

THE SOLVENT EXTRACTION OF SOME MAJOR METALS

AN OVERVIEW

Murdoch Mackenzie, Henkel Australia Pty Ltd

INTRODUCTION

The practice of hydrometallurgy contains examples of a great number of diverse solvent extraction processes. Besides the major metals there are or have been commercial solvent extraction processes operated for the recovery of metals such as tungsten, rare earths, thorium and vanadium. For every solvent extraction process which has proceeded to commercial exploitation there are literally hundreds of processes which have been developed and tested in the laboratory. The vast majority of these solvent extraction circuits have never left the laboratory although many of them are technically quite feasible. However it is those metals for which solvent extraction has proved to be a significant or potentially significant recovery route which we shall be concerned with here. Solvent extraction of metals such as copper, uranium, cobalt and nickel, besides being of great economic significance has been the spur for the development of the engineering aspects of solvent extraction. If a new and viable solvent extraction route for the recovery of a metal such as tin which is not currently recovered by solvent extraction were to be discovered then the tin solvent extraction plants would draw on copper and uranium practice for their engineering design.

Let us briefly examine the metals for which solvent extraction has succeeded and the circumstances, which caused these metals to become candidates for recovery by solvent extraction. They have some common features:

1. They are soluble in suitable lixiviants such as sulphuric acid, ammonia and cyanide
2. They are relatively valuable. Copper, which is typically priced at about US\$0.8 - 1.2/lb is the lowest priced metal recovered in significant quantities by solvent extraction. Nickel, uranium and the precious metals are significantly more valuable. In contrast zinc for which technically feasible solvent extraction routes exist has not been recovered in significant quantities by solvent extraction. The low value of zinc, typically US\$0.60 - 0.65/lb is one of the main reasons why zinc solvent extraction plants are not common.
3. They can be recovered from the concentrated strip solution in a suitable marketable or intermediate form by processes such as electrowinning or precipitation.
4. Suitable solvent extraction chemistry has been developed for these metals.

Uranium

The first metal to be recovered in significant quantities using solvent extraction was uranium. Following the development of the nuclear industry during and immediately after World War II, attention was focussed on developing technologies which could be used to upgrade and purify uranium from low grade ores and in 1957 the first commercial solvent extraction plant using amines was opened in the USA. Today most of the world's uranium is recovered in hydrometallurgical circuits which involve solvent extraction and a significant proportion of this uranium is produced in circuits which use solvent extraction as the only recovery system.

Copper

Today around 25% of the world's copper is recovered using solvent extraction and solvent extraction is considered to be the lowest cost production route for the production of quality cathode. In Chile, the world's largest copper producer, SX will soon produce 50% of that country's copper. The scope of solvent extraction for copper is only limited by the availability of acid leachable ore and it is not surprising that considerable attention is being directed towards development of suitable leaching techniques for chalcopyrite, the most ubiquitous of all copper minerals. The use of solvent extraction for copper ores dates from the Ranchers Bluebird mine which started operation in 1968. Acceptance of solvent extraction technology for copper using Henkel's (previously General Mills Chemicals Inc) oxime based extractants took a giant step forward in 1974 when ZCCM commissioned their 80,000 tonne per annum SX-EW plant at Nchanga.

Nickel

In comparison to copper and uranium the percentage of the world's nickel which is recovered using SX is relatively small, however recent developments in Australia may well change this situation. The Falconbridge plant in Kristiansand uses solvent extraction to purify nickel by removing iron, copper and cobalt from nickel chloride solution. In 1987 Queensland Nickel developed an SX circuit which was an integral part of their existing Carron nickel recovery circuit. Today a number of Australasian laterite projects are developing nickel SX circuits which are in part based on the Queensland Nickel SX technology.

Precious Metals

Although the quantity of precious metals currently recovered using circuits that involve solvent extraction is small the value of these metals is significant. Mintek has recently developed a gold refining process based on solvent extraction and there exists a potential for gold recovery by solvent extraction. In the refining of platinum group elements solvent extraction plays an important role.

THE CHEMISTRY OF THE SOLVENT EXTRACTION OF THE MAJOR METALS

Sudderth and Kordosky⁽¹⁾ have given a useful classification of the four basic classes of metal extractants and have compared these extractant classes on the basis of structure, extraction chemistry and the metal species extracted.

The four classes are:

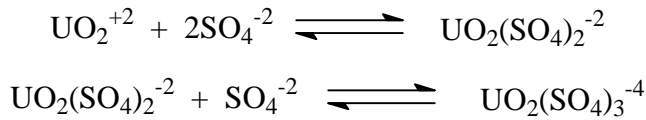
1. Chelation Extractants
2. Ion Pair Extractants
3. Neutral or Solvating Extractants
4. Organic Acid Extractants

These extractants are compared in Tables 1 to 4.

URANIUM EXTRACTION

Extraction and Stripping Chemistry

The vast majority of uranium is recovered from sulphuric acid leach solutions using C8-C10 tertiary amines. When uranium is dissolved in sulphuric acid two anionic sulphate complexes are formed:

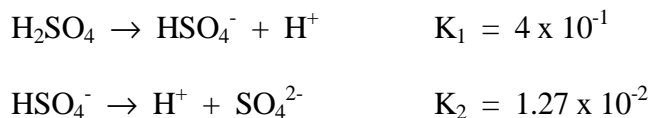


The chemistry of the extraction and stripping of these uranium anion species is given in Table 5⁽²⁾.

Uranium leaching normally involves an aggressive, oxidising agitation leach at elevated temperatures of around 40 - 80°C and such a leach is not selective for uranium. As a result the SX feed will contain a number of anion species which can cause problems in the solvent extraction of uranium. The more important of these species are:

Soluble silica	Si(OH) ₄	SiO ₂ amorphous
Tungsten	WO ₄ ²⁻	
Antimony	SbO ₄ ³⁻	
Arsenic	AsO ₃ ³⁻	
Molybdenum	MoO ₄ ²⁻	
Vanadium	VO ₃ ⁻	
Zircon	ZrO ₃ ²⁻	
Phosphate	PO ₄ ³⁻	

In addition, sulphuric acid dissociates in water as follows:



Chloride (Cl⁻) and nitrate (NO₃⁻) anions may also be present in the leach liquor.

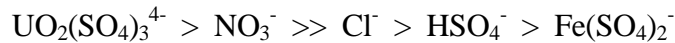
Extractant Type

Tri-octyl and tri-decyl amines are used almost exclusively for uranium extraction however trilaurylamines are used when molybdenum is present as the amine molybdenate complex formed with the C8 and C10 amines may not be sufficiently organic soluble.

In practice the theoretical maximum loading is not attained due to the presence of competing anions in the leach liquor.

Ion exchange extractants are non-selective and, although the uranyl sulphate anion is very strongly extracted by tertiary amines, other anions will also be extracted.

The order of selectivity for some anions is:



The effect of NO_3^- and Cl^- ions on the extraction of U_3O_8 by Alamine[®] 336 is shown in Figure 1. Interestingly, the effect of nitrate ions is much stronger than the effect of chloride ions. Fortunately, nitrate ions are not commonly present at high concentrations in uranium leach liquors.

The effect of pH on the extraction of U_3O_8 on Alamine[®] 336 is shown in Figure 2.

Tertiary amines have a pKa of 9.02 but they have a weak basicity with stripping commencing around pH 3.0. The increase in U_3O_8 extraction as the pH is decreased from 2.03 to 1.04 in Figure 2 probably reflects the increased protonation of the amine as the pH is lowered.

When the H_2SO_4 concentration becomes significant however, as is the case in the concentrated eluate of an ion exchange plant, then HSO_4^- competition can reduce uranium extraction.

Diluent and Modifier Type

The uranium – amine complex formed from the C8-C10 tertiary amines has limited organic solubility in the 1-20% aromatic diluents typically used and third phase inhibitors are added to the circuit organic to improve this solubility. Isodecanol at a concentration of about 50% of the amine concentration is the most commonly used modifier although high aromatic diluents can also be used. The use of isodecanol can increase phase separation times and increase crud formation. Isodecanol is also a nutrient for bacteria and can lead to bacterial activity in the circuit. The solubility of isodecanol in water is about 150-170 ppm compared to <5ppm for tertiary amine and isodecanol losses to the raffinate will be similar to the amine losses.

Tertiary Amine Stability

Tertiary amines are very stable extractants however under highly oxidising conditions (+550 vs SCE) and in the presence of nitrate ions they can degrade to form nitrosamines. Besides reducing the amine concentration nitrosamines are also carcinogenic.

Secondary amines are less stable than tertiary amines. Under highly oxidising conditions, secondary amines may be converted to hydroxylamines, which can undergo further degradation to a variety of products.

Uranium Circuit Layout

The circuit configuration of any SX plant is dictated by the extraction and stripping chemistry. A typical acid leach – SX uranium circuit is shown in Figure 3.

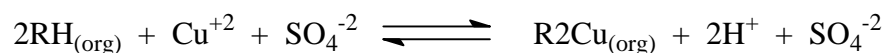
Let us consider some of the important features of this circuit.

- **Clarification**
Uranium circuits normally use an agitation leach. Clarification to remove suspended solids may involve special equipment such as hopper clarifiers.
- **Soluble silica removal.**
The leach is sufficiently aggressive to leach significant quantities of silica and this can cause crud formation and phase separation problems if allowed to go through to SX. High molecular weight polyethylene oxides or similar chemicals with significant hydrogen bonding capability are used, often in conjunction with floc bed clarifiers to precipitate soluble silica.
- **Extraction**
Uranium circuits usually aim at recoveries in excess of 95% and four stages of extraction is considered the minimum. The function of E4 may be more amine protonation than uranium recovery. Competing anions may load in E3 and E4 but are crowded off in E1.
- **Scrubbing**
Ion exchange is not a selective process and scrubbing to remove impurities such as iron, silica, and zirconates is required.
- **Stripping**
Most circuits employ a deprotonation scrub using NH₃ plus ADU precipitation spent liquor as the strip aqueous. A carefully controlled pH profile is required in strip if ADU precipitation is to be avoided. The pH decreases from about 5.0 in S4 to 3.0 in S1.
- **ADU precipitation**
Ammonia is used to precipitate ADU. The temperature must be maintained about 30°C if the sulphate content and the particle size of the precipitate are to be optimum.

COPPER EXTRACTION

- Copper extractants for acid leach solutions are exclusively oximes. For extraction from ammoniacal solutions beta diketones may be used.

The chemistry of oxime extraction of copper is relatively simple:



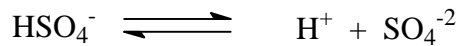
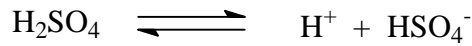
Note the following points about this equation:

When M²⁺ is extracted two hydrogen atoms are released.
Extraction of 1.0 gpl Cu produces 1.5 gpl H₂SO₄.

There are other reactions which take place in copper extraction which can influence extraction and stripping.

- **Buffering of the aqueous**

Dissociation of H₂SO₄



This dissociation depends on the SO₄²⁻ concentration and salts such as aluminium sulphate or magnesium sulphate can drive this reaction to the left and reduce the H⁺ concentration which enhances copper extraction. For this reason highly buffered solutions will yield better copper extraction than non buffered solutions.

- **Dimerisation of the oxime**

Oximes can form dimers in the organic phase and this can influence the extraction.

- **Equilibrium Modifiers**

These are used in all commercial extractants based on aldoximes and play a most significant role in the extraction of copper influencing not only the equilibrium but also the physical properties of the organic.

Extractant Types

Oxime based extractants for copper are largely based on salicyaldoximes which have been modified with one of three modifier types. Examples of the three main extractant types currently in use are:

1. **LIX® 984N**

A mixture of 2-hydroxy-5-nonylacetophenone oxime and 5-nonylsalicylaldoxime in a high flash diluent. The acetophenone oxime modifies the aldoxime and also performs as an extractant in its own right.

2. **Acorga® M5640**

5-Nonylsalicylaldoxime modified with an ester, 2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate (TXIB) in a high flash diluent.

3. **LIX® 622N**

5-Nonylsalicylaldoxime modified with tridecyl alcohol in a high flash diluent.

Each of the extractants marketed by the major chemical suppliers has been designed for a specific type of PLS with regard to pH and copper tenor. Used under the conditions for which they were designed they all deliver very similar copper net transfer values.

The physical properties of the various types of extractant do show some differences with the aldoxime/ketoxime mixtures such as LIX984N showing lower entrainments and greater tolerance to crud than the other reagents when treating some types of PLS.

The vol% concentration of the commercially available extractants is limited by organic viscosity constraints to about 30-33% and this means that the maximum net transfer of copper will be about 10g/l. For leach solutions containing significantly higher copper tenors than this the throughput O/A ratio will have to be increased above 1.0.

Typical copper and acid concentrations for an SX plant treating a dump leach solution of 3.0g/l and pH1.8 are shown in Figure 4.

Copper solvent extraction plant configurations

A variety of circuit configurations are used.

- **2E X 1S**
The usual circuit for heap leach plants
- **2E X 2S**
Used where the copper tenor is above about 7-10 g/l or the PLS pH is less than about 1.2. The decision to use a second strip stage is influenced by the life of the project and the sensitivity of the circuit to the copper tenor of the raffinate. Agitation leach plants for example are sensitive to the loss of copper in a raffinate bleed or in the wash liquor used in the solid liquid separation stages.
- **3E X 2S**
These can be justified when the PLS has a very high copper tenor, say above 20-25g/l and a high 93% plus copper recovery is desired. It is possible to use a 2EX2S circuit under these conditions but the throughput O/A ratios will be high, in excess of 2.5:1 and the capital cost of the 2EX2S plant may be higher than that of the 3EX2S plant. The 3EX2S plant will also be much more flexible in operation.
- **2E X 1W X 1S**
The wash stage is used to remove entrained impurities, usually chloride, and entrained and chemically loaded iron.
- **2E X 1P X 1S**
Series parallel circuits are used to treat high volumes of low tenor leach solutions. The parallel stage is often retrofitted to maintain copper production when the copper tenor of the PLS falls below project design and there is also the possibility to increase the volume of the PLS flow. Extractant concentrations are higher and copper recoveries are lower in series parallel circuits than in series circuits.

Examples of these circuit configurations are shown in Figure 5.

Computer modeling of copper extraction circuits

Copper SX circuits have been modeled using a number of techniques. One such model is Henkel's IsocalcTM TM programme which applies the stability constants for the equilibrium reactions involved in copper extraction to calculate the extraction isotherm for a given leach solution and circuit organic and then applies the McCabe Thiele construction to predict circuit operation. A typical Isocalc print out is shown in Figure 6.

Isocalc can be used in many ways by both project design and plant operating personnel.

- Copper recovery may be predicted for a given PLS, circuit configuration and vol% extractant concentration.
- The reagent inventory cost and copper recovery may be predicted for a variety of circuit configurations.
- A wide range of “what if?” situations may be examined, eg. what if the PLS pH changes from 1.8 to 1.5?
- Operating circuit profiles may be compared with Isocalc predictions. This comparison may indicate the presence of errors in the assumed or measured parameters of the plant, eg. the vol % extractant analysis may be in error.

Extractant stability

The oxime based extractants used to recover copper exhibit high chemical stability under normal operating conditions. Chemical attack can take place in the high acid concentrations in strip. Under normal operating temperatures this is not excessive however the degradation rate doubles for every 10°C increase in temperature. At 30°C the half-life of most copper extractants exceeds 150 days and it is only above 50°C that chemical degradation may become an issue. Manganese contamination of the tankhouse may, if the iron level of the tankhouse electrolyte is low, result in permanganate formation and this species can severely degrade both the extractant and the diluent. Bacterial oxidation of the diluent to form carboxylates is relatively common and these may have a negative effect on the physical and iron transfer characteristics of the organic.

NICKEL EXTRACTION

Unlike uranium and copper extraction where one type of extractant and circuit predominates there is a number of potential nickel extractants and circuit configurations. Sulphide nickel is usually treated using pyrometallurgical routes but in recent years there has been intensive activity in the development of hydrometallurgical routes for both sulphide concentrates and laterites. Nickel deposits can contain valuable quantities of cobalt and copper and these must also be recovered by SX if they are present in sufficient quantity.

1. Direct solvent extraction of copper, cobalt and nickel from acid leach solutions using oximes, phosphinic acids and versatic acids to extract copper, cobalt and nickel in sequence. While this circuit may function on leach solutions derived from sulphide concentrates, laterite leach solutions contain significant manganese and magnesium, both of which are extracted by phosphinic acid extractants. In addition the aqueous solubility of versatic acid at the pH used for extraction necessitates the inclusion of a versatic acid recovery stage. ⁽³⁾

2. Matte leach chloride solutions may be purified by iron extraction with TBP followed by cobalt and copper co extraction as chloride complexes with tertiary amine. Nickel does not form chloride complexes and remains in the raffinate. It may be recovered by crystallization and hydrogen reduction. This is the type of circuit used at Kristiansand. ⁽⁴⁾
3. The base metals (Ni, Cu, Co,Zn) may be precipitated as hydroxides from sulphate leach solutions, redissolved in ammonia, the cobalt may be oxidised to Co(3) and the copper and nickel co-extracted with ketoxime (LIX 84-I). ⁽⁵⁾⁽⁶⁾

These circuits are illustrated in Figures 7-9.

Of the above circuits, the ammonia re-leach circuit has received the greatest interest in the past two years for the recovery of nickel. Some features, which favour this circuit, are :

- The ammonia re-leach is both a concentration and purification stage, rejecting metals such as manganese and magnesium from the SX feed.
- The nickel SX extraction circuit has been operated for over ten years by Queensland Nickel ⁽⁷⁾
- The nickel can be stripped from the LIX 84- I to yield a catholyte of a pH suitable for electrowinning.

Improved ketoxime based reagent formulations have been developed. XI-51, a fluorinated beta diketone, can be used to extract Co from ammoniacal nickel raffinate solutions.

PRECIOUS METAL EXTRACTION

A variety of solvent extraction processes are used in the refining of the platinum group elements. Phosphinic acids (Cytac® 272) have been used to remove cobalt from nickel in sulphate leach solutions. The PGE's form a wide range of chloride complexes and this makes possible the separation of these elements using ion-exchange extractants. The majority of these separation systems are not widely discussed in the literature.

Gold as the aurocyanide complex can be extracted at pH values below 9.0 by tertiary amines and over a wide pH band by quaternary amines. The relatively low pH required for tertiary amine separation makes this an unattractive route for most circuits while the quaternary amines can only be stripped in a two stage process using zinc tetracyanide stripping followed by sulphuric acid regeneration of the organic and HCN recovery.

Recently Henkel has introduced two extractants XI-78 and LIX 79, which can extract $\text{Au}(\text{CN})_2^-$ from solutions having pH values up to 11.5. ⁽⁸⁾ These reagents also have the potential to recover both gold and copper cyanide complexes from cyanide leach solutions. Both XI-78 and LIX 79 can be stripped in 1 molar sodium hydroxide and the strip aqueous can go directly to electrowinning. Extraction isotherms for LIX 79 are shown in Figure 10. An SX circuit suitable for gold recovery using LIX 79 is shown in Figure 11.

SOLVENT EXTRACTION- SOME OPERATIONAL AND EQUIPMENT ISSUES

Contactors Design

For the major metals recovered by solvent extraction the mixer-settler contactor design predominates. However there is a range of mixer settler designs available and in recent years there has been some attention refocused on the use of pulsed columns for plants using the kinetically fast ion- exchange extractants.⁽⁹⁾ For the chelating extractants which require a minimum of two minutes mixer residence time in a well-stirred reactor, columns have not yet become commercially acceptable. Kvaerner have marketed a variety of the mixer – settler called the combined mixer- settler. As with columns, this unit has only found acceptance for ion-pair extractant systems. Some features of mixer-settlers and columns are given below.

Mixer Settlers

- Well established with literally hundreds of operating units.
- Design parameters are well established and very large units treating over 1000 cubic metres per hour of PLS can be designed from bench scale tests.
- Excellent mixing characteristics with control of the optimum droplet size claimed to be possible with modern turbine designs.⁽¹⁰⁾
- Prediction of capital and operating costs is accurate.
- The phases are readily accessible for sampling and examination in situ.
- Several design varieties are available such as the Bateman Reverse Flow Settler, the Krebs unit and the Outokumpu VSF mixer settler.⁽¹¹⁾ The Bateman and Krebs units offer the advantage of installing all of the mixers in a row avoiding the extra piping, walkways and civils involved in the typical head to toe mixer arrangement for conventional mixer settlers. The Outokumpu unit uses a special design of mixer, the vertical smooth flow spiral mixer and pumps the phases from adjacent stages using a dispersion overflow pump. Low power requirements and low entrainments are claimed for the Outokumpu unit.

Column Contactors

Advantages claimed for the column contactor include:

- Low area requirements
- Multiple stages within one unit
- Few moving parts
- Low entrainment
- Good vapor conservation

Column installations require piloting for each installation and the flooding conditions for the column must be determined. Recently Olympic Dam Corporation in South Australia has installed a large column plant for uranium extraction. The long residence times in a column compared to a mixer settler can influence the selectivity of the extraction if contaminants have slow extraction kinetics.

The main features of conventional mixer – settlers and pulsed columns are shown in Figures 12 and 13.

Crud treatment and clay treatment of circuit organics

Crud formation and treatment has been studied extensively for copper SX operations and to a lesser extent for uranium SX operations. This discussion will therefore focus on copper SX.

Most SX circuits show evidence of crud formation. The word “crud” itself is said to arise from its formation in a very early uranium SX plant at the Chalk River Mine in Canada. Crud formed in the organic of this plant and was described as Chalk River Unidentified Deposit. Whether this is true or not, there is no doubt that crud is like skin dermatitis!

■	VERY COMMON
■	DIFFICULT TO COMPLETELY CURE
■	RARELY FATAL
■	UGLY TO LOOK AT

Crud is formed when organic species adsorb onto solids and a solid-organic-water phase forms. The crud may be either:

- Preferentially organic wetted and located in the organic phase
- Preferentially aqueous wetted and located in the aqueous phase
- Wetted by both organic and aqueous and located at the organic aqueous interface

For crud to form, solids must be present in the aqueous. These can be either:

- Suspended solids derived from the leach, eg. suspended solids not clarified from an agitation leach, airborne dust carried into ponds and drains, dirty rain water run off into ponds and drains, fine particles washed off the heap solids or produced by chemical action in the heap. Suspended solids are usually oxides.
- Precipitated solids derived from dissolved species which remain in solution in the PLS pond or holding tanks may precipitate at the organic aqueous interface. This precipitation may be due to chemical changes, eg. reduced pH, which occur at the interface due to extraction or possibly are due to a locally increased concentration of a dissolved species at the interface due to adsorption at that interface.

Crud is formed when organic species adsorb onto the solids present in the SX plant aqueous solutions. The adsorption mechanism for organics onto the solids almost certainly involves hydrogen bonding.

Both oximes and modifiers contain OH groups capable of hydrogen bonding to oxygen groups in the solids. Some points which have emerged from Henkel studies of crud are:

- Copper loaded oximes adsorb onto solids at much lower levels than unloaded oximes.
- Modifiers adsorb onto solids more strongly than copper loaded or unloaded oximes.
- Adsorption of modifiers onto solids can displace or prevent adsorption of oximes.
- Modifiers are interfacially active at both the solid-liquid and liquid-liquid interfaces.
- Modifiers increase the viscosity of the organic phase. This promotes entrainment.
- Modifiers cannot load copper. If they did, then the copper loading might inhibit their adsorption onto solids as it does for oximes.

ONE REASON THAT SX CIRCUITS CONTAIN CRUD IS THAT ALDOXIMES WHICH ARE THE MAIN OXIME USED FOR COPPER RECOVERY MUST BE MODIFIED IF THEY ARE TO STRIP WITH TANKHOUSE ELECTROLYTE

ONLY CHELATING MODIFIERS, SUCH AS KETOXIMES, CAN MINIMISE THIS SITUATION.

The non-chelating modifiers used are alcohols, phenols and TXIB, all of which adsorb onto solids and contribute to crud formation. Alcohols (tridecyl alcohol) tend to show a lower level of crud forming activity than phenols and TXIB.

The components in non-modified reagents, aldoximes and ketoximes, result in lower consumption of non-modified reagents. Both these components load copper, their interfacial activity, particularly at the solid-liquid interface, is minimal in the copper loaded form. For this reason these reagents also exhibit minimum crud formation properties.

Crud Treatment

Most SX plants contain a crud treatment tank which has a low intensity agitator and take off ports at various levels in the tank. Crud can be sucked out of the settler using a crud wand located at the level in the settler where the crud is concentrated. This is often the organic-aqueous interface and pumped to the crud treatment tank.

It may be possible to wash crud out of a stage by flipping the phase continuity.

In the tank the crud is broken down using a combination of:

- Agitation
- Mixing with diluent, electrolyte, acid or PLS. (Lab tests in a beaker can be used to select the most effective solution for the promotion of crud break down)

The broken down dispersed crud may then be allowed to settle and relatively clear solutions of organic and aqueous may be removed from the tank using the side ports. Sometimes the crud persists in floating and low level ports are used to remove the organic and aqueous solutions.

If a clay treatment filter is available then the crud may be pumped through the filter which has been precoated with either clay or filter media. The filtrate is allowed to settle and the organic is decanted.

While clay treatment can be highly effective in the treatment of oxime based extractants it cannot be used for cationic extractants and would have to be carefully laboratory tested for the treatment of class 3 and class 4 extractants.

Phase Continuity

SX mixers may be operated in either the organic continuous or aqueous continuous mode. Most mixers are operated at O/A ratios close to 1.0 with the use of recycle flows if the throughput O/A is not 1.0.

The selection of the continuous phase can have significant effects on the physical aspects of the SX plant operation.

Typically on separation in the settler the continuous phase will carry entrainment of the non-continuous phase while the separated non-continuous phase will contain only low levels of entrainment of the continuous phase. For this reason E1 is usually run aqueous continuous and the raffinate stage is run organic continuous.

The phase continuity selected can also have a marked effect on the phase disengagement rate if contaminants which are selectively adsorbed into one phase are present. Figure 14 illustrates this effect.

De-entrainment of Organic and Aqueous Flows

Entrainment of organic in aqueous and aqueous in organic can create significant problems in both SX circuits and electrowinning. The main methods used for de-entrainment of SX streams are:

Coalescers in the Extraction Circuit

These usually employ some form of packed bed or porous media and may not work well when there is significant crud present in the system. Examples of coalescers include:

- **Picket Fences in the Settler**
Besides distributing a uniform flow in the settler, these can bank up the emulsion band on the upstream side and this band acts as a coalescer.
- **Packed Bed Coalescers in the Settler**
These can reduce entrainments but can also blind and cause channel flow around the edges of the packed bed or through non-blinded sections of the coalescer. For this reason, provision must be made to periodically remove the coalescers and to clean them.
- **Coalescing Material in the Loaded Organic Surge Tank**
This can help reduce aqueous entrainment to the tankhouse. Provision must be made to remove and clean the coalescing material. This can be easier to carry out than cleaning of the coalescers from the settler.
- **Coalescers Employing Multi-Media**
Woven coalescers using an aqueous wetted fibre (stainless steel) and an organic wetted plastic fibre have given good results in pilot plants but blockage by crud can be a problem in larger installations.
- **Packed Bed Raffinate Coalescers for Organic Recovery**
A coarse packed bed of 1 - 2 cm sized coke or silica particles is used in an upflow mode. Provision is made to backwash with air and water. The top of the coalescer has a “thickener froth ring” type of launder and coalesced organic remains inside this ring and is removed from time to time.
- **Organic Recovery from an After Settler ahead of the Raffinate Pond or from the Raffinate Pond Itself**
The after settler can be a purpose built unit such as a multiplate coalescer or simply a small raffinate pond.

For small pond and for raffinate pond recovery, floating booms are used to “corral” the organic prior to recovery from the top of the aqueous.

Removal of Organic from the Strip Aqueous

The methods include:

- Small after settler or holding tank
Low cost but not very effective.
- Flotation equipment
The column cell of the type developed by Magma Copper or the Jameson cell have found favour. Flotation cells of this type can remove up to 80% of the entrained organic and are simple to use. Mechanical cells of the type used in ore flotation are not effective as they employ high shear and this increases dispersion of the organic.

Flotation cells can also remove solids and, if used ahead of an electrolyte filter, will increase the filtration cycle, eg. reduce the need for backwash.

- Gravity sand filters
These can be effective but need backwash facility.
- Dual media pressure electrolyte filter (eg. Spintek and Disep filters)
These use a garnet sand-anthracite mixture. Dual media filters in general achieve the lowest organic entrainment level.

The backwash cycle is important and is automated. The backwash can be returned to leach and is a form of tankhouse bleed. In some plants, the backwash may represent the entire tankhouse bleed.

Mixer Efficiencies

The mixer efficiency is an important but often overlooked parameter of solvent extraction circuits. Variables which can effect mixer efficiencies include:

- Mixer residence time
- Turbine tip speed - 270-350 metres/min is usually optimum
- O/A ratio in the mixer. This should be close to 1.0
- Temperature
- Possible short circuiting
- Air entrainment

Well designed mixers operating on copper SX with oxime extractants should achieve mixer efficiencies of 90 – 95% in extraction and 98 – 100% in strip.

FUTURE TRENDS IN THE SOLVENT EXTRACTION OF METALS

New Extractants

In a perfect world, the chemical industry would be able to supply low cost, effective extractants for every important type of metal separation. Unfortunately this is not the case. The cost of developing a new extractant and taking it to pilot testing stage is high, around US \$2.5-3.0 million. The regulatory requirements for new chemicals can be particularly onerous. Even when the reagent has been developed, the market for it may not be great or the metallurgical industry may be reluctant to install plants using a new reagent. For some products the cost of producing the reagent may be high and this can inhibit its application. The metallurgical industry is not accustomed to paying high, say \$50/kg prices for chemicals.

New Circuits for Old Reagents

Faced with the above there is a trend to look at new circuits which use existing reagents in novel ways to recover metals. The recent activity in the Australian nickel laterite industry is an example of this.

Increased Regulation of SX Operations by Governments

Solvent extraction has progressed from being a process which solved some of the environmental problems of other metallurgical routes to being a target itself for environmental examination. The use of diluents containing aromatics may in time become prohibited in some areas.

ACKNOWLEDGEMENTS

The author acknowledges the permission of Henkel to publish this paper and the assistance he has received over the years from his colleagues in Henkel, particularly those in the Henkel Corporation Mineral Industries Division.

REFERENCES

- (1) R.B. Sudderth and G.A. Kordosky, "Some Practical Considerations in the Evaluation and Selection of Solvent Extraction Reagents" Chemical Reagents in the Mineral Processing Industry. Ed. Malhotra and Riggs. SME 1987
- (2) J.M.W. Mackenzie, "Uranium Solvent Extraction Using Tertiary Amines" ALTA 1997 Uranium Ore to Yellow Cake Seminar. ALTA Metallurgical Services, Melbourne Australia.
- (3) K. Soldenhoff, N. Hayward and D. Wilkins, "Direct Solvent Extraction of Cobalt and Nickel from Laterite Acid-Pressure Leach Liquors" EPD Congress 1998. Ed. B.Mishra (The Minerals, Metals and Materials Society, AIME) 1998 p153-165
- (4) G.M. Ritcey, "Commercial Processes for Nickel and Cobalt" In Handbook of Solvent Extraction. Ed Lo, Baird, and Hansen. John Wiley and Sons 1983. P 673
- (5) J.M.W. Mackenzie and M.J.Virnig, "Recovery of Nickel from Ammoniacal Solutions Using LIX® 84-I" Proceedings of ALTA Nickel /Cobalt Pressure Leaching and Hydrometallurgy Forum, May 1996. Perth West Australia. ALTA Metallurgical Services Melbourne.
- (6) J.M.W. Mackenzie and M.J.Virnig, "Extraction of Nickel from Ammoniacal Leach Solutions: Extractant and Solution Chemistry Issues" Proceedings of ALTA 1998 Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum. May 1998. Perth West Australia. ALTA Metallurgical Services Melbourne
- (7) M.J.Price and J.G.Reid, "Separation and Recovery of Nickel and Cobalt in Ammoniacal Systems: Process Development" Proceedings ISEC 93 , SCI London 1993 p159.
- (8) M.J.Virnig, J.M.W.Mackenzie, and C.Adamson. " The Use of Guanidine – Based Reagents for the Recovery of Gold" Hidden Wealth. South African Institute of Mining and Metallurgy. 1996 p151
- (9) R.L.Movsowitz, R.Kleinberger, and E.M.Buchalter, "Application of Pulsed Columns for Uranium SX From Pilot to Industrial Columns" ALTA 1997 Uranium Ore to Yellowcake Seminar. ALTA Metallurgical Services, Melbourne 1997
- (10) T.A.Post, M.A.Giralico, M.C.Greaves, and G.M.Frazer, "Operational Results from Optimised Lightnin SX Pumper and Auxilliary Mixer Designs" ALTA 1996 Copper Hydrometallurgy Forum. Brisbane 1996. ALTA Metallurgical Services Melbourne.
- (11) B.Nyman, R.Kuusisto, P.Taipale and J. Lyyra, "Emphaisi on Feed End Settling in Outokumpu's VSF Mixer-Settler" Ibid.

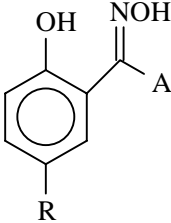
<u>EXTRACTANT CLASS</u>	CHELATING AGENTS
<p><u>FORMULA OR STRUCTURE</u></p> <div style="display: flex; align-items: center; justify-content: center;">  <div style="margin-left: 20px;"> <p>R = C₉H₁₉ or C₁₂H₂₅</p> <p>Ketoximes A = CH₃ Salicylaldoximes A = H</p> </div> </div>	
<p><u>EXTRACTION CHEMISTRY</u></p> $2RH_{(org)} + M^{+2} + SO_4^{-2} \rightleftharpoons R_2M_{(org)} + 2H^+ + SO_4^{-2}$ <p style="text-align: center;">or</p> $2RH_{(org)} + M(NH_3)_4^{+2} \rightleftharpoons R_2M_{(org)} + 2NH_3 + 2NH_4^+$	
<p><u>MODIFIERS</u> ALCOHOLS, PHENOLS, ESTERS (TXIB)</p> <p style="text-align: center;">KETOXIMES/ALDOXIME MIXTURES</p>	
<p><u>SPECIAL FEATURES</u></p> <ul style="list-style-type: none"> • Main commercial extractants for copper • Operate on hydrogen ion cycle. Stripping is reverse of extraction • Function with acid and ammoniacal leach solutions • More selective than other extractant classes • Kinetically slower than ion pair extractants • Have good physical properties in terms of phase separation, low aqueous solubility, chemical stability • Relatively expensive to manufacture 	

TABLE 1: CHELATING EXTRACTANTS

<u>EXTRACTANT CLASS</u>	ION-PAIR EXTRACTANTS
<u>FORMULA OR STRUCTURE</u>	
Quaternary Amines	$R_3R'N^+Cl^-$
Primary Amines	RNH_2
Secondary Amines	R_2NH
Tertiary Amines	R_3N
Trialkyl Guanidines	
<u>EXTRACTION CHEMISTRY – QUATERNARY AND TERTIARY AMINES</u>	
$R_3R'N^+_{(org)} + M^- \rightleftharpoons R_3R'N^+M^-_{(org)}$	
$R_3N_{(org)} + H^+ \rightleftharpoons R_3NH^+_{(org)} \quad \text{Protonation}$	
$R_3NH^+ + M^- \rightleftharpoons R_3NH^+M^-_{(org)} + H^+$	
<u>MODIFIERS</u>	ISODECANOL OR TRIDECANOL, AROMATIC DILUENT
<u>SPECIAL FEATURES</u>	
<ul style="list-style-type: none"> • Commercial extractants for uranium, thorium, vanadium, gold, cobalt and other metals • Modifiers promote solubility of the extractant - metal complex in the diluent • Kinetics, both extraction and stripping are fast • Extraction is usually of a metal anion complex such as $Au(CN)_2^-$ or $UO_2(SO_4)_3^{4-}$ • Selectivity is not high. Other anions can compete with the metal being extracted • Stripping can be ion exchange for all types or deprotonation for primary, secondary and tertiary amines and trialkylguanidines • Tertiary amines and trialkylguanidines are more selective than primary and secondary amines • For all except quaternary amines, extraction must be at pH below the pK_b of the extractant • Selectivity can be pH dependent • Primary, secondary and tertiary amines are relatively simple to produce 	

TABLE 2: ION-PAIR EXTRACTANTS

<u>EXTRACTANT CLASS</u>	NEUTRAL OR SOLVATING EXTRACTANTS	
<u>FORMULA OR STRUCTURE</u>		
Tri Octyl Phosphine Oxide (TOPO)	$R_3P = O$	
Tri Butyl Phosphate (TBP)	$(RO)_3PO$	
Ketones (MIBK)	R_2CO	$R = CH_3 \text{ and } (CH_3)_2CHCH_2$
Alcohols	ROH	
<u>EXTRACTION CHEMISTRY</u>		
Extraction is by adduct formation		
$2(RO)_3PO_{(org)} + UO_2(NO_3)_2 \rightleftharpoons UO_2(NO_3)_2 \cdot 2(RO)_3PO_{(org)}$		
Stripping is with concentrated HNO_3		
<u>SPECIAL FEATURES</u>		
<ul style="list-style-type: none"> • TBP is used extensively in nuclear fuel reprocessing • Kinetically fast • Extract neutral metal complexes • Selectivity is low • Organometallic complex must be organic soluble 		

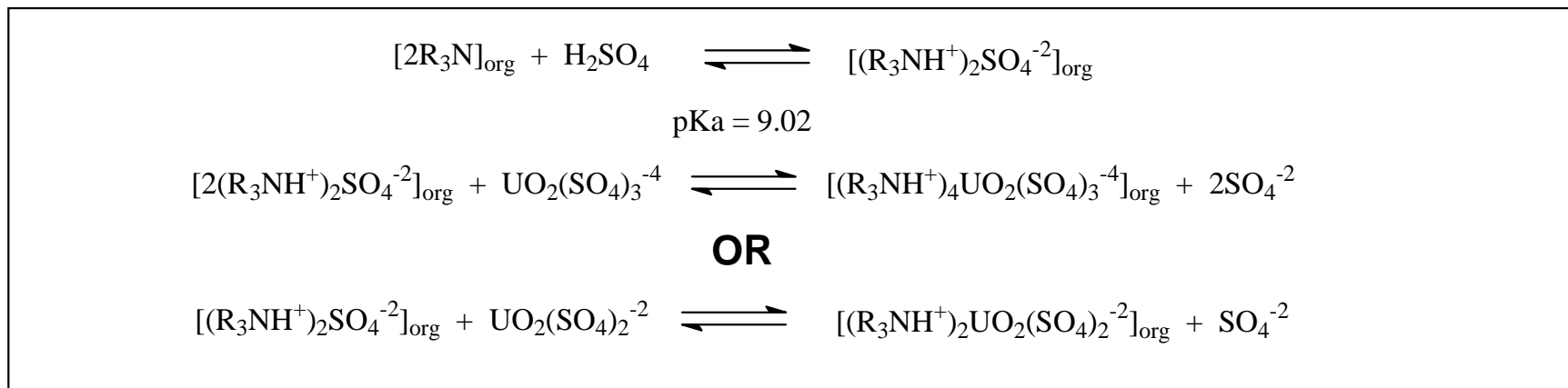
TABLE 3: NEUTRAL OR SOLVATING EXTRACTANTS

<u>EXTRACTANT CLASS</u>	ORGANIC ACID EXTRACTANTS
<u>FORMULA OR STRUCTURE</u>	
Phosphinic Acids	R ₃ P(O) OH
Sulphonic Acids	R SO ₂ OH
Carboxlic Acids	R ₃ C - COOH, Versatic Acid
Phosphoric Acids	(C ₄ H ₉ CH(C ₂ H ₅)CH ₂ O) ₂ POOH, D2HPA
<u>EXTRACTION CHEMISTRY</u>	
	$4RH_{(org)} + Zn^{+2} \rightleftharpoons R_2Zn \cdot 2RH_{(org)} + 2H^+$
<u>SPECIAL FEATURES</u>	
	<ul style="list-style-type: none"> • Phosphinic acids are widely used for cobalt extraction • Versatic acids can be used for Cu and Ni extraction • D2EHPA extracts a wide range of metals • Operate on a hydrogen ion cycle but do not display hydrogen ion stoichiometry. Often between 1 and 2 moles of extractant are required for each mole of hydrogen produced during extraction. This is because adduct formation is also involved in the extraction • Selectivity is poor and careful pH control may be required to achieve reasonable selectivity

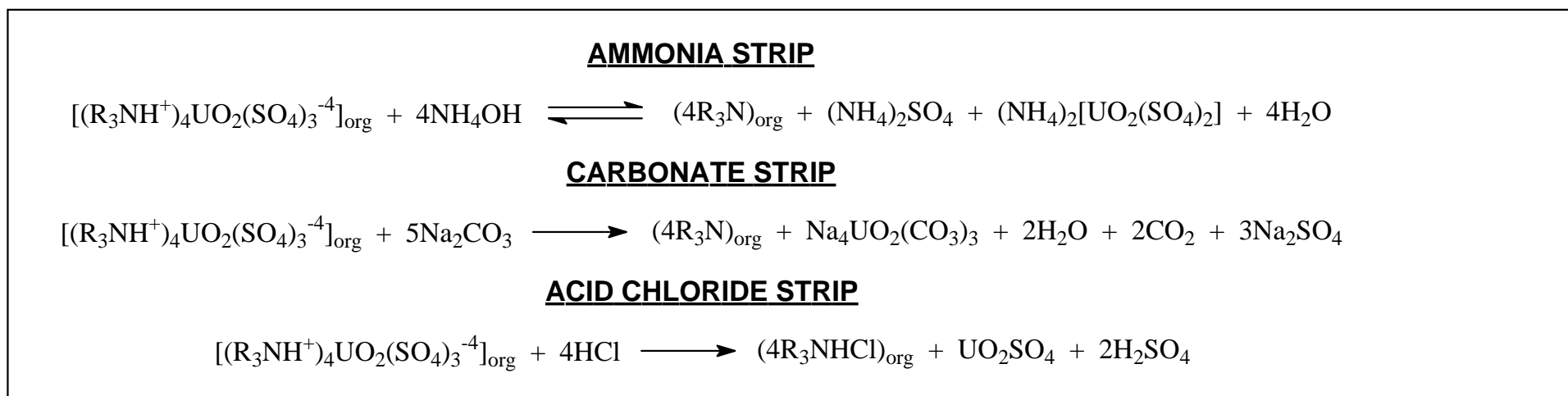
TABLE 4: ORGANIC ACID EXTRACTANTS

TABLE 5.
CHEMISTRY OF URANIUM RECOVERY USING TERTIARY AMINES

EXTRACTION



STRIPPING



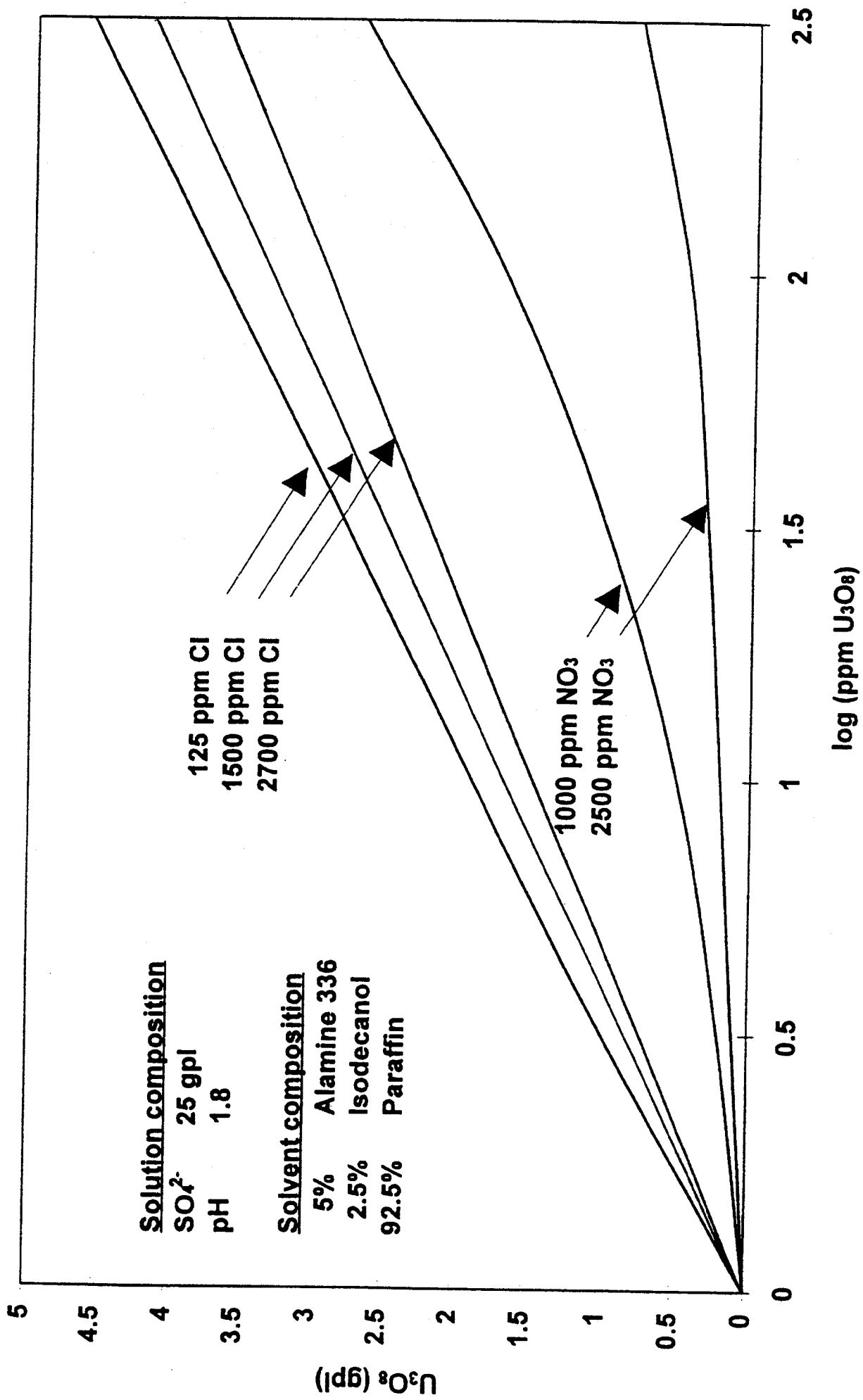


Figure 1. The Effect of Cl^- & NO_3^- on the Loading of U_3O_8 on Solvent

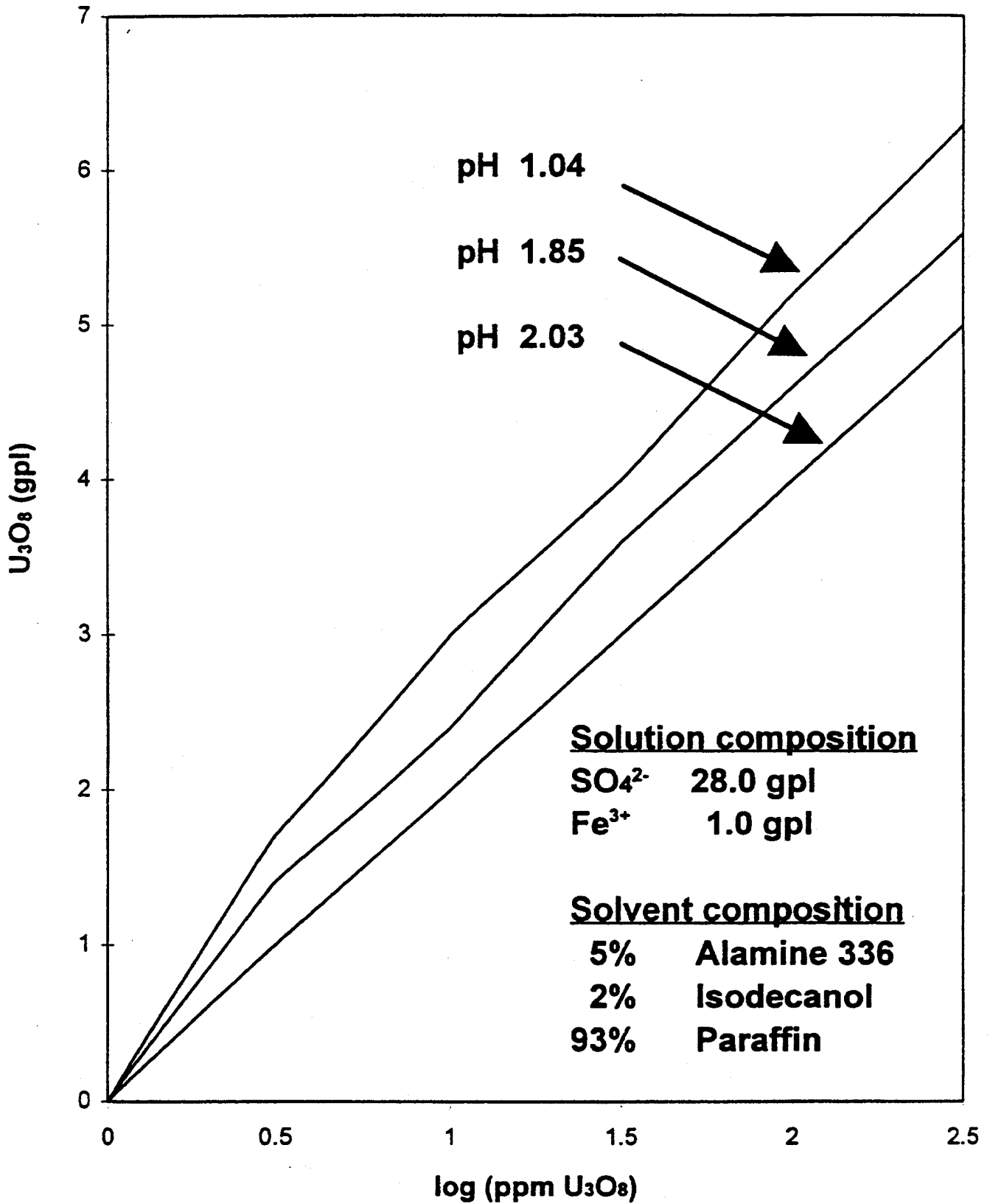


Figure 2. The Effect of pH on the Loading of U₃O₈ on Tertiary Amine Solvent

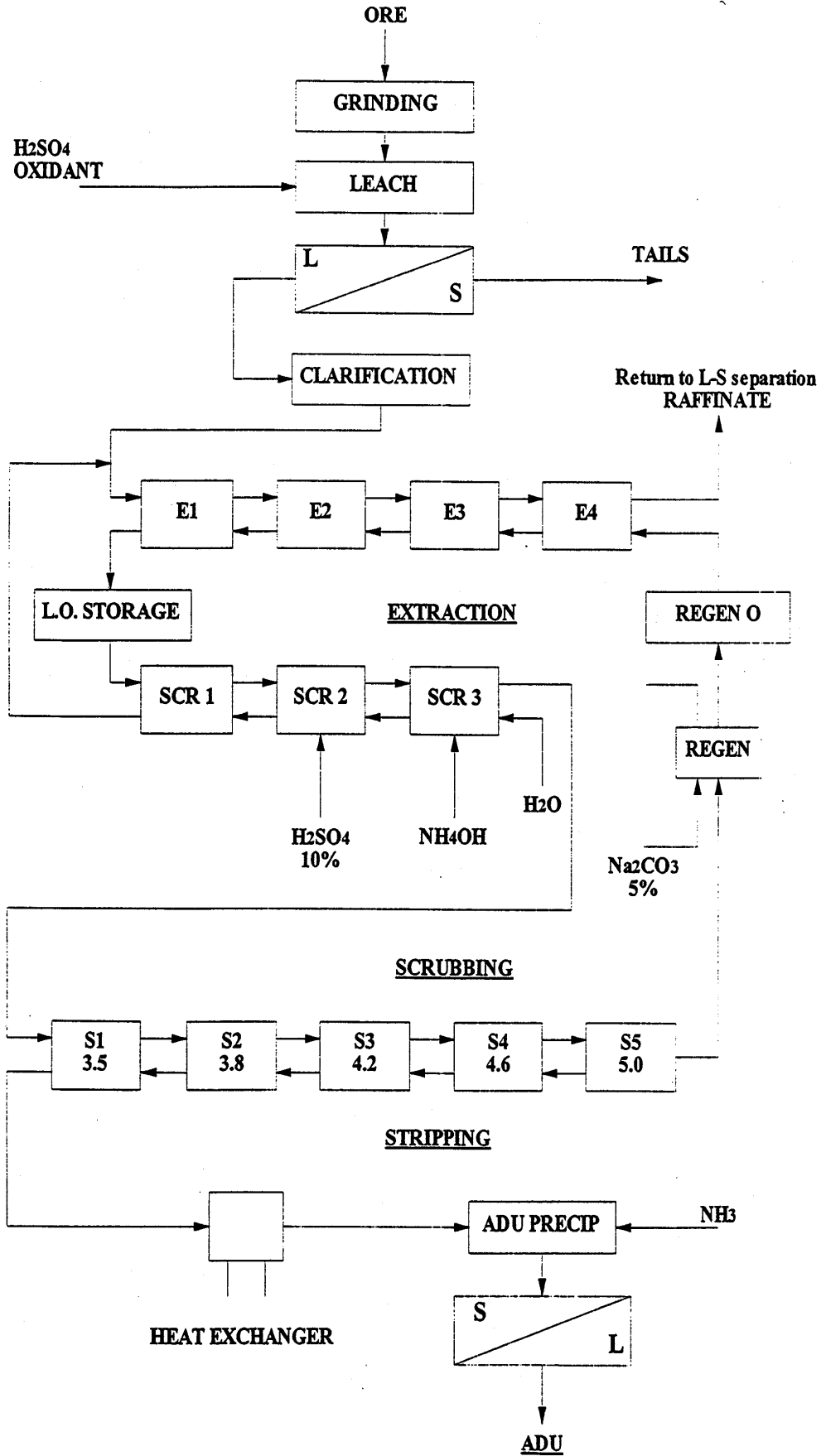


Figure 3. Typical Acid Leach - SX Uranium Circuit

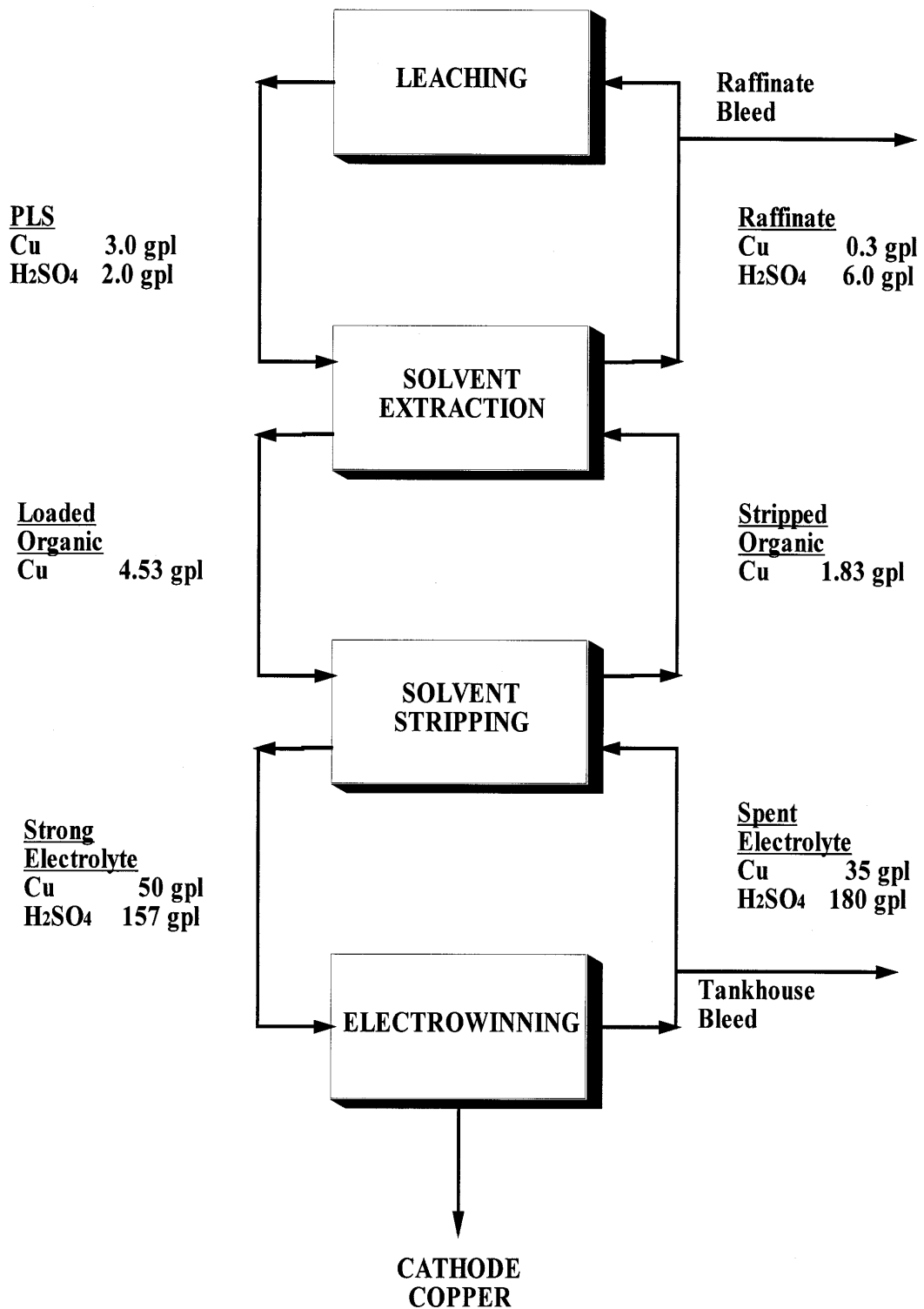


Figure 4 - Example of Copper and Acid Concentrations in a Leach-SX-EW Circuit

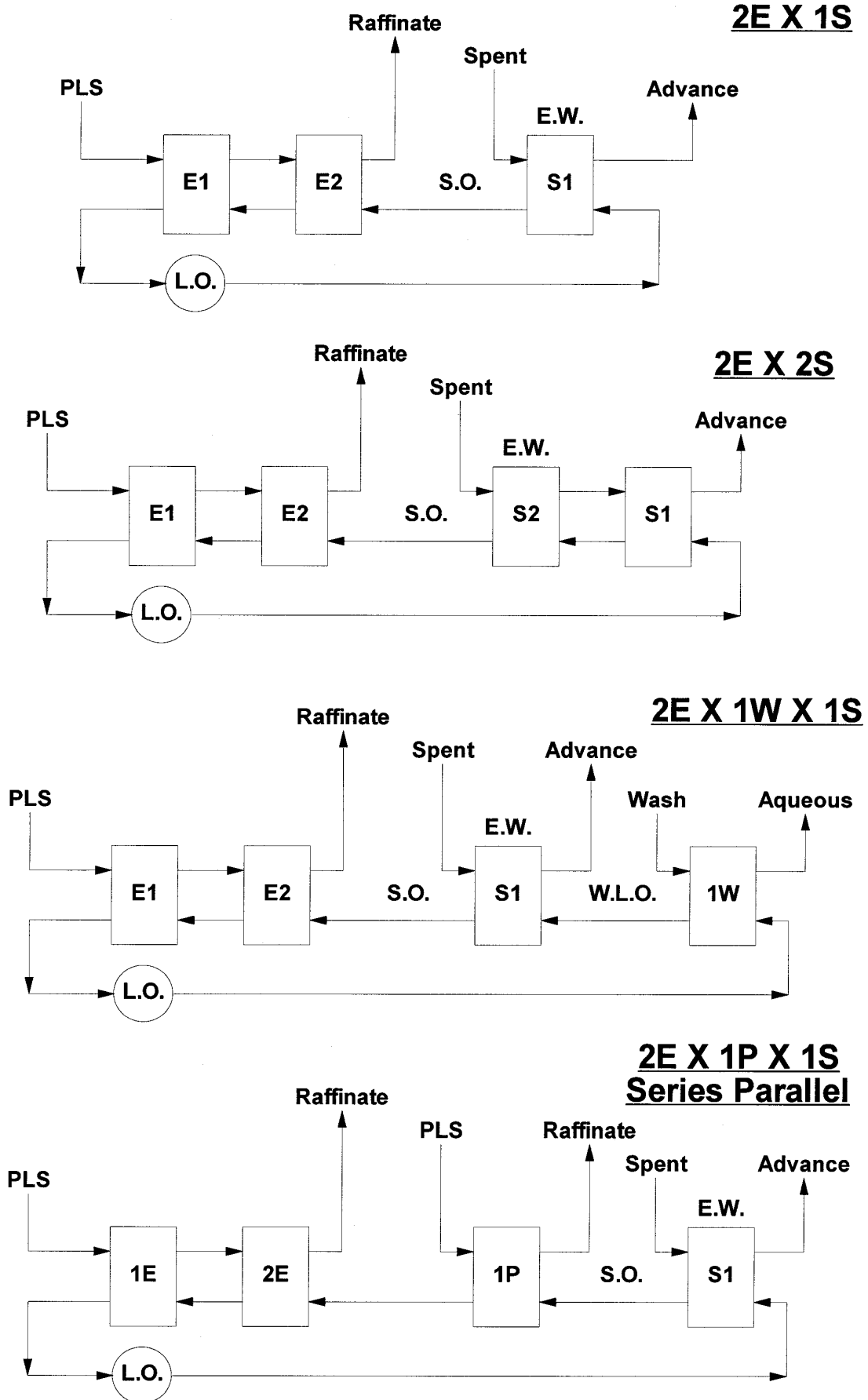


Figure 5. 2E X 1S, 2E X 2S, 2E X 1W X 1S, 2E X 1P X 1S Circuits

July 1, 1998

Henkel Australia

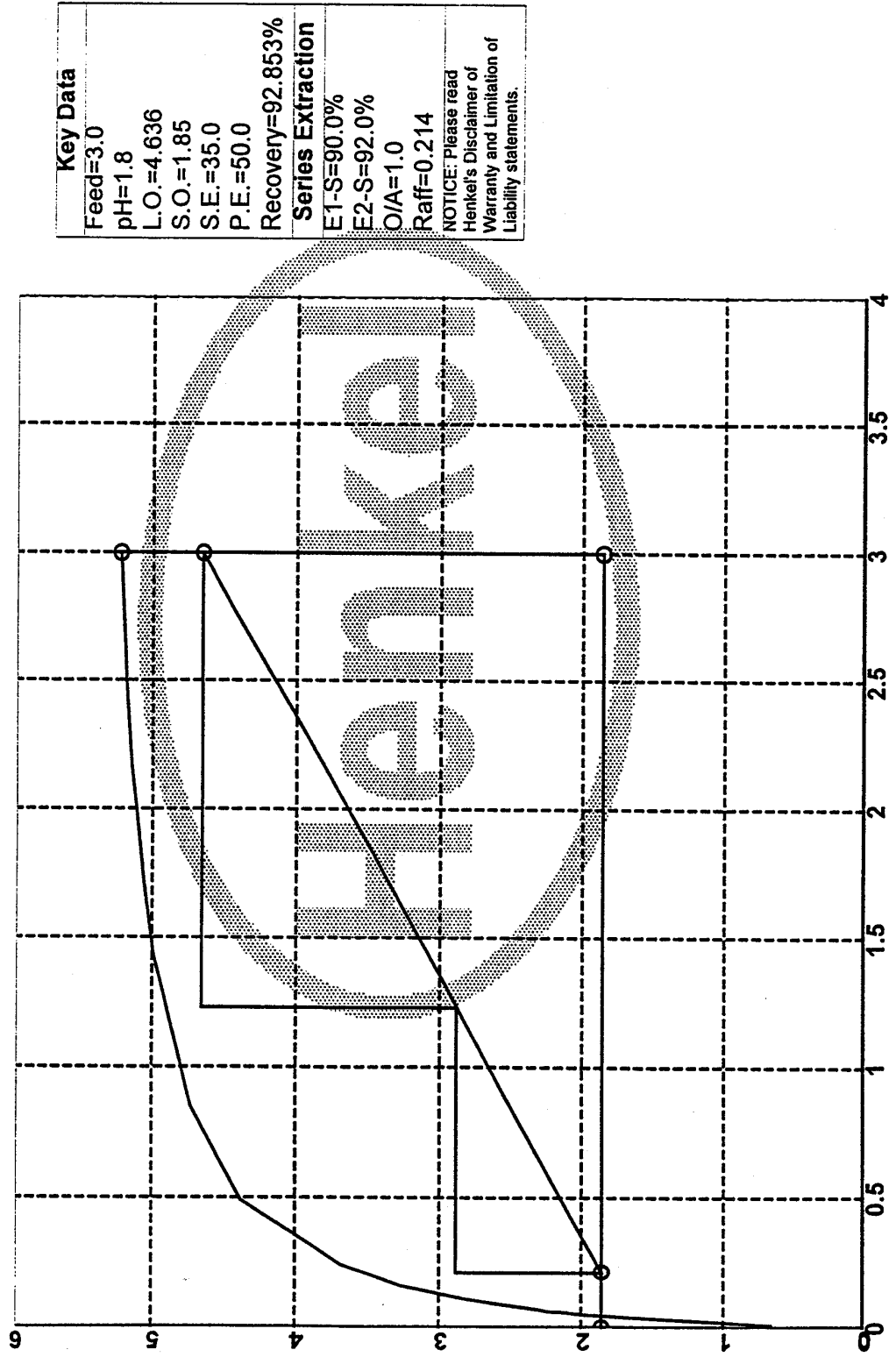


Figure 6.

Figure 6.

Isocalc™ TM - Ver. 3.01/TLJ/1997 - 1/07/98
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 Isotherm Point Calculations and Graphics / McCabe-Thieles
 NOTICE: Please read Henkel's Disclaimer of Warranty and
 Limitation of Liability statements.

Client Name/Project: Henkel Australia
 PLS g/l Cu: 3.0 PLS pH: 1.8
 PLS g/l SO4=: 80.0 PLS SO4= Activity: 15.0%
 Reagent Selected: LIX® 984N Reagent Volume Percent: 10.0
 Stripped Organic, g/l Cu: 1.85 Max Load, g/l Cu: 5.224
 No. Strip Stages: 1 Spent Elec., g/l H2SO4: 180.0
 Spent Elec., g/l Cu: 35.0 Preg. Elec., g/l Cu: 50.0
 Other Parameters/Information: 2EX1S

<u>Isotherm Results</u>	<u>Org., g/l Cu</u>	<u>Aq., g/l Cu</u>
O/A=10.0	2.144	0.064
O/A=5.0	2.434	0.081
O/A=2.0	3.268	0.164
O/A=1.5	3.690	0.241
O/A=1.0	4.351	0.499
O/A=0.5	4.984	1.433
O/A=0.2	5.163	2.337
O/A=0.1	5.200	2.665

===== McCabe-Thiele Calculations =====

O/A ratio in series extraction: 1
 Mixer efficiency for E-1 series extraction: 90%
 Mixer efficiency for E-2 series extraction: 92%
 The Materials Balance across the series extraction circuit equals (g/l Cu):

Aq. Feed [3.000]---->E-1S Aq. [1.236]---->E-2S Aq. (Raff) [0.214]
 E-1S Org. (L.O.) [4.636] <----E-2S Org. [2.871] <----Stp. Org. [1.850]

The expected recovery for the series circuit is 92.853%
 The loaded organic is 88.74% of max load.
 The net transfer is 0.279 g/l Cu per 1 vol. % of LIX® 984N.

The strip O/A=5.385 using 35.0 g/l Cu in the spent electrolyte.
 The materials balance across the strip circuit is as follows (g/l Cu):

Loaded Org. [4.636]---->S-1 Org. (St. Org.) [1.850]
 S-1 Aqu. (P.E.) [50.00] <-----Spent Elec. [35.00]

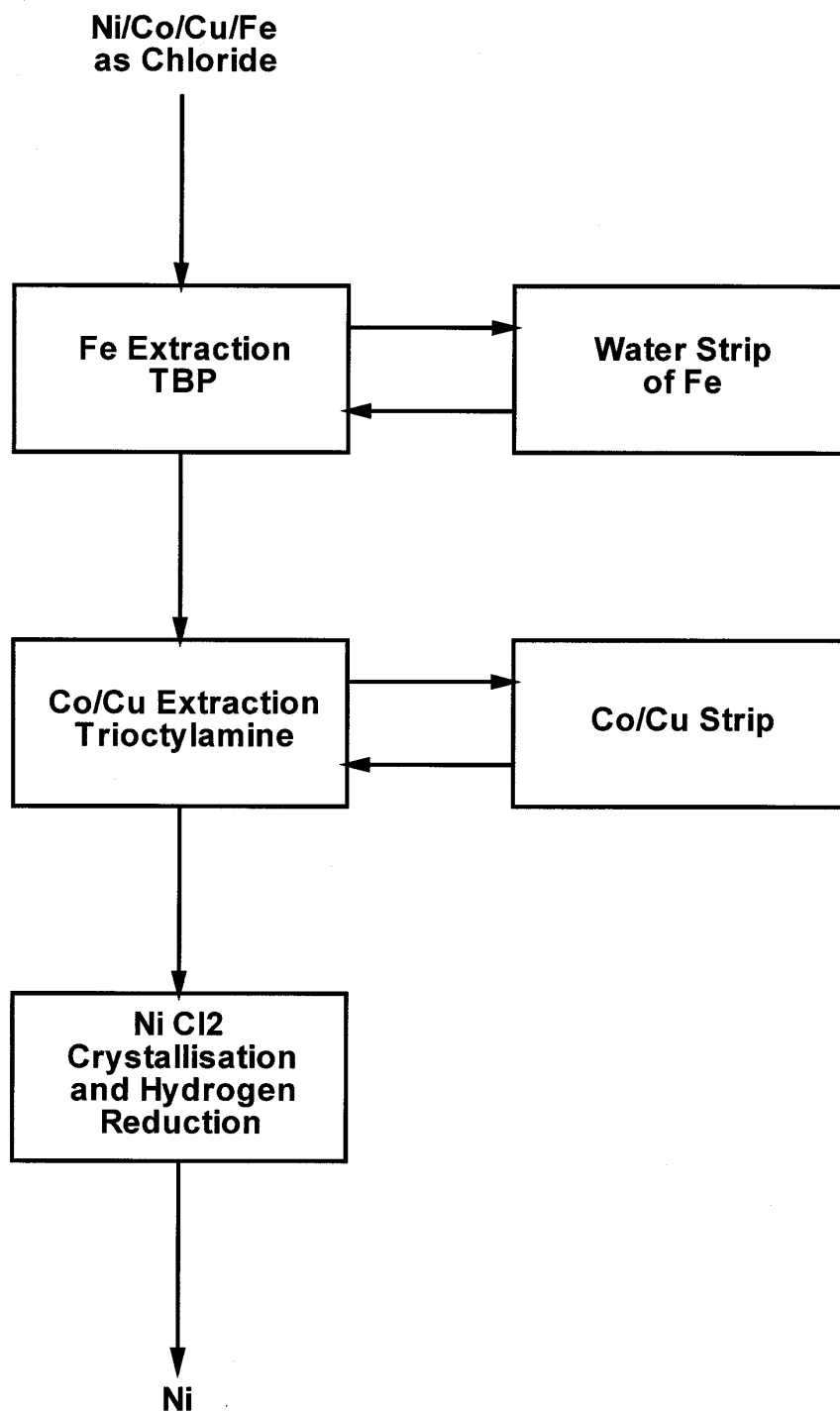


Figure 7. Nickel - Cobalt Separation using Chloride Leach Solutions and tertiary Amine Extractants

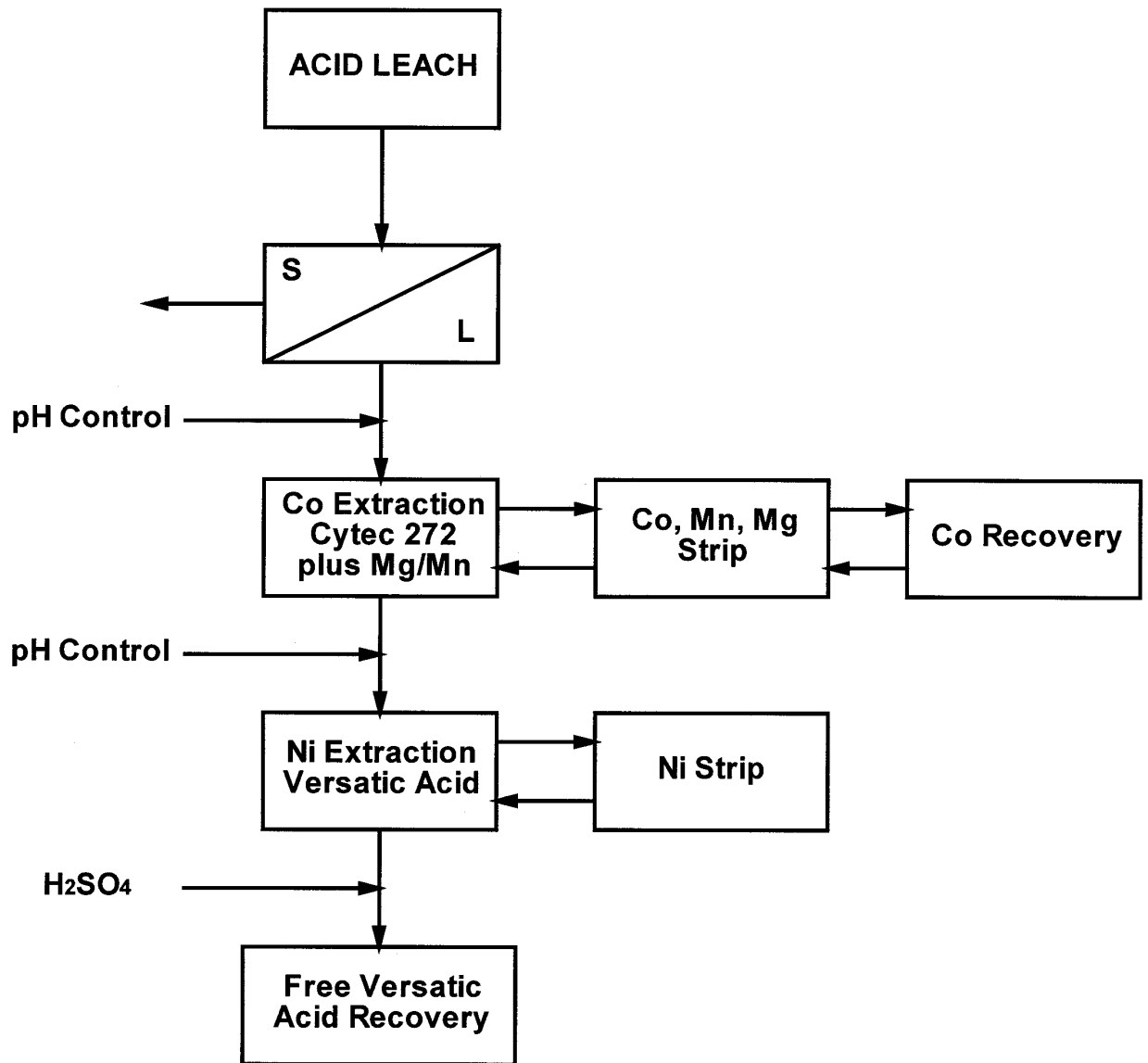


Figure 8. Nickel Recovery from Acid PLS

Ni Laterite Treatment - LIX 84-I

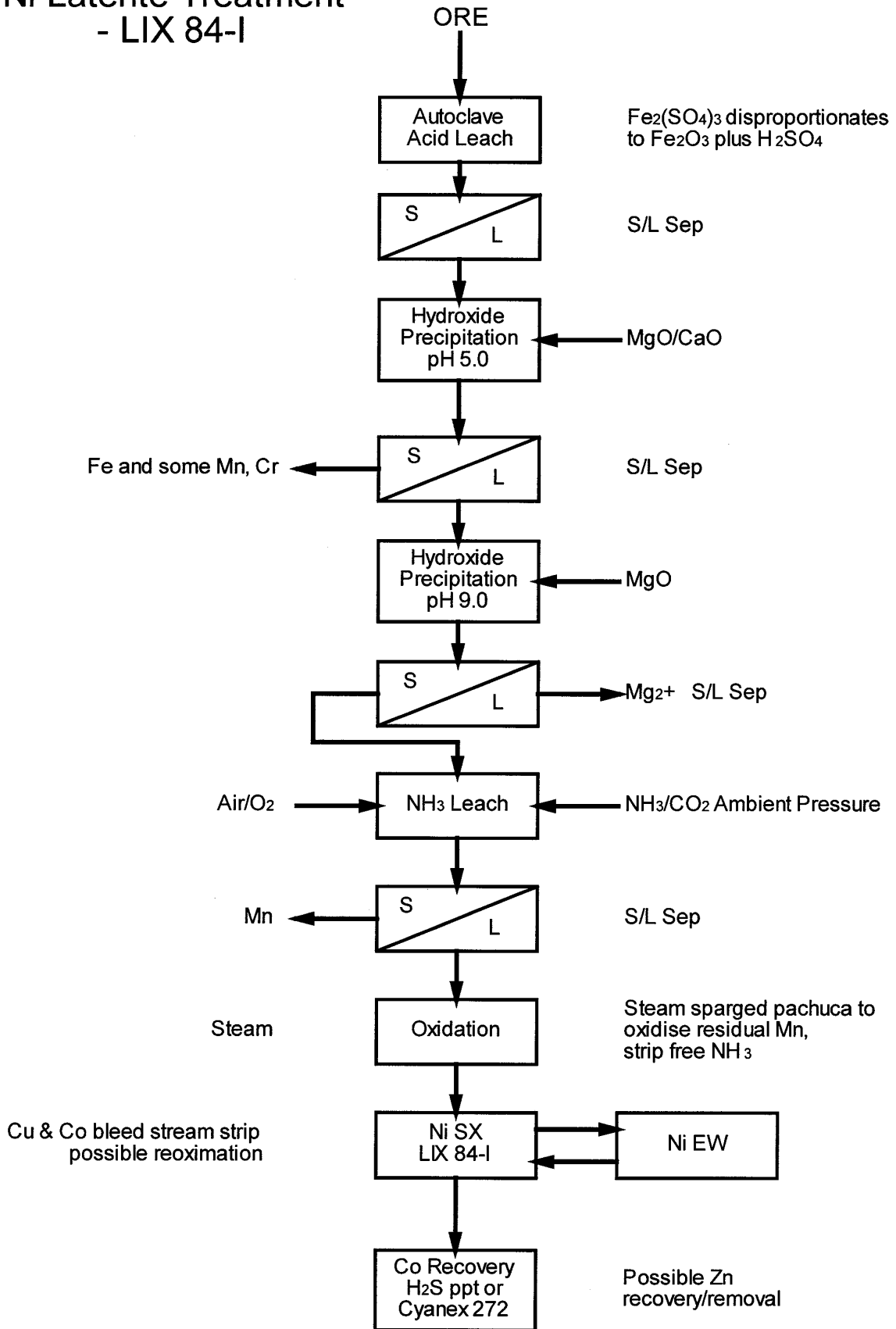


Figure 9

LIX 79 pH Isotherms

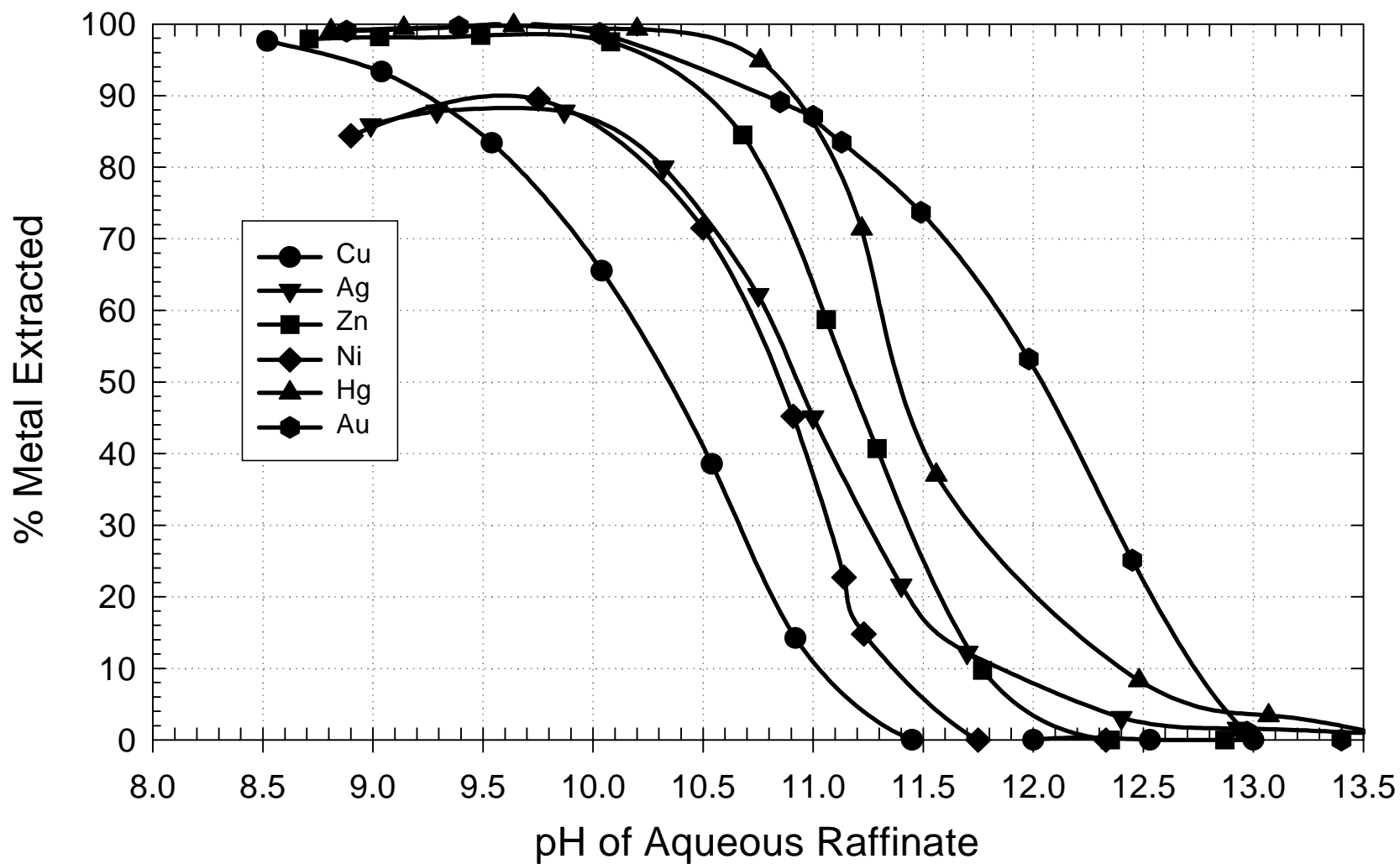


Figure 10 pH Isotherms

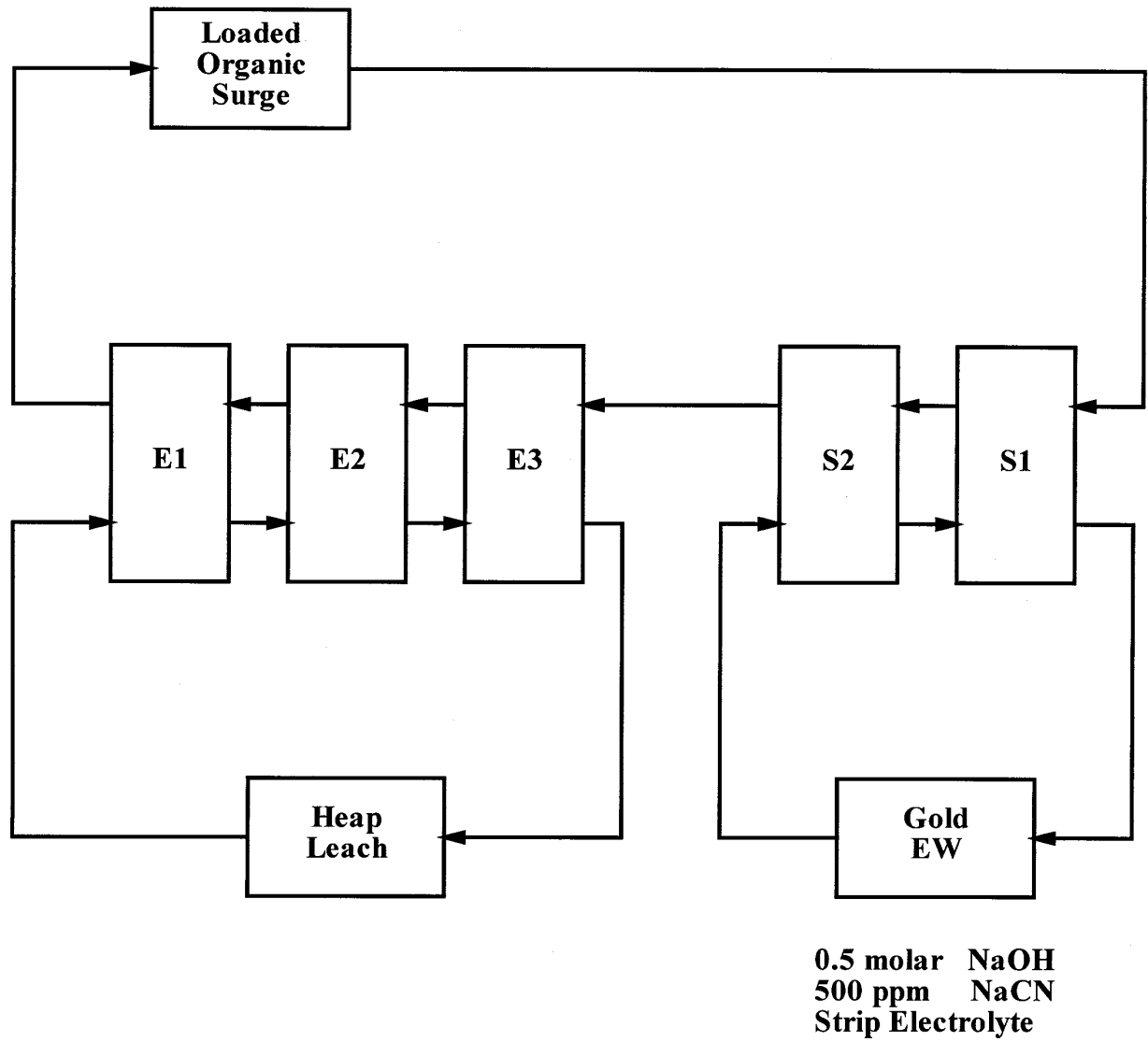
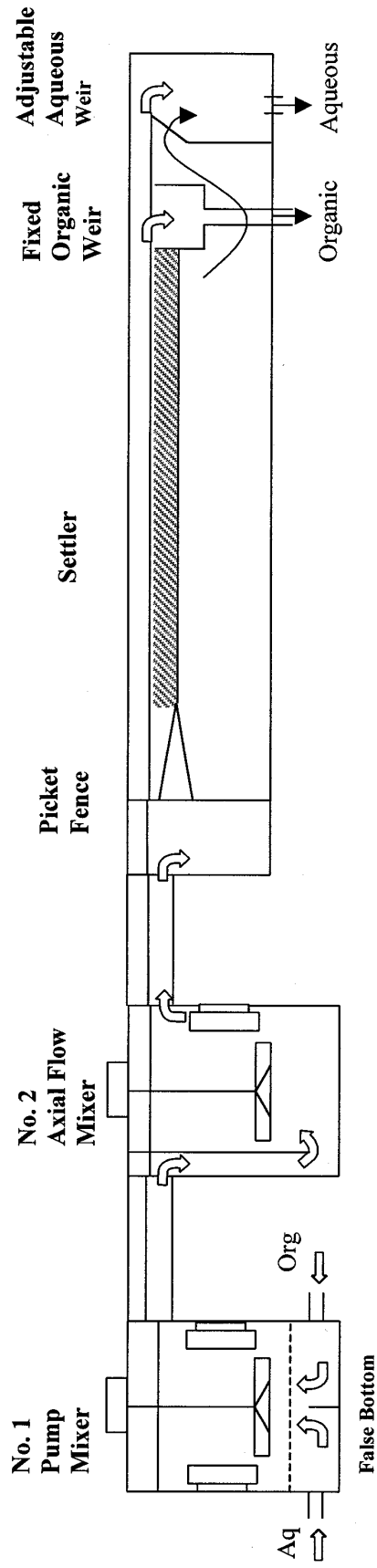


Figure 11. LIX 79 Circuit for Gold Recovery

CONVENTIONAL MIXER SETTLER



MIXER DESIGN CRITERIA

Mixer O/A (use recycles if needed)	1.1
Mixer Residence Time Copper	2 mins 3 mins if cold
Tip Speed	250 – 300 metre/min
N^3D^2	< 20
N	= rps
D	= diameter in feet

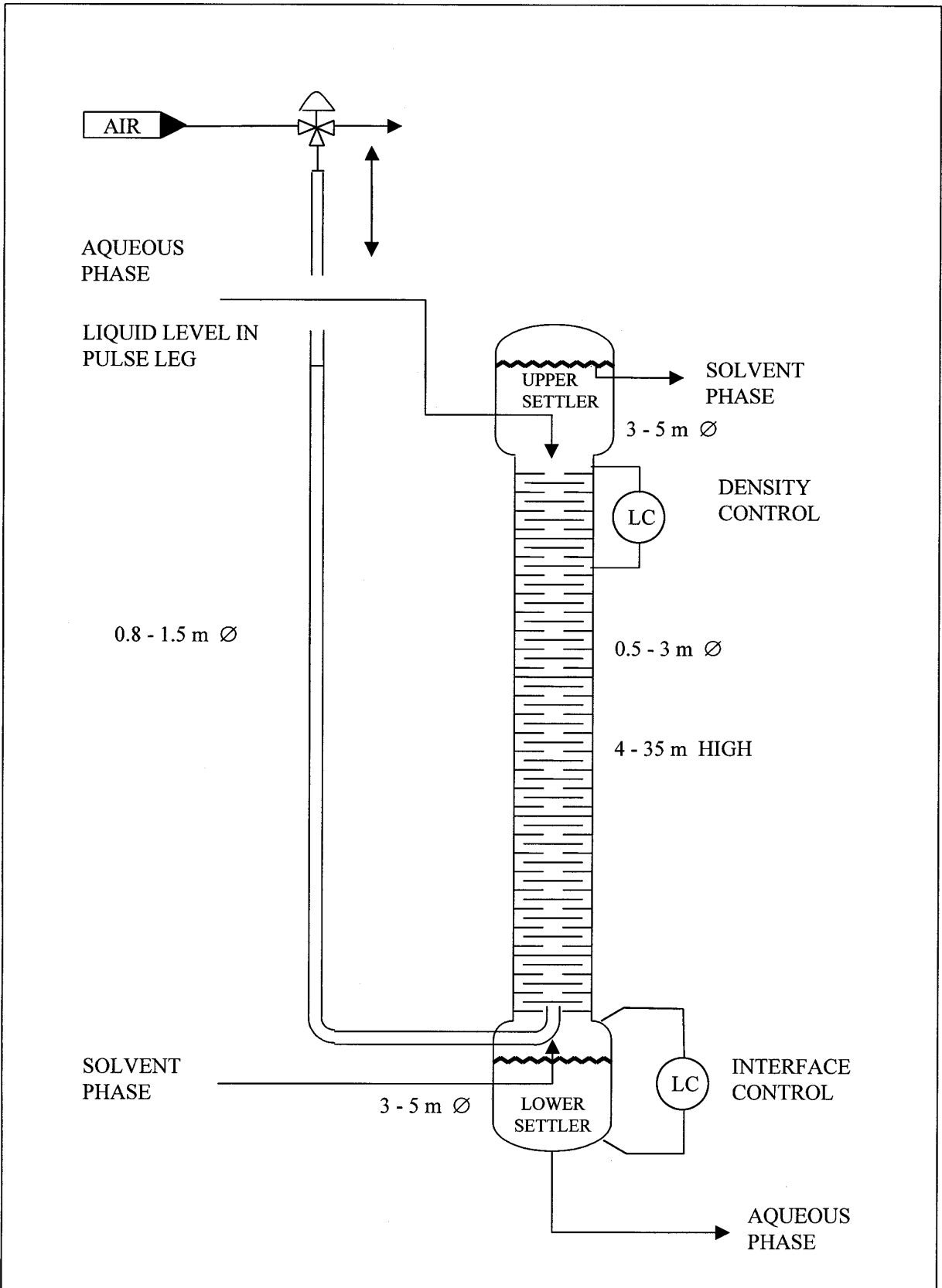
SETTLER DESIGN CRITERIA

SPECIFIC FLOW RATE	4.0 – 5.0 $m^3/m^2/hr$ (Total flow)
If cold	3.0 – 3.5 $m^3/m^2/hr$
ORGANIC SPACE VELOCITY	3 – 6 cm/sec.
ORGANIC DEPTH	200 – 250 mm

From total organic flow calculate settler width from organic space velocity and organic depth.

From specific flow rate calculate settler area and settler length.

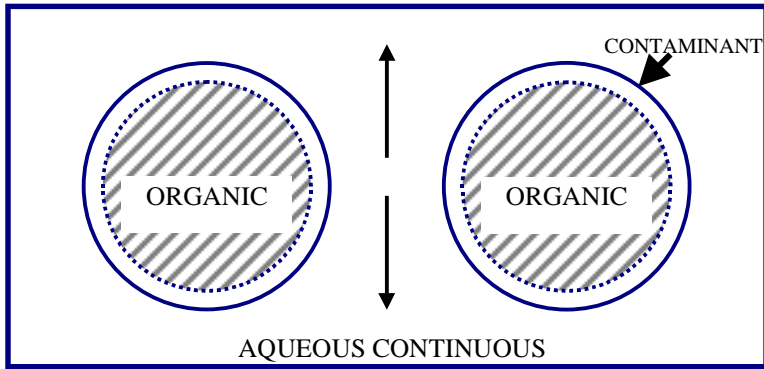
Figure 12



BATEMAN PULSED COLUMN

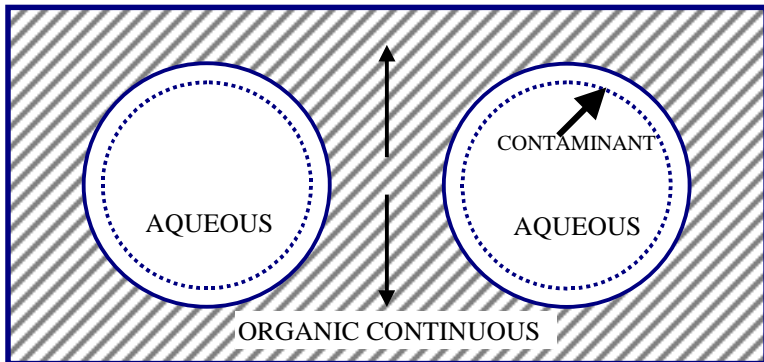
Figure 13

Diagram supplied with permission from Alta Metallurgical Services Pty Ltd and Bateman



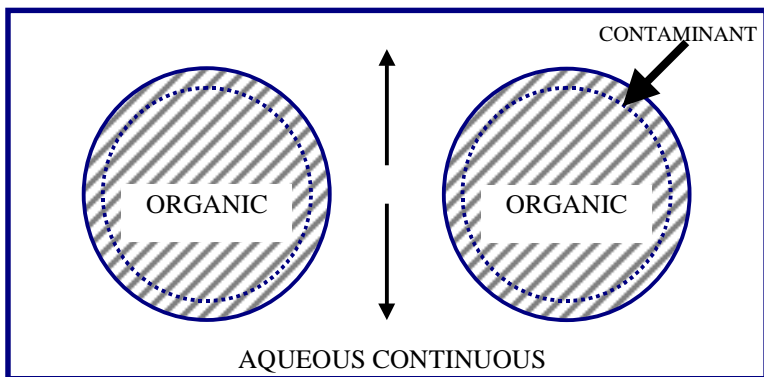
Aqueous Continuous Emulsion
- Aqueous Wetted Contaminants

Aqueous film must thin to molecular dimensions before coalescence takes place. Aqueous wetted contaminant can structure this film and inhibit thinning and coalescence.



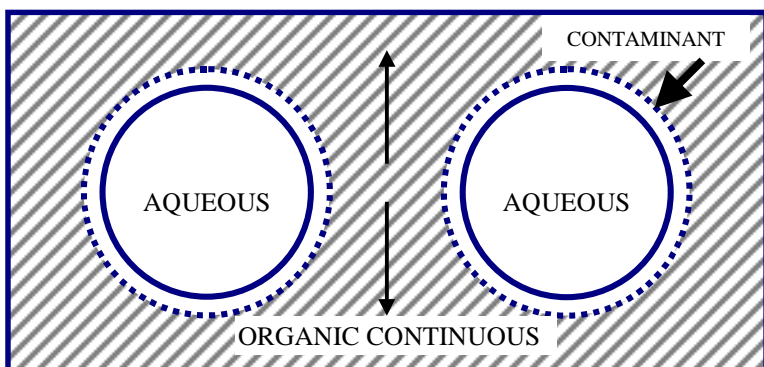
Organic Continuous Emulsion
- Aqueous Wetted Contaminants

Organic film must thin to molecular dimensions before coalescence takes place. Aqueous wetted contaminant does not inhibit organic film thinning.



Aqueous Continuous Emulsion
- Organic Wetted Contaminants

Aqueous film must thin to molecular dimensions before coalescence takes place. Organic wetted contaminant does not inhibit aqueous film thinning.



Organic Continuous Emulsion
- Organic Wetted Contaminants

Aqueous film must thin to molecular dimensions before coalescence takes place. Organic wetted contaminant can structure this film and inhibit coalescence.

Figure 14.