GLOBAL SURVEY OF COPPER SOLVENT EXTRACTION OPERATIONS AND PRACTICES

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ABSTRACT

Global practice in copper solvent extraction is reviewed, based on individual plant operating data for 2012. Trends in feed and electrolyte compositions and flow rates, and extractant and diluent selection, together with their impact on copper recovery and reagent utilisation, are reviewed. Optimisation of copper transfer and copper production by changing circuit configurations with changing feed composition during the life of mine is discussed. Emerging trends in equipment design are assessed. The rapid adoption and expansion of this technology in the African Copper Belt is also addressed, along with the unique challenges pertaining to operating conditions in this region.
INTRODUCTION

Continuing from similar surveys carried out in 1997, 1999, 2003, and 2007 [1-4], global operating practice in copper solvent extraction (SX) in 2012 is reviewed. Contributing operations include established sites from the USA (10), Chile (11), Peru (1) and Mexico (1), as well as newer operations from Africa (4). Trends in operating conditions and performance, as well as equipment design and process technology choices are analysed. The significant expansion in production in the African Copper Belt is also discussed. The detailed survey results are provided on the CD-ROM of the proceedings.

In contrast to past experience, there is an increasing reluctance of many operations to participate in this survey, indicating a more competitive commercial operating environment: a more sophisticated understanding of this technology is evolving, such that optimisation of process conditions may add competitive advantage. Several new operations currently commissioning or ramping up to full production in Africa and Europe declined to participate since their operations are not yet at stable performance. It is also notable that more than 100 copper SX plants exist today in China [5]. Although most of these are smaller than 1,000 t/a Cu and none of the Chinese operations participated in this survey, they represent a growing and important influencer in this industry, particularly through the explosion of Chinese-owned operations outside China, notably in Africa. Most Australian operations have closed in recent years.

There are currently some 75 operations worldwide with cathode production above 10,000 t/a. The top ten producers account for approximately 45% of the total SX copper production, which is in the order of 4 million t/a. The largest of the plants that participated in the survey is Morenci, AZ (245 kt Cu in 2012), while the smallest is Pinto Valley, AZ (2.77 kt). It is significant that 72% of the operations produced below their nameplate capacities in 2012 (Figure 1). In Chile and southwestern USA, this is largely due to declining ore grades, while in Africa this reflects recently commissioned operations that are still ramping up. A notable performance is that of Tenke Fungurume (Democratic Republic of Congo, DRC), which produced 37% above design capacity.

TRENDS IN OPERATING CONDITIONS AND PROCESS PERFORMANCE

Distinct characteristics emerge when one examines copper SX on a regional basis.

North America is the most mature region, with mostly low grade, mixed oxide/secondary sulfide ores. The pregnant leach solutions (PLS) are typified by low Cu, low Fe, high Mn, and a wide range of pH values. The circuits are mostly configured in series-parallel to allow for increased PLS throughput. At a number of sites the high PLS flowrates give extraction organic-to-aqueous (O:A) ratios well below 1:1, which results in raffinate stages being operated in aqueous phase continuity. Emphasis on organic recovery is therefore important (e.g., increased retention time in the raffinate pond; use of equipment such as Pace Setters, Jameson cells, and pond skimmers).
In South America the operations process mostly medium-grade ‘oxide’ and secondary sulfide deposits and are primarily located in the Atacama Desert. The circuits are usually configured in series, i.e., 2E+2S and 2E+1S. Leaching of the predominant mineral in the region, atacamite (Cu₂Cl(OH)₃), results in elevated levels (1 to 30 g/L) of chloride in the PLS. Wash stages are common to control chloride transfer to the electrolyte. Several operations have experienced nitration issues associated with high levels of nitrates dissolved in the PLS.

In Central Africa, ore copper grades are significantly higher than in other parts of the world, ranging from 2.5 to 5%. The minerals are predominantly malachite and heterogenite, which are processed by grinding and agitated leaching rather than by heap leaching. Most SX circuits are series with either two or three extraction stages combined with two strip stages. In many of the operations, cobalt is produced as a by-product.

**PLS Composition**

The nature of the PLS varies considerably (0.23 to 43 g/L Cu), depending largely on geographic location (Table 1). Chilean operations (mainly heap, dump, and run-of-mine leaching) frequently have elevated levels of Fe in the PLS due to secondary sulfides (as well as chloride, nitrate, and elements such as W and Re); the African agitated leach operations contain Co in the PLS and much higher levels of total suspended solids (TSS) which exacerbate crud formation. Average Mn levels are similar across the globe, but the ratio of Fe:Mn is usually lowest in African plants and highest in North American plants.
Table 1 – Variation of average PLS composition with location

<table>
<thead>
<tr>
<th>Location</th>
<th>Cu (g/L)</th>
<th>pH</th>
<th>Fe (g/L)</th>
<th>Mn (g/L)</th>
<th>Co (g/L)</th>
<th>Cl (mg/L)</th>
<th>TSS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>1.1</td>
<td>2.1</td>
<td>1.8</td>
<td>0.98</td>
<td>-</td>
<td>62</td>
<td>33</td>
</tr>
<tr>
<td>South America</td>
<td>3.2</td>
<td>1.9</td>
<td>5.8</td>
<td>1.01</td>
<td>0.06</td>
<td>870</td>
<td>44</td>
</tr>
<tr>
<td>Africa</td>
<td>17.3</td>
<td>1.7</td>
<td>3.4</td>
<td>0.90</td>
<td>6.7</td>
<td>-</td>
<td>137</td>
</tr>
</tbody>
</table>

Advance and Spent Electrolyte Composition

There is little variation in the composition of the advance electrolyte produced in the SX process, due to the well-known parameters that are required to achieve electrowinning of high quality copper cathode (Table 2). The average ΔCu across the SX strip circuit is 11.9 g/L, with the spent electrolyte advancing from 36.1 to 48.0 g/L. The acid content of the spent electrolyte influences the electrolyte conductivity as well as the stripping efficiency and copper transfer across SX: this parameter averages 183 g/L for the survey data. The high Co content of the electrolytes in Africa results from aqueous-in-organic entrainment of the high Co-containing PLS to the loaded organic phase. The large differences in Fe content of the electrolyte result from varying regional Cu contents of the PLS: the higher the Cu content of the PLS, the greater the degree of acidification of the raffinate, and the lower consequent extent of chemical transfer of iron to the electrolyte by co-extraction on the loaded organic phase. It is well known that the presence of Fe(III) is detrimental to the current efficiency of copper electrowinning [5].

Table 2 – Variation of average electrolyte composition with location

<table>
<thead>
<tr>
<th>Location</th>
<th>Cu (g/L)</th>
<th>H₂SO₄ (g/L)</th>
<th>Co (mg/L)</th>
<th>Cu (g/L)</th>
<th>Fe (mg/L)</th>
<th>Mn (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>36.1</td>
<td>182</td>
<td>125</td>
<td>46.3</td>
<td>1780</td>
<td>57</td>
</tr>
<tr>
<td>South America</td>
<td>37.0</td>
<td>183</td>
<td>169</td>
<td>47.9</td>
<td>793</td>
<td>125</td>
</tr>
<tr>
<td>Africa</td>
<td>35.3</td>
<td>187</td>
<td>1890</td>
<td>50.9</td>
<td>407</td>
<td>91</td>
</tr>
</tbody>
</table>

Extractant and Diluent

Cytec currently dominates the global supply of extractant with their ACORGA® range of extractants, most of which are modified aldoximes and modified aldoxime-ketoximes. The other major supplier is BASF, with the LIX® range of extractants, which are typically ketoxime-aldoxime blends. SNF Flomin has recently entered the market, supplying the CuPRO MEX extractants, and which are currently being tested at three Chilean operations. Extractant concentration employed (Table 3) obviously bears a direct relationship to the Cu tenor of the PLS (Table 1) and extraction efficiency required: in this survey, extractant concentration ranged from 3 vol.% for a PLS containing 0.23 g/L Cu (Pinto Valley, AZ) to 35 vol.% for the treatment of a PLS containing 22.5 g/L Cu
(Mutanda, DRC). The low solids’ content of the PLS and excellent attention to operating conditions allow the Chilean operations to achieve both high extractant utilisation (high net copper transfer) and low extractant consumptions (Table 3).

<table>
<thead>
<tr>
<th>Location</th>
<th>Concentration (vol.%</th>
<th>Net transfer (g/L Cu/vol.%</th>
<th>Consumption (kg/t Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>8.7</td>
<td>0.19</td>
<td>3.9</td>
</tr>
<tr>
<td>South America</td>
<td>15.4</td>
<td>0.28</td>
<td>2.7</td>
</tr>
<tr>
<td>Africa</td>
<td>30.3</td>
<td>0.23</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Safety and carbon footprint considerations dominate diluent selection (Table 4). In Chile, many operations have recently changed from partially aromatic diluents to those containing <0.5% aromatic content. These aliphatic diluents typically have high flashpoints (>80°C) and low volatility. In North American operations, aromatic content is somewhat higher, with a spread between operations using non-aromatic and partially aromatic diluents; in Africa, diluents containing higher aromatic content are preferred for the enhanced solvating capacity that this offers for the higher extractant concentrations in use in this region. It is notable that indications of a widespread move towards aliphatic diluents, predicted for the SX industry some years ago, does not seem to have materialised: it is evident that some aromatic component in the diluent (8 to 25 vol.%) is preferred, because of the chemical and physical advantages that this imparts [6,7].

<table>
<thead>
<tr>
<th>Location</th>
<th>Aromatic content (vol.%</th>
<th>Flashpoint (°C</th>
<th>Consumption (kg/t Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>12.2</td>
<td>79</td>
<td>31.4</td>
</tr>
<tr>
<td>South America</td>
<td>10.0</td>
<td>80</td>
<td>22.9</td>
</tr>
<tr>
<td>Africa</td>
<td>18.0</td>
<td>87</td>
<td>12.4</td>
</tr>
</tbody>
</table>

**Extraction and Stripping Efficiencies**

Despite the wide range of PLS Cu concentrations treated, extraction efficiency remains high (average 94.2%) under most conditions (Figure 2) – testimony to the versatility of extractant performance and range of circuit configurations that today enable these high efficiencies to be achieved. High overall recoveries from high PLS tenors are also often facilitated by use of a split circuit or processing through a second SX circuit.

Complete stripping of the loaded organic phase is never achieved because of the chelating nature of copper extractants. The acidity of the spent electrolyte is the main parameter influencing the extent of stripping that is possible (Figure 3), however stripping also depends on the specific extractant chemistry (ketoxime and/or modified
aldoxime), circuit staging, and other operating conditions. Operating at higher spent electrolyte acidity permits a lower Cu concentration on the stripped organic phase and increases the electrolyte conductivity (lowers the electrowinning energy requirements), however, strong sulfuric acid also hydrolytically degrades the extractant and can result in increased extractant consumption. The highest spent electrolyte acidity recorded in this survey is 202 g/L H₂SO₄ at Quebrada Blanca (Chile). A compromise of operating conditions to minimise operating costs, while maintaining product quality, is always necessary.

Figure 2 – Relationship between Cu content of PLS and extraction efficiency

Figure 3 – Relationship between spent electrolyte acidity and stripping efficiency
Organic Losses and Reagent Consumptions

Organic losses to the raffinate vary between 7 and 125 mg/L, while those to the advance electrolyte are given as 1 to 250 mg/L. It would, however, generally be expected that entrainment losses to the electrolyte would be lower than those to the raffinate because of the higher acidity of the electrolyte and greater density difference compared to the organic phase. Extractant consumptions (Table 3) vary widely across the plants surveyed, from 1.7 to 8.7 kg/t cathode Cu, with a strong dependence on extractant concentration and solids’ content of the PLS. A high TSS content in the PLS generally correlates with high organic losses to the raffinate, although there are notable exceptions to this (Figure 4). Figure 5 indicates little apparent relationship between organic entrainment losses to the raffinate and advance electrolyte and overall extractant consumption: this is likely due to difference in efficiencies of organic reclamation from ponds and crud. This unexpected observation also highlights probable errors in reporting of entrainment figures: accurate direct measurements of entrainment losses are difficult to achieve due to the inherent inaccuracies of sampling a highly variable and non-homogeneous fluid, and analysis methods remain less than ideal [8,9]. The most reliable indication of control of organic losses is generally the extractant consumption, as measured by the volume of extractant added to the organic phase over a given period. High extractant consumptions can also be due to other factors, such as high rates of degradation (such as by nitration at Lomas Bayas, Chile [10]) or high temperatures.

Diluent loss occurs primarily through evaporation, with secondary sources of loss by organic entrainment and crud. Diluent consumption therefore varies widely (Table 4), depending on ambient temperature and relative humidity, and on whether the settlers are open, have covers, or have building roofs. The low consumptions measured on the African plants are influenced by the much lower proportion of diluent in the organic phase due to the high extractant concentrations employed (Table 3).

Figure 4 - Effect of solids’ content of PLS on organic losses to the raffinate
Staging

Most older plants in North and South America have two extraction stages and a single strip stage. With declining PLS grade, many of these circuits have converted their original series configuration to include several stages in which a parallel PLS stream is introduced, thereby allowing copper production to be maintained from an increased total PLS flow. In the recently commissioned African plants, the higher tenors of the agitation leach circuits (>30 g/L Cu) require a greater number of stages to maintain extraction efficiency. The viscosities of modern extractants permit a maximum extractant concentration of ~35 vol.% to be employed, so high net copper transfer is maintained by use of higher O:A flowrate ratios and increasing the number of stages. Kamoto Copper (DRC), for example, commissioned in late 2012, has three trains of three extraction and two strip stages, which is typical for new plant designs in this part of the world.

In Chile, where the PLS typically contains high chloride (and sometimes nitrate) from leaching of minerals from the Atacama Desert, one wash stage is usual. Wash stages are not commonly found in the African or North American circuit designs, although Sierrita and several of the Morenci plants do include a wash stage for limiting iron transfer to the electrolyte by aqueous-in-organic entrainment.

Mixers and Settlers

With respect to mixer design, the newer plants use cylindrical mixing boxes with a primary and secondary mixer in each stage. Mixer residence times of 3 min are
typically employed. There is a wide range in the style of impellers used: those surveyed range from 9 to 83 m³ in volume and from 7.5 to 134 kW in power. Outotec’s Spirok and DOP mixer designs have received some application in copper, including at Kokkola (Finland), Casserones, Radamo Tomić, Zaldivar, Franke (Chile), Milpillas (Mexico), Sepon (Laos), Cobre Las Cruces (Spain), and Chambishi (Zambia). Tenova Bateman Technologies recently presented a new impeller design, claimed to improve mass transfer and reduce entrainment losses [11]. Both extraction and strip circuits almost universally run organic-continuous, although older plants, pushing for production targets at high PLS flowrates and low tenors, increasingly run aqueous continuity in their extraction stages and accept the higher organic losses that this will inevitably introduce.

Modern settlers are designed with settling duties of 3 to 5 m³/m²/h. There is considerable variation in the design of settlers from dimensions to the number of picket fences and additional settler furniture. Most settlers are 1 m deep, while length ranges from 12 to 34.5 m, and width ranges from 3.7 to 30 m. Organic depth averages 0.27 m in both extraction and strip stages, with a range of 0.1 to 0.5 m. New plants are increasingly employing stainless steel as the material of construction—although considerably more expensive than the alternatives, it offers valuable resistance to fire initiation and propagation. Increasing use of reverse flow settlers is evident, such as recently installed at Milpillas and Kamoto Copper. Coalescence in settlers is usually facilitated by the installation of one to three picket fences. Some plants use hydrophobic coalescing packs. Quebrada Blanca has modified their settler internals using PIP technology, developed by Igor Polski, in the feed distribution, the picket fences, and in the settler overflow. These modifications allow a reduction of 70% in aqueous entrainment [12].

Ancillary Equipment

Crud is usually removed by pumps and treated by centrifuge to recover the organic component. Most operations treat the recovered organic with clays, zeolites, or diatomaceous earths before returning it to the SX circuit. Organic recovery from aqueous streams is facilitated by the use of aftersettlers, flotation columns, carbon columns, and directly from the surfaces of aqueous tanks and ponds. The use of coalescence packs in loaded organic tanks assists with removal of entrained PLS ahead of the strip circuit.

Modern Plant Design Trends

Where capital constraints permit, new or refurbished SX circuits are more frequently designed upfront for multiple pipe configurations, thereby allowing processing flexibility and for combinations of series and parallel staging to be readily implemented over the lifetime of plant, as the nature of the ore body, PLS, or economic conditions change. Where footprint and topography permit, processing of the PLS through three or four parallel trains, spaced some distance apart from each other, is the preferred approach to minimising the risk of fire spreading through all parts of a circuit as well as mitigating the business interruption loss that occurs following a fire event [13]. This approach is well exemplified by the Spence (Chile) design and layout.
Optimisation of new and existing mixers and settlers is increasingly facilitated by computer-aided modelling and computational fluid dynamic simulations. This is seldom carried out for specific plant designs because of cost, but engineering companies and research consortia are sponsoring interesting work in this area, the results of which should manifest in the designs of the future [8,14,15]. Contacting equipment other than mixer settlers is unlikely ever to be used in the copper industry, mainly due to the small number of stages that are required for extraction and stripping and the relatively slow extraction kinetics of oxime extractants.

Fire-fighting systems are receiving increasing attention in recent designs [16]. One of the more significant developments is high pressure water fog systems (installed at Sepon and Cobre Las Cruces). Traditionally, fluoroprotein (FP) and aqueous film-forming foam (AFFF) systems have typically been employed, but these are difficult to test once installed since they affect the phase disengagement properties of the organic phase (FP more than AFFF) and it can take some time for the situation to restore itself. Water fog does not have this problem. Although the capital cost for water fog is greater than that of foam systems, the life-cycle cost is estimated to be cheaper. However, a new patented, proprietary formulation foaming agent, recently tested, apparently washed out of the organic phase within two plant cycles and showed excellent characteristics. This is combined with a unique foam make up and delivery system that is reported to reduce the installed cost to 25% of a conventional foam system. It is currently being designed for three large African plants.

**COMMISSIONING OPERATIONS AND PROJECTS**

In Europe, two interesting flowsheets are under commissioning and ramp-up. Cobre Las Cruces (Spain) (72 kt Cu/a commissioned in 2008), treats a copper concentrate by agitated ferric leaching at 90°C, which produces an SX feed containing ~10 g/L Cu and 50 g/L Fe. This high iron content in the PLS gives rise to some challenges in achieving selectivity of copper transfer to the advance electrolyte [17]. Assarel Medet (Bulgaria) is a 2,000 t/a Cu plant designed by Outotec, which is ramping up from commissioning in 2009. This operation faces challenges of -20°C temperatures and ambient wind speeds of 25 m/s. This plant is the first to combine both straight- and reverse-flow mixer settlers, and has very compact settlers with stage efficiencies of 95% and settling rates double the industry standard at 8.8 to 9.7 m³/m²h [18].

Most large, new copper projects under design, construction, or commissioning today are in the African Copper Belt (Table 5). The combined cathode capacity coming on line is likely to ensure that this region overtakes Chile as the primary producer of SX copper within the next decade. Most operations are agitated atmospheric or pressure leaching operations, which produce PLS tenors above 30 g/L Cu and contain relatively high TSS, although heap leaching accounts for a small proportion of the intended production. Most of these operations also produce a cobalt product.
Table 5 - Copper Belt projects in design, construction, and commissioning

<table>
<thead>
<tr>
<th>Project / Plant</th>
<th>Location</th>
<th>Total prodn (kt/a Cu)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chambishi</td>
<td>Kitwe, Zambia</td>
<td>60</td>
<td>Ramping up</td>
</tr>
<tr>
<td>Kamoto Copper</td>
<td>Kolwezi, DRC</td>
<td>270</td>
<td>Commissioning SX2&amp;3</td>
</tr>
<tr>
<td>Tenke Fungurume</td>
<td>Tenke, DRC</td>
<td>220</td>
<td>Commissioning additional SX</td>
</tr>
<tr>
<td>Kansanshi</td>
<td>Solwezi, Zambia</td>
<td>150</td>
<td>Commissioning additional SX</td>
</tr>
<tr>
<td>Kipoi</td>
<td>Likasi, DRC</td>
<td>50</td>
<td>Construction</td>
</tr>
<tr>
<td>Roan Tailings</td>
<td>Kolwezi, DRC</td>
<td>105</td>
<td>Detailed design</td>
</tr>
<tr>
<td>Sicomines</td>
<td>Kolwezi, DRC</td>
<td>80</td>
<td>Detailed design</td>
</tr>
</tbody>
</table>

CONCLUSIONS

This 2012 survey shows that a wide range of PLS compositions are successfully processed by SX to produce high-purity copper cathode from the downstream electrowinning process. Traditional operations in the southwestern USA and Chile typically treat low tenor solutions from heap leaching, which have low solids’ content and operate essentially trouble-free. In contrast, operations in Africa treat very high tenor liquors from agitation and pressure leaching, with high solids’ contents, and in far more difficult operating environments. The proliferation of projects in the African Copper Belt indicate that this will become the dominant copper-producing region of the world within the next decade, introducing many new challenges for equipment and reagent vendors, as well as for operators.

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REFERENCES