# Table of Contents

List of Figures............................................................................................................. 3
1.0 Introduction........................................................................................................ 4
2.0 SX Design Factors ........................................................................................... 5
   2.1 SX Reagents.................................................................................................... 6
   2.2 Acid Management ........................................................................................ 8
   2.3 Liquor Temperature ..................................................................................... 11
   2.4 Crud Management ........................................................................................ 11
3.0 The Effect of Impurities and Additives ......................................................... 13
   3.1 Leaching Aids ............................................................................................... 13
   3.2 Nitrate .............................................................................................................. 14
   3.3 Silica .................................................................................................................. 15
   3.4 Chloride ........................................................................................................... 16
   3.5 Manganese ..................................................................................................... 17
   3.6 Iron .................................................................................................................... 20
   3.7 Antimony and Bismuth .................................................................................. 21
4.0 Solvent Extraction Equipment ......................................................................... 22
   4.1 Mixer-Settlers .............................................................................................. 22
   4.2 Pulsed Columns ............................................................................................ 23
   4.3 Molecular Recognition Technology ......................................................... 26
   4.4 Non-Dispersive Solvent Extraction ............................................................. 27
   4.5 Emulsion Liquid Membranes ......................................................................... 29
5.0 Summary............................................................................................................. 31
6.0 References......................................................................................................... 34
**List of Abbreviations**

A/O or O/A – Aqueous/Organic, referring to volume ratio in the contactor  
ELM – Emulsion Liquid Membrane  
EW – Electrowinning  
IX – Ion Exchange  
MRT – Molecular Recognition Technology  
NDSX – Non Dispersive Solvent Extraction  
PGM(s) – Platinum Group Metal(s)  
PLS – Pregnant Leach Solution  
SX – Solvent Extraction

**List of Figures**

Figure 1 - *Schematic of equilibrium loading as a function of pH*  
Figure 2 - *A conventional SX mixer settler design*  
Figure 3 - *Schematic design of a Bateman Solvent Extraction Pulsed Column*  
Figure 4 - *Celgard Liqui-Cell Extra Flow Membrane Contactor*  
Figure 5 - *Schematic of an ELM globule*


1.0 Introduction

Over the last several decades copper solvent extraction-electrowinning has proven to be a cost effective and adaptable technique for producing high grade copper. Solvent extraction has been used to produce high grade copper in since the invention of appropriate organic reagents in 1968 by General Mills Chemicals. Over the last 40 years solvent extraction circuits and operations have been improved through better process control, equipment improvements, and the invention of more robust and effective solvent extraction reagents. The International Copper Study Group estimates that 16% of the refined copper production from ores in 2006 used SX-EW. It has become more popular recently as increasingly low grade and dirty concentrates have made smelting less attractive than hydrometallurgical processing. Today it is used to produce cathode copper from a diverse range of leach liquors, from low tenor, low acid chalcocite heap leach streams to high tenor, high acid chalcopyrite pressure oxidation streams. Through a wide range of process variables, equipment setups, extraction reagents, and flow sheet options SX-EW can be adapted to fit the requirements of many copper producers. This paper will seek to cover several factors that must be considered in operating a copper SX-EW plant, the impact of various
common impurities, as well as a look at possible equipment setups and secondary processes that relate to copper SX-EW.

2.0 SX Design Factors

There are many important factors that must be considered when operating a copper SX-EW plant. First and foremost is the makeup and tenor of the pregnant leach solution. The design strategies for processing heap leach liquor will be very different from those for a pressure oxidation reactor. The solution tenor is important because it affects the flowrate of the aqueous PLS (pregnant leach solution) – for a given rate of copper production the aqueous flowrate of a low tenor solution will necessarily be higher than that of a high tenor solution (Sole and Feather 2003). This relationship also determines the optimal A/O ratio in extraction, and therefore will also affect the loading capacity and kinetic requirements of the organic reagent. The acidity will also affect the choice of extractant, as loading and stripping rates are strong functions of pH. As a result, stability of the electrolyte and PLS pH is important to the efficient operation of the plant as shifts of +/- 0.5 units can significantly alter loading/stripping capacity and kinetics (Bergh and Yianatos 2001). As such, a dynamic plant model including stripping and loading kinetics, phase separation, crud
formation, entrainment, degradation and losses is very useful in operating and fine tuning a plant (Komulainen et al. 2006). The choice of organic diluent plays a role in the performance of a given solvent extraction reagent as well as it will affect the physical properties of the organic phase as well as the degradation of the organic (Van de Voorde et al. 2005).

2.1 SX Reagents

The most important piece of a solvent extraction circuit is the formulation and mixture of the organic extraction reagent. Not only is the reagent inventory an expensive part of the initial capital cost, but the choice of organic reagent will also influence process and operational variables such as pH and temperature. The rest of the plant flow sheet will also be affected because impurity control, loading and stripping kinetics, and circuit tolerance of leach modifiers or electrowinning enhancers is contingent on the performance and characteristics of the organic reagent. The reverse is true as well. By customizing the reagent formulation to be most suitable for the circuit and ore body an SX reagent can be tailor made to best suit a circuit and offer more efficient extraction.
The two main classes of copper solvent extraction reagents are aldoxime reagents and ketoxime reagents. Ketoxime reagents were invented shortly after the beginning of industrial copper SX use in 1968 using formulations of 2-hydroxybenzophenone oxime. Later ketoxime reagents were made using 2-hydroxy-5-nonylacetophenone, which made them more effective for dilute acid low copper tenor solutions. Aldoxime reagents were invented by Acorga Limited in 1979, using a 5-nonyl-salicylaldoxime formulation. These reagents were much stronger than ketoxime class extractants and proved to be difficult to strip using conventional spent electrolytes (Maes et al. 2003).

Over the next decade it was discovered that by using non chelating modifiers on aldoxime reagents SX performance could be improved in several areas. Alkyl phenol was the first such modifier that allowed the commercialization of aldoxime reagents. Aliphatic alcohol use resulted in better copper:iron selectivity, faster phase separation and better resistance to environmental degradation. Reagents modified with ester have better copper: iron selectivity still, as well as better physical properties that lead to less entrainment and crud generation (Maes et al. 2003). Ester modified aldoxime reagents are commonly used today,
particularly in new plants where flow sheet designs are not constrained by pre-existing equipment and solvent inventories.

2.2 Acid Management

The management and control of acidity is the most important operational variable in a solvent extraction circuit. Acidity can affect the efficiency of the plant in several ways. First and foremost, the equilibrium loading/stripping curves of organic reagents are strong functions of pH (see Figure 1).

![Figure 1. Schematic of equilibrium loading as a function of pH (Soderstrom 2007)](image)

The pH of the PLS must be managed so that copper will move from the aqueous phase to the organic, while the pH of the electrolyte is higher
so that it strips the organic effectively. If these variables are not controlled properly the loading capacity and kinetics of the organic reagent will be effectively diminished. Control strategies for pH include the reduction of aqueous entrainment in the organic to prevent PLS-electrolyte contamination, neutralization of excess acid with basic salts or lime, and careful management of any bleed recycle streams from the electrolyte.

Acid management can also be a challenge when treating high acid and high copper tenor solutions. The copper solvent extraction produces acid in the aqueous phase, as shown in equation 1.

\[
2RH_{\text{org}} + Cu^{2+}_{\text{aq}} \leftrightarrow R_2Cu_{\text{org}} + 2H^{+}_{\text{aq}} \quad (\text{Eq. 1})
\]

For each mole of copper removed from the aqueous it is replaced with 2 moles of protons, the equivalent acidity of 1 mole of sulphuric acid. In low tenor copper solutions this is insignificant because the change in copper concentration through the circuit is relatively small. However, in high copper tenor solutions such as concentrate pressure oxidation liquors where copper concentrations can be in excess of 40 g/L, equation 1 adds a significant amount of acid to the PLS. This in turn can affect the loading behavior of the organic extractant by shifting the equilibrium towards stripping. Several solutions are available to this problem. The simplest and most expensive solution is by directly
neutralizing acid in the mixers. This requires no additional equipment or flowsheet changes, but reagent costs can be prohibitive (Grinbaum 2007). Another solution is to adsorb acid with ion exchange resins. However, this yields a relatively useless dilute acid (Grinbaum 2007). The loading stage can also be split into multiple cells to allow partial neutralization of the intermediate raffinate with lime or carbonate. This necessitates gypsum treatment down stream. Bateman Engineering approached this problem by developing an acid solvent extraction circuit for Chambishi Metals in Zambia (Grinbaum 2007). The optimal solution for a given plant is very site dependent as the primary variable is the cost of neutralization agents.

One more way acidity can impact plant performance is if washing systems are used to control crud. The development of localized high pH zones can enhance the formation of high volume, low density siliceous gel-crud which is difficult to manage. All of these factors demonstrate the importance of tight pH control throughout copper SX circuits.
2.3 Liquor Temperature

The temperature of the aqueous stream entering the SX circuit may not always be near room temperature. Heated atmospheric leaches and pressure oxidation streams can be near boiling point when they first leave the leach reactors. Even if cooling towers are used the stream may still be above room temperature. The temperature of the leach liquor entering the circuit will alter the chemical behavior and physical properties of the organic. Higher temperature organic will cause increased hydrolytic degradation and increase the viscosity of the liquid, changing mixing/settling properties (Soderstrom 2007). If a mixed formulation of organic reagents is used, the formulation may alter over time if one reagent is more sensitive to temperature than the others. Elevated temperature will also increase the loss of organic solvent via evaporation (Bishop et al. 1999). Similarly, this will increase the risk of fire and other safety hazards.

2.4 Crud Management

Crud, or scum, is the name for a solid stabilized emulsion formed by mixing an aqueous phase containing fine suspended solids with an organic extractant phase. A thin, compact layer of crud at the organic-
aqueous interface in the settler has a positive effect on cross phase contamination and phase separation speed. However, crud must be managed effectively as excess crud buildup in the settler will eventually spread to the rest of the circuit and can cause serious disruptions downstream. As crud is typically 50% organic by weight or greater, crud treatment such as centrifuging or clay application is commonly used to recover the high value organic extractant (Bishop et al. 1999, Hartmann and Corbella 2007). Depending on the choice of solvent extraction contacting equipment crud can be controlled more easily. Column SX typically has less problems relating to crud control (Nielson and Vancas 1999).

Crud is a problem at most solvent extraction plants and its formation in the context of a full circuit is complex. The solid particles that give the emulsion stability are typically modeled as silica, but any fine solid (<2 micron) that passes thickeners can cause crud formation. Clays, jarosites, gypsum, quartz, and micas have all been linked to crud formation in copper solvent extraction (Readett and Miller 1995, Virnig et al. 1999).
Excessive mixing can also enhance crud formation through strong shear forces that break droplets into micro droplets, which settle poorly and have high interfacial surface area.

The presence of coagulants and flocculants from upstream flotation circuits can also lead to an increase of crud formation. This can be caused if the modifier binds to suspended particulate and makes it more hydrophobic (Virnig et al. 1999). Hydrophobic particles have a higher potential to stabilize crud emulsions than hydrophilic particles.

### 3.0 The Effect of Impurities and Additives

#### 3.1 Leaching Aids

Some copper processes use leaching aids during the leaching stage to improve recovery and/or kinetics. Often these chemical aids are in the form of surfactants that improve the ability of the leach solution to penetrate the pores of ground minerals by reducing the surface tension of the leach solution, such as Dearcodox or Dowfax 2AO (Kordosky and Virnig 2007). These chemicals are not removed from the PLS before entering the SX-EW segment of the circuit and so they can affect downstream performance. Specifically, the lower surface...
tension in the aqueous can help stabilize dispersions, increasing the
time for settling and phase separation. This in turn can increase
aqueous entrainment in the organic and electrolyte. Surfactants can
also increase the rate of organic reagent degradation either via
hydrolysis, or via nitration should the solution contain nitrate ions
(Kordosky and Virnig 2007). As a result, it is important to consider the
possible negative effects of leaching aids on the SX-EW process and
how to best mitigate them.

3.2 Nitrate

Nitrate is occasionally present in copper ore deposits in small amounts
and as such it can find its way into PLS solutions. Through recycle
streams the nitrate concentration can build up to significant and levels
that have a negative impact on SX-EW performance. This was
witnessed at the Lomas Bayas mine in Chile, where nitrate
concentrations of >25 g/L in the PLS accelerated nitration of the
organic extractant. This problem was eventually solved at Lomas
Bayas by replacing the extractant from LIX 622N to LIX 84-IC.
Nitration of aldoxime extractants forms nitro aldoxime which binds too
strongly to copper for strip solutions to remove, effectively lowering
extraction capacity. The presence of equilibrium modifiers and chloride
ions increase the rate of this type of nitration degradation (Virnig et al. 2003). This problem is exacerbated by a high solution potential in the PLS or electrolyte. Nitration problems have a tendency to become worse if left unchecked as the byproducts of the nitration reaction enhance degradation (Virnig et al. 2003). It has been shown that nitration degradation can be a problem even in plants with low (1-4g/L) levels of nitrate in the PLS although the rate of degradation is slower (Kordosky and Virnig 2007). In any plant with the potential for nitrate ions to enter the PLS it is important to choose an appropriate organic extractant or otherwise mitigate the effects of nitrate buildup.

3.3 Silica

Silica can often be present in copper leach solutions as a result of silicon in the copper ore or in the host rock. It can be present both as fine silica particles that are not removed during flotation, or as dissolved silica after the dissolution of the copper minerals. In either case the presence of silica in the copper leach solution can cause difficulties downstream in the solvent extraction circuit. Fine silica particles stabilize emulsions, slowing phase separation and leading to the formation of crud (Menacho and Zivkovic 1994). Dissolved silica
precipitates and polymerizes as chains of colloidal siloxane, as per equation 2.

\[ Si(OH)_4 + \left( H_4SiO_4 \right)_n \rightarrow \left( H_4SiO_4 \right)_n \]  

(Eq. 2)

This colloidal silica gel is of low density and is difficult to separate from the aqueous phase. The gel absorbs organic and does not compact easily. This problem was studied in detail after silica issues in the Girilambone copper SX-EW plant. There it was found that by running organic continuous instead of aqueous continuous reduced aqueous entrainment in the organic and decreased silica levels in the high acid strip where silica precipitation was most prevalent (Readett and Miller 1995).

### 3.4 Chloride

Chloride can be present in copper leach liquors for several reasons. Most obviously are processes where chloride is the leaching agent, such as the CLEAR process, CYMET, CESL, and the BHAS process (Peacey et al. 2004). However, these processes typically electrowin copper from the leach solution rather than relying on solvent extraction. Chloride can also enter with the mineral, although this is uncommon. More commonly in sulphate SX-EW processes chloride enters with water, depending on the water source. This is particularly
true if saline water is used. A certain concentration of chloride is desirable in electrolytes as it increases the conductivity of the solution (de Maere and Winand 1995). However, excess chloride can cause problems if the solution potential is high enough to cause the evolution of chlorine gas. Chlorine gas will accelerate corrosion of the surrounding equipment. The problem of chlorine gas evolution is exacerbated by the presence of high valence manganese ions which increase the solution potential (Miller 1995). A MRT (molecular recognition technology) pilot unit made by IBC Advanced Technologies Inc. was successfully used in the Chuquicamata Division of Codelco, Chile to maintain low levels of chloride (Dale et al. 1999).

3.5 Manganese

Manganese is often associated with copper minerals and can build up in processing circuits. The control of dissolved manganese in copper SX-EW circuits is very important as it has significant negative effects in both the solvent extraction circuit as well as the electrowinning tankhouse. Manganese control is particularly important because once significant quantities of manganese build up in the electrolyte the solution potential will increase causing more manganese to enter the system in a positive feedback loop (Miller 1995, Zhang 2007).
Manganese (II) in the SX plant initially has limited effects, but when it is transferred to the electrolyte via aqueous entrainment problems arise. Once in the electrolyte manganese (II) can be oxidized to higher valence manganese (III), manganese (IV) and manganese (VII), leading to lower current efficiency of the plating operation. Energy is not only wasted on these side oxidation reactions, but also because the presence of manganese can lower the conductivity of the electrolyte. The formation of MnO$_2$ from manganese (IV) also has negative effects on electrode performance, such as causing faster degradation of lead anodes via formation of a lead oxide layer that sloughs off (Hecker et al. 1995). Manganese also causes nodular growth of copper on cathodes, reducing final copper quality (Hakakari 1995).

The presence of MnO$_4^-$ and other high valence manganese ions in the spent electrolyte drives the solution potential up. This causes several problems in series. First is that organic reagent degradation is enhanced by increased solution potential. Naturally this causes a decrease in loading capacity and effectively, kinetics. Second, the products of these organic degradation reactions are surface active, which makes them stabilize emulsions and slow down phase
separation in settlers (Miller 1995). This enhances aqueous entrainment in the organic phase, which in turn leads to more manganese build up in the electrolyte. In this way manganese buildup can cascade through a circuit, leading to a drastic reduction in plant performance.

Several strategies, both physical and chemical, can be used to minimize the negative effects of manganese in copper SX-EW circuits. Physically, picket fences or mesh netting can help promote coalescence and prevent entrainment. Scrupulous crud removal and treatment also helps (Miller 1995). Chemically, since manganese primarily causes problems via high valence ions increasing the solution potential, control of the potential via the addition of a reducing agent can help. Sparging SO$_2$ was shown to be effective at maintaining a solution potential of 400-450 mv provided there was 1 g/L ferrous iron in solution. However, excess SO$_2$ can react with dissolved oxygen to form HOSO$_3$, itself a strong oxidant, so this technique can be risky if used long term (Miller 1995).
3.6 Iron

Iron is ubiquitous in copper solvent extraction circuits, whether because it is dissolved from the mineral feed as in the case of pressure oxidation of chalcopyrite, or because ferrous iron salts are added to the circuit. In either case it affects the design and operation of a solvent extraction plant in several ways. First is how the organic extractant behaves with respect to iron. Copper: iron selectivity has improved a great deal over the course of solvent extraction development and currently ester modified reagents offer the best copper: iron selectivity (Sole et al. 2007). It is primarily ferric iron that competes with copper for absorption (Cupertino et al. 1999). The presence of excessive dissolved iron in the strip electrolyte is undesirable because tankhouse current efficiency is reduced by the cyclical oxidation of iron (II) to iron (III). Iron in the electrolyte can be reduced by improving organic extractant selectivity and also by reducing entrainment of the aqueous PLS in the strip. However, in the case of leach solutions high in manganese but low in iron, iron can be added to the PLS to insure that manganese is not extracted by the organic (Sole et al. 2007). The problems caused by manganese are worse than those caused by iron. Iron (II) is also added to solutions as a way to lower solution potential and reduce high other high valence
metal ions (Cupertino et al. 1999). Once in the electrolyte iron can be removed via the recycle of a bleed stream back to the PLS. However, this is inefficient as it represents a loss of acid and copper. Another solution is the use of ion exchange resins to treat a bleed from the electrolyte and selectively remove iron. This is the Fenix Iron Control Process and it was effective at controlling iron in the Mount Gordon copper plant (Shaw et al. 2006).

3.7 Antimony and Bismuth

Antimony, arsenic, and bismuth are not usually present in PLS solutions in amounts significant enough to cause problems in solvent extraction. However, unless there is a specific method for removing them via an electrolyte bleed stream, they can gradually build up due to aqueous entrainment and reduce the quality of final cathodes. As these elements typically build up slowly, ion exchange or MRT ligand systems are ideal to maintain the purity of the electrolyte. Antimony and bismuth removal ion exchange with phosphonic acid based resin from copper refinery electrolytes was demonstrated at a lab scale in 1995 (Dreisinger and Scholey 1995). Bismuth removal via MRT was piloted successfully at the Caraiba Metais copper refinery in Brazil in 1999 (Dale et al. 1999).
4.0 Solvent Extraction Equipment

4.1 Mixer-Settlers

The simplest and most prolific solvent extraction contactor is a mixer-settler. The two phases are introduced into a tank with a fast moving impeller that creates a dispersion. This dispersion is then mixed with a slower moving auxiliary mixer and given time for contact. Then the dispersion is moved to a settling tank where the phases are given time to separate. The less dense organic floats to the top and passes over a spillway while the heavy aqueous sinks and leaves the cell through a launder (See figure 2). Several design variables can improve the performance of a mixer settler, such as picket fences for flow distribution into the settler, roofs to seal the tanks and prevent airborne contamination, and specialized discharge launders to reduce cross phase contamination (Giralico et al. 2003, Pekkala et al. 1999, Vancas 2003). As mixer settlers are in contact with air, evaporative losses can be significant (Bishop et al. 1999). The primary advantage of conventional mixer settlers is simplicity and low capital cost. However, high flow rates can make operational optimization of mixer settlers difficult, and reagent inventory must be higher to compensate for higher losses and lowered efficiency.
4.2 Pulsed Columns

One alternative to conventional open air mixer settlers in SX is the use of pulsed columns. Pulsed columns have been used in SX for decades but only recently have they been applied to industrial scale copper production. In a pulsed column the aqueous phase is into the top of the column while the organic enters from the bottom. A pulse, typically generated by a blast of compressed air, agitates and mixes the liquids while they pass each other in countercurrent fashion. A series of disc-shaped baffles and rings force the fluids to travel in a serpentine path rather than short circuiting down the center. At the top and bottom
decanters separate the phases and allow collection of the barren liquor and the loaded organic (Nielson and Vancas 1999). A schematic design is shown in figure 3. Unlike conventional mixer-settlers, pulsed columns can be run continuous with respect to either minor-phase or major-phase. The position of the organic/aqueous interface will depend on whether the column is running organic continuous or aqueous continuous. For the former, the interface is in the bottom decanter and in the upper decanter for the latter.

Figure 3. Schematic design of a Bateman Solvent Extraction Pulsed Column (Nielson and Vancas 1999)
One improvement of the pulsed column is to add an intermediate decanter in the middle of the column to allow stripping and extraction to take place within a single column. This design was piloted in 2003 by Bateman Engineering and Mexicana de Cananea (Lerner et al. 2003).

There are several important design variables for a pulsed column – phase continuity, phase ratios, flux rate, and pulse intensity. The choice of phase continuity is decided by the construction materials of the column. They should be wetted by whichever phase is to be continuous – plastic for organic continuous, metal for aqueous continuous. Organic continuous will lead to more aqueous entrainment in the organic, and vice versa. Entrainment can be reduced by extending the length of the decanters to allow more time for separation.

Phase ratios are determined by the tenor of incoming liquor and the loading capacity of the diluted extractant. The A/O ratio for heap leach liquor will be higher than for high grade pressure oxidation liquor. Pulse intensity is a product of the pulse frequency and the pulse amplitude. Pulse intensity affects the dispersion of the phases. Flux rate is the total flow rate per unit area. Typical pulsed column fluxes
are in the range of 30 to 50 m³/h/m², roughly an order of magnitude higher than conventional mixer settlers (Nielson and Vancas 1999, Lerner et al. 2003). This leads to a much smaller physical footprint for a pulsed column setup, although of course the vertical space needed is higher.

Several advantages of pulsed columns have generated industry interest. As the columns are completely sealed, evaporative losses are nil and no particulate matter can enter the liquids. This is not only a benefit for reagent consumption but also for safety since many SX vapours can be dangerous or flammable. As pulsed columns form larger droplets than mixer settlers, less crud is formed, leading to less organic losses to crud entrainment and other related problems. On the other hand, pulsed columns have a higher capital cost than conventional mixer-settlers.

4.3 Molecular Recognition Technology

Molecular recognition technology (MRT) uses highly selective ligand molecules to separate or recover specific ions. MRT can be used to recover dilute ions in the ppb range even the presence of high concentrations of competing ions. MRT columns achieve high selective
loading with single passes. The cost of the ligand reagents is high so it is unlikely that MRT will be used for primary metal production. However, it has shown success in the recovery of PGMs from anode slimes in copper electrowinning as well as the purification of copper electrolytes via the removal and control of elements such as bismuth, antimony, and free chloride (Dale et al. 1999, Bruening et al. 2003). Bismuth removal from a copper electrolyte by MRT is performed in a circuit designed by Bateman Engineering and IBC Advanced Technologies at Port Kembla Copper, Australia, since 1997. At this plant bismuth is managed at 100-200 ppm in the electrolyte by bleed treatment, keeping bismuth concentration in the copper cathode to <0.3 ppm. Once the ligand resin reaches capacity the bed is eluted with strong sulphuric acid solution and the bismuth is recovered from the eluate as a saleable salt (Izatt et al. 2000). MRT circuit flowsheets resemble ion exchange flowsheets, with MRT ligand columns in place of IX resin columns.

4.4 Non-Dispersive Solvent Extraction

Non-dispersive two phase reactors are commonly used in the pharmaceutical industry but they can also be applied to solvent extraction. In non-dispersive solvent extraction (NDSX) the aqueous
and organic phases contact one another across a tubular membrane. The hydrophobicity of the membrane material governs whether the organic flows on the inside or outside of the tubes. If the material is hydrophobic, the organic should be inside the tube with a slight overpressure applied to the aqueous phase to prevent organic entrainment in the aqueous (Gabelman and Hwang 1999). Celgard GmhB has developed a microporous hollow fiber membrane module for solvent extraction (see Figure 4). The cell operates with flow across the fibers by means of a central baffle. The advantage of NDSX technology is that hollow fiber membrane cells can achieve high levels of interfacial surface area between the organic and aqueous phases while minimizing common challenges in conventional mixer-settlers, such as emulsification problems, the need for dispersion and coalescence, and crud issues. NDSX is best suited for use as a method of removing low concentrations ions from large volumes of solution. This is particularly true as conventional mixer-settlers have difficulty recovering copper below 1 g/L without an excessively large organic inventory. NDSX has been demonstrated on a bench scale as effective at recovering dilute copper from an ammoniacal solution. This was achieved in a circuit of single stage extraction and single stage stripping using β-diketone LIX 54 (Gameiro et al. 2007).
Figure 4. Celgard Liqui-Cell Extra Flow Membrane Contactor (Gamiero et al. 2007)

4.5 Emulsion Liquid Membranes

Emulsion liquid membranes (ELMs) were first invented in 1968 by Li for the hydrocarbon processing industry, but since then they have also
shown potential for the solvent extraction of heavy metal ions (Li 1968). During ELM extraction a water in oil emulsion is created and stabilized with surfactants. The oil phase contains the solvent extraction reagent while the aqueous phase within the droplet is the stripping solution. This allows stripping and extraction to take place within a single unit operation (see Figure 5). After the emulsion contacts the pregnant solution the loaded emulsion is separated from the feed stream and demulsified. The metal in the separated strip solution can then be electrowon or crystallized for recovery (Sengupta et al. 2006a). Advantages of ELM processing are a substantially lower requirement of organic inventory, high specific surface area leading to fast extraction/stripping kinetics, and a removal of equilibrium limitations of extraction leading to high recovery and low metal concentrations in the barren liquor. The primary challenge relating to ELM solvent extraction is the rupture of emulsion droplets. This problem has several causes. Inadequate surfactant in the organic phase will reduce the strength of the emulsion layer, increasing rupture likelihood. Strong mixer agitation in the cell will break the emulsion layer with excessive shear stress. Rupture can also occur after a droplet has absorbed a lot of water, swelling it beyond its original capacity (Sengupta et al. 2006b). In all cases rupture is a costly problem as the high grade strip solution is lost and the pH of the
Pregnant solution will be modified by the high acid strip solution. This technology has been studied for use in low tenor ammoniacal solutions (Sengupta et al. 2007) as well as acidic mine waste water but as of this writing there has been no commercialization due to concerns about the stability of ELMs.

Figure 5. Schematic of an ELM globule (not to scale)

5.0 Summary

Copper solvent extraction is a mature and robust technology that can be applied to a wide variety of leach liquors, from high acid high copper tenor pressure oxidation solutions to dilute acid heap leach
leachates. Organic extractants fall under aldoxime and ketoxime classes, with ester modified aldoxime reagents playing the most important role in industry today. The formulation of the organic extractant should be chosen to avoid degradation and co-extraction of other ions in the system. As organic extractant capacity and kinetics are strong functions of pH, acid management in solvent extraction is very important to maintain efficient operation of SX circuits. Acidity can also affect the amount of siliceous crud formed through the circuit. Crud must be managed to insure that a thin layer of compact crud forms to enhance phase separation but to prevent the excess crud buildup, particularly low density crud which is difficult to remove. Various impurities can affect the operation of the SX circuit. Excess dissolved silica will precipitate as low density crud. Nitrate, even in small amounts, can increase the rate of hydrolytic degradation of the organic reagent. The presence of manganese or iron can increase solution caused and enhance organic degradation. Antimony and bismuth have minimal effect on the SX circuit but negatively impact copper cathode quality in the tankhouse. Alternatives to the conventional solvent extraction mixer settler setup have been developed recently, including pulsed columns and non dispersive contactors. Ion exchange resins and molecular recognition technology can be useful ways to control electrolyte impurities without resorting
to wasteful bleed recycles. Emulsion liquid membranes are in development but have not been shown to be feasible for industrial use so far.
6.0 References


