Solvent : 50 v/o CYANEX 923 extractant in Exxsol D-80 diluent*
Aqueous : 31.3 g/l Cu, 8.4 g/l Ni (as sulfates), 7.30 g/l As, 0.35 g/l Sb, 1.10 g/l Bi, 167.4 g/l H_2SO_4
Contact Time : 5 minutes
Temperature : 50^{o}C

Equilibrium Metal Concentration (g/1)

	Arsenic		Antimony	
O/A	Organic	Aqueous	Organic	Aqueous
1	1.60	5.70	0.15	0.20
2	1.43	4.45	0.08	0.20
5	1.04	2.10	0.03	0.22
10	0.63	1.03	0.01	0.24

Bismuth quantitatively extracted at all O/A ratios

TABLE 5
Sulfuric Acid Scrubbing Using Water

Solvent : 50 v/o CYANEX 923 extractant in Exxsol D-80 diluent; loaded to 16.4 g/l H_2SO_4 and 1.90 g/l As, 0.14 g/l Sb and 1.10 g/l Bi
Scrub Feed : Distilled Water
Contact Time : 5 minutes
Temperature : 50^{o}C

Equilibrium H_2SO_4 Concentration

O/A	Organic	Aqueous
0.5	0	9.1
1	0	17.4
5	0.7	78.4
10	5.4	110.0
20	9.9	130.2

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* *A product of Exxon Co., U. S. A.*

TABLE 6
Arsenic, Antimony and Bismuth Stripping Isotherms

Solvent : 50 v/o CYANEX 923 extractant in Exxsol D-80 diluent; loaded to 1.38 g/l As, 0.061 g/l Sb. 0.19 g/l Bi
Strip Feed : Distilled Water
Contact Time : 5 minutes
Temperature : 50^{o}C

Equilibrium Metal Concentration g/l

	As		Sb		Bi	
O/A	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
0.5	0	0.71	0	0.033	0.01	0.09
1	0.28	1.10	0	0.061	0.02	0.17
2	0.53	1.71	0	0.14	0.08	0.22
5	0.89	2.45	0.009	0.26	0.14	0.26
10	1.08	3.05	0.029	0.32	-	-

FIG. 5 — ARSENIC AND ANTIMONY EXTRACTION ISOTHERMS

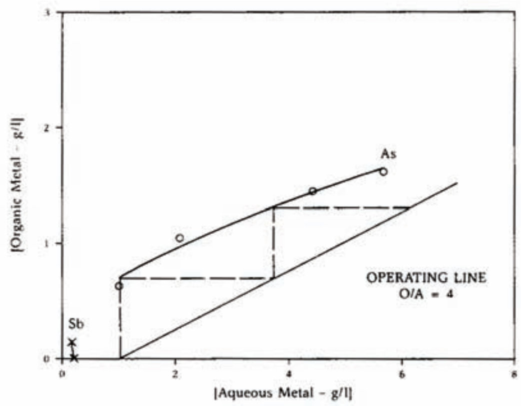


FIG. 6 — SULFURIC ACID SCRUBBING

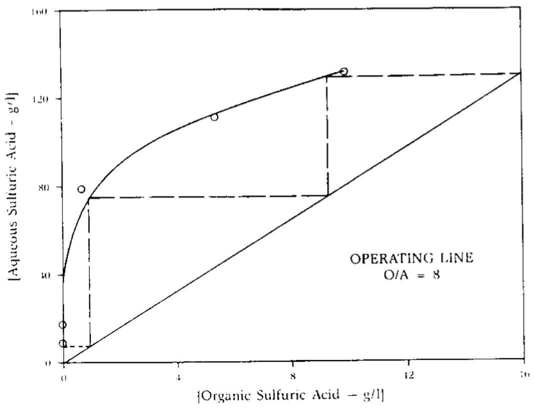
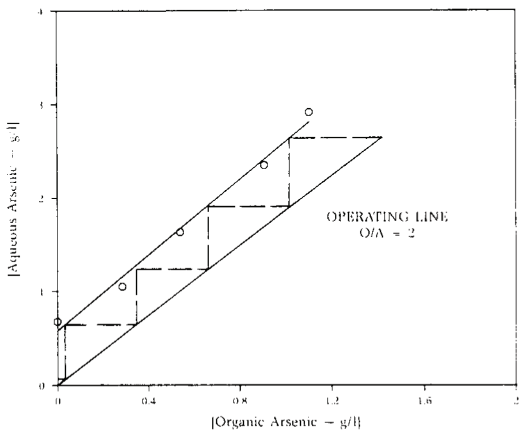


FIG. 7 — ARSENIC STRIPPING ISOTHERM



Uranium Extraction From Wet Process Phosphoric Acid

The conventional process for recovering uranium from wet process phosphoric acid involves extraction with a synergic mixture of D2EHPA and TOPO. CYANEX 923 extractant is a potential substitute for TOPO in this process and offers a materials handling advantage in that it is a liquid, while TOPO is a solid at normal temperatures (melting point approximately 50°C) and must be melted for ready removal from its container.

The feasibility of using CYANEX 923 extractant in this application is illustrated by the results of shake-out tests which are presented in Table 7 and Figure 8.

TABLE 7
Uranium Recovery from Wet-Process Phosphoric Acid Using Synergic Mixtures of Phosphine Oxides and D2EHPA

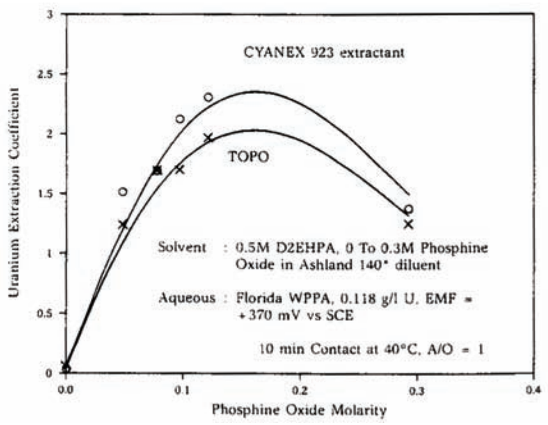
Solvent : All 0.5M D2EHPA in Ashland 140 diluent*. Varying in Phosphine Oxide concentration from 0 to 0.3M.
Aqueous : Florida WPPA 0.118 g/l U, oxidized with H_2O_2 to + 370 mV (vs.SCE).
A/0 : 1
Temperature : 40°C
Contact Time : 10 minutes

Phosphine Oxide Molarity	Uranium Extraction Coefficient (E_A^O) TOPO	 CYANEX 923 Extractant
0	0.08	0.05
0.05	1.26	1.54
0.08	1.73	1.72
0.10	1.73	2.16
0.125	2.00	2.34
0.3	1.26	1.39

$$E_A^O \quad \frac{\text{Uranium Concentration In Solvent}}{\text{Uranium Concentration In Aqueous}} = \text{At Equilibrium}$$

**Ashland 140, an aliphatic diluent, is a product of Ashland Chemical Co.*

FIG. 8 — EFFECT OF PHOSPHINE OXIDE MOLARITY ON URANIUM EXTRACTION FROM WPPA



Niobium - Tantalum Separation

Niobium - tantalum separation is normally effected using MIBK. The disadvantage here is the high aqueous solubility of the ketone (approximately 20 g/1) and the consequent need to treat the raffinate for recovery of the extractant. Recent work' has shown that TOPO has utility in niobium - tantalum separation and is reported to produce higher purity niobium oxide than MIBK.

The advantage of using CYANEX 923 extractant in place of TOPO is again related to its liquid state and higher organic solubility.

A strong diluent effect was observed in preliminary experiments on niobium extraction. This is illustrated by the results of extraction isotherms given in Table 8 and plotted in Figure 9. Aromatic 150* proved to be the superior diluent in comparison to both Aromatic 100* and Exxsol D-80.

The process for niobium - tantalum separation, as with MIBK and TOPO, consists of extracting both metals followed by a selective strip; first of niobium and then of tantalum. This is illustrated in Table 9 and Figure 10 where selective stripping of niobium. from a niobium - tantalum loaded solvent was observed using a strip feed containing 0. 1 N NH_4OH and 1 % NH_4F. Tantalum was subsequently stripped using a more basic strip feed of 0.4 N NH_4OH and 4% NH_4F.

*A product of Exxon Co., U.S.A.

TABLE 8

The Effect of Diluent Type on Niobium Extraction

Solvent : 277 g/l (0.8M) CYANEX 923 extractant in the appropriate diluent.
Diluents : Exxsol D-80, Aromatic 100 and Aromatic 150
Aqueous : 88.5 or 91.4 g/l Nb, 4N HF, 8N H_2SO_4
Temperature : 24^{o}C
Contact Time : 5 minutes

Equilibrium Nb Concentration (g/1)

	EXXSOL D-80		Aromatic 100		Aromatic 150	
O/A	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
2	43.8	66.6	38.7	72.0	61.3	60.7
1	36.6	51.9	39.7	51.7	61.9	29.5
0.5	36.6	15.3	36.5	18.5	44.8	1.86
0.3	-	-	-	-	27.2	0.73
0.2	17.4	1.53	18.2	0.30	18.2	0.56
	8.84	0.07	9.12	0.13	9.13	0.05

FIG. 9 — EFFECT OF DILUENT TYPE ON NIOBIUM EXTRACTION

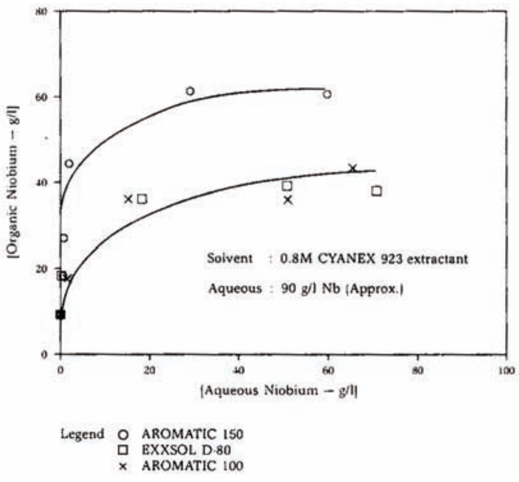


TABLE 9
Niobium Stripping From a Solvent Containing Niobium and Tantalum

Solvent	:	277 g/l (0.8M) CYANEX 923 extractant in Aromatic 150 diluent. Loaded to 22.4 g/1 Nb and 3.61 g/l Ta.
Strip Feed	:	0.1N NH_4OH, 1% NH_4F
Contact Time	:	5 minutes
Temperature	:	24°C

Equilibrium Nb Concentration g/l		
A/0	Organic	Aqueous
5	0	4.66
2	0	11.6
1	0	22.7
0.05	3.30	38.2
0.2	10.9	57.3
0.1	14.8	75.6

TABLE 10
Tantalum Stripping Isotherm

Solvent	:	277 g/l (0.8M) CYANEX 923 extractant in Aromatic 150 diluent. Loaded to 6.78 g/1 Ta.
Strip Feed	:	0.4N NH_4OH, 4% NH_4F
Contact Time	:	5 minutes
Temperature	:	24°C

Equilibrium Ta Concentration g/l		
O/A	Organic	Aqueous
2	0	3.39
1	0.61	5.93
0.5	0.74	11.6
0.2	2.66	19.4
0.1	4.71	18.3

FIG. 10 — NIOBIUM STRIPPING ISOTHERM

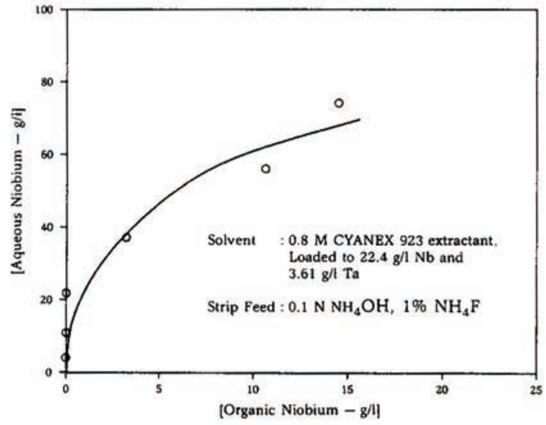
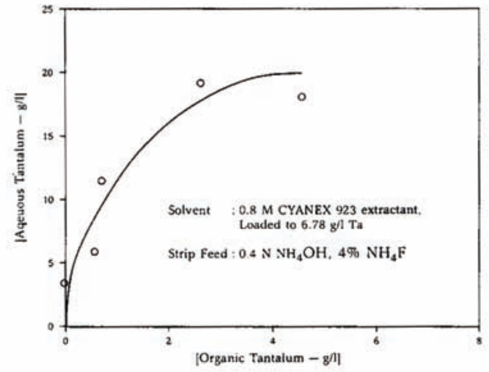


FIG. 11 — TANTALUM STRIPPING ISOTHERM



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[1] *R. Hahn and H. Retelsdorf. Production of Pure Niobium Using a New Extraction Process for Niobic Oxide and Optimal Reduction Processes. Erzmetal, 37, (9), 444-448 (1984).*

12 Potential Applications

Cadmium Removal from Phosphoric Acid

Cadmium sometimes occurs as an undesirable impurity in phosphoric and other acids. The data given in Table 11 illustrate the ability of CYANEX 923 to readily reduce the concentration of cadmium from 10 mg/l to below a target of 2 mg/l; the specification in this particular application. McCabe-Thiele interpolations from the isotherm (Figure 12) indicate minimal staging requirements and that cadmium can be reduced from 10 mg/1 to < 2 mg/1 in two theoretical stages at A/0 = 4.

Cadmium, as well as co-extracted acids, are efficiently stripped from the loaded solvent with water as shown by the data in Table 12. The stripping isotherm (Figure 13) again indicates minimal staging requirements.

TABLE 11
Extraction of Cadmium from HCl/H_3PO_4 Using 2.5 v/o CYANEX 923

Solvent : 2.5 v/o CYANEX 923 in Exxsol D-80
Aqueous : 10.2 mg/1 Cd^{2+}, 100 g/l HCl, 133 g/1 H_3PO_4
Phase Contact : 10 mins at 40°C

Equilibrium Concentration

	Cd(mg/l)		HCl (g/l)		H_3PO_4 (g/l)	
A/O	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
0.25	2.46	0.36	0.6	97.6	0.75	130
0.5	4.85	0.51	1.3	97.4	0.5	132
1	9.37	0.83	2.5	97.5	1	132
2	17.6	1.40	2.4	98.8	2	132
5	40.6	2.08	6.0	98.8	5	132

FIG. 12 – CADMIUM EXTRACTION ISOTHERM: 2.5 v/o CYANEX 923

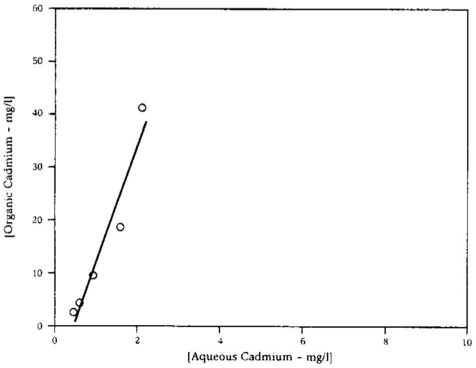


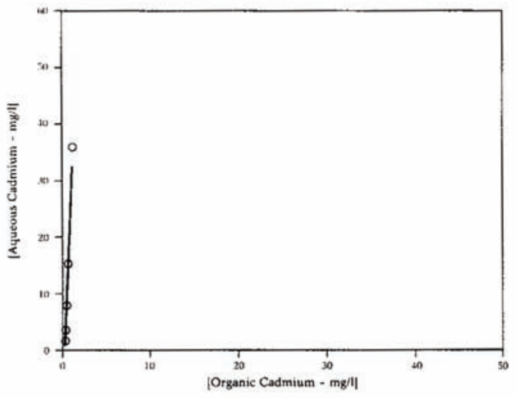
TABLE 12
Cadmium Stripping from 2.5 v/o CYANEX 923

Solvent : 2.5 v/o CYANEX 923 in Exxsol D-80 loaded to 8.05 mg/1 Cd, 1.3 g/1 HC1, 1.2 g/1 H_3PO_4
Strip Feed : Water
Phase Contact : 10 mins at 40°C

Equilibrium Concentration

	Cd(mg/l)		HCl (g/l)		H_3PO_4 (g/l)	
A/O	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
5	0.15	1.58	0	0.2	0	0.3
2	0.15	3.95	0	0.6	0	0.7
1	0.40	7.65	0	01.0	0	1.3
0.5	0.50	15.1	0	2.2	0	2.5
0.2	0.79	36.3	0	5.4	0	6.4

FIG. 13 – CADMIUM STRIPPING ISOTHERM: 2.5 v/o CYANEX 923



ANALYSIS IN ORGANIC SOLVENTS

As described, the gas chromatographic procedure is suitable for analyzing solvents containing approximately 120 g/l CYANEX 923 extractant. Other concentrations may be determined by diluting the solvent appropriately or adjusting the composition of the standard solution.

CYANEX 923 extractant is a mixture containing four major components, as follows: Trihexylphosphine oxide (1), dihexylmonooctyl- phosphine oxide (2), dioctylmonohexyl-phosphine oxide (3) and trioctylphosphine oxide (4).

The method is based upon the fact that, within the limits of experimental error, the response factors for components 1, 2 and 3 are the same as for 4 and that 4 (TOPO) is readily available and may be easily purified to AR grade.

Reagents

1. Didecylphthalate (AR grade - internal standard)
2. TOPO (purified - see note 1)
3. Process diluent (e.g. Escaid* 110 diluent)

Calibration

1. Accurately weigh 1g (± 1 mg) of pure TOPO and 2g (± 0. 1 g) of didecylphthalate into a 50 ml volumetric flask. Dissolve and make up to volume with the process diluent.
2. Analyze the above standard solution as described under "Gas Chromatographic Conditions" to determine the relative response factor of TOPO vs. didecylphthalate.

Procedure

1. Centrifuge the solvent to be analyzed or filter through PS paper" to remove entrained aqueous or suspended solids.
2. Accurately weigh 2g (±0.1g) of didecylphthalate into a 50 ml volumetric flask and pipette 25 ml of the clarified solvent into the same flask. Make up to volume with the process diluent.
3. Determine the relative response factor of each component of CYANEX 923 extractant vs. that of the internal standard as described under "Gas Chromatographic Conditions".

Calculations

Total Concentration of Trialkylphosphine Oxides (g/1)

$$\sum \left[\frac{R_{4S}}{R_{na}} \right] \times 2 \times C_{4S}$$

Where R_{4S} = Relative response factor for TOPO in the standard solution

R_{na} = Relative response factor for the n^{th} component in the analyte solution.

C_{4S} = Concentration of TOPO in the standard solution (g/1)

Gas Chromatographic Conditions

Instrument	:	Perkin Elmer Sigma 115 or equivalent
Column	:	30 in x 0.32 mm fused silica capillary column coated with 0.25 µm of DB1
Detector	:	FID
Carrier Gas	:	Helium at 18 psig
Vent Flow	:	100 ml/min
Column Flow	:	4.3 ml/min
Split Ratio	:	23/1
Temperatures ^{o}C		
Detector	:	340
Injection Port	:	340
Column	:	220 to 330 at 10^{o}C/min
Sample Injection Volume	:	0.1 µl
Peak Areas	:	Determined by electronic integration

Notes

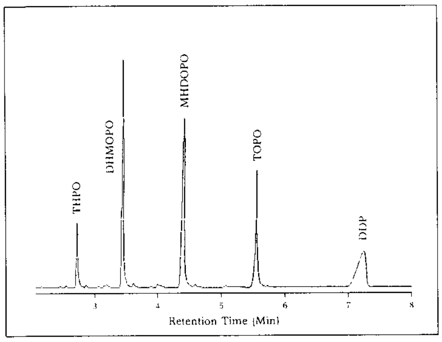
1. A chromatograrn of commercial CYANEX 923 extractant is shown in Figure 1A.
2. Pure TOPO (>99.5%) can be obtained by recrystallizing commercial grade TOPO from hexane (three recrystallizations are necessary).
3. Megabore columns may be used as an alternative to capillary columns. A thermal conductivity detector may also be used in place of an FID.
4. The method is based upon a single point determination. If required, a calibration curve can be constructed by varying the concentration of TOPO in the standard solution while maintaining a constant concentration of the internal standard.
5. This method has not been validated.

---

* *A product of Exxon Co., U.S.A.*

** *Phase separation paper available from Whatman, Inc., Clifton, NJ*

FIG. 2A — CHROMATOGRAM OF CYANEX 923 EXTRACTANT CONTAINING DIDECYLPHTHALATE (DDP) AS AN INTERNAL STANDARD



ANALYSIS IN AQUEOUS SOLUTION

The aqueous solubility of each component of CYANEX 923 extractant will normally be <2 mg/l. The method is based on analysis of the aqueous sample by gas chromatography. The response factors of the four active components are equal within the limits of experimental error.

Reagents

1. Tetrahydrofuran (THF). "Baker Analyzed Reagent, 100%."
2. TOPO (purified - see note 1.)

Calibration

1. Prepare a stock solution by accurately weighing (± 1 mg) approximately 0.5 g of TOPO into a 50 ml volumetric flask. Dilute to 50 ml with THF and dissolve the TOPO.
2. Dilute aliquots of the stock solution with distilled water to prepare standard solutions containing 2, 5, 10 and 30 mg/l of TOPO.
3. Analyze the solutions as described under "Gas Chromatographic Conditions.

Procedure

1. Filter the aqueous solution to remove entrained organic
2. Inject 3µl of the analyte solution and analyze as described under "Gas Chromatographic Conditions."

Calculation

1. *Response Factor for TOPO (R) =

$$\frac{\text{Conc. of TOPO in Standard (mg/1)}}{\text{Area of TOPO Standard Peak}}$$

2. Concentration of Component in Aqueous (mg/1) = Area of Component Peak (analyte) x R

*Response factor for the standard closest in concentration to the sample.

Gas Chromatographic Conditions

Instrument : Hewlett Packard 5730A or equivalent
Column : 2 ft x 1/4 inch x 2 mm ID glass Column packed with 9% OV-17 and 12% SP2401 on 80/100 mesh Supelcoport
Detector : FID
Carrier Gas : Helium at 57 psi (Flowrate 40 ml/minute)
Temperatures °C
    FID : 300
    Injection Port : 250
    Column : 230 (Isothermal)
Sample Injection Volume : 3 µl

Notes

1. Pure TOPO can be obtained by recrystallizing commercial grade TOPO from hexane. (Three recrystallizations are necessary).
2. Retention time for TOPO is approximately 12 minutes.
3. Detection limit approximately 2 mg/l.
4. This method has not been validated.

DETERMINATION OF WATER

The method is based on distilling water from CYANEX 923 extractant in the form of an azeotrope with toluene. On contacting a condenser, the water and toluene separate and fall into a graduated trap. The volume of the distillate is then measured.

Apparatus

1. 500 ml round-bottomed, short-necked glass flask with a 40/50 ground glass fitting.
2. Water-cooled condenser. Cold-finger type.
3. Dean and Stark type trap. 10 ml capacity graduated in 0.1 ml divisions with a 40/50 ground glass fitting.
4. Heating mantle controlled by a rheostat.

Reagents

1. AR grade toluene (water-free)

Procedure

1. Weigh 50 g of the sample (± 0.5 g) into the 500 ml flask.
2. Add approximately 200 ml of toluene to the flask and assemble the apparatus.
3. Heat the contents of the flask to boiling and allow to reflux for 30 to 60 minutes or until the volume of water in the trap is constant.
4. Read the volume of water in the trap at room temperature.

Calculation

$$\% \text{ Water} = \frac{\text{Volume of Water in Trap (ml)}}{\text{Sample weight (g)}} \times 100$$

Notes

1. This method has not been validated.
2. Karl-Fisher titration is not recommended.

Technical Papers (listed chronologically)

1. **A Liquid Phosphine Oxide; Solvent Extraction of Phenol, Acetic Acid and Ethanol**
   Watson, E.K.; et.al.
   Solvent Extr. Ion Exch., 6, No. 2, Pages 207-20; (1988)

2. **Solvent Extraction Separation of Niobium and Tantalum at MHO**
   Haesebroek, G.; et.al.
   Process Metall., 7B, Pages 1115-20; (1992)

3. **Simulation of Countercurrent Multistage Extraction Process for Recovery of Titanium**
   Kagaku Kogaku Ronbunshu, 19, No. 2,
   Pages 214-19; (1993)

4. **Computer Modelling of Countercurrent Multistage Extraction for Titanium (IV) - Sulfuric Acid - CYANEX 923 System**
   Technal. Rep. Kansai Univ., 35, Pages 59-67; (1993)

5. **Phenol Recovery with SLM using CYANEX 923**
   Garea, A.; et.al.
   Chem. Eng. Commer., 120, Pages 85-97; (1993)

6. **Computer Modelling of Countercurrent Multistage Extraction for Ti(4 +) – H_2S0_4 CYANEX 923 System**
   Int. Conf. Process. Mater. Prob.
   Pages 521-4, Ed. Henein, H. Pub.
   Miner. Met. Mater. Soc., Warrendale PA; (1993)

7. **Gold (I) Extraction Equilibrium in Cyanide Media by the Synergic Mixture of Primene 81R-CYANEX 923**
   Coravaca, C.
   Hydrometallurgy, 35, No. 1, Pages 27-40; (1994)

8. **The Phosphine Oxides CYANEX 923 and CYANEX 923 as Extractants for Gold (1) Cyanide Aqueous Solutions**
   Alquacil, F.J.; et.al.
   Hydrometallurgy, 16, No. 3, Pages 369-84; (1994)

Patents (listed chronologically)

1. **Liquid Phosphine Oxide Systems for Solvent Extraction**
   Robertson, A.J. and Rickelton, W.A.
   European Pat. Appl. EP 132700 Al (1985)

2. **Procede de Separation des Terres Rares par Extraction Liquide-Liquide**
   Dellaye, T.; et.al.
   European Pat. Appl. 0284504 (1988)

3. **Recovery of Uranium from Wet Process Phosphoric Acid Using Asymetrical Phosphine Oxid**es
   Rickelton, W.A.
   U.S. Patent 4778663 (1988)

4. **Process for Solvent Extraction Using Phosphine Oxide Mixtures**
   Rickelton, W.A. and Robertson, A.J.
   U.S. Patent 4909939 (1990)

5. **Recovery of Indium from Acidic Solutions by Solvent Extraction Using Trialkylphosphine Oxide**
   Rickelton, W.A.
   Canadian Pat. Appl. CA 2077601 (1994)

6. **Method for Recovering Carboxylic Acids from Aqueous Solutions**
   Gentry, J.C.; et.al.
   U.S. Patent 5399751 (1995)

As of July 26, 1995

16 Health and Safety

The oral and dermal toxicity of CYANEX 923 extractant is low. CYANEX 923 extractant produces mild eye irritation and severe skin irritation upon contact. Repeated dermal exposure for 28 consecutive days produced severe skin irritation, but no systemic toxicity. CYANEX 923 extractant did not produce dermal sensitization in guinea pigs after repeated dermal exposure. This product did not produce mutations in bacteria nor did it produce chromosomal effects in the mouse micronucleus or human lymphocyte aberration assays. CYANEX 923 extractant is highly toxic to fish and invertebrates and great care should be exercised to avoid environmental exposure.

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SIGMA-ALDRICH

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006
Version 3.0 Revision Date 29.12.2008
Print Date 02.09.2009
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKING

Product name	:	Iron(II) chloride tetrahydrate
Product Number	:	220299
Brand	:	Sigma-Aldrich
Company	:	Sigma-Aldrich (Pty.) Ltd. 17 Pomona Street Aviation Park, Unit 4 KEMPTON PARK 1619 SOUTH AFRICA
Telephone	:	+27 11 979 1188
Fax	:	+27 11 979 1119
Emergency Phone #	:	

2. HAZARDS IDENTIFICATION

Risk advice to man and the environment
Harmful if swallowed. Irritating to skin. Risk of serious damage to eyes.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Synonyms	:	Ferrous chloridetetrahydrate
Formula	:	$Cl_2Fe \cdot 4H_2O$
Molecular Weight	:	198,81 g/mol

CAS-No.	EC-No.	Index-No.	Classification	Concentration
Ferrous chloride tetrahydrate				
13478-10-9	231-843-4	-	Xn, R22 - R38 - R41	-

4. FIRST AID MEASURES

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled
If breathed in, move person into fresh air. If not breathing give artificial respiration Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Special protective equipment for fire-fighters
Wear self contained breathing apparatus for fire fighting if necessary.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions
Use personal protective equipment. Avoid dust formation. Avoid breathing dust. Ensure adequate ventilation.

Environmental precautions
Do not let product enter drains.

Methods for cleaning up
Pick up and arrange disposal without creating dust. Keep in suitable, closed containers for disposal.

7. HANDLING AND STORAGE

Handling
Avoid contact with skin and eyes. Avoid formation of dust and aerosols.
Provide appropriate exhaust ventilation at places where dust is formed. Normal measures for preventive fire protection.

Storage
Store in cool place. Keep container tightly closed in a dry and well-ventilated place.

Air sensitive. hygroscopic Store under inert gas.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Personal protective equipment

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a dust mask type N95 (US) or type P1 (EN 143) respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Hand protection
The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it. Handle with gloves.

Eye protection
Safety glasses

Skin and body protection
Choose body protection according to the amount and concentration of the dangerous substance at the work place.

Hygiene measures
Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form	Fine crystals and fragments
Colour	light green

Safety data

pH	2,5 at 100 g/l at 20 °C

Melting point	105 - 110 °C
Boiling point	no data available
Flash point	no data available
Ignition temperature	no data available
Lower explosion limit	no data available
Upper explosion limit	no data available
Vapour pressure	13,3 hPa at 693 °C
Density	1,93 g/cm3
Water solubility	no data available
Partition coefficient: n-octanol/water	log Pow: -1,5

10. STABILITY AND REACTIVITY

Storage stability
Stable under recommended storage conditions.

Conditions to avoid
Exposure to moisture.

Materials to avoid
A mixture of this product and sodium or potassium will explode on impact., Strong bases, Strong acids, Ethylene oxide, Strong oxidizing agents

Hazardous decomposition products
Hazardous decomposition products formed under fire conditions. - Hydrogen chloride gas, Iron oxides

11. TOXICOLOGICAL INFORMATION

Acute toxicity

LD50 Intraperitoneal - mouse - 92,5 mg/kg

Irritation and corrosion

no data available

Sensitisation

no data available

Chronic exposure

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

Signs and Symptoms of Exposure

Overdose of iron compounds may have a corrosive effect on the gastrointestinal mucosa and be followed by necrosis, perforation, and stricture formation. Several hours may elapse before symptoms that can include epigastric pain, diarrhea, vomiting, nausea, and hematemesis occur. After apparent recovery a person may experience metabolic acidosis, convulsions, and coma hours or days later. Further complications may develop leading to acute liver necrosis that can result in death due to hepatic coma., Symptoms may be delayed., Effects due to ingestion may include:, Epigastric pain., Diarrhoea, Vomiting, Nausea, hematemesis

Potential Health Effects

Inhalation May be harmful if inhaled. May cause respiratory tract irritation.

Skin	May be harmful if absorbed through skin. Causes skin irritation.
Eyes	Causes serious eye irritation.
Ingestion	Harmful if swallowed.

Additional Information
RTECS: NO5600000

12. ECOLOGICAL INFORMATION

Elimination information (persistence and degradability)

no data available

Ecotoxicity effects

no data available

Further information on ecology

no data available

13. DISPOSAL CONSIDERATIONS

Product

Observe all federal, state, and local environmental regulations. Contact a licensed professional waste disposal service to dispose of this material. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber.

Contaminated packaging

Dispose of as unused product.

14. TRANSPORT INFORMATION

ADR/RID
UN-Number: 3260 Class: 8 Packing group: III
Proper shipping name: CORROSIVE SOLID, ACIDIC, INORGANIC, N.O.S. (Ferrous chloride tetrahydrate)

IMDG
UN-Number: 3260 Class: 8 Packing group: III EMS-No: F-A, S-B
Proper shipping name: CORROSIVE SOLID, ACIDIC, INORGANIC, N.O.S. (Ferrous chloride tetrahydrate)
Marine pollutant: No

IATA
UN-Number: 3260 Class: 8 Packing group: III
Proper shipping name: Corrosive solid, acidic, inorganic n.o.s. (Ferrous chloride tetrahydrate)

15. REGULATORY INFORMATION

Labelling according to EC Directives

Hazard symbols

Xn	Harmful

R-phrase(s)

R22	Harmful if swallowed.
R38	Irritating to skin.
R41	Risk of serious damage to eyes.

S-phrase(s)

S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S39	Wear eye/face protection.

16. OTHER INFORMATION

Further information

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Co., shall not be held liable for any damage resulting from handling or from contact with the above product. See reverse side of invoice or packing slip for additional terms and conditions of sale.

Safety data sheet

MERCK

According to EC Directive 91/155/EEC
04.2000 from CD-ROM 2000/1

1. Identification of the substance/preparation and of the company/undertaking

Identification of the product

Catalogue No.:	100313
Product name:	Hydrochloric acid 32% extra pure

Manufacturer/supplier identification

Company:	Merck KGaA * 64271 Darmstadt * Germany * Tel: ++49 (0)6151 72-2440
Regional representation:	This information is given on the authorised Safety Data Sheet for your country.
Emergency telephone No.:	Please contact the regional Merck representation in your country.

2. Composition/information on ingredients

Aqueous solution.

Hazardous ingredients:

Name according to EC Directives: Hydrochloric acid

Hazard symbols:	C	R-phrases:	34-37
EC-Index-No.:	017-002-01-X	Causes burns. Irritating to respiratory system.	
CAS-No..:	7647-01-0	Content:	32 %

3. Hazards identification

Causes burns. Irritating to respiratory system.

4. First aid measures

After inhalation: fresh air. Summon doctor.
After skin contact: wash off with plenty of water. Dab with polyethylene glycol 400. Immediately remove contaminated clothing.
After eye contact: rinse out with plenty of water for at least 10 minutes with the eyelid held wide open. Immediately summon eye specialist.
After swallowing: make victim drink plenty of water, avoid vomiting (risk of perforation!). Immediately summon doctor. Gastric lavage.

5. Fire-fighting measures

Suitable extinguishing media:
In adaption to materials stored in the immediate neighbourhood.

Special risks:
Non-combustible. Hydrogen may form upon contact with metals (danger of explosion!). Ambient fire may liberate hazardous vapours. The following may develop in event of fire: hydrochloric acid.

Special protective equipment for fire fighting:
Do not stay in dangerous zone without suitable chemical protection clothing and self-contained breathing apparatus.

Other information:
Prevent fire-fighting water from entering surface water or groundwater. Contain escaping vapours with water.

6. Accidental release measures

Person-related precautionary measures:
Avoid substance contact. Do not inhale vapours/aerosols. Ensure supply of fresh air in enclosed rooms.

Environmental-protection measures:
Do not allow to enter sewerage system.

Procedures for cleaning / absorption:
Take up with liquid-absorbent material (e.g. Chemizorb®). Forward for disposal. Clean up affected area.

Additional notes:
Render harmless: neutralize with diluted sodium hydroxide solution or by throwing on lime, lime sand, or sodium carbonate.

7. Handling and storage

Handling:

No further requirements.

Storage:

Tightly closed. Dry. At +15°C to +25°C. The data apply to the entire pack.

8. Exposure controls/personal protection

Specific control parameter

MAK Germany (max. workplace conc.) Hydrogen chloride:
$5\ ml/m^3$ or $7.6\ mg/m^3$

EC-value/cat. Hydrogen chloride:
$5\ ml/m^3$ or $8\ mg/m^3$

Personal protective equipment:

Respiratory protection:	required when vapours/aerosols are generated.
Eye protection:	required
Hand protection:	required

Protective clothing should be selected specifically for the working place, depending on concentration and quantity of the hazardous substances handled. The resistance of the protective clothing to chemicals should be ascertained with the respective supplier.

Other protective equipment: Acid-resistant protective clothing.

Industrial hygiene:
Immediately change contaminated clothing. Apply skin- protective barrier cream. Wash hands and face after working with substance.

9. Physical and chemical properties

Form:		liquid			
Colour:		colourless to yellowish			
Odour:		pungent			
pH value		(20 °C)	< 1		
Viscosity	dynamic	(15 °C)	1.9	mPa*s	
Melting point			-40	°C	
Solidification point			~ 50	°C	
Boiling point			not available		
Ignition temperature					not applicable
Flash point					not applicable
Explosion limits	lower				not applicable
	upper				not applicable
Vapour pressure		(20 °C)	21.3	hPa	
Relative vapour density_			not available		
Density		(20 °C)	1.15	g/cm^3	
Solubility in					
water		(20 °C)	soluble		

10. Stability and reactivity

Conditions to be avoided

Heating.

Substances to be avoided

aluminium, amines, carbides, hydrides, fluorine, alkali metals, metals, potassium permanganate, strong alkalis, salts of oxyhalogenic acids, conc. sulfuric acid, aldehydes, sulfides, lithium silicide, vinylmethyl ether, semimetallic oxides, semimetallic hydrogen compounds.

Hazardous decomposition products

in the event of fire: See chapter 5.

Further information

unsuitable working materials: metals, metal alloys.

11. Toxicological information

Acute toxicity

LC_{50} (inhalation, rat): 3124 ppm(V) /1 h (calculated on the pure substance) .

Subacute to chronic toxicity

Applicable to the toxicologically determinant component:
An embryotoxic effect need not be feared when the threshold limit value is observed.

Further toxicological information

Strongly corrosive substance.
After inhalation of vapours: Irritation symptoms in the respiratory tract.
After skin contact: burns.
After eye contact: burns, Risk of blindness!
After swallowing: Damage of: mouth, oesophagus and gastrointestinal tract. Risk of perforation in the oesophagus and stomach. After a latency period: cardiovascular failure..

Further data

The product should be handled with the care usual when dealing with chemicals.

12. Ecological information

Ecotoxic effects:
Biological effects: Toxic for aquatic organisms. Toxic effect on fish and plankton. Forms corrosive mixtures with water even if diluted. Damage to plant growth.

Further ecologic data:
The following applies to HCl in general: Harmfull effect on aquatic organisms. Harmful effect due to pH shift. Biological effects: hyrochloric acid (including such due to reaction): lethal for fish as from 25 mg/l; Leuciscus idus LC_{50}: 862 mg/l (1N-solution). Harmful effects begin at: plants 6 mg/l. Does not cause biological oxygen deficit.

Do not allow to enter waters, waste water, or soil!

13. Disposal considerations

Product:

There are no uniform EC Regulations for the disposal of chemicals or residues. Chemical residues generally count as special waste. The disposal of the latter is regulated in the EC member countries through corresponding laws and regulations. We recommend that you contact either the authorities in charge or approved waste disposal companies which will advise you on how to dispose of special waste.

Packaging:

Disposal in compliance with official regulations. Handle contaminated packaging in the same way as the substance itself. If not officially specified differently, non-contaminated packaging may be treated like household waste or recycled.

14. Transport information

Transport over land ADR/RID and GGVS/GGVE (Germany)
GGVS/GGVE class: 8 Number and letter: 5b
ADR/RID class: 8 Number and letter: 5b
Name of material: 1789 CHLORWASSERSTOFFSAEURE (SALZSAEURE)

River transport ADN/ADNR
not examined

Sea transport IMDG
IMDG class: 8 UN-No.: 1789 Packaging group: II
Ems: 8-03 MFAG: 700
Correct technical name: HYDROCHLORIC ACID,32 %

Air transport ICAO-TI and IATA-DGR
ICAO/IATA class: 8 UN/ID-No.: 1789 Packaging group: II
Correct technical name: HYDROCHLORIC ACID

The transport regulations are cited according to international regulations and in the form applicable in Germany (GGVS/GGVE). Possible national deviations in other countries are not considered.

15. Regulatory information

Labelling according to EC Directives

Symbol:	C	Corrosive
R-phrases:	34-37	Causes burns. Irritating to respiratory system.
S-phrases:	26-36/37/39-45	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves and eye/face protection. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

16. Other information

Reduced labelling on the container due to small quantity.
Reason for alteration
Change in transport classification.

Date of issue: 21.12.1999 Supersedes edition of 09.07.1996

Safety Data Sheet

According to EC Directive 91/155/EEC

Date of issue:	30.03.2006
Supersedes edition of	09.01.2004

1. Identification of the substance/preparation and of the company/undertaking

Identification of the product

Catalogue No.:	100441
Product name:	Nitric acid 65% Suprapur®

Use of the substance/preparation

Reagent for analysis
Chemical production

Company/undertaking identification

Company:	Merck KGaA * 64271 Darmstadt * Germany * Phone: +49 6151 72-0
Emergency telephone No.:	Please contact the regional Merck representation in your country.

2. Composition/information on ingredients

Hazardous ingredients:

Name according to EC Directives: *CAS-No.*	*EC No.*	*EC-Index-No.*	*Classification*	*Content:*
Nitric acid 7697-37-2	231-714-2	007-004-00-1	O; R8 C; R35	65 %

(Full text of R-Phrases in heading 16)

3. Hazards identification

Causes severe burns.

4. First aid measures

After inhalation: fresh air. Call in physician.
After skin contact: wash off with plenty of water. Dab with polyethylene glycol 400. Immediately remove contaminated clothing.
After eye contact: rinse out with plenty of water for at least 10 minutes with the eyelid held wide open. Immediately call in ophtalmologist.
After swallowing: make victim drink plenty of water (if necessary several litres), avoid vomiting (risk of perforation!). Immediately call in physician. Do not attempt to neutralize.

5. Fire-fighting measures

Suitable extinguishing media:
In adaption to materials stored in the immediate neighbourhood.

Special risks:
Non-combustible. Ambient fire may liberate hazardous vapours. The following may develop in event of fire: nitrogen oxides.

Special protective equipment for fire fighting:
Do not stay in dangerous zone without self-contained breathing apparatus. In order to avoid contact with skin, keep a safety distance and wear suitable protective clothing.

Other information:
Cool container with spray water from a save distance. Contain escaping vapours with water. Prevent fire-fighting water from entering surface water or groundwater.

6. Accidental release measures

Person-related precautionary measures:
Avoid substance contact. Do not inhale vapours/aerosols. Ensure supply of fresh air in enclosed rooms.

Environmental-protection measures:
Do not allow to enter sewerage system.

Procedures for cleaning / absorption:
Take up with liquid-absorbent and neutralizing material (e.g. Chemizorb® H^+, Art. No. 101595). Forward for disposal. Clean up affected area.

7. Handling and storage

Handling:

No further requirements.

Storage:

Tightly closed. Store at +2°C to +25°C.

8. Exposure controls/personal protection

Specific control parameter

EC

Name	nitric acid
Short term (<15 min.)	1 ml/m^3 2.6 mg/m^3

Personal protective equipment:

Protective clothing should be selected specifically for the working place, depending on concentration and quantity of the hazardous substances handled. The resistance of the protective clothing to chemicals should be ascertained with the respective supplier.

Respiratory protection: required when vapours/aerosols are generated. filter NO- Filter P 3 (acc. to DIN 3181) for solid and liquid particles of toxic and very toxic substances.

Eye protection: required

Hand protection: In full contact:

Glove material:	viton
Layer thickness:	0.70 mm
Breakthrough time:	> 480 Min.

In splash contact:

Glove material:	natural latex
Layer thickness:	0.6 mm
Breakthrough time:	> 120 Min.

The protective gloves to be used must comply with the specifications of EC directive 89/686/EEC and the resultant standard EN374, for example KCL 890 Vitoject® (full contact), 706 Lapren® (splash contact). The breakthrough times stated above were determined by KCL in laboratory tests acc. to EN374 with samples of the recommended glove types.
This recommendation applies only to the product stated in the safety data sheet and supplied by us as well as to the purpose specified by us. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN374 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).

Other protective equipment: Acid-resistant protective clothing.

Industrial hygiene:
Immediately change contaminated clothing. Apply skin- protective barrier cream. Wash hands and face after working with substance.

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9. Physical and chemical properties

Form: liquid
Colour: colourless
Odour: pungent

pH value		(20 °C)	0		strongly acid
Melting point			~ -32	°C	
Boiling point			121	°C	
Ignition temperature			not applicable		
Flash point			not applicable		
Explosion limits	lower		not available		
	upper		not available		
Vapour pressure		(20 °C)	~ 9.4	hPa	
Density		(20 °C)	1.39	g/cm^3	
Solubility in water		(20 °C)	soluble		
log Pow		(25 °C)	-2.3		(anhydrous substance) (OECD 107)

10. Stability and reactivity

Conditions to be avoided

Heating.

Substances to be avoided

Risk of explosion with: / Risk of ignition or formation of inflammable gases or vapors with: acetonitrile, acetylidene, alcohols, anilines (Spontaneously flammable.), antimony hydride, arsenic hydride, amines, ammonia, combustible substances, phosphides, aldehydes, dichloromethane, hydrazines, dioxane, acetic acid / acetone, acetic acid anhydride, fluorine, formaldehyde, glycerol / sulfuric acid, hydrogen iodide, chlorates / organic substances, carbon/soot, hydrocarbons, alkali metals, lithium silicide, organic solvents, metals in powder form, organic substances / sulfuric acid, phosphorus, pyridine, sulfur dioxide, hydrogen sulfide, hydrogen selenide, hydrogen peroxide.

Violent reactions possible with: nitriles, antimony, arsenic, boron, ferric oxide, alkalis, sodium hypochlorite.

Hazardous decomposition products
in the event of fire: See chapter 5.

Further information

strong oxidizing agent;
unsuitable working materials: metals, metal alloys.

11. Toxicological information

Acute toxicity

LDLo (oral, human): 430 mg/kg (calculated on the pure substance) (IUCLID).

Subacute to chronic toxicity

Bacterial mutagenicity: Ames test: negative. (in vitro) (calculated on the pure substance)

Further toxicological information

Strongly corrosive substance.
After inhalation of vapours: burns of mucous membranes, coughing, dyspnoea. Inhalation may lead to the formation of oedemas in the respiratory tract.
After skin contact: burns.
After eye contact: burns, Risk of blindness!
After swallowing: tissue damage (mouth, oesophagus, gastrointestinal tract), strong pain (risk of perforation!), bloody vomiting, death.

Other notes:
The following applies to nitrites/nitrates in general: methaemoglobinaemia after the uptake of large quantities.

Further data

The product should be handled with the care usual when dealing with chemicals.

12. Ecological information

Behavior in environmental compartments:
Distribution: log Pow: -2.3 (25 °C) (anhydrous substance) (OECD 107).
No bioaccumulation is to be expected (log Pow <1).

Ecotoxic effects:
Biological effects:
Toxic effect on fish and plankton. Harmful effect due to pH shift. Forms corrosive mixtures with water even if diluted. Does not cause biological oxygen deficit. Hazard for drinking water supplies.

Fish toxicity: Gambusia affinis LC_{50}: 72 mg/l /96 h (calculated on the pure substance) (IUCLID).

Further ecologic data:
The following applies to nitrates in general: may contribute to the eutrophication of water supplies. Hazard for drinking water. Fish: $LC_{50} > 500$ mg/l.

Do not allow to enter waters, waste water, or soil!

13. Disposal considerations

Product:

Chemicals must be disposed of in compliance with the respective national regulations. Under www.retrologistik.de you will find country- and substance-specific information as well as contact partners.

Packaging:

Merck product packaging must be disposed of in compliance with the country-specific regulations or must be passed to a packaging return system. Under www.retrologistik.de you will find special information on the respective national conditions as well as contact partners.

14. Transport information

Road & Rail ADR, RID
UN 2031 SALPETERSAEURE, 8, II

Inland waterway ADN, ADNR not tested

Sea IMDG-Code
UN 2031 NITRIC ACID MORE THAN 50% BUT NOT MORE THAN 70%, 8, II
Ems F-A S-B

Air
UN 2031 NITRIC ACID
CAO 8, II
PAX 8, II prohibited

The transport regulations are cited according to international regulations and in the form applicable in Germany . Possible national deviations in other countries are not considered.

15. Regulatory information

Labelling according to EC Directives

Symbol:	C	Corrosive
R-phrases:	35	Causes severe burns.
S-phrases:	23-26-36/37/39-45	Do not breathe vapour. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves and eye/face protection. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

Reduced labelling (1999/45/EC,Art.10,4)

Symbol:	C	Corrosive
R-phrases:	35	Causes severe burns.
S-phrases:	26-36/37/39-45	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice. Wear suitable protective clothing, gloves and eye/face protection. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

16. Other information

Text of any R phrases referred to under heading 2:

8	Contact with combustible material may cause fire.
35	Causes severe burns.

Reason for alteration

Chapter 8: specific control parameter.
Chapter 10: stability and reactivity.
Chapter 11: toxicological information.
Chapter 12: ecological information.

General update.

Regional representation:

This information is given on the authorised Safety Data Sheet for your country.

Shell Chemicals

ShellSol A150
Version 4.

Effective Date 15.03.2007

according to EC directive 2001/58/EC

Material Safety Data Sheet

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND COMPANY/UNDERTAKING

Material Name : **ShellSol A150**
Uses : Industrial Solvent.
Product Code : Q7493

Manufacturer/Supplier : **Shell South Africa Chemicals**
Reunion Rocks Road
4110 Isipingo
South Africa

Telephone : +27 (0)31 913 2000
Fax : +27 (0)31 902 5228 / 902 5768

Emergency Telephone Number : South Africa :+27 (0)31 902 4075 or +27 (0) 836291307 Zimbabwe : Normal; (04) 703115/117 or 011 200072/73 Kenya :0925411 491 328

Other Information : ShellSol is a trademark owned by Shell Trademark Management B.V. and Shell Brands Inc. and used by affiliates of Royal Dutch Shell plc.

2. COMPOSITION/INFORMATION ON INGREDIENTS

Material Formal Name : Solvent naphtha (petroleum), heavy aromatic
CAS No. : 64742-94-5
INDEX No. : 649-424-00-3
EINECS No. : 265-198-5

Hazardous Components

Chemical Name	CAS	EINECS	Symbol(s)	R-phrase(s)	Conc.
Benzene	71-43-2	200-753-7	F, T	R45; R46; R11; R36/38; R48/23/24/25; R65	>= 0,00 - < 0,10 %W
Naphthalene	91-20-3	202-049-5	Xn, N	R22; R40; R50/53	>= 0,00 - < 10,00 %W
1,3,5-Trimethyl benzene	108-67-8	203-604-4	Xi, N	R10; R37; R51/53	>= 1,00 - <= 1,50 %W
1,2,4-Trimethyl benzene	95-63-6	202-436-9	Xn, N	R10; R20; R36/37/38; R51/53	>= 10,00 - <= 12,00 %W
1,2,3-Trimethyl benzene	526-73-8	208-394-8			>= 5,50 - <= 7,00 %W

3. HAZARDS IDENTIFICATION

Health Hazards : Vapours may cause drowsiness and dizziness. Slightly irritating to respiratory system. May cause moderate irritation to skin. Repeated exposure may cause skin dryness or cracking. Moderately irritating to eyes. Harmful: may cause lung damage if swallowed. Limited evidence of carcinogenic effect.

Signs and Symptoms : Respiratory irritation signs and symptoms may include a temporary burning sensation of the nose and throat, coughing, and/or difficulty breathing. Breathing of high vapour concentrations may cause central nervous system (CNS) depression resulting in dizziness, light-headedness, headache, nausea and loss of coordination. Continued inhalation may result in unconsciousness and death. Skin irritation signs and symptoms may include a burning sensation, redness, swelling, and/or blisters. Defatting dermatitis signs and symptoms may include a burning sensation and/or a dried/cracked appearance. Eye irritation signs and symptoms may include a burning sensation, redness, swelling, and/or blurred vision. If material enters lungs, signs and symptoms may include coughing, choking, wheezing, difficulty in breathing, chest congestion, shortness of breath, and/or fever.

Safety Hazards : Combustible liquid. In use, may form flammable/explosive vapour-air mixture. Electrostatic charges may be generated during pumping. Electrostatic discharge may cause fire.

Environmental Hazards : Expected to be toxic to aquatic organisms. May cause long-term adverse effects in the aquatic environment.

4. FIRST AID MEASURES

Inhalation : Remove to fresh air. If rapid recovery does not occur, transport to nearest medical facility for additional treatment.

Skin Contact : Remove contaminated clothing. Flush exposed area with water and follow by washing with soap if available.

Eye Contact : Flush eyes with water while holding eyelids open. Rest eyes for 30 minutes. If redness, burning, blurred vision, or swelling persist, transport to the nearest medical facility for additional treatment.

Ingestion : If swallowed, do not induce vomiting: transport to nearest medical facility for additional treatment. If vomiting occurs spontaneously, keep head below hips to prevent aspiration. If any of the following delayed signs and symptoms appear within the next 6 hours, transport to the nearest medical facility: fever greater than 101° F (37° C), shortness of breath, chest congestion or continued coughing or wheezing.

Advice to Physician : Potential for chemical pneumonitis. Consider: gastric lavage with protected airway, administration of activated charcoal. Call a doctor or poison control center for guidance. Causes central nervous system depression. Dermatitis may result from prolonged or repeated exposure.

5. FIRE FIGHTING MEASURES

Clear fire area of all non-emergency personnel.

Specific Hazards	:	Carbon monoxide may be evolved if incomplete combustion occurs. Will float and can be reignited on surface water. The vapour is heavier than air, spreads along the ground and distant ignition is possible.
Extinguishing Media	:	Foam, water spray or fog. Dry chemical powder, carbon dioxide, sand or earth may be used for small fires only. Do not discharge extinguishing waters into the aquatic environment.
Unsuitable Extinguishing Media	:	Do not use water in a jet.
Protective Equipment for Firefighters	:	Wear full protective clothing and self-contained breathing apparatus.
Additional Advice	:	Keep adjacent containers cool by spraying with water.

6. ACCIDENTAL RELEASE MEASURES

Observe all relevant local and international regulations.

Protective measures	:	Avoid contact with spilled or released material. Immediately remove all contaminated clothing. For guidance on selection of personal protective equipment see Chapter 8 of this Material Safety Data Sheet. For guidance on disposal of spilled material see Chapter 13 of this Material Safety Data Sheet. Shut off leaks, if possible without personal risks. Remove all possible sources of ignition in the surrounding area. Use appropriate containment (of product and fire fighting water) to avoid environmental contamination. Prevent from spreading or entering drains, ditches or rivers by using sand, earth, or other appropriate barriers. Attempt to disperse the vapour or to direct its flow to a safe location for example by using fog sprays. Take precautionary measures against static discharge. Ensure electrical continuity by bonding and grounding (earthing) all equipment. Monitor area with combustible gas indicator.
Clean Up Methods	:	For small liquid spills (< 1 drum), transfer by mechanical means to a labelled, sealable container for product recovery or safe disposal. Allow residues to evaporate or soak up with an appropriate absorbent material and dispose of safely. Remove contaminated soil and dispose of safely. For large liquid spills (> 1 drum), transfer by mechanical means such as vacuum truck to a salvage tank for recovery or safe disposal. Do not flush away residues with water. Retain as contaminated waste. Allow residues to evaporate or soak up with an appropriate absorbent material and dispose of safely. Remove contaminated soil and dispose of safely.
Additional Advice	:	See Chapter 13 for information on disposal. Notify authorities if any exposure to the general public or the environment occurs or is likely to occur.

7. HANDLING AND STORAGE

General Precautions	:	Avoid breathing vapours or contact with material. Only use in well ventilated areas. Wash thoroughly after handling. For

guidance on selection of personal protective equipment see Chapter 8 of this Material Safety Data Sheet. Use the information in this data sheet as input to a risk assessment of local circumstances to help determine appropriate controls for safe handling, storage and disposal of this material.

Handling : Extinguish any naked flames. Do not smoke. Remove ignition sources. Avoid sparks. Avoid contact with skin, eyes, and clothing. Electrostatic charges may be generated during pumping. Electrostatic discharge may cause fire. Ensure electrical continuity by bonding and grounding (earthing) all equipment. Restrict line velocity during pumping in order to avoid generation of electrostatic discharge (<= 1 m/sec until fill pipe submerged to twice its diameter, then <= 7 m/sec). Avoid splash filling. Do NOT use compressed air for filling, discharging, or handling operations.

Storage : Must be stored in a diked (bunded) area. Bulk storage tanks should be diked (bunded). Keep away from flammables, oxidizing agents, and corrosives. Storage Temperature: Ambient.

Product Transfer : Keep containers closed when not in use. Do not use compressed air for filling, discharging or handling.

Recommended Materials : For containers, or container linings use mild steel, stainless steel. For container paints, use epoxy paint, zinc silicate paint.

Unsuitable Materials : Avoid prolonged contact with natural, butyl or nitrile rubbers.

Container Advice : Containers, even those that have been emptied, can contain explosive vapours. Do not cut, drill, grind, weld or perform similar operations on or near containers.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Occupational Exposure Limits

In the absence of occupational exposure standards for this product, it is recommended that the following are adopted.

Material	Source	Type	ppm	mg/m3	Notation
RCP Aromatic solvents 180 - 215	EU HSPA	TWA (8 h)		100 mg/m3	

Additional Information : Wash hands before eating, drinking, smoking and using the toilet.

Exposure Controls : The level of protection and types of controls necessary will vary depending upon potential exposure conditions. Select controls based on a risk assessment of local circumstances. Appropriate measures include: Adequate explosion-proof ventilation to control airborne concentrations below the exposure guidelines/limits. Eye washes and showers for emergency use.

Personal Protective Equipment : Personal protective equipment (PPE) should meet recommended national standards. Check with PPE suppliers.

Respiratory Protection : If engineering controls do not maintain airborne concentrations to a level which is adequate to protect worker health, select respiratory protection equipment suitable for the specific conditions of use and meeting relevant legislation. Check with respiratory protective equipment suppliers. Where air-filtering respirators are suitable, select an appropriate combination of mask and filter. Select a filter suitable for organic gases and vapours [boiling point >65 °C (149 °F)] meeting EN141. Where air-filtering respirators are unsuitable (e.g., airborne concentrations are high, risk of oxygen deficiency, confined space) use appropriate positive pressure breathing apparatus.

Hand Protection : Longer term protection: Nitrile rubber gloves Incidental contact/Splash protection: PVC or neoprene rubber gloves Personal hygiene is a key element of effective hand care. Gloves must only be worn on clean hands. After using gloves, hands should be washed and dried thoroughly. Application of a non-perfumed moisturizer is recommended.

Eye Protection : Chemical splash goggles (chemical monogoggles).

Protective Clothing : Use protective clothing which is chemical resistant to this material. Safety shoes and boots should also be chemical resistant.

Monitoring Methods : Monitoring of the concentration of substances in the breathing zone of workers or in the general workplace may be required to confirm compliance with an OEL and adequacy of exposure controls. For some substances biological monitoring may also be appropriate. Examples of sources of recommended air monitoring methods are given below or contact supplier. Further national methods may be available. National Institute of Occupational Safety and Health (NIOSH), USA: Manual of analytical Methods http://www.cdc.gov/niosh/nmam/nmammenu.html Occupational Safety and Health Administration (OSHA), USA: Sampling and Analytical Methods http://www.osha-slc.gov/dts/sltc/methods/toc.html Health and Safety Executive (HSE), UK: Methods for the Determination of Hazardous Substances http://www.hsl.gov.uk/search.htm

Environmental Exposure Controls : Local guidelines on emission limits for volatile substances must be observed for the discharge of exhaust air containing vapour.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance : Colourless. Liquid.
Odour : Aromatic.
Boiling point : 179 - 214 °C / 354 - 417 °F
Pour point : Typical -20 °C / -4 °F
Flash point : Typical 62 - 65,6 °C / 144 - 150,1 °F (ASTM D-93 / PMCC)
Explosion / Flammability limits in air : 0,6 - 7 %(V)
Auto-ignition temperature : 449 - 510 °C / 840 - 950 °F (ASTM E-659)
Vapour pressure : < 1,3 kPa at 20 °C / 68 °F
Specific gravity : 0,88 - 0,91 at 20 °C / 68 °F

Density : Typical 893 kg/m3 at 15 °C / 59 °F (ASTM D-4052)
Water solubility : Insoluble.
Volatile organic carbon : 90 % (EC/1999/13)

content		
Evaporation rate (nBuAc=1)	:	< 1,0 (ASTM D 3539, nBuAc=1)

10. STABILITY AND REACTIVITY

Stability	:	Stable under normal conditions of use.
Conditions to Avoid	:	Avoid heat, sparks, open flames and other ignition sources.
Materials to Avoid	:	Strong oxidising agents.
Hazardous Decomposition Products	:	Thermal decomposition is highly dependent on conditions. A complex mixture of airborne solids, liquids and gases, including carbon monoxide, carbon dioxide and other organic compounds will be evolved when this material undergoes combustion or thermal or oxidative degradation.

11. TOXICOLOGICAL INFORMATION

Basis for Assessment	:	Information given is based on product data and on data on the components and the toxicology of similar products.
Acute Oral Toxicity	:	Low toxicity: LD50 >2000 mg/kg , Rat Aspiration into the lungs when swallowed or vomited may cause chemical pneumonitis which can be fatal.
Acute Dermal Toxicity	:	Low toxicity: LD50 >2000 mg/kg , Rat
Acute Inhalation Toxicity	:	Low toxicity: LC50 greater than near-saturated vapour concentration. / 4 hours, Rat High concentrations may cause central nervous system depression resulting in headaches, dizziness and nausea.
Skin Irritation	:	May cause moderate skin irritation (but insufficient to classify). Prolonged/repeated contact may cause defatting of the skin which can lead to dermatitis.
Eye Irritation	:	Moderately irritating to eyes (but insufficient to classify).
Respiratory Irritation	:	Inhalation of vapours or mists may cause irritation to the respiratory system. Insufficient to classify.
Sensitisation	:	Not a skin sensitiser.
Mutagenicity	:	Not expected to be mutagenic.
Carcinogenicity	:	Limited evidence of carcinogenic effect. (Naphthalene)
Reproductive and Developmental Toxicity	:	Causes foetotoxicity in animals at doses which are maternally toxic. Not expected to impair fertility.

12. ECOLOGICAL INFORMATION

Acute Toxicity		
Fish	:	Expected to be toxic: 1 < LC/EC/IC50 <= 10 mg/l
Aquatic Invertebrates	:	Expected to be toxic: 1 < LC/EC/IC50 <= 10 mg/l
Algae	:	Expected to be toxic: 1 < LC/EC/IC50 <= 10 mg/l
Microorganisms	:	Expected to be toxic: 1 < LC/EC/IC50 <= 10 mg/l
Mobility	:	Adsorbs to soil and has low mobility. Floats on water.
Persistence/degradability	:	Expected to be readily biodegradable. Oxidises rapidly by photo-chemical reactions in air.
Bioaccumulation	:	Has the potential to bioaccumulate.

13. DISPOSAL CONSIDERATIONS

Material Disposal	: Recover or recycle if possible. It is the responsibility of the waste generator to determine the toxicity and physical properties of the material generated to determine the proper waste classification and disposal methods in compliance with applicable regulations. Do not dispose into the environment, in drains or in water courses. Waste product should not be allowed to contaminate soil or water.
Container Disposal	: Drain container thoroughly. After draining, vent in a safe place away from sparks and fire. Residues may cause an explosion hazard if heated above the flash point. Do not puncture, cut or weld uncleaned drums. Send to drum recoverer or metal reclaimer.
Local Legislation	: Disposal should be in accordance with applicable regional, national, and local laws and regulations. Local regulations may be more stringent than regional or national requirements and must be complied with.

14. TRANSPORT INFORMATION

ADR

Class	: 9
Packing group	: III
Classification code	: M6
Hazard indentification no.	: 90
UN No.	: 3082
Danger label (primary risk)	: 9
Proper shipping name	: ENVIRONMENTALLY HAZARDOUS SUBSTANCE, LIQUID, N.O.S. (ALKYL (C3-C8) BENZENES)

IMDG
This material is not classified as dangerous under IMDG regulations.

IATA (Country variations may apply)
This material is not classified as dangerous under IATA regulations.

Additional Information	: **Packaging and Transportation of Dangerous Goods is in compliance with Chapter VIII of the Regulations in terms of the National Road Traffic Act of 1996. This regulation is supported by SABS codes of practice SABS 0229 - Packaging of DG for Road Transport, SABS 0233 - IBC for DG and SABS 0232 Parts 1 & 3 - Emergency Response.**

15. REGULATORY INFORMATION

The regulatory information is not intended to be comprehensive. Other regulations may apply to this material.

EC Label Name	:	SOLVENT NAPHTHA (PETROLEUM), HEAVY AROM.	
EC label/EC Number	:	265-198-5	
EC Classification	:	Harmful. Dangerous for the environment.	
EC Annex I Number	:	649-424-00-3	
EC Symbols	:	Xn Harmful. N Dangerous for the environment.	
EC Risk Phrases	:	R40 Limited evidence of carcinogenic effect. R65 Harmful: may cause lung damage if swallowed. R66 Repeated exposure may cause skin dryness or cracking. R67 Vapours may cause drowsiness and dizziness. R51/53 Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.	
EC Safety Phrases	:	S23 Do not breathe vapour. S24 Avoid contact with skin. S61 Avoid release to the environment. Refer to special instructions/Safety data sheets. S62 If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label. S36/37 Wear suitable protective clothing and gloves.	
DSL	:	Listed.	
INV (CN)	:	Listed.	
TSCA	:	Listed.	
EINECS	:	Listed.	265-198-5
KECI (KR)	:	Listed.	KE-31656
PICCS (PH)	:	Listed.	

National Legislation

OE_HPV	:	Listed.
Other Information	:	In compliance with the Occupational Health and Safety Act 85 of 1993 and satisfying the requirements of Regulation GN1179 being the Hazardous Chemicals Subsatnce Regulation. Ambient Air Quality Regulation (New) 94/69/EC (21st ATP). The benzene content of this product is less than 0.1%. Nota P applies. Classification and labelling as carcinogen (R45) is not required.

16. OTHER INFORMATION

R-phrase(s)

R10	Flammable.
R11	Highly flammable.
R20	Harmful by inhalation.
R22	Harmful if swallowed.
R36/37/38	Irritating to eyes, respiratory system and skin.
R36/38	Irritating to eyes and skin.
R37	Irritating to respiratory system.
R40	Limited evidence of carcinogenic effect.
R45	May cause cancer.
R46	May cause heritable genetic damage.
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R65	Harmful: May cause lung damage if swallowed.
R66	Repeated exposure may cause skin dryness or cracking.
R67	Vapours may cause drowsiness and dizziness.

MSDS Version Number : 4.

MSDS Effective Date : 15.03.2007

MSDS Revisions : A vertical bar (|) in the left margin indicates an amendment from the previous version.

MSDS Regulation : The content and format of this safety data sheet is in accordance with Commission Directive 2001/58/EC of 27 July 2001, amending for the second time Commission Directive 91/155/EEC.

Uses and Restrictions : Industrial Solvent.

MSDS Distribution : The information in this document should be made available to all who may handle the product

Disclaimer : This information is based on our current knowledge and is intended to describe the product for the purposes of health, safety and environmental requirements only. It should not therefore be construed as guaranteeing any specific property of the product.

Safety data sheet

MERCK

According to EC Directive 91/155/EEC
02.2001 from CD-ROM 2001/1 Date of issue: 04.10.1999 Supersedes edition of 28.09.1987

1. Identification of the substance/preparation and of the company/undertaking

Identification of the product

Catalogue No.: 106404
Product name: Sodium chloride GR for analysis ACS,ISO

Manufacturer/supplier identification

Company: Merck KGaA * 64271 Darmstadt * Germany * Tel: +49 6151 72-2440
Emergency telephone No.: Please contact the regional Merck representation in your country.

2. Composition/information on ingredients

CAS-No.: 7647-14-5
M: 58.44 g/mol
EC-No.: 231-598-3
Molecular formula: (Hill) ClNa
Molecular formula: (struc.) NaCl

3. Hazards identification

No hazardous product as specified in Directive 67/548/EEC.

4. First aid measures

After inhalation: fresh air.
After skin contact: wash off with water.
After eye contact: rinse out with water.
After swallowing (large amounts): consult doctor if feeling unwell.

5. Fire-fighting measures

Suitable extinguishing media:
In adaption to materials stored in the immediate neighbourhood.

Special risks:
Non-combustible.

Other information:
Prevent fire-fighting water from entering surface water or groundwater.

6. Accidental release measures

Environmental-protection measures:
Do not allow to enter sewerage system.

Procedures for cleaning / absorption:
Take up dry. Forward for disposal. Clean up affected area.

7. Handling and storage

Handling:

No further requirements.

Storage:

Tightly closed. Dry. Storage temperature: no restrictions.

8. Exposure controls/personal protection

Personal protective equipment:

Protective clothing should be selected specifically for the working place, depending on concentration and quantity of the hazardous substances handled. The resistance of the protective clothing to chemicals should be ascertained with the respective supplier.

Respiratory protection:	required when dusts are generated.
Eye protection:	required
Hand protection:	Use recommended

Industrial hygiene:
Wash hands after working with substance.

Change contaminated clothing. Wash hands after working with substance.

9. Physical and chemical properties

Form:		solid		
Colour:		colourless		
Odour:		odourless		
pH value at 100 g/l H_2O		(20 °C)	4.5-7.0	
Melting point			801	°C
Boiling point		(1013 hPa)	1461	°C
Ignition temperature			not available	
Flash point			not available	
Explosion limits	lower		not available	
	upper		not available	
Vapour pressure		(865 °C)	1.3	hPa
Density		(20 °C)	2.17	g/cm^3
Bulk density			~ 1140	kg/m^3
Solubility in				
water		(20 °C)	358	g/l
ethanol		(25 °C)	0.51	g/l

10. Stability and reactivity

Conditions to be avoided

no information available

Substances to be avoided

alkali metals.

Hazardous decomposition products

no information available

11. Toxicological information

Acute toxicity

LD_{50} (oral, rat): 3000 mg/kg.
LD_{50} (dermal, rabbit): >10000 mg/kg.

Specific symptoms in animal studies:
Skin irritation test (rabbit): Slight irritations.
Eye irritation test (rabbit): Slight irritations.

Subacute to chronic toxicity

Noncarcinogenic in animal experiments.
No mutagenic effect in animal experiments.
No impairment of reproductive performance suspected.
No teratogenic effect in animal experiments.

Bacterial mutagenicity:
Escherichia coli: negative.
Ames-Test: negative.

Mikronucleus-Test: negative.

Further toxicological information

After skin contact: Slight irritations.
After eye contact: Slight iritations.
After swallowing of large amounts: nausea, vomiting.

Further data

No toxic effects are to be expected when the product is handled appropriately.

12. Ecological information

Biologic degradation:
Methods for the determination of biodegradability are not applicable to inorganic substances.

Behavior in environmental compartments:
Concentration in organisms is not to be expected.
Passage from aqueous solution into the atmosphere is not to be expected.

Ecotoxic effects:
Biological effects:
Fish toxicity: P.promelas LC_{50}: 7650 mg/l /96 h; L.macrochirus LC_{50}: 9675 mg/l /96 h (in hard water);
Daphnia toxicity: Daphnia magna EC_{50}: 1000 mg/l /48 h.

Further ecologic data:
No ecological problems are to be expected when the product is handled and used with due care and attention.

13. Disposal considerations

Product:

There are no uniform EC Regulations for the disposal of chemicals or residues. Chemical residues generally count as special waste. The disposal of the latter is regulated in the EC member countries through corresponding laws and regulations. We recommend that you contact either the authorities in charge or approved waste disposal companies which will advise you on how to dispose of special waste.

Packaging:

Disposal in compliance with official regulations. Handle contaminated packaging in the same way as the substance itself. If not officially specified differently, non-contaminated packaging may be treated like household waste or recycled.

14. Transport information

Not subject to transport regulations.

15. Regulatory information

Labelling according to EC Directives

Symbol: ---
R-phrases: ---
S-phrases: ---

16. Other information

Reason for alteration

General update.

Regional representation:

This information is given on the authorised Safety Data Sheet for your country.

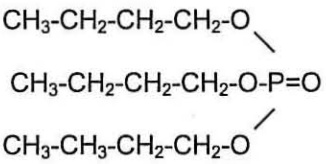
Tributyl phosphate

(Tri-n-butyl phosphate; TBP; Antifoam T; Baysolvex® TBP)

Description

Tributyl phosphate is a clear, colorless liquid of low viscosity with a slightly pungent odor.

Structural formula



$$\begin{array}{l} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O \\ CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}P{=}O \\ CH_3\text{-}CH_3\text{-}CH_2\text{-}CH_2\text{-}O \end{array}$$

Empirical formula

$C_{12}H_{27}O_4P$

General properties

Molar mass

266 g/mole TBP

Soluble in common organic solvents such as aliphatic, aromatic and chlorinated carbons, alcohols, esters, ketones, glycol ethers. Solubility of TBP in water at 20°C: approx. 0.04 % by wt.

Density at 20°C
0.977 g/cm^3

Viscosity at 20°C
3.8 mPa.s

Boiling point at 5 mbar
130°C

Refractive index n_D^{20}
1.424

Hazen color value
Approx. 10

Hazard characteristics

harmful

Application

Antifoam T

As a defoamer in:

- concrete additives (especially in concrete containing lignin sulfonate as a fluidizer);
- textile processing chemicals (especially in combination with wetting agents, e.g. our MERSOLAT® brands);
- glues and adhesives, paper coating slurries, plastic dispersions, drilling fluids, cementations, lubricants, coatings, electroplating.

Baysolvex® TBP

As an extracting agent in liquid-liquid extraction, e.g. for the separation and recovery of rare earths and platinum metals, in the concentration of uranium and thorium, in the cleaning of phosphoric acid, sulfuric acid, nitric acid, hydrofluoric acid.

Miscellaneous

As a very strong, aprotic and polar solvent, e.g. for the production of synthetic resin and natural rubber solutions.

Further information
See TBP brochure, no. AI 12 034/4 (issue 2.97), Antifoam T, no. AI 12 049 (issue 7.96), Baysolvex® TBP, issue 06/93.

Bayer AG, Specialty Products Business Group
D-51368 Leverkusen
Tel.: +49 (0)214-30-26003
Fax: +49 (0)214-30-62985
E-mail: spechem@bayer-ag.de

⊙ Material Safety Data Sheet for Zinc chloride

Print

MATERIAL SAFETY DATA SHEET		**Date Issued:** Wednesday, January 19, 2005

Company Details
Name: Associated Chemical Enteprises (Pty) Ltd.
Address: 10 Amethyst Street, Theta, Johannesburg
Tel: +27 (0) 11 496-3300
Emergency tel. no :+27 (0) 11 496-3300
Fax : +27 (0) 11 496-3311

⊙Product and Company Identification	
Chemical Abstract Number:	7440-66-6
Trade Name:	Zinc chloride
Chemical Name:	Zinc chloride
UN no:	2331
⊙Composition	
EEC classification:	231-592-0
Risk Phrases:	R34 Causes burns
Safety Phrases:	S28 After contact with skin, wash immediately with plenty of water S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible) S8 Keep container dry S7 Keep container tightly closed
⊙Hazards Identification	
Flammability:	Flammable
Eye effects - eyes:	Irritating to eyes
Health effects - skin:	Causes burns
Health effects - ingestion:	Fever, muscular symptom, pain, cardiovascular disorder, nausea and vomiting
Health effects - inhalation:	Irritating to respiratory tract
Carcinogenicity:	Has been found to cause cancer in laboratory animals
Mutagenicity:	Evidence of reproductive effects
⊙First Aid Measures	
Product in eyes:	Irrigate thoroughly with water for at least 10 minutes. If discomfort persists obtain medical attention
Product on skin:	Wash off skin thoroughly with water. Remove contaminated clothing. In severe cases, obtain medical attention
Product ingested:	Wash out mouth thoroughly with water. Obtain medical attention
Product inhaled:	Remove from exposure, rest and keep warm. In severe cases, obtain medical attention
⊙Fire Fighting Measures	
Special hazards:	May evolve toxic fumes in fire
Protective clothing:	Plastic apron, boots, gloves, goggles/face shield
⊙Accidental Release Measures	
Personal precautions:	Wear appropriate protective clothing
Environmental precautions:	Transfer to container and arrange removal by disposal company

Small spills:	Wash site of spillage thoroughly with detergent and water
Large spills:	Liquids should be contained with sand or earth and transferred to salvage containers
Handling and Storage	
Suitable material:	Do not use metal equipment or containers
Handling/storage precautions:	Store at room temperature (15-25°C recommended). Keep well closed and protected from direct sunlight and moisture
Exposure Controls / Personal Protection	
Engineering control measures:	Ventilation: extraction hood
Personal protection - respiratory:	Dust respirator
Personal protection - hand:	Rubber/plastic gloves
Personal protection - eye:	Goggles/face shield
Personal protection - skin:	Sleeves
Other protection:	Plastic apron, boots
Physical and Chemical Properties	
Appearance:	White very deliquesc granules, or fused pieces or rods
Odour:	Odourless
pH:	5 (100g/l H_2O)
Boiling Point:	732°C
Melting Point:	262°C
Flammability:	Flammable
Solubility - water:	Very soluble
Stability and Reactivity	
Incompatible materials:	Do not use metal equipment or containers
Toxicological Information	
Skin and eye contact:	Irritation. Causes burns on skin contact
Carcinogenicity:	Has been found to cause cancer in laboratory animals
Mutagenicity:	Evidence of reproductive effects
Reproductive hazards:	Hazardous properties cannot be excluded but unlikely when handled appropriately
Ecological Information	
Bio-accumulation:	No environmental hazard is anticipated provided that the material is handled and disposed with care
Disposal Considerations	
Disposal of packaging:	Rinse out empty containers thoroughly before returning for recycling
Transport Information	
UN no:	2331
ADR/RID class:	8.11'(c)
IMDG - class:	8
IMDG - packaging group:	III
IATA - class:	2331
Regulatory Information	
ECC hazard classification:	231-592-0
Risk Phrases:	R34 Causes burns
Safety Phrases:	S28 After contact with skin, wash immediately with plenty of water S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible) S8 Keep container dry S7 Keep container tightly closed
Uses	
Chemical uses:	Deodorant, disinfecting and embalming material, alone or with pheno and other antiseptics for preserving railway ties, fireproofing lumber, with ammonium chloride as flux for soldering, etching metals, manufacturing parchment paper, artificial

	silk, dyes, activated carbon, cold-water glues, vulcanized fiber, browning steel, galvanizing iron, copper-plating iron, in magnesia cements, petroleum oil refining, cement for metals and for facing stone, mordant in printing and dyeing textiles, carbonizing woolen goods, producing crepe and crimping fabrics, mercerizing cotton, sizing and weighting fabrics, vulcanizing rubber, solvent for cellulose, preserving anatomical specimens, in microscopy for seperating silk, wool and plant fibres as dehydrating agent in chemical syntheses

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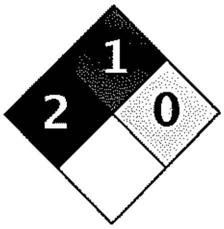

Health	2
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet
Zinc nitrate hexahydrate MSDS

Section 1: Chemical Product and Company Identification

Product Name: Zinc nitrate hexahydrate

Catalog Codes: SLZ1234

CAS#: 10196-18-6

RTECS: ZH4775000

TSCA: TSCA 8(b) inventory: Zinc nitrate hexahydrate

CI#: Not available.

Synonym:

Chemical Formula: H12N2O12Zn

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Zinc nitrate hexahydrate	10196-18-6	100

Toxicological Data on Ingredients: Zinc nitrate hexahydrate: ORAL (LD50): Acute: 1190 mg/kg [Rat]. 926 mg/kg [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects:
Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation.

Potential Chronic Health Effects:
Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.
CARCINOGENIC EFFECTS: Not available.
MUTAGENIC EFFECTS: Not available.
TERATOGENIC EFFECTS: Not available.
DEVELOPMENTAL TOXICITY: Not available.
The substance is toxic to mucous membranes.
Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Do not use an eye ointment. Seek medical attention.

Skin Contact:
After contact with skin, wash immediately with plenty of water. Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cold water may be used. Cover the irritated skin with an emollient. If irritation persists, seek medical attention. Wash contaminated clothing before reusing.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation: Allow the victim to rest in a well ventilated area. Seek immediate medical attention.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention.

Ingestion:
Do not induce vomiting. Examine the lips and mouth to ascertain whether the tissues are damaged, a possible indication that the toxic material was ingested; the absence of such signs, however, is not conclusive. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: Not available.

Flammable Limits: Not available.

Products of Combustion: Not available.

Fire Hazards in Presence of Various Substances: Flammable in presence of reducing materials.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available.
Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:
Oxidizing material.
Do not use water jet. Use flooding quantities of water. Avoid contact with organic materials.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill: Use appropriate tools to put the spilled solid in a convenient waste disposal container.

Large Spill:
Oxidizing material.
Stop leak if without risk. Avoid contact with a combustible material (wood, paper, oil, clothing...). Keep substance damp using water spray. Do not touch spilled material. Prevent entry into sewers, basements or confined areas; dike if needed. Eliminate all ignition sources. Call for assistance on disposal.

Section 7: Handling and Storage

Precautions:
Keep away from heat. Keep away from sources of ignition. Keep away from combustible material Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Wear suitable protective clothing In case of insufficient ventilation, wear suitable respiratory equipment If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes

Storage:
Keep container dry. Keep in a cool place. Ground all equipment containing material. Oxidizing materials should be stored in a separate safety storage cabinet or room.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:
Splash goggles. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Crystalline solid.)

Odor: Not available.

Taste: Not available.

Molecular Weight: 297.47 g/mole

Color: White.

pH (1% soln/water): 6 [Acidic.]

Boiling Point: Decomposes.

Melting Point: 36.4°C (97.5°F)

Critical Temperature: Not available.

Specific Gravity: 2.065 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: See solubility in water.

Solubility: Easily soluble in cold water.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Not available.

Incompatibility with various substances: Not available.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity: Not available.

Polymerization: No.

Section 11: Toxicological Information

Routes of Entry: Eye contact. Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 926 mg/kg [Mouse].

Chronic Effects on Humans: The substance is toxic to mucous membranes.

Other Toxic Effects on Humans: Hazardous in case of skin contact (irritant), of ingestion, of inhalation.

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans: Not available.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may

arise.

Toxicity of the Products of Biodegradation: The products of degradation are more toxic.

Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:

Section 14: Transport Information

DOT Classification: CLASS 5.1: Oxidizing material.

Identification: : Zinc nitrate : UN1514 PG: II

Special Provisions for Transport: Marine Pollutant

Section 15: Other Regulatory Information

Federal and State Regulations: TSCA 8(b) inventory: Zinc nitrate hexahydrate

Other Regulations: OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).

Other Classifications:

WHMIS (Canada):
CLASS C: Oxidizing material.
CLASS D-2B: Material causing other toxic effects (TOXIC).

DSCL (EEC):
R22- Harmful if swallowed.
R36/38- Irritating to eyes and skin.

HMIS (U.S.A.):

Health Hazard: 2

Fire Hazard: 1

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 2

Flammability: 1

Reactivity: 0

Specific hazard:

Protective Equipment:
Gloves.
Lab coat.
Dust respirator. Be sure to use an
approved/certified respirator or

equivalent. Wear appropriate respirator
when ventilation is inadequate.
Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/11/2005 12:56 PM

Last Updated: 11/06/2008 12:00 PM

APPENDIX B

STANDARD OPERATING PROCEDURES

B. APPENDIX B: STANDARD OPERATING PROCEDURES

The standard operating procedures followed in carrying out the experimental work are given in this appendix.

B.1 Safety and environment

1. PPE must be worn at all times when working in the solvent extraction laboratory. The required PPE is:
    a. Lab coat or overalls
    b. Closed shoes
    c. Safety glasses or goggles (if wearing spectacles);
    d. Latex gloves.
2. Experiments must be carried out in a fume-hood.
3. When working with concentrated acid, as much as practically possible, this must be carried out in a fume hood.
4. In case of irreparable damage to any glassware during the test work, the pieces must be collected carefully (do not pick up the pieces with your bare hands) and discarded in the glass waste-bin.
5. All volumetric flasks, beakers and sample bottles that contain solutions should be properly labelled at all times.
6. Waste solutions should be discarded into the provided jerry cans. Do not dispose any solutions down the drain

B.2 Extraction experiments procedures

Extraction experiments work procedure

1. Prepare the required volume of organic phase as required for the planned number of tests in a volumetric flask.
2. Set up the required number of beakers (maximum 5) of appropriate size (250 ml) and label according to test work labels provided.
3. Set up 5 separating funnels of appropriate size (250 ml) and label according to test work labels provided.
4. Label sample bottles, with project number, experiment number, phase ratio, responsible person’s initials and date.

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5. Prepare hardened ash-less filter paper (allows aqueous through).
6. Prepare phase-separating filter paper (allows organic through).
7. Pipette the required amount (50 ml) of aqueous phase into each beaker.
8. Pipette the required amount (50 ml) of organic phase into each beaker.
9. Add a magnetic stirrer, place on a stirrer hotplate and agitate for 15 min.
10. Switch off, remove magnetic stirrer from beaker using the magnet stirrer stick.
11. Decant the entire volume of solution into the appropriate separating funnel and allow the two phases to separate.
12. Drain off aqueous phase through hardened ash-less filter paper into the sample bottles. Samples must be properly sealed and packaged and then to sent for chemical analysis (de Bruyn Spectroscopic Solutions).
13. Drain off organic phase through phase separating filter paper into the sample bottle Samples must be properly sealed and packaged and then to sent for chemical analysis (de Bruyn Spectroscopic Solutions).
14. Place an order with de Bruyn Spectroscopic solutions for the analysis of:
    a. Aqueous phase for Zn, Fe, Na and Cl.
    b. Organic phase for Zn, Fe, and Na.
15. Pack aqueous and organic samples for each set of experiments in separate sample bags and label with which phase they are (aqueous or organic).
16. Organise removal permit for samples to be taken out of site and specify that solutions will be returned to site.
17. Any waste aqueous or organic solutions should be placed into the appropriate jerry cans in the lab.
18. Samples should be returned to site once analysis has been completed and be analysed for H^+ and Fe(II) in the Technology acid lab.

Procedure for preconditioning of the Alamine 336 organic phase

1. Make up 2000 ml of 6 M HCl by adding 500 ml de-ionised water to flask, then slowly adding 1000 ml concentrated HCl with stirring, then make up to the mark with DI water.
2. Make up 1000 ml organic phase as per recipe.

3. Place organic in 5 l beaker with stirring.
4. Add 1000 ml of 6 M HCl to beaker and stir vigorously by magnetic stirring for 15 minutes.
5. Transfer to separating funnel, tap off aqueous phase and discard.
6. The organic phase is now preconditioned and can be used in experiment.
7. Use this preconditioned organic for your SO samples – not the freshly made organic.

B.3 Stripping experiments procedures

Preparation Procedure of Loaded organic (LO)

1. Pipette 200ml of organic phase into a beaker.
2. Pipette 400ml of aqueous phase (PLS) into each beaker.
3. Add a magnetic stirrer, place on a stirrer hotplate and agitate for 15 min.
4. Switch off, remove magnetic stirrer from beaker using the magnet stirrer stick.
5. Decant the entire volume of solution into the appropriate separating funnel and allow the two phases to separate.
6. Drain off aqueous phase and discard it.
7. Contact the remaining organic with fresh 400ml of aqueous phase (PLS) into the beaker.
8. Add a magnetic stirrer, place on a stirrer hotplate and agitate for 15 min.
9. Switch off, remove magnetic stirrer from beaker using the magnet stirrer stick.
10. Decant the entire volume of solution into the appropriate separating funnel and allow the two phases to separate.
11. Drain off aqueous phase and discard it.
12. Use the loaded organic for the stripping experiments.

Stripping experiments work procedure

1. Table 2 provide the volumes that will be required for the various phase ratios to be used to produce the stripping isotherm.
2. Set up the required number of beakers of appropriate size and label according to test work labels provided.
3. Set up 5 separating funnels of appropriate size and label according to test work labels provided.
4. Label sample bottles, with project number, experiment number, phase ratio, responsible person’s initials and date.

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O:A 2
9 December 2008
TG

5. Prepare hardened ash-less filter paper (allows aqueous through).
6. Prepare phase-separating filter paper (allows organic through).
7. Pipette the required amount of aqueous phase into each beaker.
8. Pipette the required amount of organic phase into each beaker.
9. Add a magnetic stirrer, place on a stirrer hotplate and agitate for 15 min.
10. Switch off, remove magnetic stirrer from beaker using the magnet stirrer stick.
11. Decant the entire volume of solution into the appropriate separating funnel and allow the two phases to separate.
12. Drain off aqueous phase through hardened ash-less filter paper into the sample bottles. Samples must be properly sealed and packaged and then to sent for chemical analysis (de Bruyn Spectroscopic Solutions).
13. Drain off organic phase through phase separating filter paper into the sample bottle Samples must be properly sealed and packaged and then to sent for chemical analysis (de Bruyn Spectroscopic Solutions).
14. Place an order with de Bruyn Spectroscopic solutions for the analysis of:
    a. Aqueous phase for Zn, Fe, Na and Cl.
    b. Organic phase for Zn, Fe, and Na.
15. Pack aqueous and organic samples for each set of experiments in separate sample bags and label with which phase they are (aqueous or organic).
16. Organise removal permit for samples to be taken out of site and specify that solutions will be returned to site.
17. Any waste aqueous or organic solutions should be placed into the appropriate jerry cans in the lab.
18. Samples should be returned to site once analysis has been completed and be analysed for H^+ and Fe(II) in the Technology acid lab.

Table B-1 Experimental conditions for the stripping test work.

O:A	Volume organic (ml)	Volume aqueous (ml)
0.1	20	200
0.25	20	80
0.5	20	40
1	20	20
2	40	20
5	100	20
10	200	20
Total	**420**	**400**

Anglo Research
A Division of Anglo Operations Limited

Date: 12 February 2008
Revision: 2

STANDARD OPERATING PROCEDURE FOR TOTAL ACID DETERMINATION

1.0 PPE REQUIRED

- Safety overalls/laboratory coat
- Safety shoes/boots
- Safety gloves
- Safety goggles

2.0 PRINCIPLE

To determine the total acid content in a sample by acid-base titration i.e. neutralization.

3.0 APPARATUS AND CHEMICALS REQUIRED

Metrohm 794 Basic Titrino, 776 Dosimats
pH Electrode
0.1M Sodium Hydroxide
280g/l Potassium oxalate (pH ~ 11)

4.0 PROCEDURE

Make sure the environment in which you are working is clean and organized. To guarantee safety, check for the presence and position of (emergency) stop buttons on all moving machinery.

4.1 Instrument Set up.

a) Install Sodium Hydroxide (0.1M) exchange unit on 794 Basic Titrino. Ensure exchange unit is pushed fully to the back. If unit is not correctly installed the warning “no exchange unit “will be displayed.

b) Install Potassium Oxalate (280g/l) exchange unit on either of the two 776 Dosimat units. On the particular 776 Dosimat keyboard select RECALL 2, ENTER.

c) Check the Potassium Nitrate in the pH electrode; fill up to the opening in the electrode.

d) Place the pH electrode and burettes from the exchange units on the stirrer stand. The burettes should be positioned (in the holder) behind the electrode in the direction of stirring. Try to maximize the distance between burettes and electrode.

e) Flush the stirrer, electrode and burettes into a waste beaker with distilled water from wash bottle pump system.

4.2 Method Selection

a) Press User Method Key and ENTER.

b) Press Select Key until method “TOT ACID” is on display and ENTER.

4.3 Sample Preparation

a) Add a known aliquot of sample into plastic cup. (Guideline: 1ml for 0.2g/l H^+)

b) Add distilled water up to 50ml mark to cover the pH electrode during titration.

c) Mount the cup on the stand, insert stirrer and probes. Stirrer will start automatically when positioned at the correct height.

4.4 Titration

a) Press START on the 794 Basic Titrino or the 794 Basic Titrino Keyboard.

b) Wait until there is a request for id#1 or C21, input date using ddmmyy and press ENTER.

c) The display will show id#2 or C22, input sample id by pressing REPORT KEY select letters, digits, Characters by pressing MODE button and then ENTER. When done press Quit button and ENTER.

d) The display will show id#3 or C23, Input the dilution factor. Press ENTER.

e) The display will request Sample size. Input Sample size as above and press ENTER. Titration will start automatically.

f) After the titration is finished record the result and lift up the stand so as to stop the stirrer and flush with distilled water.

g) Repeat the above for the next sample from point 4.3.

h) If at any point you want to stop the titration e.g. plastic titration cup is overflowing press STOP on the 794 Basic Titrino or the 794 Basic Titrino Keyboard. If required reduce the sample aliquot.

ANGLO AMERICAN

Anglo Research
A Division of Anglo Operations Limited

Date: 13 February 2008
Revision: 1

STANDARD OPERATING PROCEDURE FOR FERROUS QUANTITY DETERMINATION

1.0 PPE REQUIRED

- Safety overalls/laboratory coat
- Safety shoes/boots
- Safety gloves
- Safety goggles

2.0 PRINCIPLE

To determine the quantity of ferrous ion in a sample by titration i.e. oxidation of ferrous ion to ferric using the dichromate ion, which is reduced to Cr^{3+} ion, as illustrated by the equation below.

$$6Fe^{2+} + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + Cr^{3+}$$

3.0 APPARATUS REQUIRED

Mettler Toledo DL50 Autotitrator
Computer
Eh electrode
0.1M $K_2Cr_2O_7$
Mixed Acid (Spekker)
Pipettes
100ml Plastic Cup (DL50 specific)

4.0 PROCEDURE

Make sure the environment in which you are working is clean and organized. To guarantee safety, check for the presence and position of (emergency) stop buttons on all moving machinery.

4.1 Logging into Computer Programme and Method Selection.

f) On Desktop double click on Lab X icon.

NB: Computer has username “student” and password “student”

g) Double click on “Titrator 2”, then “samples” then “Ferrous” then “Ferrous oxidation”.
h) Fill in the number of samples to be analyzed and press Enter. Go to file and press “Save”.
i) Select the “Titrator 2” tab at the bottom of screen.

4.2 Sample and Plant Preparation

NB: The following procedure has been programmed for a 20ml sample volume and in the event that a smaller sample is used the result is multiplied by a correction factor to volume 20ml.

d) Add a 20ml sample aliquot of sample into 100ml plastic cup.
e) Add 20ml of Spekker acid.
f) Add distilled water up to 60ml.
g) Place the cup into cold water bath for cooling.
h) Insert Eh probe and burette on the DL50 stirrer holder.
i) Mount the 100ml plastic cup on the DL50 Auto – titrator, by rotating the grey clamp lid to the right.

4.3 Running the Titration

i) Right click on “Ferrous Oxidation” icon and select “Run”, or go to “Analysis” and click on “Start Series”.
j) Wait for Confirmation request.
k) When Confirmation requested click “Confirmation” icon or go to “Analysis” and click on “Sent Confirmation” to start the titration.
l) After the programme is finished, the computer automatically records the result or you may record the result.
m) Flush the stirrer and Eh probe with water.
n) Repeat the above for the next sample run from point 4.2.

APPENDIX C

EXTRACTION AND STRIPPING EXPERIMENTAL RESULTS

C. APPENDIX C: EXTRACTION AND STRIPPING EXPERIMENT RESULTS

Table C-1 gives the metal analysis of the organic samples used as feed organic in the study.

Table C-1 Composition of the feed solutions used to investigate the effect of initial zinc concentration on zinc extraction.

Sample	**Na**	**Fe**	**Zn**
	µg/ml	**µg/ml**	**µg/ml**
Alamine	44	6.62	18
CYANEX	44	10	18.6
TBP	44	6.68	18

C.1 Effect of zinc concentration

Table C-2 gives the quantities of reagents used to prepare a 250 ml bulk synthetic solution for each set of experimental conditions. Table C-3 gives the composition of the various feed solutions used in the experiments to investigate the effect of zinc concentration on zinc extraction.

Table C-2 Amount of reagents used to prepare a 250 ml bulk synthetic solution for each set of experiments.

Label	**Target Zn**	**$ZnCl_2$**	**HCl**	**$Zn(NO_3)_2$**	**NaCl**
	M	**g**	**g**	**g**	**g**
Z1	0.01	0.26	79.13	-	35.02
Z2	0.02	0.52	79.13	-	34.79
Z3	0.04	1.30	79.13	-	34.12
Z4	0.08	2.61	79.13	-	33.01
Z5	0.15	5.21	79.13	-	30.77
Z6	0.30	10.22	79.13	-	26.47
Z7	0.50	17.04	79.13	-	20.63
Z8	0.80	27.26	79.13	-	11.86
Z9	1.00	34.07	79.13	-	6.02
Z10	1.50	41.09	79.13	21.87	-
Z11	2.00	41.09	79.13	59.05	-
Z12	2.50	41.09	79.13	96.24	-
Z13	2.75	41.09	79.13	114.83	-

Table C-3 Composition of the feed solutions used to investigate the effect of initial zinc concentration on zinc extraction.

Label	**Target Zn**	**Zn**	**Cl**	**H**	**Na**
	M	***M***	***M***	***M***	***M***
Z1	0.01	0.01	5.05	2.80	2.34
Z2	0.02	0.02	5.08	1.84	2.39
Z3	0.04	0.04	5.16	2.60	2.33
Z4	0.08	0.08	5.12	2.78	2.28
Z5	0.15	0.15	5.12	2.75	2.13
Z6	0.30	0.29	5.11	2.78	1.84
Z7	0.50	0.49	5.04	2.63	1.45
Z8	0.80	0.78	5.04	2.51	0.85
Z9	1.00	0.98	5.01	2.48	0.43
Z10	1.50	1.49	5.20	2.53	0.03
Z11	2.00	2.00	5.02	1.94	0.03
Z12	2.50	2.54	5.07	2.21	0.03
Z13	2.75	2.78	4.98	2.25	0.02

Tables C-4 to C-6 provide the data obtained from the extraction experiments using Alamine 336, CYANEX 923 and TBP to investigate the influence of initial zinc concentration on zinc extraction.

Table C-4 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using Alamine 336 as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
AZ1	0.00	0.01	92.54	118.13	**125.58**	2.45	0.0026	-4.38	104.49
AZ2	0.00	0.02	97.08	104.53	107.44	2.45	0.0024	-2.51	102.61
AZ3	0.00	0.04	98.88	99.29	100.41	2.37	0.0023	-1.64	101.74
AZ4	0.00	0.08	99.31	96.74	97.43	2.30	0.0022	-1.07	101.16
AZ5	0.02	0.14	84.47	88.46	103.99	2.13	0.0022	0.03	100.07
AZ6	0.15	0.15	47.92	51.18	103.26	1.44	0.0023	21.77	78.35
AZ7	0.33	0.15	32.58	31.57	98.99	0.83	0.0026	42.58	57.59
AZ8	0.59	0.16	24.32	20.59	96.27	0.43	0.0024	49.80	50.48
AZ9	0.82	0.16	16.77	16.71	99.95	0.42	0.0024	3.21	97.34
AZ10	1.33	0.15	10.47	10.05	99.58	0.03	0.0023	-6.92	115.99
AZ11	1.71	0.12	14.50	5.92	91.43	0.03	0.0022	-1.04	109.67
AZ12	2.30	0.10	9.19	3.81	94.62	0.02	0.0021	0.35	108.17
AZ13	2.59	0.09	6.90	3.14	96.25	0.02	0.0023	2.29	107.05
				Average	**101.17**			**Average**	**94.98**
			Standard deviation		**8.45**		**Standard deviation**		**20.20**

Table C-4 (continued)

	Cl		**H**		**Distribution coefficient**			**Molar ratio**		
Label	**Aq**	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***						
AZ1	3.43	1.62	2.87	-0.07	15.84	0.47	0.00	35	0.19	-4
AZ2	3.29	1.79	2.86	-1.02	35.83	0.55	0.00	19	0.17	0
AZ3	3.24	1.93	2.88	-0.29	88.60	0.60	0.00	8	0.16	-1
AZ4	3.05	2.07	2.89	-0.11	140.16	0.68	0.00	4	0.15	-3
AZ5	2.82	2.29	2.86	-0.11	5.70	0.81	0.00	2	0.13	-3
AZ6	2.68	2.43	2.90	-0.12	0.98	0.91	0.00	2	0.12	-3
AZ7	2.70	2.34	2.83	-0.20	0.47	0.87	0.00	2	0.13	-2
AZ8	2.57	2.47	3.19	-0.67	0.27	0.96	0.01	2	0.12	0
AZ9	2.66	2.35	2.89	-0.41	0.20	0.88	0.01	2	0.13	-1
AZ10	2.68	2.52	2.83	-0.29	0.11	0.94	0.08	2	0.12	-1
AZ11	2.74	2.28	2.72	-0.78	0.07	0.83	0.09	3	0.13	0
AZ12	2.86	2.21	2.65	-0.44	0.04	0.77	0.09	3	0.14	-1
AZ13	2.89	2.09	2.57	-0.32	0.03	0.72	0.10	3	0.15	-1

*Calculated by mass balance.

L: Ligand/extractant

Table C-5 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using CYANEX 923 as an extractant.

Label	**Zn**					**Na**			
	Aq	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**		***M***	***M***	**%**	**%**
CZ1	0.00	0.01	93.75	108.75	**115.00**	2.49	0.0024	-6.43	106.53
CZ2	0.00	0.02	97.99	109.36	**111.37**	2.48	0.0023	-3.86	103.95
CZ3	0.00	0.04	99.36	103.93	104.57	2.41	0.0024	-3.39	103.49
CZ4	0.00	0.08	99.73	99.48	99.75	2.35	0.0024	-3.06	103.17
CZ5	0.00	0.17	99.81	109.22	109.41	2.18	0.0026	-2.34	102.46
CZ6	0.01	0.28	95.49	97.25	101.76	1.89	0.0024	-2.87	103.00
CZ7	0.12	0.35	75.00	71.77	96.76	1.47	0.0023	-1.40	101.56
CZ8	0.35	0.41	54.72	52.72	98.01	0.85	0.0025	-0.18	100.48
CZ9	0.53	0.42	45.67	42.22	96.55	0.43	0.0027	-0.08	100.70
CZ10	1.10	0.36	25.87	24.01	98.13	0.02	0.0028	6.06	105.02
CZ11	1.71	0.29	14.47	14.47	100.00	0.03	0.0027	-1.39	112.22
CZ12	2.31	0.24	8.95	9.55	100.59	0.02	0.0023	20.00	89.04
CZ13	2.63	0.23	5.59	8.36	102.77	0.02	0.0022	0.35	108.64
				Average	**102.67**			**Average**	**103.10**
			Standard deviation		**5.86**		**Standard deviation**		**5.35**

Table C-5 (continued)

Label	**Cl**		**H**		**Distribution coefficient**			**Molar ratio**		
	Aq	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***						
CZ1	4.16	0.90	2.22	0.58	17.40	0.22	0.00	125	1	2
CZ2	4.06	1.02	2.21	-0.38	54.35	0.25	0.00	60	1	-3
CZ3	3.88	1.28	2.25	0.35	162.15	0.33	0.00	25	1	3
CZ4	3.82	1.31	2.25	0.53	362.79	0.34	0.00	12	1	2
CZ5	3.65	1.46	2.29	0.45	590.11	0.40	0.00	6	1	2
CZ6	3.46	1.66	2.37	0.41	21.58	0.48	0.00	4	1	2
CZ7	3.37	1.67	2.44	0.19	2.87	0.50	0.00	3	1	5
CZ8	3.35	1.70	2.61	-0.09	1.16	0.51	0.00	2	1	-11
CZ9	3.30	1.70	2.68	-0.20	0.78	0.52	0.01	2	1	-5
CZ10	3.41	1.79	2.43	0.10	0.32	0.52	0.12	3	1	10
CZ11	3.69	1.33	2.32	-0.38	0.17	0.36	0.11	3	1	-3
CZ12	3.87	1.21	2.14	0.07	0.10	0.31	0.11	4	1	14
CZ13	3.84	1.14	1.95	0.30	0.09	0.30	0.09	4	1	3

*Calculated by mass balance.

L: Ligand/extractant

Table C-6 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using TBP as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
TZ1	0.01	1.56E-03	13.33	21.25	107.92	2.44	0.0024	-4.17	104.27
TZ2	0.01	2.95E-03	13.88	19.42	105.53	2.39	0.0023	-0.14	100.24
TZ3	0.03	5.20E-03	10.81	13.37	102.56	2.37	0.0022	-1.52	101.62
TZ4	0.06	1.29E-02	23.80	15.71	91.90	2.28	0.0023	-0.25	100.35
TZ5	0.13	2.36E-02	15.65	15.29	99.64	2.17	0.0024	-1.71	101.82
TZ6	0.27	4.05E-02	7.67	13.89	106.22	1.86	0.0026	-1.01	101.15
TZ7	0.46	6.07E-02	5.31	12.46	107.16	1.45	0.0023	-0.48	100.64
TZ8	0.70	9.18E-02	10.88	11.72	100.85	0.84	0.0023	1.05	99.23
TZ9	0.89	1.13E-01	9.82	11.46	101.64	0.42	0.0023	3.08	97.46
TZ10	1.45	8.75E-02	2.44	5.88	103.44	0.03	0.0024	-12.11	121.54
TZ11	2.01	5.05E-02	-0.24	2.52	102.76	0.03	0.0022	-11.44	120.10
TZ12	2.59	3.37E-02	-1.97	1.33	103.30	0.03	0.0023	-11.83	121.04
TZ13	2.86	3.03E-02	-2.63	1.09	103.72	0.03	0.0022	-11.64	120.46
				Average	**102.82**			**Average**	**106.92**
			Standard deviation		**4.08**		**Standard deviation**		**9.75**

Table C-6 (continued)

	Cl		**H**		**Distribution coefficient**			**Molar ratio**		
Label	**Aq**	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***						
TZ1	3.77	1.28	2.79	0.01	0.25	0.34	0.00	641	0.8	97
TZ2	3.58	1.50	2.77	-0.93	0.23	0.42	0.00	339	0.7	-1
TZ3	3.53	1.63	2.78	-0.18	0.15	0.46	0.00	192	0.6	-6
TZ4	3.40	1.73	2.77	0.01	0.21	0.51	0.00	78	0.6	79
TZ5	3.32	1.79	2.77	-0.02	0.18	0.54	0.00	42	0.6	-56
TZ6	3.26	1.85	2.78	0.00	0.15	0.57	0.00	25	0.5	-388
TZ7	3.16	1.88	2.73	-0.10	0.13	0.60	0.00	16	0.5	-10
TZ8	3.12	1.93	2.81	-0.29	0.13	0.62	0.00	11	0.5	-3
TZ9	3.03	1.97	2.80	-0.32	0.13	0.65	0.01	9	0.5	-3
TZ10	3.15	2.04	2.55	-0.01	0.06	0.65	0.08	11	0.5	-68
TZ11	3.20	1.82	2.22	-0.28	0.03	0.57	0.08	20	0.5	-4
TZ12	3.29	1.79	2.06	0.15	0.01	0.54	0.08	30	0.6	7
TZ13	3.22	1.76	1.90	0.36	0.01	0.55	0.08	33	0.6	3

*Calculated by mass balance.

L: Ligand/extractant

C.2 Effect of chloride concentration

Table C-7 gives the quantities of reagents used to prepare a 250 ml bulk synthetic solution for each set of experimental conditions. Table C-8 gives the composition of the various feed solutions used in the experiments to investigate the effect of chloride concentration on zinc extraction.

Table C-7 Amount of reagents used to prepare a 250 ml bulk synthetic solution for each set of experiments.

Label	Target Cl	$ZnCl_2$	HCl	$Zn(NO_3)_2$	HNO_3	NaCl
	M	g	g	g	g	g
CL1	0.10	-	-	75.86	79.57	1.46
CL2	0.20	-	-	75.86	79.57	2.92
CL3	0.50	-	-	75.86	79.57	7.31
CL4	1.00	-	-	75.86	79.57	14.61
CL5	2.00	-	-	75.86	79.57	29.22
CL6	3.00	34.76	-	-	79.57	14.03
CL7	4.00	34.76	-	-	79.57	28.64
CL8	5.00	34.76	79.13	-	-	2.66
CL9	6.00	34.76	79.13	-	-	17.27
CL10	6.21	34.76	79.13	-	-	20.27

Table C-8 Composition of the feed solutions used to investigate the effect of initial chloride concentration on zinc extraction.

Label	Target Cl	Cl	Zn	H	Na
	M	*M*	*M*	*M*	*M*
CL1	0.10	0.10	1.08	2.19	0.10
CL2	0.20	0.20	1.04	1.97	0.21
CL3	0.50	0.52	1.03	1.95	0.52
CL4	1.00	1.09	1.03	1.97	1.06
CL5	2.00	1.83	1.01	1.82	2.07
CL6	3.00	2.71	1.01	2.90	1.02
CL7	4.00	3.69	0.99	2.83	2.08
CL8	5.00	4.66	1.01	2.71	0.20
CL9	6.00	5.70	1.00	1.44	1.26
CL10	6.21	5.93	1.00	2.65	1.48

Tables C-9 to C-11 provide the data obtained from the extraction experiments using Alamine 336, CYANEX 923 and TBP to investigate the influence of initial chloride concentration on zinc extraction.

Table C-9 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using Alamine 336 as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
ACL1	1.03	0.02	4.54	1.82	97.28	0.11	0.0027	-7.73	110.47
ACL2	1.02	0.03	1.54	2.61	101.07	0.21	0.0025	-2.06	103.26
ACL3	0.98	0.05	5.76	5.07	99.31	0.52	0.0027	0.03	100.48
ACL4	0.94	0.09	8.34	8.33	99.99	1.01	0.0026	4.54	95.70
ACL5	0.89	0.12	12.04	11.80	99.76	2.02	0.0025	2.44	97.68
ACL6	0.91	0.09	9.86	8.67	98.81	0.97	0.0025	4.96	95.28
ACL7	0.89	0.10	10.02	9.96	99.94	2.01	0.0025	3.40	96.72
ACL8	0.84	0.17	16.56	16.94	100.38	0.22	0.0025	-7.43	108.65
ACL9	0.84	0.17	16.20	16.95	100.75	1.20	0.0028	4.30	95.92
ACL10	0.83	0.16	16.90	16.53	99.63	1.40	0.0026	4.92	95.25
				Average	**99.69**			**Average**	**99.94**
			Standard deviation		**1.08**		**Standard deviation**		**5.69**

Table C-9 (continued)

	Cl		**H**		**Distribution coefficient**			**Molar ratio**		
	Aq	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
Label	***M***	***M***	***M***	***M***						
ACL1	0.38	-0.28	0.14	2.05	0.02	-0.73	0.03	16	-1	0.15
ACL2	0.46	-0.27	0.29	1.68	0.03	-0.57	0.01	11	-1	0.18
ACL3	0.70	-0.18	0.05	1.90	0.05	-0.26	0.01	6	-2	0.16
ACL4	1.18	-0.10	0.06	1.92	0.09	-0.08	0.00	4	-3	0.16
ACL5	2.21	-0.38	0.14	1.68	0.13	-0.17	0.00	3	-1	0.18
ACL6	1.81	0.90	2.91	-0.01	0.10	0.49	0.00	3	0.34	-21
ACL7	2.82	0.87	2.86	-0.03	0.11	0.31	0.00	3	0.35	-11
ACL8	3.52	1.14	2.91	-0.20	0.20	0.32	0.01	2	0.27	-1
ACL9	4.59	1.12	2.88	-1.44	0.20	0.24	0.00	2	0.27	0
ACL10	4.76	1.18	2.82	-0.16	0.20	0.25	0.00	2	0.26	-2

*Calculated by mass balance. L: Ligand/extractant

Table C-10 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using CYANEX 923 as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
CCL1	0.81	0.27	24.72	25.37	100.65	0.11	0.0025	-11.55	114.12
CCL2	0.78	0.31	25.00	30.08	105.08	0.22	0.0024	-2.70	103.86
CCL3	0.69	0.34	33.48	32.98	99.50	0.56	0.0024	-6.96	107.42
CCL4	0.58	0.42	43.11	41.42	98.31	1.08	0.0025	-1.97	102.20
CCL5	0.54	0.46	46.07	45.63	99.56	2.18	0.0025	-5.24	105.36
CCL6	0.84	0.18	15.96	17.97	102.01	1.08	0.0027	-5.82	106.08
CCL7	0.84	0.17	14.82	17.22	102.39	2.17	0.0024	-4.09	104.21
CCL8	0.59	0.39	41.77	38.79	97.02	0.22	0.0027	-6.57	107.92
CCL9	0.61	0.38	38.49	37.90	99.41	1.29	0.0024	-2.90	103.10
CCL10	0.62	0.37	38.27	36.61	98.34	1.51	0.0024	-2.23	102.40
				Average	**100.23**			**Average**	**105.67**
			Standard deviation		**2.38**		**Standard deviation**		**3.57**

Table C-10 (continued)

	Cl		H		Distribution coefficient			Molar ratio		
Label	**Aq**	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***						
CCL1	0.00	0.10	1.59	0.60	0.34	22.46	0.02	4	10	2
CCL2	0.01	0.19	1.53	0.44	0.40	20.04	0.01	3	5	2
CCL3	0.04	0.48	1.37	0.58	0.50	12.42	0.00	3	2	2
CCL4	0.23	0.86	0.01	1.96	0.73	3.78	0.00	2	1	1
CCL5	1.00	0.83	0.01	1.80	0.85	0.84	0.00	2	1	1
CCL6	2.42	0.29	1.83	1.06	0.21	0.12	0.00	6	3	1
CCL7	3.47	0.22	2.19	0.64	0.20	0.06	0.00	6	5	2
CCL8	3.72	0.94	2.62	0.09	0.67	0.25	0.01	3	1	11
CCL9	4.77	0.94	2.52	-1.08	0.62	0.20	0.00	3	1	-1
CCL10	4.95	0.98	2.46	0.19	0.59	0.20	0.00	3	1	5

*Calculated by mass balance. L: Ligand/extractant

Table C-11 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using CYANEX 923 as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
TCL1	1.02	0.00	5.36	0.10	94.74	0.11	0.0023	-11.23	113.63
TCL2	1.00	0.00	3.44	0.31	96.87	0.21	0.0023	1.39	99.73
TCL3	0.98	0.01	5.52	1.45	95.92	0.53	0.0023	-2.44	102.88
TCL4	0.98	0.04	4.16	3.99	99.83	1.04	0.0023	2.03	98.19
TCL5	0.93	0.08	7.57	7.95	100.38	2.07	0.0024	0.10	100.01
TCL6	1.00	0.01	0.82	1.15	100.34	1.06	0.0023	-3.07	103.29
TCL7	0.99	0.01	0.35	1.02	100.67	2.15	0.0024	-2.98	103.09
TCL8	0.90	0.12	11.24	11.75	100.51	0.22	0.0023	-6.36	107.49
TCL9	0.86	0.11	13.63	11.01	97.38	1.25	0.0024	0.15	100.04
TCL10	0.86	0.11	13.73	10.77	97.04	1.50	0.0025	-1.62	101.78
				Average	**98.37**			**Average**	**103.02**
			Standard deviation		**2.21**		**Standard deviation**		**4.55**

Table C-11 (continued)

	Cl		**H**		**Distribution coefficient**			**Molar ratio**		
Label	**Aq**	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***						
TCL1	0.10	0.00	1.88	0.31	0.00	0.01	0.02	934	657	3
TCL2	0.20	0.00	2.11	-0.14	0.00	-0.02	0.01	307	-269	-7
TCL3	0.52	0.00	2.08	-0.13	0.02	-0.01	0.00	67	-250	-8
TCL4	0.97	0.12	1.95	0.02	0.04	0.12	0.00	24	9	43
TCL5	2.00	-0.17	1.90	-0.08	0.09	-0.09	0.00	13	-6	-12
TCL6	3.17	-0.46	2.34	0.55	0.01	-0.14	0.00	86	-2	2
TCL7	4.32	-0.63	2.29	0.54	0.01	-0.15	0.00	99	-2	2
TCL8	5.10	-0.45	2.86	-0.15	0.13	-0.09	0.01	8	-2	-7
TCL9	6.07	-0.37	2.78	-1.34	0.13	-0.06	0.00	9	-3	-1
TCL10	6.27	-0.34	2.74	-0.08	0.12	-0.05	0.00	9	-3	-12

*Calculated by mass balance. L: Ligand/extractant

C.3 Effect of pH on zinc extraction

Table C-12 gives the quantities of reagents used to prepare a 250 ml bulk synthetic solution for each set of experimental conditions. Table C-13 gives the composition of the various feed solutions used in the experiments to investigate the effect of acid concentration on zinc extraction.

Table C-12 Amount of reagents used to prepare a 250 ml bulk synthetic solution for each set of experiments.

Label	**Target H**	**$ZnCl_2$**	**HNO_3**	**NaCl**
	M	**g**	**g**	**g**
H1	0.25	34.76	7.10	46.02
H2	0.5	34.76	14.21	46.02
H3	1	34.76	28.42	46.02
H4	2	34.76	56.83	46.02
H5	3	34.76	85.25	46.02
H6	4	34.76	113.67	46.02

Table C-13 Composition of the feed solutions used to investigate the effect of initial acid concentration on zinc extraction.

Label	**Target H**	**H**	**pH**	**Zn**	**Cl**	**Na**
	M	***M***		***M***	***M***	***M***
H1	0.25	0.21	-0.08	0.96	5.84	3.27
H2	0.5	0.47	-0.4	0.96	5.65	3.37
H3	1.0	1.05	-0.7	0.96	5.69	3.35
H4	2.0	2.05	-1.0	0.95	5.52	3.31
H5	3.0	3.09	-1.1	0.96	5.48	3.35
H6	4.0	4.12	-1.3	0.96	5.41	3.34

Tables C-14 to C-16 provide the data obtained from the extraction experiments using Alamine 336, CYANEX 923 and TBP to investigate the influence of initial acid concentration on zinc extraction.

Table C-14 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using Alamine 336 as an extractant.

	Zn					Na			
Label	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**	**Aq**
	M	**%**	**%**	**%**	***M***	***M***	**%**	**%**	***M***
ApH1	0.85	0.15	11.50	15.93	104.43	3.43	0.0024	-4.95	105.03
ApH2	0.84	0.15	12.59	15.88	103.29	3.37	0.0024	-0.15	100.23
ApH3	0.86	0.14	10.47	14.17	103.70	3.25	0.0023	2.94	97.12
ApH4	0.86	0.12	9.52	12.14	102.62	3.31	0.0023	0.20	99.87
ApH5	0.88	0.10	8.53	9.94	101.41	3.27	0.0022	2.54	97.52
ApH6	0.89	0.08	6.93	8.16	101.23	3.18	0.0024	4.86	95.21
				Average	102.78			**Average**	99.16
			Standard deviation		1.28		**Standard deviation**		3.42

	Cl		**H**			**Distribution coefficient**			**Molar ratio**		
Label	**Aq**	***Org**	**Aq**	***Org**	**Equilibrium**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***	**pH**						
ApH1	5.63	0.21	0.32	-0.11	-0.19	0.18	0.04	0.00	2	1	-3
ApH2	5.33	0.32	0.57	-0.10	-0.45	0.18	0.06	0.00	2	1	-3
ApH3	5.28	0.40	1.10	-0.04	-0.67	0.16	0.08	0.00	2	1	-7
ApH4	5.20	0.32	2.05	0.01	-0.89	0.13	0.06	0.00	3	1	58
ApH5	5.14	0.34	2.97	0.12	-1.03	0.11	0.07	0.00	3	1	2
ApH6	5.09	0.32	3.75	0.37	-1.15	0.09	0.06	0.00	4	1	1

[*] Calculated by mass balance. L: Ligand/extractant

Table C-15 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using CYANEX 923 as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
CpH1	0.70	0.47	27.08	48.33	**121.26**	3.90	0.0022	-19.37	**119.43**
CpH2	0.59	0.43	38.54	44.50	105.97	3.36	0.0022	0.31	99.75
CpH3	0.64	0.34	33.72	35.28	101.56	3.27	0.0024	2.63	97.44
CpH4	0.77	0.21	19.12	21.95	102.83	3.26	0.0023	1.78	98.28
CpH5	0.88	0.10	7.87	10.16	102.29	3.28	0.0021	2.28	97.78
CpH6	0.94	0.04	1.27	4.03	102.75	3.32	0.0024	0.68	99.39
				Average	106.11			**Average**	102.01
			Standard deviation		7.57		**Standard deviation**		8.58

	Cl		**H**			**Distribution coefficient**			**Molar ratio**		
Label	**Aq**	***Org**	**Aq**	***Org**	**Equilibrium**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***	**pH**						
CpH1	5.92	-0.08	0.18	0.03	0.10	0.66	-0.01	0.00	2	-12	34
CpH2	5.08	0.57	0.37	0.10	-0.24	0.72	0.11	0.00	2	2	10
CpH3	5.10	0.58	0.79	0.27	-0.51	0.53	0.11	0.00	3	2	4
CpH4	4.94	0.58	1.57	0.48	-0.76	0.27	0.12	0.00	5	2	2
CpH5	5.14	0.35	2.29	0.81	-0.94	0.11	0.07	0.00	10	3	1
CpH6	5.13	0.29	3.10	1.02	-1.05	0.04	0.06	0.00	26	4	1

* Calculated by mass balance. L: Ligand/extractant

Table C-16 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using TBP as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
TpH1	0.92	0.08	4.91	8.25	103.34	3.35	0.0032	-2.49	102.59
TpH2	0.91	0.07	5.22	7.33	102.11	3.26	0.0023	3.15	96.92
TpH3	0.93	0.05	2.97	4.82	101.84	3.28	0.0022	2.13	97.94
TpH4	0.97	0.02	-1.24	1.61	102.85	3.22	0.0021	2.92	97.14
TpH5	0.97	0.00	-1.20	0.43	101.64	3.21	0.0027	4.30	95.78
TpH6	0.98	0.00	-2.11	0.14	102.25	3.21	0.0023	3.77	96.30
				Average	**102.34**			**Average**	**97.78**
			Standard deviation		**0.64**		**Standard deviation**		**2.47**

	Cl		**H**			**Distribution coefficient**			**Molar ratio**		
Label	**Aq**	***Org**	**Aq**	***Org**	**Equilibrium**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***	**pH**						
TpH1	6.26	-0.42	0.12	0.09	0.01	0.09	-0.07	0.00	13	-2	11
TpH2	5.58	0.07	0.35	0.12	-0.31	0.08	0.01	0.00	14	14	8
TpH3	5.51	0.18	0.74	0.31	-0.57	0.05	0.03	0.00	22	6	3
TpH4	5.47	0.05	1.54	0.51	-0.78	0.02	0.01	0.00	65	21	2
TpH5	5.38	0.10	2.36	0.73	-0.95	0.00	0.02	0.00	240	10	1
TpH6	5.27	0.14	3.24	0.88	-1.06	0.00	0.03	0.00	769	7	1

*Calculated by mass balance. L: Ligand/extractant

C.4 Effect of extractant concentration

The feed composition of the solution used for the experiments to investigate the effect of extractant concentration on zinc extraction was 0.99 *M* Zn, 5.63 *M* Cl^-, 2.76 *M* H^+ and 0.38 *M* Na. A one litre bulk synthetic solution was prepared for these experiments using 139.03 g of zinc chloride, 316.53 g of hydrochloric acid and 21.73 g of sodium chloride to reach the specified chloride concentration. Tables C-17 to C-19 provide the data obtained from the extraction experiments using Alamine 336, CYANEX 923 and TBP to investigate the influence of extractant concentration on zinc extraction.

Table C-17 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using Alamine 336 as an extractant.

	Zn					**Na**			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
AV1	0.98	0.01	0.31	1.42	101.11	0.41	0.0025	-8.84	109.52
AV2	0.96	0.03	2.10	2.73	100.63	0.40	0.0026	-7.14	107.82
AV3	0.93	0.06	5.20	6.17	100.97	0.40	0.0024	-7.79	108.43
AV4	0.88	0.12	11.01	11.96	100.95	0.41	0.0025	-8.46	109.12
AV5	0.83	0.17	15.68	16.89	101.20	0.40	0.0025	-7.78	108.45
				Average	**100.97**			**Average**	**108.67**
				Standard deviation	**0.22**		**Standard deviation**		**0.66**

	Cl		**H**		**Distribution coefficient**			**Molar ratio**		
Label	**Aq**	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***						
AV1	5.38	0.25	2.79	-0.03	0.01	0.05	0.01	1	0.1	-1
AV2	5.32	0.31	2.84	-0.08	0.03	0.06	0.01	2	0.1	-1
AV3	5.34	0.29	2.89	-0.13	0.07	0.05	0.01	2	0.4	-1
AV4	5.20	0.44	2.92	-0.16	0.13	0.08	0.01	2	0.5	-1
AV5	5.11	0.52	2.95	-0.19	0.20	0.10	0.01	2	1	-2

*Calculated by mass balance. L: Ligand/extractant

Table C-18 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using CYANEX 923 as an extractant.

	Zn					Na			
Label	Aq	Org	Extraction (Aq)	Extraction (Org)	Mass Balance	Aq	Org	Extraction (Aq)	Mass Balance
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
CV1	0.86	0.02	13.00	1.62	**88.62**	0.39	0.0020	-5.16	105.68
CV2	0.71	0.06	28.37	5.59	**77.22**	0.40	0.0020	-7.42	107.95
CV3	0.57	0.43	41.86	43.23	101.37	0.41	0.0023	-9.27	109.87
CV4	0.39	0.60	59.95	60.88	100.94	0.41	0.0032	-9.35	110.21
CV5	0.38	0.60	61.82	61.35	99.53	0.41	0.0027	-8.43	109.14
CV6	0.57	0.40	42.54	40.86	98.32	0.41	0.00	-9.02	109.80
				Average	**94.33**			**Average**	**108.78**
			Standard deviation		**9.61**		**Standard deviation**		**1.72**

	Cl		H		Distribution coefficient			Molar ratio		
Label	Aq	*Org	Aq	*Org	Zn	Cl	Na	L:Zn	L:Cl	L:H
	M	***M***	***M***	***M***						
CV1	5.04	0.60	2.81	-0.05	0.02	0.12	0.00	16	0.4	-5
CV2	4.67	0.96	2.83	-0.07	0.08	0.21	0.00	11	1	-9
CV3	4.28	1.35	2.71	0.05	0.74	0.31	0.01	2	1	21
CV4	3.75	1.89	2.60	0.17	1.52	0.50	0.01	2	1	9
CV5	3.61	2.03	2.45	0.31	1.61	0.56	0.01	3	1	6
CV6	4.09	1.54	2.52	0.24	0.71	0.38	0.01	6	2	11

*Calculated by mass balance. L: Ligand/extractant

Table C-19 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using TBP as an extractant.

	Zn					Na			
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**
TV1	0.98	0.14	0.89	13.71	**112.82**	0.40	0.0020	-6.65	107.20
TV2	0.95	0.31	3.16	31.82	**128.66**	0.41	0.0021	-8.67	109.23
TV3	0.89	0.13	9.50	12.78	103.28	0.41	0.0021	-9.61	110.16
TV4	0.76	0.28	23.33	28.15	104.81	0.43	0.0027	-14.19	114.90
TV5	0.71	0.32	27.71	32.25	104.55	0.42	0.0022	-12.62	113.22
TV6	0.63	0.39	36.40	39.40	103.00	0.44	0.00	-17.96	118.65
TV7	0.53	0.48	46.49	48.88	102.39	0.46	0.00	-21.24	122.03
TV8	0.42	0.57	57.81	57.76	99.96	0.47	0.00	-24.18	125.06
				Average	**107.43**			**Average**	**115.06**
			Standard deviation		**9.36**		**Standard deviation**		**6.38**

	Cl		H		Distribution coefficient			Molar ratio		
Label	**Aq**	***Org**	**Aq**	***Org**	**Zn**	**Cl**	**Na**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	***M***	***M***						
TV1	5.46	0.17	2.78	-0.02	0.14	0.03	0.01	2	2	-13
TV2	5.46	0.17	2.75	0.01	0.33	0.03	0.01	2	4	70
TV3	5.29	0.35	2.80	-0.04	0.14	0.07	0.01	8	3	-27
TV4	4.97	0.67	2.77	-0.01	0.37	0.13	0.01	5	2	-273
TV5	4.82	0.81	2.75	0.01	0.45	0.17	0.01	6	2	273
TV6	4.59	1.04	2.71	0.05	0.62	0.23	0.01	6	2	53
TV7	4.30	1.33	2.65	0.11	0.91	0.31	0.01	6	2	27
TV8	3.98	1.65	2.58	0.18	1.37	0.42	0.01	6	2	20

[*] Calculated by mass balance. L: Ligand/extractant

C.5 Effect of ferrous concentration

Table C-20 gives the quantities of reagents used to prepare a 250 ml bulk synthetic solution for each set of experimental conditions. Table C-21 gives the composition of the various feed solutions used in the experiments to investigate the effect of iron(II) concentration on zinc extraction.

Table C-20 Amount of reagents used to prepare a 250 ml bulk synthetic solution for each set of experiments.

Label	**Target Fe**	**$ZnCl_2$**	**HCl**	**NaCl**	**$FeCl_2$**
	M	**g**	**g**	**g**	**g**
F1	0.01	34.76	79.13	5.21	0.38
F2	0.02	34.76	79.13	4.99	0.76
F3	0.05	34.76	79.13	3.97	2.49
F4	0.08	34.76	79.13	3.20	3.80
F5	0.10	34.76	79.13	2.51	4.97

Table C-21 Composition of the feed solutions used to investigate the effect of initial iron(II) concentration on zinc extraction.

Label	**Target Fe**	**Fe**	**Zn**	**Cl**	**H**	**Na**
	M	***M***	***M***	***M***	***M***	***M***
F1	0.01	0.01	1.00	5.65	2.77	0.37
F2	0.02	0.02	1.00	5.64	2.74	0.35
F3	0.05	0.05	0.99	5.61	2.78	0.28
F4	0.08	0.08	0.97	5.30	2.78	0.23
F5	0.10	0.10	0.97	5.31	2.91	0.19

Tables C-22 to C-24 provide the data obtained from the extraction experiments using Alamine 336, CYANEX 923 and TBP to investigate the influence of concentration on zinc extraction.

Table C-22 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using Alamine 336 as an extractant.

	Zn					**Fe**				
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**	**%**
AF1	0.83	0.16	16.88	16.39	99.50	0.01	0.00	13.24	18.04	104.79
AF2	0.83	0.16	17.36	16.27	98.91	0.01	0.00	6.21	9.84	103.63
AF3	0.83	0.16	15.72	16.69	100.97	0.05	0.00	1.48	3.92	102.44
AF4	0.83	0.17	14.27	17.19	102.93	0.08	0.00	0.05	2.88	102.83
AF5	0.82	0.17	15.84	16.99	101.15	0.10	0.00	3.02	2.54	99.52
				Average	**100.69**				**Average**	**102.64**
			Standard deviation		**1.57**		**Standard deviation**			**1.96**

	Na				**Cl**		**H**		**Distribution coefficient**				**Molar ratio**		
Label	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**	**Aq**	**Org**	**Aq**	**Org**	**Zn**	**Cl**	**Na**	**Fe**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	**%**	**%**	***M***	***M***	***M***	***M***							
AF1	0.36	0.00	2.41	98.33	5.13	0.53	2.95	-0.18	0.20	0.10	0.01	0.21	2	1	-2
AF2	0.34	0.00	1.84	98.82	5.14	0.50	2.91	-0.17	0.20	0.10	0.01	0.10	2	1	-2
AF3	0.27	0.00	1.18	99.68	5.13	0.48	3.00	-0.22	0.20	0.09	0.01	0.04	2	1	-1
AF4	0.23	0.00	2.10	98.81	5.11	0.19	2.98	-0.21	0.20	0.04	0.01	0.03	2	2	-1
AF5	0.19	0.00	0.00	101.87	5.01	0.30	2.89	0.02	0.20	0.06	0.02	0.03	2	1	19
			Average	**99.50**											
		Standard deviation		**1.41**											

[*] Calculated by mass balance. L: Ligand/extractant

Table C-23 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using CYANEX 923 as an extractant.

	Zn					**Fe**				
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**	**%**
CF1	0.56	0.42	43.61	41.65	98.04	0.01	0.00	20.78	24.66	103.88
CF2	0.57	0.42	43.36	42.05	98.69	0.01	0.00	10.89	15.46	104.57
CF3	0.57	0.43	42.49	43.32	100.83	0.05	0.00	2.51	5.73	103.22
CF4	0.57	0.41	41.17	42.13	100.96	0.08	0.00	-0.35	4.03	104.39
CF5	0.57	0.42	41.74	43.24	101.49	0.10	0.00	2.56	3.20	100.64
				Average	**100.00**				**Average**	**103.34**
				Standard deviation	**1.53**				**Standard deviation**	**1.60**

	Na				**Cl**		**H**		**Distribution coefficient**				**Molar ratio**		
Label	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**	**Aq**	**Org**	**Aq**	**Org**	**Zn**	**Cl**	**Na**	**Fe**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	**%**	**%**	***M***	***M***	***M***	***M***							
CF1	0.36	0.00	2.23	98.40	4.22	1.43	2.70	0.07	0.74	0.34	0.01	0.31	2	1	15
CF2	0.35	0.00	-0.09	100.75	4.27	1.37	2.67	0.07	0.74	0.32	0.01	0.17	2	1	14
CF3	0.28	0.00	-0.97	101.84	4.27	1.33	2.65	0.13	0.75	0.31	0.01	0.06	2	1	8
CF4	0.23	0.00	0.98	100.00	4.26	1.05	2.67	0.11	0.72	0.25	0.01	0.04	2	1	9
CF5	0.18	0.00	4.16	97.07	4.20	1.10	2.79	0.11	0.74	0.26	0.01	0.03	2	1	9
			Average	**99.61**											
				1.89											

[*] Calculated by mass balance. . L: Ligand/extractant

Table C-24 Chemical analyses results, extraction and mass balance calculations for the extraction experiments using TBP as an extractant.

	Zn					Fe				
Label	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**	**Aq**	**Org**	**Extraction (Aq)**	**Extraction (Org)**	**Mass Balance**
	M	***M***	**%**	**%**	**%**	***M***	***M***	**%**	**%**	**%**
TF1	0.88	0.11	11.57	11.41	99.84	0.01	0.00	10.05	13.38	103.33
TF2	0.89	0.12	11.70	11.57	99.87	0.01	0.00	5.97	9.84	103.86
TF3	0.89	0.12	9.62	11.81	102.19	0.05	0.00	0.78	4.74	103.96
TF4	0.89	0.11	8.48	11.56	103.08	0.08	0.00	-1.01	3.58	104.60
TF5	0.88	0.12	9.65	11.98	102.32	0.10	0.00	0.66	3.54	102.88
				Average	**101.46**				**Average**	**103.73**
				Standard deviation	**1.50**			**Standard deviation**		**0.65**

	Na				Cl		H		Distribution coefficient				Molar ratio		
Label	**Aq**	**Org**	**Extraction (Aq)**	**Mass Balance**	**Aq**	**Org**	**Aq**	**Org**	**Zn**	**Cl**	**Na**	**Fe**	**L:Zn**	**L:Cl**	**L:H**
	M	***M***	**%**	**%**	***M***	***M***	***M***	***M***							
TF1	0.36	0.00	2.03	98.53	5.09	0.56	2.82	-0.05	0.13	0.11	0.01	0.15	9	2	-19
TF2	0.35	0.00	0.67	99.90	5.09	0.55	2.78	-0.04	0.13	0.11	0.01	0.10	9	2	-25
TF3	0.28	0.00	-2.58	103.30	5.15	0.45	2.85	-0.07	0.13	0.09	0.01	0.05	9	2	-15
TF4	0.23	0.00	1.42	99.41	5.12	0.18	2.87	-0.09	0.13	0.04	0.01	0.04	9	5	-11
TF5	0.18	0.00	3.39	97.80	5.08	0.23	2.91	-0.01	0.13	0.04	0.01	0.04	9	4	-190
			Average	**99.79**											
				2.12											

[*] Calculated by mass balance. L: Ligand/extractant

C.6 Stripping using water

The results obtained in the stripping test work using water as a strip liquor are given in tables C-25 and C-26.

Table C-25 Chemical analyses results, strip and mass balance calculations for the stripping experiments using CYANEX 923 as an extractant and water as the strip liquor.

		Zn						**Cl**
Label	**Phase ratio**	**LO**	**Aq**	**Org**	**Strip (Aq)**	**Strip (Org)**	**Mass Balance**	**Aq**
	O:A	***M***	***M***	***M***	**%**	**%**	**%**	***M***
SWC1	0.1	0.42	0.03	0.18	60.53	57.47	103.05	0.07
SWC2	0.25	0.42	0.04	0.32	38.15	23.90	114.25	0.11
SWC3	0.5	0.42	0.05	0.36	21.49	13.95	107.54	0.17
SWC4	1.0	0.42	0.05	0.41	12.47	1.10	111.37	0.22
SWC5	2.0	0.42	0.053	0.42	6.30	-0.48	106.78	0.35
SWC6	5	0.42	0.04	0.42	2.13	0.60	101.53	0.65
SWC7	10	0.42	0.04	0.42	1.05	-0.81	101.86	1.04
						Average	**106.63**	
					Standard deviation		**4.88**	

Table C-26 Chemical analyses results, strip and mass balance calculations for the stripping experiments using TBP as an extractant and water as the strip liquor.

		Zn						**Cl**
Label	**Phase ratio**	**LO**	**Aq**	**Org**	**Strip (Aq)**	**Strip (Org)**	**Mass Balance**	**Aq**
	O:A	***M***	***M***	***M***	**%**	**%**	**%**	***M***
SWT1	0.1	0.12	0.01	0.00	95.40	99.76	95.64	0.07
SWT2	0.25	0.12	0.03	0.00	96.70	99.76	96.94	0.11
SWT3	0.5	0.12	0.06	0.00	98.97	99.70	99.27	0.17
SWT4	1.0	0.12	0.12	0.00	101.73	99.38	102.35	0.22
SWT5	2.0	0.12	0.231	0.00	94.13	97.38	96.75	0.35
SWT6	5	0.12	0.50	0.02	81.88	84.56	97.32	0.65
SWT7	10	0.12	0.73	0.04	59.85	65.49	94.37	1.04
						Average	**97.52**	
					Standard deviation		**2.61**	

C.7 Stripping using water

The results obtained in the stripping test work using a 1 *M* sodium chloride solution as a strip liquor are given in tables C-27 and C-28.

Table C-27 Chemical analyses results, strip and mass balance calculations for the stripping experiments using CYANEX 923 as an extractant and a 1 M sodium chloride solution as the strip liquor.

		Zn						**Cl**
Label	**Phase ratio**	***LO**	**Aq**	**Org**	**Strip (Aq)**	**Strip (Org)**	**Mass Balance**	**Aq**
	O:A	***M***	***M***	***M***	**%**	**%**	**%**	***M***
SWC1	0.1	0.42	0.00	0.41	9.99	2.07	107.92	0.97
SWC2	0.25	0.42	0.01	0.44	6.21	-4.28	110.49	1.01
SWC3	0.5	0.42	0.01	0.45	4.27	-7.62	111.89	1.06
SWC4	1.0	0.42	0.01	0.46	2.83	-9.96	112.79	1.13
SWC5	2.0	0.42	0.016	0.44	1.92	-4.43	106.35	1.25
SWC6	5	0.42	0.03	0.42	1.27	-0.61	101.87	1.52
SWC7	10	0.42	0.05	0.41	1.12	1.74	99.38	1.88
						Average	**107.24**	
					Standard deviation		**5.08**	

*Loaded organic

Table C-28 Chemical analyses results, strip and mass balance calculations for the stripping experiments using TBP as an and a 1 M sodium chloride solution as the strip liquor.

		Feed						**Cl**
Label	**Phase ratio**	***LO**	**Aq**	**Org**	**Strip (Aq)**	**Strip (Org)**	**Mass Balance**	**Aq**
	O:A	***M***	***M***	***M***	**%**	**%**	**%**	***M***
SWT1	0.1	0.12	0.01	0.00	89.67	99.72	89.96	0.98
SWT2	0.25	0.12	0.03	0.00	92.56	98.99	93.57	1.03
SWT3	0.5	0.12	0.06	0.00	93.24	97.68	95.55	1.11
SWT4	1.0	0.12	0.12	0.01	95.27	95.45	99.81	1.24
SWT5	2.0	0.12	0.205	0.01	83.48	90.11	93.37	1.48
SWT6	5	0.12	0.41	0.03	66.50	75.24	91.26	2.05
SWT7	10	0.12	0.62	0.05	50.27	61.09	89.18	2.69
						Average	**93.24**	
					Standard deviation		**3.65**	

*Loaded organic

APPENDIX D

EXTRACTION REACTION STOICHIOMETRY

D. APPENDIX D: EXTRACTION REACTION STOICHIOMETRY

The molar ratios of total extractant to chloride and protons were plotted on graphs for the various solution parameters investigated (studies of the effect of zinc, chloride, proton and extractant concentration on zinc extraction). It is expected that at higher concentrations the molar ratios should reach a minimum value and remain constant at that value. This value would thus give an indication of the nature of the extracted zinc complex. The graphs from the studies into the effect of zinc, chloride, proton and extractant concentration on zinc extraction are provided in this appendix. No conclusive results could be derived from the graphs.

D.1 Effect of Feed Zinc Concentration

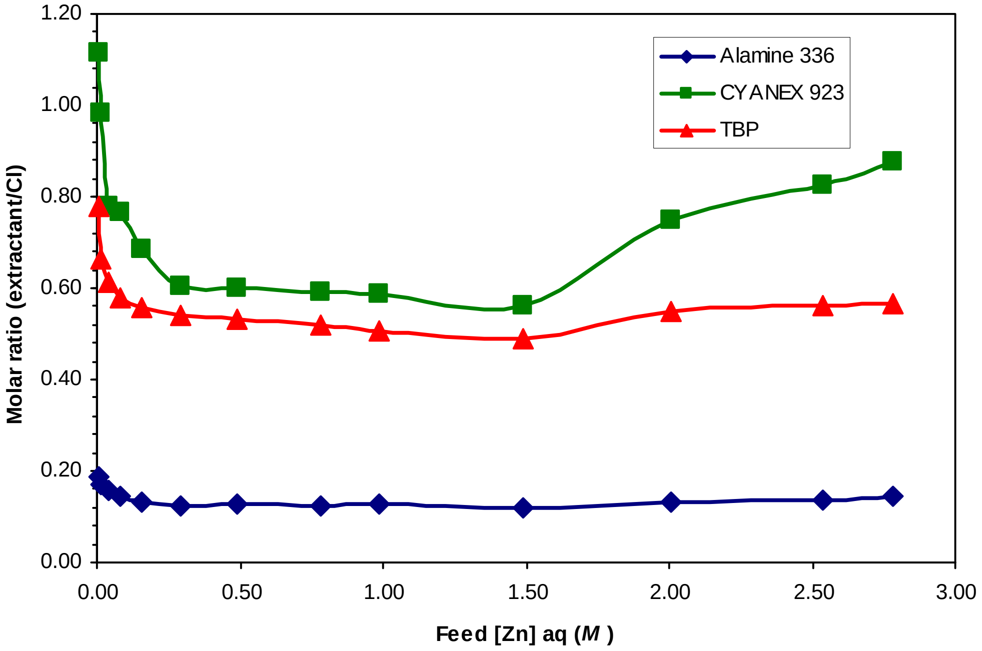

Figure D-1 Effect of zinc concentration in the aqueous feed on the molar ratio of extractant to chloride in the organic phase.

Aqueous phase: 5.2 *M* Cl^- and 2.8 *M* H^+ at varying zinc concentration.

Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.

Conditions: Phase ratio of 1; room temperature.

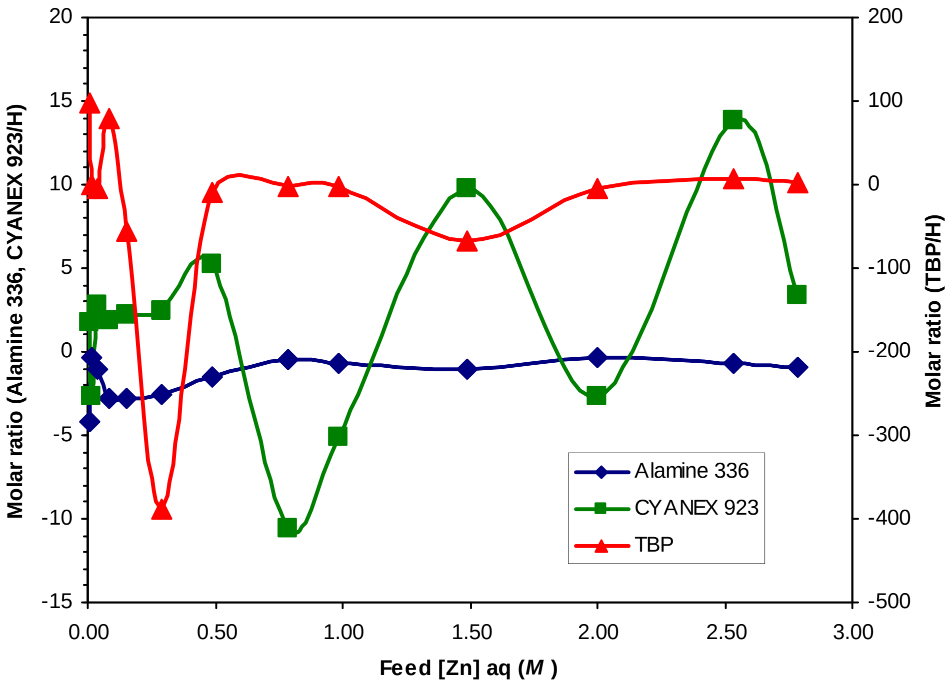

Figure D-2 Effect of zinc concentration in the aqueous feed on the molar ratio of extractant to proton in the organic phase.

Aqueous phase: 5.2 M Cl^- and 2.8 M H^+ at varying zinc concentration.

Organic phase: CYANEX 923 and TBP at 1 M and Alamine 336 at 0.3 M in Shellsol A150.

Conditions: Phase ratio of 1; room temperature.

D.2 Effect of Feed Chloride Concentration

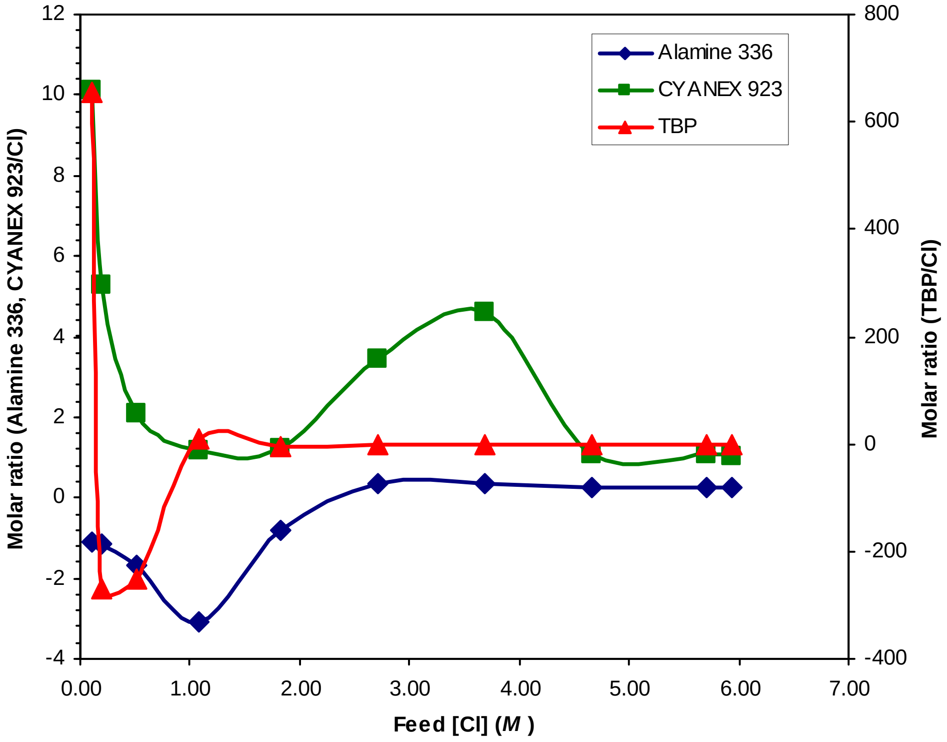

Figure D-3 Effect of chloride concentration in the aqueous feed on the molar ratio of extractant to chloride in the organic phase.

Aqueous phase:	1.0 *M* Zn and 2.8 *M* H^+ at varying chloride concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

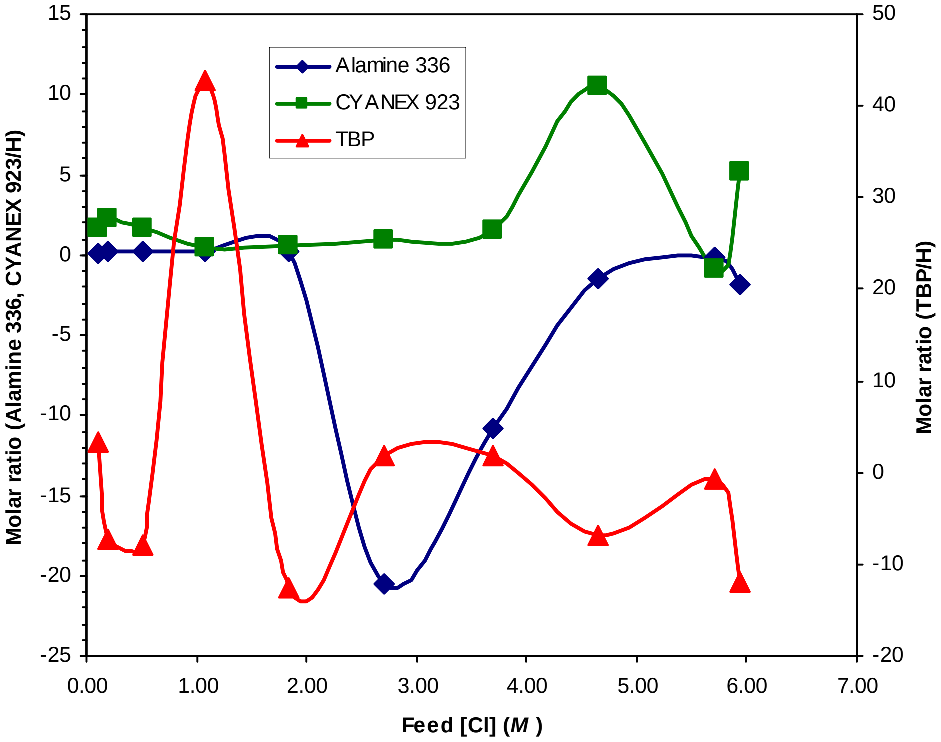

Figure D-4 Effect of chloride concentration in the aqueous feed on the molar ratio of extractant to proton in the organic phase.

Aqueous phase:	1.0 *M* Zn and 2.8 *M* H^+ at varying chloride concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

D.3 Effect of pH

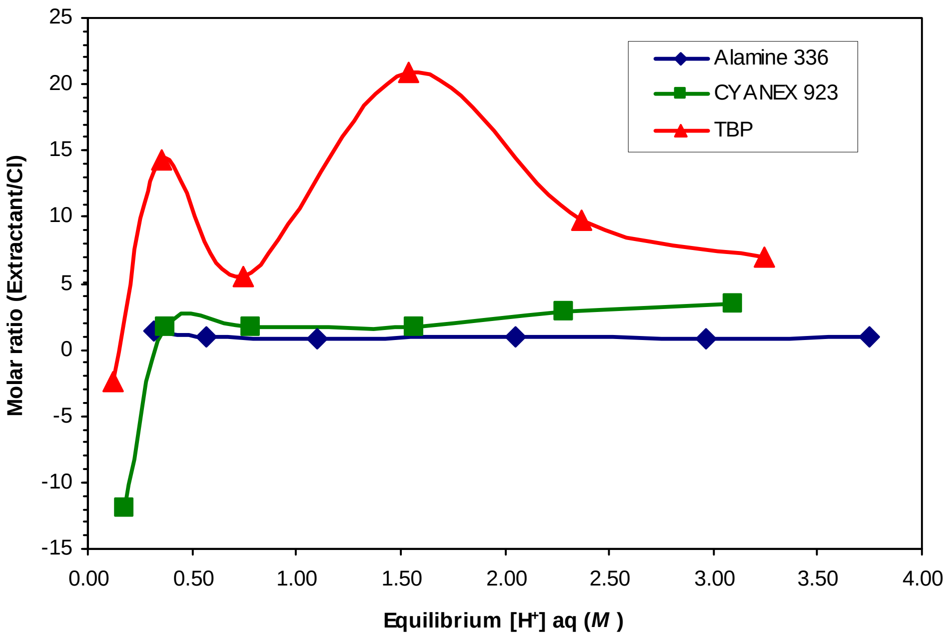

Figure D-5 Effect of acid concentration on the molar ratio of extractant to chloride in the organic phase.

Aqueous phase:	1.0 *M* Zn and 5.2 *M* Cl^- at varying chloride concentration.
Organic phase:	CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.
Conditions:	Phase ratio of 1; room temperature.

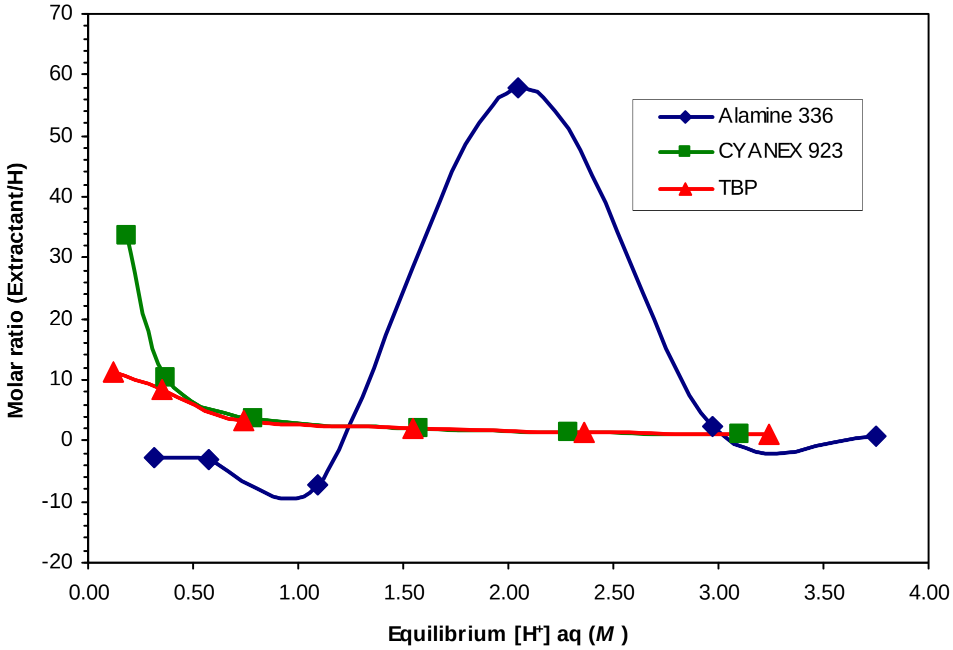

Figure D-6 Effect of acid concentration on the molar ratio of extractant to proton in the organic phase.

Aqueous phase: 1.0 *M* Zn and 5.2 *M* Cl^- at varying chloride concentration.

Organic phase: CYANEX 923 and TBP at 1 *M* and Alamine 336 at 0.3 *M* in Shellsol A150.

Conditions: Phase ratio of 1; room temperature.

D.4 Effect of Extractant Concentration

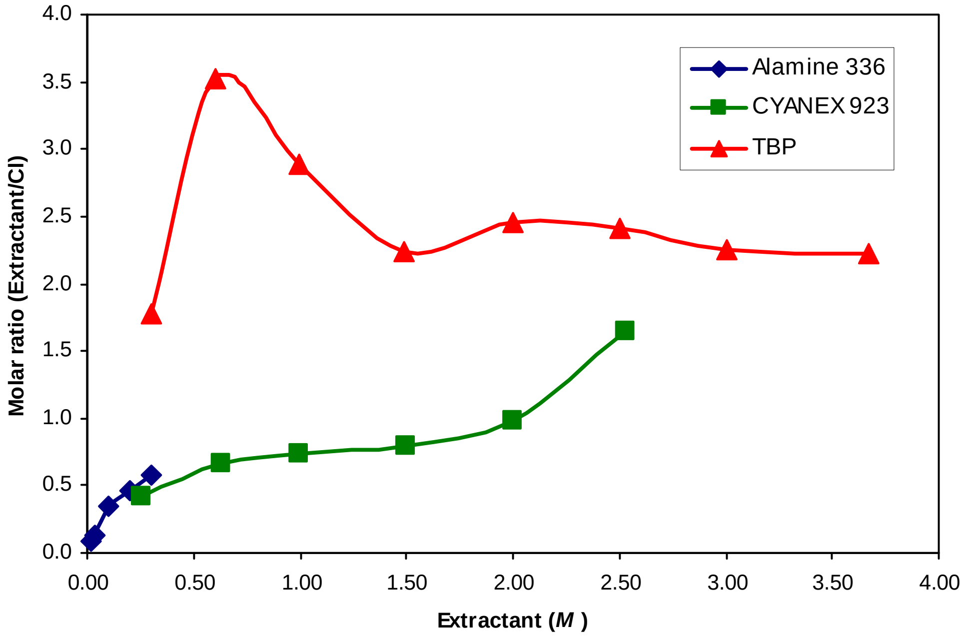

Figure D-7 Effect of extractant concentration on the molar ratio of extractant to chloride in the organic phase.

Aqueous phase:	1.0 M Zn, 5.2 M Cl^- and 2.8 M H^+.
Organic phase:	Varying extractant concentrations.
Conditions:	Phase ratio of 1; room temperature.

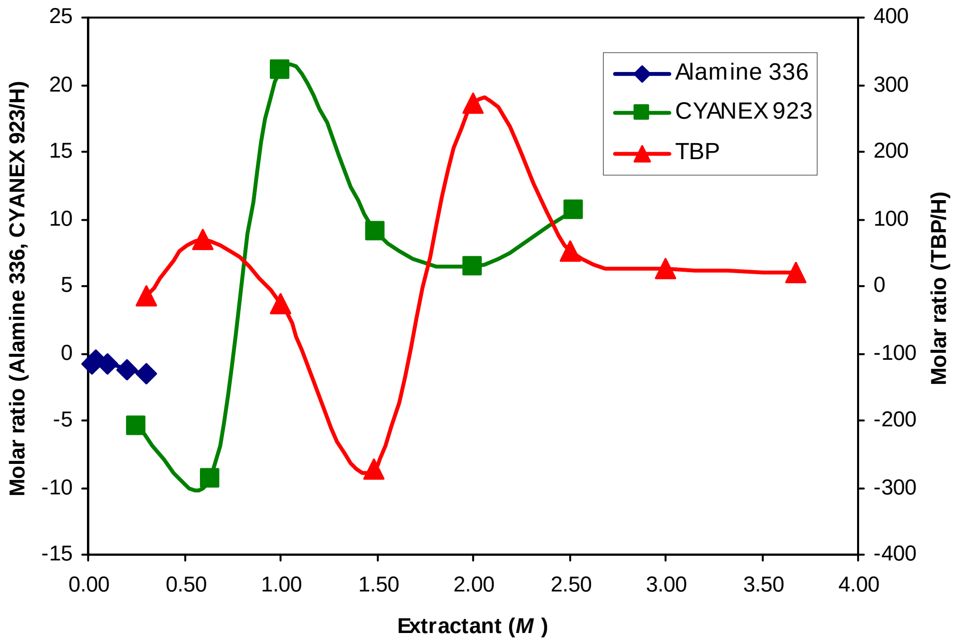

Figure D-8 Effect of extractant concentration on the molar ratio of extractant to proton in the organic phase.

Aqueous phase:	1.0 M Zn, 5.2 M Cl^- and 2.8 M H^+.
Organic phase:	Varying extractant concentrations.
Conditions:	Phase ratio of 1; room temperature.