

# Intec Base Metal Processes

## *Realising the potential of Chloride Hydrometallurgy*

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## **Abstract**

*The application of chloride hydrometallurgy to the treatment of base metal sulfide concentrates and its inherent advantages has been well documented for over a century. The chloride/bromide based Intec Copper Process and Intec Zinc Process offer a unique approach to such treatment, central to which is the ability to generate the powerful oxidant,  $\text{BrCl}_2^-$  at the anode. The benefits of this approach are evident in all process stages and are wide ranging, to offer superior, low cost and sustainable production of high purity metal. In the leaching stage, high metal extractions that include precious metals are achieved under the mild conditions of 85°C and atmospheric pressure in the one circuit. Oxygen input through air injection and minimal sulfur oxidation to sulfate combine to result in the lowest energy consumption during leaching when compared to equivalent hydrometallurgical processes. In the purification of the PLS, the Intec Processes use low cost cementation and precipitation through alkali addition. In comparison, all other hydrometallurgical processes use SX, which is burdened by onerous cost and complicated operations. In the electrowinning stage, the Intec Processes benefit from their ability to generate soluble  $\text{BrCl}_2^-$  at the anode rather than oxygen.*

## **Introduction**

Dutrizac [1], in a 1991 review of chloride hydrometallurgy for sulfide minerals, concluded that “Despite the successes and apparent advantages of the chloride route, there has been little commercial activity”. Since then, research activity in the field has steadily declined with the emergence of numerous sulfate-based hydrometallurgical processes for base metal treatment. As a consequence, the chloride option was becoming increasingly marginalised as numerous proponents have espoused the virtues of sulfate-based processes.

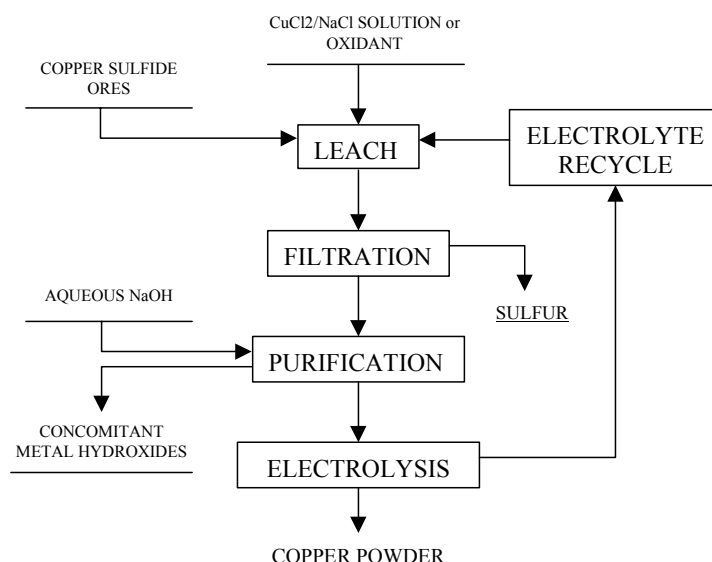
Against these trends of the past decade, the chloride based Intec Copper Process has emerged. It has reached commercial availability through a thorough development program, highlighted by the operation of a 350tpa demonstration plant [2]. The Intec Zinc Process [3] has capitalised on the experience gained from the development of the Intec Copper Process, with which it shares similar unit operations.

The Intec base metal Processes (“Intec Processes”) are unique in their ability to process sulfide concentrates to high purity metal at significantly lower capital and operating cost than conventional smelting. These benefits are delivered with the least environmental impact, as quantified in a Life Cycle Analysis (LCA), comparing the Intec Copper Process with both conventional and emerging technologies [4].

This paper benchmarks the Intec Processes with existing hydrometallurgical and emerging sulfate-based processes. In particular, the performance of key components of these processes are compared in terms of chemistry, engineering and operational perspectives.

## **Base Metal Chloride Hydrometallurgy**

The generalised flowchart in Figure 1 for processing copper sulfide concentrates to recover copper was first conceptualised by Hoepfner [5] in 1893. This bears considerable similarity to zinc hydrometallurgy, whereby zinc oxide from roasting is leached into a solution, which is subsequently purified before an electrowinning step. The Roast Leach Electrowin (RLE) Process for zinc has achieved widespread application over a number of years proving itself a low cost (typically US10-15¢/lb Zn) method of achieving metal production from sulfide concentrates.



**Figure 1:** Generalised flow chart for processing and recovery of copper [5].

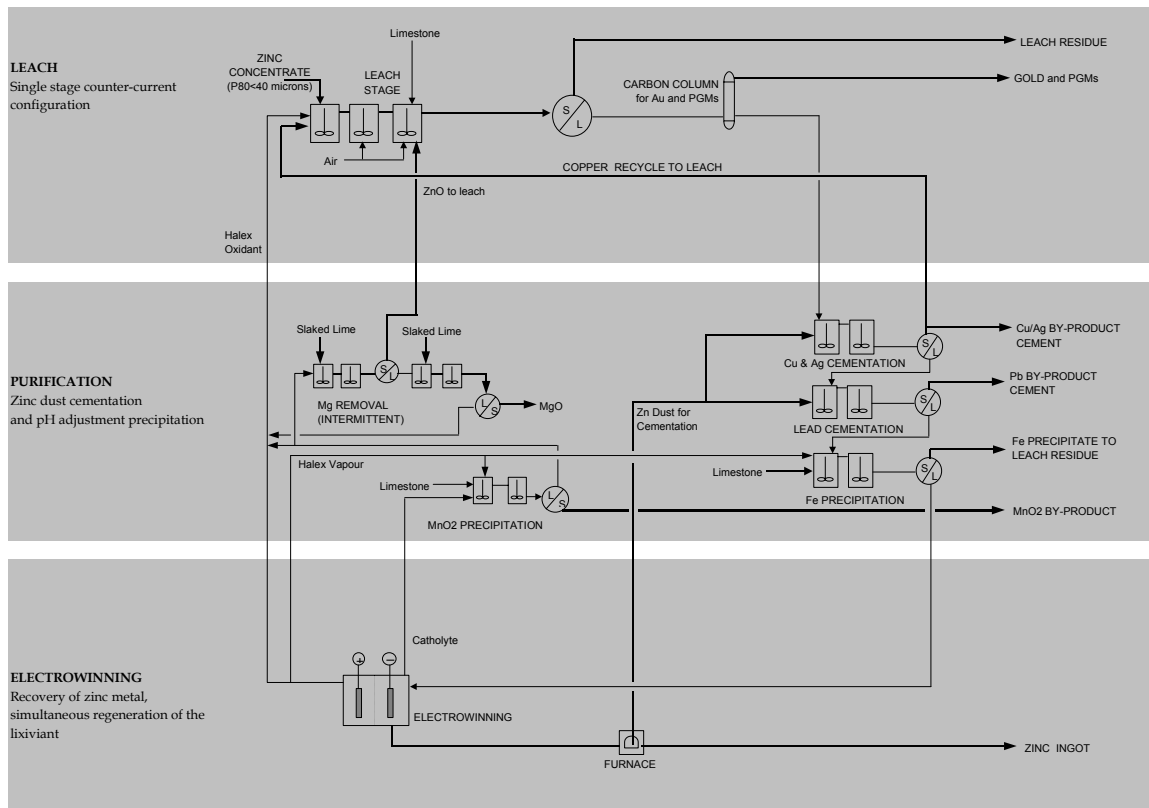
Simply substituting chloride for the sulfate media used in the RLE Process, has the potential to further reduce the cost of zinc production as the capital intensive roasting step can be eliminated. Instead of acid, chlorine gas can be generated at the anode for subsequent direct leaching of sulfide minerals. The ability to economically generate chlorine gas has been realised through the availability of titanium anodes in recent years, and is commercially practiced in the Falconbridge matte-leach and Sumitomo MCLE nickel and cobalt refining processes.

When this leach/electrowinning route is applied to copper, chloride hydrometallurgy has distinct advantages over sulfate systems, primarily through the stability of the cuprous ion ( $\text{Cu}^+$ ) in the chloride media. Cupric ( $\text{Cu}^{2+}$ ) as an oxidant can be used for leaching under relatively mild conditions, whilst electrowinning from cuprous requires half the electrons to that of cupric. Indeed, the CLEAR Process demonstration plant which operated at 30,000tpa copper production over 6 years until 1982 validated the suitability of the chloride route for refractory sulfides such as chalcopyrite [1]. In addition, the CLEAR program demonstrated the suitability of fibre-reinforced plastics and titanium in containing chloride solutions. Some of the shortcomings of the CLEAR Process were lack of solution purification, undesirable chlorine generation at the electrowinning cell graphite anode and high power consumption due to a high applied current density.

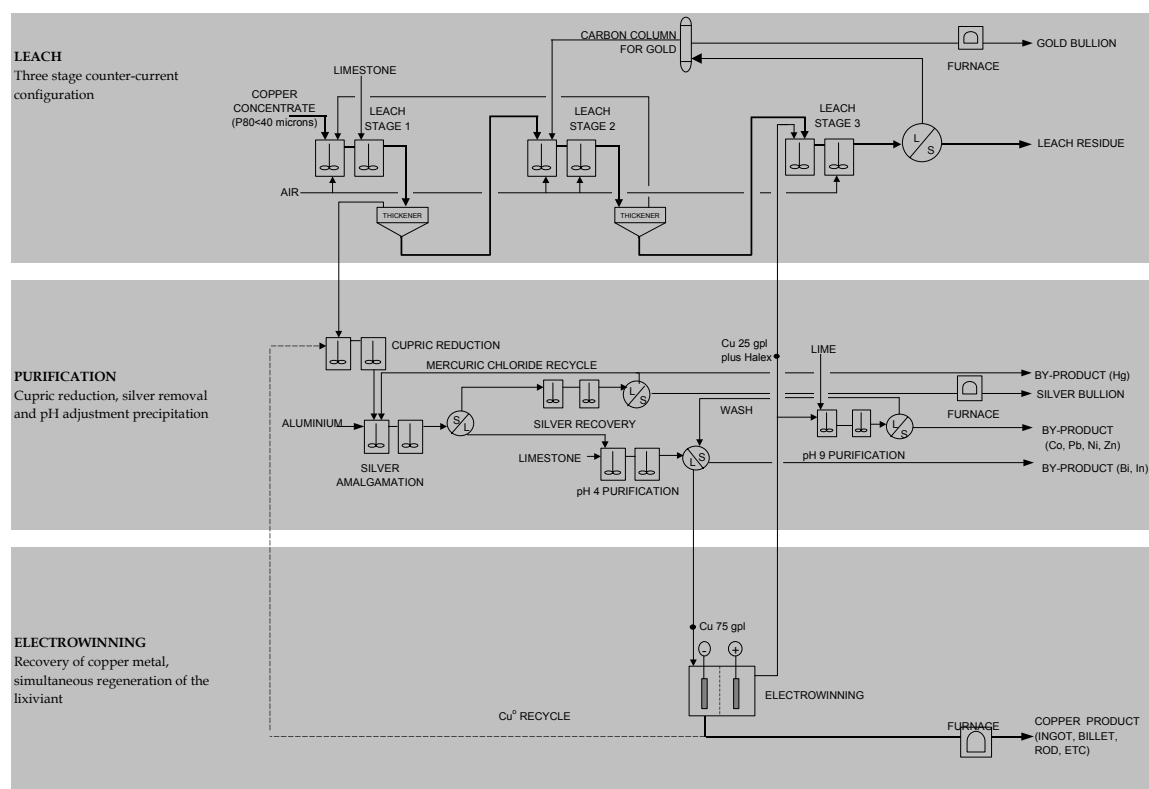
The respective flow diagrams for the Intec Zinc and Copper Processes shown in Figures 2 and 3 further rationalise the production of base metals from sulfides concentrates, through their unique ability to generate the soluble polyhalogen anion  $\text{BrCl}_2^-$  (Halex™) rather than chlorine gas at the anode. Key features include:

- the ability to recovery precious metals in the one process;
- solution purification without the need for solvent extraction, and
- the capability to produce LME Grade A purity copper.

The implications of the above are discussed in detail in the sections that follow.



**Figure 2:** Flow diagram of the Intec Zinc Process.



**Figure 3:** Flowchart of the Intec Copper Process

## Leaching

Leaching in a chloride medium offers numerous advantages over leaching in a sulfate medium. These begin with basic thermodynamics as chloride ions impact through increased stability of metals in solution as well as increased activity of acid. This is highlighted in the work by Peters [6] where the beneficial impact of increasing chloride concentration upon sphalerite, chalcopyrite

and gold dissolution is calculated. In particular, the potential for gold dissolution was calculated at 790mV (versus SHE), making it amenable to leaching by ferric ( $\text{Fe}^{3+}$ ) and a small excess of chlorine.

The impact of chloride on metal dissolution parallels that of cyanide, which is widely used in the production of gold. Cyanide complexes strongly with gold and, with oxygen input through aeration, has the ability to leach gold at atmospheric pressure and ambient temperature. As a consequence, equipment selection, materials of construction and operations are relatively straight forward, which is evident in the ability to economically exploit gold ores containing as little as 1gpt gold. Compared to cyanide, chloride is a weaker complex and thus requires higher temperatures to achieve similar results. Despite this, conditions are sufficiently mild to maintain straight forward equipment selection, materials of construction and operation.

In addition to chloride, the Intec Processes contain bromide, which complexes more strongly with base and precious metals than chloride [7,8]. This permits leaching at atmospheric pressure and 85°C temperature, significantly milder than other known chloride processes which range upwards of 95°C and in most instances at significantly higher pressure [1,8].

The Intec Zinc Process employs a single stage leach and is capable of a wide range of base and precious metals extractions. Alternatively, the Intec Copper Process employs a counter-current leach to capitalise on the stability of cuprous in the chloride medium. This enables a high concentration of cuprous in the pregnant liquor stream (PLS), whilst achieving high metal extractions overall. In both Intec Processes, the presence of  $\text{BrCl}_2^-$ , with an oxidising potential in excess of 1000mV (versus SHE), enables high extraction of gold, which is recovered by adsorption onto carbon.

An important aspect in leaching is the input of oxygen to reject dissolved iron, as occurs in chalcopyrite dissolution. In the Intec Processes air is used to supply oxygen, as it also performs the function of rejecting water in the form of steam. The high efficiency of oxygen uptake by cuprous assists in minimising the air input and consequent heat loss, to enable the balancing of water input and water output through evaporation. At the increased temperatures of other processes, steam loss to spent air increases exponentially and thus oxygen is used to minimise the amount of offgas generated. For a chalcopyrite concentrate with iron rejection as hematite ( $\text{Fe}_2\text{O}_3$ ), each tonne of copper production requires approximately 750kg of oxygen. Jones [9] quotes energy consumption for an oxygen plant at 400kWh/t oxygen, with oxygen plant capital cost estimated at US\$10 million for a 100,000tpa copper plant.

Oxygen consumption is also affected by the degree of sulfate formation in the leach. Leaching in chloride solutions is known to suppress sulfate generation as the majority of sulfur is not oxidised beyond the elemental state. Further, the degree of sulfate formation increases with temperature and pressure, with the mild temperatures of the Intec Processes achieving best practice at less than 5% sulfur oxidation. Sulfate formation is further penalised by the reagent cost of limestone that is used to neutralisation (availability of an copper oxide heap in the immediate vicinity can capitalise on the weak acid generated).

A summary of the leach characteristics for current copper hydrometallurgical processes is presented in Table 1. The Intec Copper Process is the only chloride-based process currently commercially available and is compared with competing sulfate-based processes [9,10,11,12,13].

Property	Intec	CESL	Activox	Total Pressure Oxidation	Bacterial Leaching
Grind Size (P80)	40 $\mu$	40 $\mu$	7-15 $\mu$	40 $\mu$	<10 $\mu$
<b>Grinding Energy</b>	<b>35</b>	<b>35</b>	<b>125</b>	<b>35</b>	<b>125</b>
Leach Configuration	3 stage FRP tanks	Autoclave	Autoclave	Autoclave	Rubber Lined Steel
Temperature	85°C	130-150°C	100-110°C	220°C	45-60°C
Pressure	atmospheric	15 bar	3-10 bar	>30 bar	atmospheric
Residence Time	14 hours	1 hour	1-2 hours	1 hour	>6 days
Cu Extraction	>98.5%	>96%	98%	>98%	>97%
<b>Leach Operation Energy</b>	<b>400 (73)</b>	<b>230</b>	<b>305</b>	<b>590</b>	<b>1655</b>
Precious Metal Leaching	Within Cu Leach	Cyanide Leach of Residue	Cyanide Leach of Residue	Cyanide Leach of Residue	Cyanide Leach of Residue
<b>Precious Metal Recovery Energy</b>	-	<b>200 [9] (42)</b>	<b>200 [9] (93)</b>	<b>200 [9] (93)</b>	<b>200 [9] (93)</b>
O <sub>2</sub> Source	Air	Oxygen Plant	Oxygen Plant	Oxygen Plant	Air
S <sup>o</sup> →SO <sub>4</sub> <sup>2-</sup>	<5%	5-15%	5-15%	100%	>90%
Air Required (kg/t-Cu)	4047	-	-	-	23800
O <sub>2</sub> Required (kg/t-Cu)	-	1140	1140	3000	-
<b>Energy for O<sub>2</sub> production</b>	-	<b>455</b>	<b>455</b>	<b>1205</b>	-
<b>Total Energy</b>	<b>435 (73)</b>	<b>920 (42)</b>	<b>1085 (93)</b>	<b>2030 (93)</b>	<b>1980 (93)</b>

**Table 1:** Leach characteristics of hydrometallurgical processes for treatment of chalcopyrite concentrates. All data for energy consumption refers to electrical energy as kWh/t-Cu. Data in brackets is natural gas consumption in kg/t-Cu for the purpose of heating.

The data in Table 1 highlights the significantly reduced energy consumption for leaching by the Intec Copper Process when compared with sulfate-based processes. The economic consequences of the Intec approach are low operating costs, as energy is a major input to leaching operations. Capital costs also benefit from the absence of an oxygen plant and cyanide leaching for precious metals recovery, which also simplifies operational complexity.

From a maintenance perspective, Intec is advantaged by the reduced temperature and pressure of operations. In the Intec Processes, liquors and slurries are transported with basic centrifugal and hose pumps, which achieve high availability. Alternatively autoclaves require relatively demanding unit operations such as high pressure slurry pumping through check valves, staged heating of feed and slurry let-down in flash tanks. Recent HPAL (high pressure acid leach) plant experience for nickel laterites highlights the problems with the high temperature and pressure approach. Mechanical failures experienced to date [13] include pump, valve and seal failures in the preheat circuit, wear plate erosion and cracks in the autoclave, while flash tanks have experienced titanium liner and overhead piping failures. Low service life of key equipment means frequent downtime for maintenance, thus impacting negatively on availability.

From an environmental perspective, iron rejection in the form of jarosite is often associated with sulfate-based leaching. This is the case for the zinc RLE Process where there is increasing regulatory pressure to eliminate jarosite residues [14,15], with hematite considered more

environmentally acceptable. In the Intec Processes, iron is rejected as hematite due to the presence of minimal sulfate (<0.5g/l) in solution. Further, heavy metals such as mercury, silver and lead are extracted during leaching for recovery as by-products rather than reporting to the leach residue as is the case in sulfate-based systems. Furthermore, unlike the RLE Process, there is no need for roasting, which results in SO<sub>2</sub> emissions to atmosphere with levels dependent on the degree of capital expenditure on scrubbing and acid generation.

Thus, in summary the Intec approach to base metal leaching offers high metal extractions with extensive by-product recovery in the one circuit. Further, when compared to sulfate-based processes, Intec offers superior energy efficiency in an operationally robust and environmentally sustainable manner.

## **Purification of PLS**

The Intec Processes are similar to the zinc RLE Process, in that low cost cementation and precipitation reactions (by limestone and lime addition) are used. This compares with the use of solvent extraction (SX) in all sulfate-based processes. Yet with SX there is still a requirement to remove impurities from the raffinate, which is typically performed by precipitation from a bleed stream [9].

SX thus requires additional unit operations for associated settling, extraction and stripping operations. Supporting these main operations are organic coalescers, filters and cleaning equipment as well as crud treatment and removal systems. Purification by SX is thus burdened by:

- high capital cost at approximately US\$280/at-Cu [10], exclusive of indirect costs;
- significant energy consumption at approximately 500kWh/t-Cu (based on heap leach operations) [16] which along with organic reagent inputs impacts on operating cost;
- complicated commissioning, operation and control impacting on plant availability as SX is interdependent upon upstream leaching and downstream electrowinning;
- environmental concerns of organic loss through entrainment and evaporative loss of organic diluent [17].

Although, the Intec Copper Process and Intec Zinc Process both use cementation and precipitation reactions for purification, the philosophical approach of each process varies greatly. This is due to the difference in chemical properties of copper and zinc. Copper is a relatively noble metal, onto which only silver and mercury cement in the Intec Copper Process. Thus the first step in purification is the cementation of these elements. This is followed by limestone (CaCO<sub>3</sub>) addition to raise the pH to 4 to precipitate impurities such as bismuth, indium and germanium. After filtration of the precipitates, the clear filtrate is fed to electrowinning. All remaining impurities, which include Zn, Ni, Co, Pb, Cd, etc, are less noble than copper and hence copper purity is not affected by their presence. Instead, to prevent their accumulation, a bleed of catholyte is firstly treated to allow removal of copper by precipitation at pH<4, with subsequent removal of the remaining impurities by lime (Ca(OH)<sub>2</sub>) addition at pH 4-9.

Zinc, alternatively, is less noble than most impurities and thus cementation is the predominant method of liquor purification. This is also the case in the RLE Process, but in the presence chloride, zinc is stabilised through complexation relative to metals such as nickel and cobalt [8]. This facilitates the removal of such elements by cementation, that in the sulfate medium are sluggish and often require the addition of additives such as arsenic. The Intec Zinc Process also includes limestone precipitation, which when combined with the addition of the BrCl<sub>2</sub><sup>-</sup> oxidant (Eh>1100mV) has the ability to remove residual iron and manganese from the liquor. This is a distinct advantage over the RLE process in which manganese precipitates as MnO<sub>2</sub> at the anode leading to serious impact on both cell operations and materials handling.

The cementation and precipitation reactions used by the Intec Processes, are performed in simple agitated tanks. Subsequent solids/liquor separation is either by filtration or thickening. Energy consumption is in the order of 100kWh/t metal (Cu and Zn), whilst reagent inputs are recycled metal product and low cost limestone and lime. As a consequence, capital and operating costs are significantly lower than sulfate-based alternatives. Cementation products can be sold to refineries as by-products, whilst the ability to sell precipitation by-products is a function of the impurities and their grade. In particular, payable silver exceeds that for conventional smelting whilst values can be realised for metals such as nickel and cobalt that, conventionally, are not payable.

## Electrowinning

The theory behind electrowinning of various metals in a number of media has been extensively investigated and reviewed by Winand [18]. In particular, Winand identified fields of stability for the possible types of polycrystalline deposits as a function of mass transfer and inhibition intensity. Winand noted that metals can be classified into three groups based on their increasing tendency to adsorb inhibitors:

- normal (Cd, Zn, Sn, Ag);
- intermediate (Au, Cu); and
- inert (Fe, Ni, Co, Pt, Cr, Mn)

Further, anions can be similarly classified by their tendency to inhibit:

- activating ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ );
- intermediate ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ); and
- inhibiting ( $\text{BF}_4^-$ ,  $\text{NH}_2\text{SO}_2^{2-}$ ,  $\text{ClO}_4^-$ ).

Conventionally, the metal produced from electrowinning operations is in the form of a cathode plate. Consistent with Winand's classification above, conventional zinc production by the RLE Process is hampered by the high activity of zinc, which over time results in nodule formation and decreasing current efficiency. As a consequence, plate stripping is typically carried out every 24 hours with the observed overall current efficiency typically <91% and energy consumption at 3,100kWh/t of zinc [19]. Similar performance has been demonstrated in chloride electrolyte by MacKinnon et al. [20], although the addition agent tetrabutylammonium chloride was found to be more effective than glue in producing a flat plate. In both chloride and sulfate systems, the types of impurities significantly influence the performance of zinc electrowinning [20,21]. Consequently, optimisation of electrowinning operations is mainly a function of purification, addition agents and general cell parameters such as current density, stripping cycle, cell configuration and degree of agitation.

The use of chloride instead of sulfate has a more pronounced impact on the electrowinning of copper, due to Cu(I) stabilisation. This is mainly due to the capability to electrodeposit copper by the passage of one electron instead of two as in sulfate solutions. Also benefiting, is anodic oxidation of Cu(I) to Cu(II) rather than oxygen evolution, as in sulfate solutions. These factors, combined with better reversibility of reactions and high solution electrical conductivity, mean copper electrowinning in chloride can operate at approximately one quarter of the specific energy consumption needed for sulfate solutions [18].

Although the energy savings offered by the chloride route are potentially significant, additional capital expenditure is required to operate in the presence of chloride. Stainless steel cathodes used in the sulfate medium are not suitable and this is also the case with lead anodes. Instead titanium must be used for both cathodes and anodes, with the anode enclosed in a porous or non

porous membrane. These features add to the capital cost of electrowinning, and are offset by operating at higher current density and thus increased cell voltage. As a consequence, the benefits of lower energy consumption can be negated to a considerable extent [22]. Further, at these higher current densities, dendritic copper is produced, thus necessitating installation of systems to dislodge and transport the copper from the cell.

Electrowinning in the Intec Processes mirrors the above observation for chloride systems. In the Intec Zinc Process, zinc cathode plate is produced at conditions similar to those for the sulfate-based RLE Process, resulting in similar energy consumption. Where the Intec Zinc Process has a significant advantage is in the anodic reaction where  $\text{BrCl}_2^-$  instead of oxygen is generated at a reduced potential. This is particularly beneficial to the treatment of zinc concentrates with manganese contamination. In the conventional RLE Process, the manganese ultimately precipitates onto the anode as  $\text{MnO}_2$ , requiring onerous anode handling and cell cleaning to enable its removal. In the Intec Zinc Process,  $\text{BrCl}_2^-$  formation occurs at sufficiently low Eh and pH to prevent  $\text{MnO}_2$  precipitation from occurring at the anode. Instead manganese is precipitated as  $\text{MnO}_2$  at controlled Eh and pH in a dedicated circuit.

In the Intec Copper Process, copper is electrowon from Cu(I) at a current density of  $1,000\text{A/m}^2$ , which is greater than six times the productivity of conventional electrowinning in sulfate solutions. Overall the capital cost for electrowinning is approximately US\$300/tpa of copper capacity, similar to that of sulfate-based operations. Energy consumption for the Intec Copper Process at  $1650\text{kWh/t}$  of copper (inclusive of 13% recycle) is significantly lower than that for sulfate solutions. Unlike cathode plate produced in sulfate-based electrowinning, the dendritic product from electrowinning is melted to prevent its oxidation. Although, this increases energy consumption by a further  $400\text{kWh/t}$  of copper, opportunity exists in the melting step to produce value added products such as billet or rod. As in the Intec Zinc Process,  $\text{BrCl}_2^-$  is also generated at the anode to provide significant benefits to leaching as previously described.

## Conclusion

In the treatment of base metal sulfide concentrates to recover high purity metal products, the chloride medium provides significant advantages over sulfate-based processing. Among these benefits are:

- significantly reduced capital and operating cost;
- high metal extraction and recovery in the one circuit including precious metals;
- low energy consumption; and
- sustainable environmental practices with no liquid effluent, benign offgas emissions and stable residues.

The chloride based Intec Copper Process and Intec Zinc Process realise these potential advantages, by combining their unique mixed-halide chemistry with inherently simple unit operations.

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