The Intec Copper Process: A Detailed Environmental Analysis

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ABSTRACT

The Intec Copper Process is an environmentally advantageous hydrometallurgical process for the production of high purity copper and associated precious metals from copper sulphide concentrates.

The process uses a mixed chloride-bromide lixiviant in an elegant cyclic circuit to leach the copper into solution, rejecting the iron as stable hematite rather than as unstable jarosite. After purification of the pregnant liquor, copper is electrowon at London Metal Exchange Grade A purity, while the anodic energy of the cell is stored as the soluble species, Halex[TM], for recycle as the regenerated lixiviant to the leach circuit. Both gold and silver are leached and recovered directly from this cyclic process without resorting to cyanide leaching of the residue.

No liquid emissions result from the Intec Copper Process, whilst spent air and water vapour from the leach are released to the atmosphere. The sulphur in the minerals reports to the solids residue in elemental form, without the need for expensive handling of voluminous gaseous sulphur dioxide streams found in smelters. A significant difference to competing smelting and hydrometallurgical processes is that any mercury entering the process from the sulphide concentrate feed is recovered rather than reporting directly to waste or polluting the environment.

Outside the process circuit itself, the Intec Copper Process has several notable environmental advantages over competing technologies:

1. Flexibility of scale with low capital and operating costs allow operation directly at the mill head at production rates as low as 15 000 tpa, significantly reducing environmental impacts from concentrates transport.

2. The ability to handle low-grade and dirty concentrates often allows greater recoveries in the mill, improving both the economics and environmental acceptability of a mine by reducing metal losses to tailings.

3. A comparison of the total energy requirements of the Intec Copper Process with those of competing technologies shows that the Intec Copper Process has the lowest energy consumption of any of the known hydrometallurgical processes, as well as improving upon pyrometallurgy under appropriate conditions.

INTRODUCTION

The Intec Copper Process is a proven, patented hydrometallurgical process for the production of pure copper and precious metals from sulphide concentrates.

The process is based on the electrolytic deposition at the cathode of LME (London Metal Exchange) Grade A purity copper from a purified sodium chloride-sodium bromide electrolyte. During electrowinning, the mixed halide species $BrCl_2^-$ ('Halex[TM]') is generated in solution at the anode and exhibits powerful leaching characteristics when it is re-circulated to treat incoming concentrate feed.

The Intec Copper Process has been developed and proven over the last ten years at a cost of US$16 million. Development commenced at bench scale, progressed through to a continuous 50 kg-Cu per day pilot plant and was subsequently proven in a 350 tpa-Cu demonstration plant. Accordingly, design methodologies, materials of construction and process control have all been validated. Following a thorough review, H.G.

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Engineering of Toronto, Canada, have concluded that the Intec Copper Process is suitable for commercial application.

DESCRIPTION OF THE INTEC COPPER PROCESS

The patented Intec Copper Process was developed for the production of copper at LME Grade A purity from sulphide concentrates. Essentially, the Intec Copper Process consists of the three sequential circuits of leaching, purification and electrowinning. A simple flow diagram for the Intec Copper Process is shown in Figure 1. The leach section is a three stage countercurrent configuration with concentrate fed to Stage 1 and oxidant fed to Stage 3. Purification consists of cupric reduction, silver removal and precipitation by pH adjustment. Electrowinning consists of the recovery of copper metal and the simultaneous regeneration of the leach liquor (lixiviant).

Electrowinning

Electrowinning is at the heart of the Intec Copper Process, with LME Grade A purity copper metal being electrowon from a purified electrolyte at 1000 A/m^2 current density in a unique electrowinning cell.

Electrolyte, principally comprising 250 g/L sodium chloride (NaCl), 30 g/L sodium bromide (NaBr), 30 g/L calcium chloride ($CaCl_2$) and 75 g/L cuprous (Cu^+) ion, is fed to the cathode compartment of the diaphragm cell where 50 g/L copper is stripped by the formation of copper dendrites at the cathode. The spent catholyte passes through a porous diaphragm (filter cloth) to the anode compartment where the residual 25 g/L cuprous is oxidised to cupric, with the remaining energy being consumed in the production of the oxidant ($BrCl_2^-$). Reactions at the anode thus regenerate the oxidising strength of the electrolyte, which is returned to the leach. The oxidant, $BrCl_2^-$, is referred to as Halex[TM].

The lixiviant

The Halex[TM] laden lixiviant, generated at the anode, is the most significant of the various unique aspects of the Intec Copper Process. It represents a simple method for storing a powerful oxidising agent in soluble form, whereas previous chloride-based technologies operating at similar oxidizing potential have produced chlorine gas. This lixiviant is at an oxidation potential (Eh) of 1000 mV (all Eh values are relative to Ag/AgCl), which readily leaches gold. It is this liquor that is used for the leaching of copper sulphide concentrates.

Extraction

The leach circuit operates at 85°C with oxygen supplied by air at atmospheric pressure.

Copper concentrate ground to P_{80} 40 microns is fed to Stage 1 of the leach, and then progresses through the circuit to Stage 3. Copper extraction is typically 98.5per cent and is achieved with a leach residence time of 12 to 14 hours. The fresh Halex[TM] lixiviant from the anode is fed to Stage 3, increasing its tenor as it progresses through the leach circuit, eventually exiting stage 1 as 70 g/L copper primarily in the cuprous form.

Gold is dissolved in Stage 3 at an Eh of 550 to 650 mV and adsorbed onto a carbon filter, from which it is subsequently recovered.
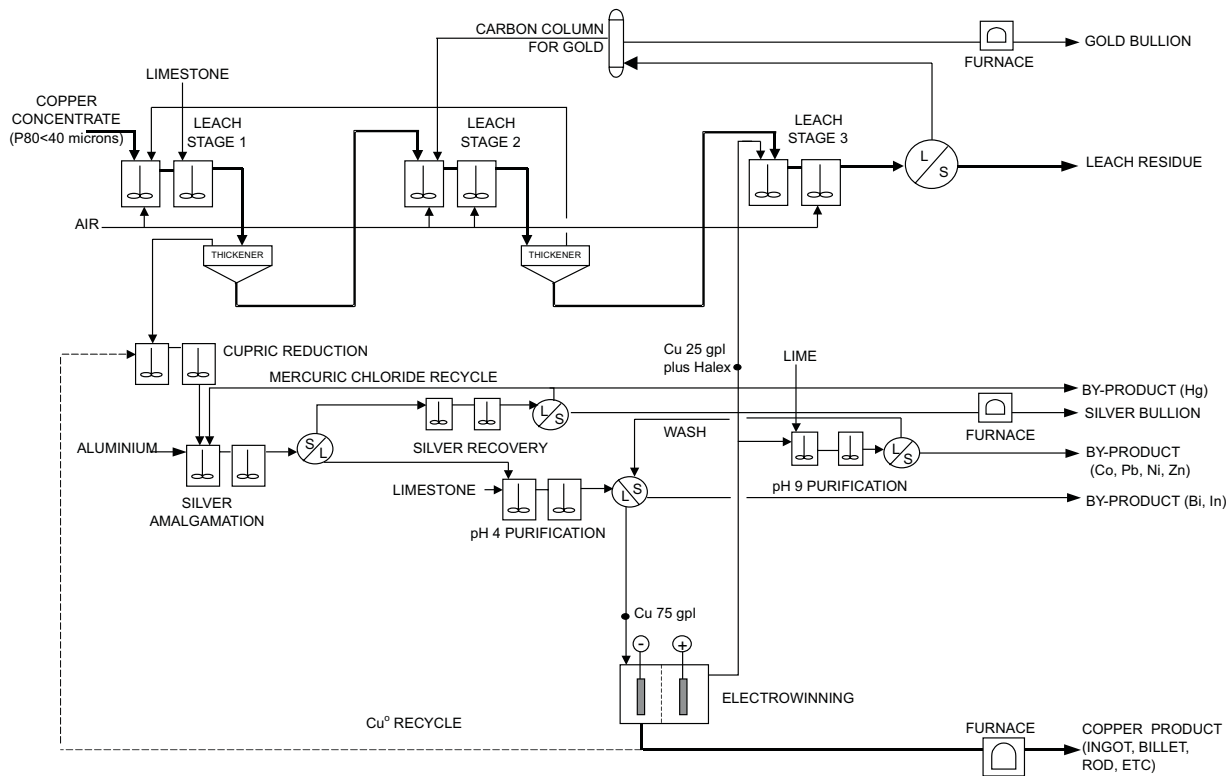
FIG 1 - Intec Copper Process flow diagram.

The leach residue is separated and washed in a filter press before discharge to either a landfill or a tailings dam.

The pregnant liquor leaves the leach circuit containing a number of impurities, such as cobalt, nickel, indium, mercury, silver, zinc and lead, which readily leach from the concentrate feed.

Purification

The pregnant electrolyte is purified in a three-stage system prior to electrowinning. The first stage involves the conversion of any residual cupric ion to cuprous (by passing the pregnant electrolyte over copper dendrites) to condition it for the remaining two stages of purification. During this operation the copper tenor increases to 75 g/L.

The second stage involves the addition of aqueous mercury (Hg^{2+}) and metallic aluminium to the pregnant liquor. The aluminium forms a 'copper sponge', which provides a large surface area that enables the silver to be galvanically removed from the liquor as an amalgam (Equation 1). The amalgam is subsequently treated to produce aqueous mercury for recycle to the front of the circuit and a silver bullion by-product.

$$3Cu^+ + Ag^+ + Hg^{2+} + 2Al \rightarrow 2Cu^\circ + Cu/Ag/Hg \text{ (amalgam)} + 2Al^{3+} \quad (1)$$
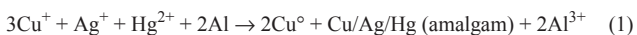
In the third stage, impurities such as residual iron, indium, and bismuth are precipitated at pH 4.0 - 4.5 by the addition of ground limestone.

The resultant purified copper solution is then sent for electrolysis as described earlier, in order to produce high purity copper metal and regenerate the lixiviant for recycle to the leach section.

A separate bleed stream takes a small flow of electrolyte (at minimum copper tenor) from the cathode compartment of the electrowinning cells, and treats it to remove zinc, lead, cadmium, cobalt, manganese, magnesium and nickel as solid precipitates at pH 9 and above using lime with the liquor returning to the process. These metals have no effect on product purity and thus may be removed after electrowinning.

RESIDUES FROM THE INTEC COPPER PROCESS

The Intec Copper Process produces no liquid or noxious gaseous emissions. Excluding spent air from the leach that is scrubbed prior to release to the atmosphere, elements entering the process through the concentrate or reagents are either recovered as products and by-products (Cu, Ag, Au, Hg) or are precipitated and removed as solid residues (Fe, Bi, As, Sb, Se, Pb, Zn, etc). Depending on the copper concentrate or blend of concentrates being fed to the process, economic quantities of the latter elements may be present in the residues, particularly those precipitated by alkali addition, under which circumstances re-treatment of the solids would be a viable option.

The overwhelming majority (typically >90 per cent by mass) of the solid residues from the Intec Copper Process come from the leach section of the process (leach residue). As is described below, this residue consists primarily of hematite (α-Fe_2O_3), elemental sulphur (S) and gypsum ($CaSO_4.2H_2O$) plus unaltered gangue minerals from the concentrate (primarily quartz). The remainder of the solid residue is formed during the electrolyte purification process, consisting of a complex and concentrate-specific mixture of metal oxides and hydroxides plus unreacted alkalis (primarily limestone). These residues are blended together for the purposes of disposal.

Extensive studies have been commissioned on the residues from the Intec Copper Process to assess the stability of the residue for disposal in the environment. These have consisted of a combination of empirical studies and residue characterisation studies, the latter forming a useful platform from which to draw upon the extensive amount of scientific literature on environmental stability.

Experimental

The studies described below have focussed on the residues from the Intec Copper Demonstration Plant, operated during 1998/99. These residues represent a conservative base for discussions, firstly because the large-scale operations represent the most realistic view of the process capabilities, and secondly because the blend of copper concentrates fed to the Demonstration Plant included a metallurgically complex feed containing significant levels of mercury, lead, zinc and arsenic.

Solid residues were filtered using plate-and-frame filter presses in the Demonstration Plant Operation. The residues were washed *in situ* to recover soluble salts using brine and then water before being squeezed and discharged. Representative sampling was difficult because of the size of the batch discharges (in excess of one tonne each for the leach residues). Experiments during the operations period indicated only minor fluctuations in the homogeneity of the filter cake, but an effort was made to take samples in as representative a fashion as was practicable. Several grab samples were taken for each batch, dried in an oven at 70°C to determine the moisture content, and blended.

Samples of the leach and purification residues were tested by the Toxicity Characteristics Leaching Procedure (TCLP) and/or Specific Contaminant Concentration (SCC) test at an independent laboratory, Australian Laboratory Services (ALS) throughout the Demonstration Plant operation, either individually or as blends of leach and purification residues containing 80 - 96 per cent leach residue.

After concluding the Demonstration Plant operations in 1999, blended samples of the leach residue and purification residue were prepared and labelled LRB and ARB, respectively. Portions of these samples were sent, along with a sample of a leach residue that had been prepared by batch processes in the laboratory, to the Australian Nuclear Science and Technology Organisation (ANSTO) for modified TCLP testing (rainwater and mine tailings water leaching solutions) and for Sequential Leach studies. The laboratory sample was notable because its colour (yellow-brown) differed markedly from the brick-red colour observed for the leach residues produced by continuous operations in the Demonstration Plant.

A blended sample of ten per cent ARB and 90 per cent LRB was sent to ALS for Multiple Extraction Procedure (MEP) testing to gain further empirical evidence of the stability of the blended materials (at Demonstration Plant production rates of blending) for disposal.

Residues from the Demonstration Plant (DP) and laboratory (Lab) leach residue were characterised by XRD, TGA, DTA, FTIR, Raman and Mossbauer Spectroscopy to determine the phases present in these samples. Derivative samples from the Demonstration Plant and laboratory leach residues were prepared by extracting gypsum by washing with demineralised water, and by then extracting elemental sulphur with tetrachloroethylene (TCE). DTA and TGA analyses were then performed in an argon atmosphere on the four extracted samples, with XRD analyses both before and after heating.

Elemental analyses were obtained by neutron activation analyses at Becquerel Laboratories, at the ANSTO nuclear reactor at Lucas Heights, Sydney.

Results of empirical studies

Absolute studies (total digestion and analysis, termed Specific Contaminant Concentration (SCC) tests by the NSW Environment Protection Authority) of the Demonstration Plant residues have been performed at various rates of blending between the purification and leach residues. For the majority of NSW EPA notifiable elements, these studies have shown contaminant levels with 95 per cent upper confidence limits (UCLs) below the threshold levels for classification as 'Solid' or

'Inert' waste (EPA, 1999), either of which require tracking under current NSW environmental legislation.

For the elements with 95 per cent UCLs exceeding the NSW EPA threshold levels (Pb and Se), additional studies have been performed to demonstrate the stability of the elements within the residues in the environment. While the limitations of the Toxicity Characteristics Leaching Procedure (TCLP) have been widely commented upon, this method is commonly used as a first measure of environmental stability, and is specifically used by the NSW EPA as one means of examining this issue. Extensive studies of the Intec Copper Process Demonstration Plant residues have routinely returned TCLP results well within the NSW EPA threshold levels for characterisation of the residues as 'Solid Waste'.

Given the limitations of the use of acetic acid as a leachate in the standard (US EPA) TCLP method, modified TCLP studies have been performed on the Demonstration Plant residues using rainwater and mine tailings water, both yielding results in line with the standard method (Lowson *et al*, 1999). Building upon these modified TCLP studies, a number of Sequential Leach experiments were carried out, under which the residues were subjected to a series of leachants of increasing severity (water, Tamm's acid oxalate, Schumann's reagent), the results of which demonstrated that:

1. the iron oxides in the residues are primarily crystalline (>95 per cent), showing very high stability; and

2. the residues show low leachability even under conditions exceeding those that would be expected in an unmanaged, uncapped landfill (Lowson *et al*, 1999).

A separate study investigated the stability of the Demonstration Plant (blended leach and purification) residues using the Multiple Extraction Procedure (MEP) technique. The results from this study demonstrated that, after an initial dissolution of gypsum from the blended residue, the leaching of the residue dropped off to negligible levels. No iron leaching was observed in any of the sequence of extractions.

Based upon this empirical evidence, as well as theoretical data and advice from experts in the field, the NSW EPA issued to Intec Ltd an Immobilisation Approval under the POEA 1997. This document specifically recognises the stability of the residues for disposal with particular reference to the elements exceeding the NSW EPA threshold levels noted above.

Characterisation of the residues and theoretical stability

In addition to the empirical evidence, it was considered important that Intec should generate as thorough a knowledge of the specific nature of the Intec Copper Process residues as was practicable. To this end, Intec commissioned a range of studies designed to characterise the residues. These are noted below, with a brief description of the information generated by each technique.

Overall, the DP sample was found to contain 35 per cent hematite, 33 per cent gypsum, 25 per cent elemental sulphur, six per cent quartz and adsorbed moisture. The latter figure was, of course, reduced substantially by the drying required for sample preparation. Incorporating the typical figure of ten per cent moisture associated with the filter cakes as disposed into this composition, these figures are diluted slightly.

X-Ray diffraction (XRD) analysis of the DP leach residue identified hematite, gypsum, elemental sulphur and quartz. The latter phase has carried over unreacted from the concentrate. This result is as expected. Hematite and elemental sulphur are generated by the main leaching reaction:

$$2\ CuFeS_2 + 2\ Cu^{2+} + 1.5\ O_2 \rightarrow 4\ Cu^+ + 4S° + Fe_2O_3$$
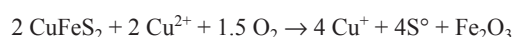
By maintaining a background of calcium in solution (5 - 10 g/L), any sulphate formed by oxidation at high redox potential of small amounts of pyrite or elemental sulphur in the leach is precipitated immediately as gypsum. This inhibits the formation of jarosite by low soluble sulphate levels.

By comparison, XRD analysis of the Lab sample identified only one crystalline phase – elemental sulphur. No iron phase was clearly discernable until the sample was washed in demineralised water, at which point akaganeite could be resolved. Iron phases may have been difficult to identify in these samples due to a combination of the small particle size, identified by SEM as being <1 micron, and absorption of the Co X-rays by the iron, which would reduce the signal and increase the background. As the laboratory sample had been produced without an excess of calcium in the electrolyte, it did not contain significant quantities of gypsum.

DTA and TGA traces gave the most data on the gypsum and sulphur contents of the two leach residues (Figures 2 and 3). They showed an endothermic loss of adsorbed water to around 100°C, followed by a sulphur melting endotherm to around 180°C. This is immediately followed by a major concurrent sulphur oxidation and volatilisation exotherm in an air atmosphere, or sulphur volatilisation endotherm in an argon atmosphere. Both reactions were complete by 280°C.
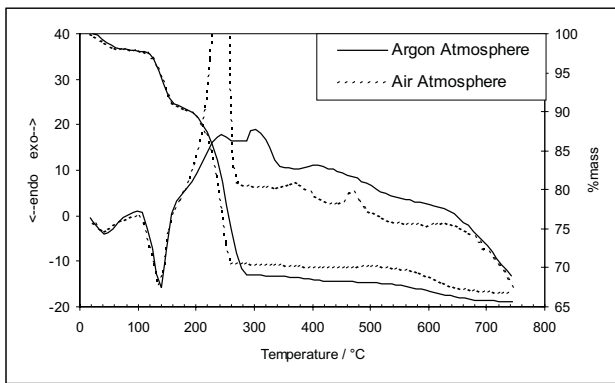

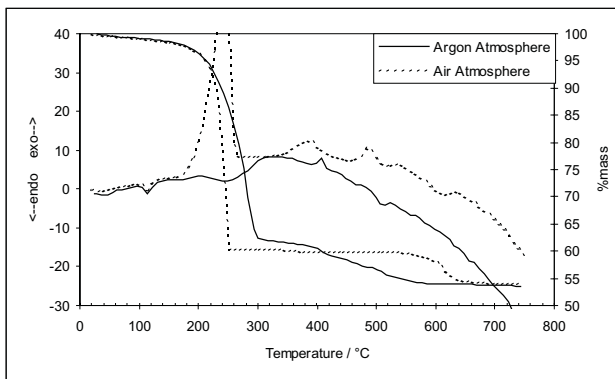FIG 2 - DTA/TGA traces for DP sample in air and argon atmospheres.

FIG 3 - DTA/TGA traces for Lab sample in air and argon atmospheres.

Given the expected compositions of the residues, any thermal events above 300°C would be correlated with iron compounds. As can be seen in Figures 4 to 7, some events are observed for both samples, all of which become complete upon the decomposition of iron compounds to hematite by 750°C (hence the similar mass losses observed in both air and argon atmospheres.
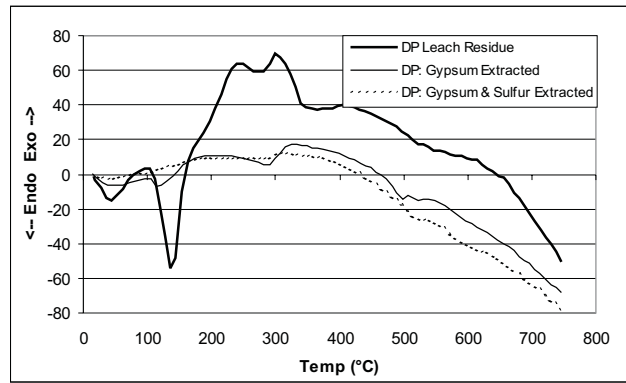

FIG 4 - DTA traces for DP leach residue in an argon atmosphere, including gypsum and sulphur extracted samples (normalised for mass loss during extractions).
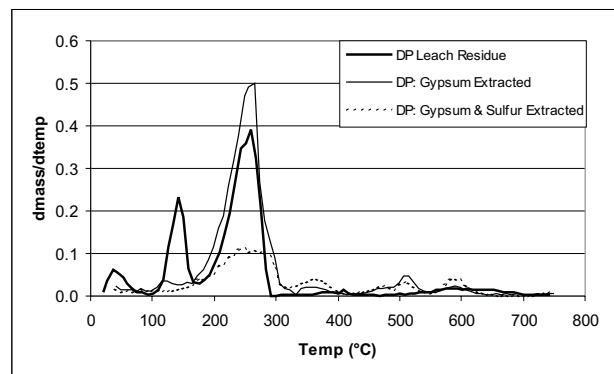

FIG 5 - TGA traces for DP leach residue in an argon atmosphere, including gypsum and sulphur extracted samples (normalised for mass loss during extractions).

The difference in traces associated with the air and argon atmospheres above 300°C in Figure 2 may have been due to the temporary sequestering of evolved sulphur as ferric sulphate before decomposition above 400°C. As can be seen in Figure 5, three small mass losses were observed in the 300 - 600°C region. One of these may have been associated with the decomposition of a small quantity of akaganeite in the primarily hematite iron phase of the DP residue, but the data are insufficient to make an absolute determination.

The absence of significant thermal events above 300°C supports the XRD identification of hematite in the DP residue sample. By comparison, a sharp exothermic peak occurred at around 400°C in the Lab sample (Figure 6). Given that akaganeite was the primary iron phase identified by XRD, this is likely to be be associated with the decomposition of akaganeite to hematite, as there was an associated mass loss (Figure 7). No explanation is offered for the small event at 500°C.

After thermal treatment in air, XRD analysis showed hematite, anhydrite ($CaSO_4$) and quartz for the DP sample, and only hematite and quartz for the Lab sample. This is consistent with the suggestion that the laboratory sample contained little or no gypsum to start with. No difference was observed after thermal treatment in an argon atmosphere for the DP sample, but the Lab sample showed the presence of magnetite (Fe_3O_4). This may have been due to the formation of a reducing atmosphere during the sulphur volatilisation in the early stages of heating, or it may have been due to the internal structural mechanism proposed by Ozdemir and Dunlop (2000).
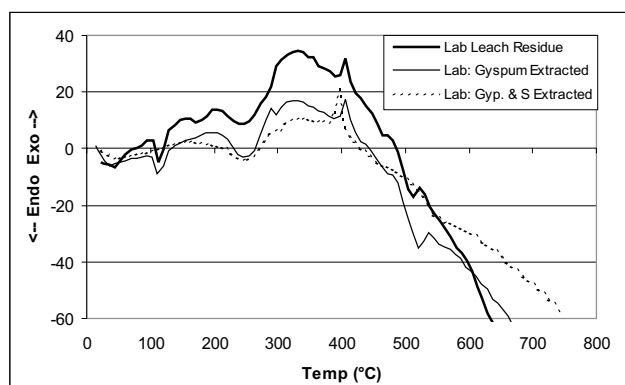
FIG 6 - DTA traces for Lab leach residue in an argon atmosphere, including gypsum and sulphur extracted samples (normalised for mass loss during extractions).
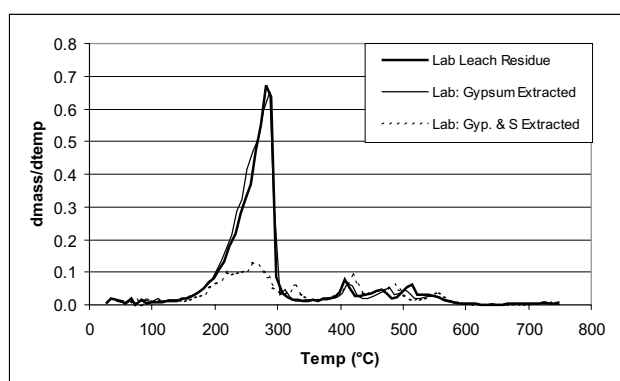

FIG 7 - TGA traces for Lab leach residue in an argon atmosphere, including gypsum and sulphur extracted samples (normalised for mass loss during extractions).

The FTIR traces for the two leach residues are difficult to interpret, due to the complex composition of the residue mixtures. Importantly, however, the FTIR data for the DP sample show a small peak at 847 cm^{-1} which may be associated with akaganeite (indicating the presence of a small akaganeite fraction), while the Lab sample shows a large peak at 846 cm^{-1}, which would correlate to the higher akaganeite content of the residue. The DP residue also showed a small peak at 880 cm^{-1} which may be associated with the presence of goethite in the residue, using data from Schwertmann and Cornell (1991, Table 3-1).

The Mossbauer analysis of the DP sample indicated the absence of appreciable quantities of jarosite. This is expected, given that the Intec Copper Process leach circuit operates with a background level of calcium (typically ~10 g/L), which would precipitate most sulphate rapidly as gypsum (hence the observed gypsum in the DP sample), and would thus prevent the formation of jarosites. The analysis also indicated the presence of some akaganeite, consistent with the results from the FTIR.

Raman spectroscopy confirmed the presence of hematite in the DP sample, showing no indications of any FeOOH polymorphs (goethite, akaganeite or lepidocrocite). This analysis does not preclude the presence of akaganeite. Raman analysis of the Lab sample indicated primarily hematite. Assuming that the akaganeite portion of the iron oxide phase is indistinguishable by this method, then the confirmation of hematite in the Lab sample indicates that the two iron oxides may have formed by competing mechanisms.

The SEM micrographs for the two residues are consistent with the findings of the previous analyses. The DP residue, expected to be primarily hematite, shows irregular hexagonal plates (Figure 8), as suggested by Schwertmann and Cornell (1999, Table 3-1), while the Lab sample consists of rod-like crystals up to several hundred nanometres in length (Figure 9), which might be correlated to akaganeite (Schwertmann and Cornell, 1999, Table 3-1).
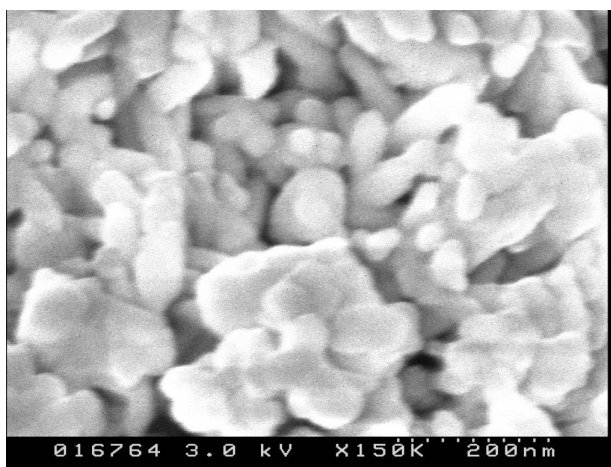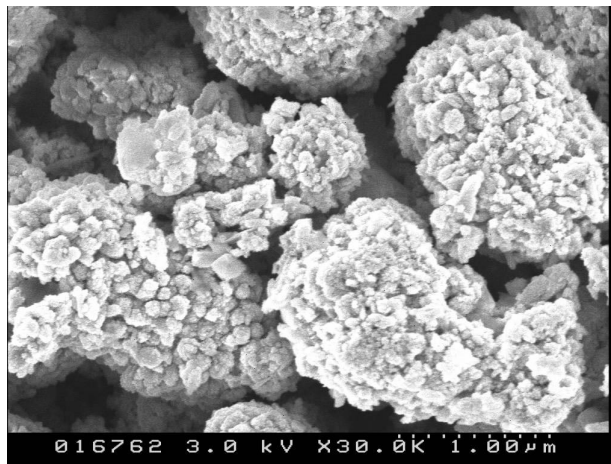

FIG 8 - SEM micrographs of DP sample.

Having correlated the data from the multiple analytical techniques used to characterise the residues, direct concentration data provided by neutron activation analysis was then used in conjunction with the mass loss data from the TGA analyses to generate mass balances for the residues.

Overall, these calculations show that the DP residues consisted of a mixture of hematite, gypsum, elemental sulphur and quartz, with a low but undetermined quantity of akaganeite. The gypsum level in the residue, however, was much higher than would be expected for typical Intec Copper Process residues since the specific mineralogy of one of the copper concentrates fed to the Demonstration Plant allowed a substantially higher-than-normal amount of pyrite to leach from the concentrate. This produced higher levels of sulphate, and thus higher levels of gypsum. Reducing this back to more normal levels, a typical Intec Copper Process leach residue would be expected to contain around 45 per cent hematite, 32 per cent elemental sulphur, 14 per cent gypsum and eight per cent quartz, excluding the moisture that would be associated with normal plant filtration practices (around 20 per cent).
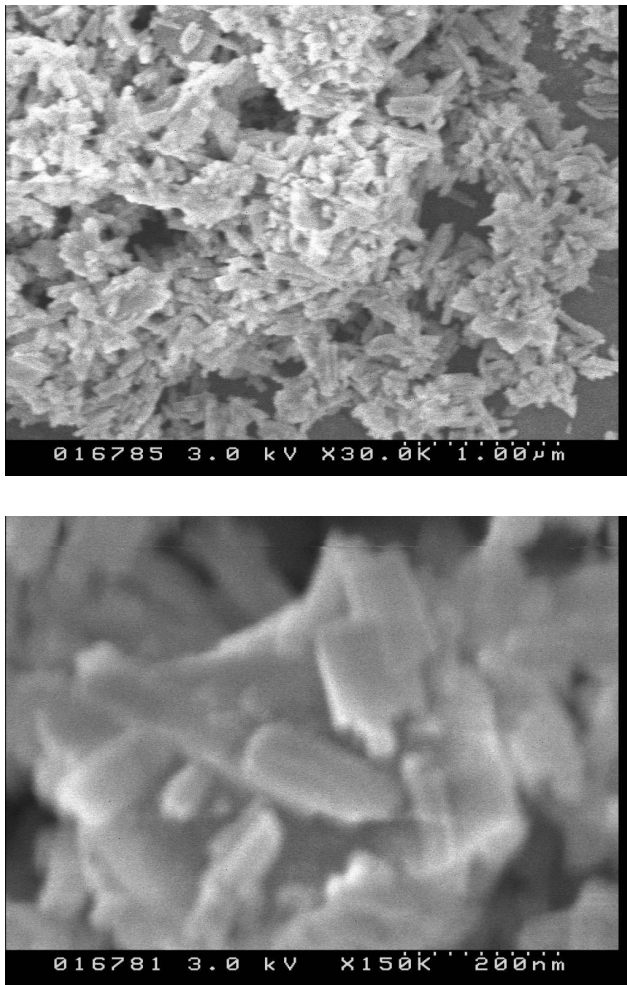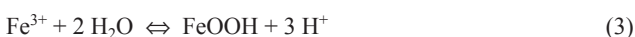
FIG 9 - SEM micrographs of Lab sample.

Iron precipitation in the Intec Copper Process system

The scientific literature offers varying descriptions of the mechanisms for the precipitation of iron oxides from solution. In many cases, these descriptions are predicated on alkaline conditions or on the addition of fixed alkali:iron ratios, resulting in changing pH regimes as the acid generated during hydrolysis of ferric ions lowers the overall solution pH. While the relevance to conditions in the Intec Copper Process electrolytes may vary, some broad conclusions can be drawn from the literature.

Overall, two basic mechanisms for the precipitation of ferric from a chloride solution appear common. Either the iron is precipitated directly from solution as hematite:

$$2\ Fe^{3+} + H_2O \Leftrightarrow Fe_2O_3 + 6\ H^+ \tag{2}$$
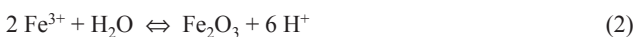
or it precipitates as either goethite (α-FeOOH) or akaganeite (β-FeOOH):

$$Fe^{3+} + 2\ H_2O \Leftrightarrow FeOOH + 3\ H^+ \tag{3}$$

As hematite is the more thermodynamically stable (eg Berner, 1969), the latter oxides (particularly akaganeite) may transform over time, principally by a dissolution/reprecipitation mechanism.

Most researchers (eg Cornell *et al*, 1989) appear to agree that, on addition of an alkali, ferric ions form monomeric and dinuclear hydroxide species, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe_2(OH)_4^{2+}$. Depending on a number of factors, these are then believed to join to form small, relatively labile polynuclear species, which then proceed via deprotonation of surface water, agglomeration of polynuclears into chains or rafts (possibly with precipitation as amorphous ferric hydroxide), and internal rearrangement to give hematite. Alternatively, direct precipitation of the monomeric and dinuclear or small polynuclear species has also been considered (eg Dutrizac and Riveros, 1999; Knight and Sylva, 1974).

Of the two hematite formation mechanisms, it seems reasonable that the latter, although less well documented, is the more likely for the Intec Copper Process system. Were the hematite observed in the Demonstration Plant residue (sample DP) to have formed via the precipitation of amorphous ferric hydroxide, the residue should still have contained an appreciable quantity of amorphous materialsince the transformation mechanism has often been documented to be slow even at elevated temperatures (Welham *et al*, 2000). As shown in the sequential extraction results, this was not the case. On the contrary, the residue appears to consist of microcrystalline hematite – stable with respect to ammonium oxalate but of too small crystal size to be readily determined by XRD spectroscopy. Such a morphology might be expected as a result of the very rapid nucleation from solution, such as might occur at elevated temperatures.

As noted by Schwertmann and Cornell (1991), akaganeite cannot form above pH 5 because at higher pHs the OH⁻ is far more competitive for structural sites than the chloride. Chloride directs the formation of the embryonic particle by forming an outer sphere linkage at the position of minimum energy (Cornell *et al*, 1989). Given the low pH of the leach circuit (<2.5 dropping to <1) and the high chloride levels in solution (~4.8 M), it might be expected that the chloride would be sufficiently competitive with hydroxide ions that akaganeite formation should dominate over goethite, as has been observed in laboratory situations.

The presence of ~0.3M bromide, however, complicates the issue. Deliyanni *et al* (2001) noted that large ions such as chloride are necessary for the formation of the tunnel structure observed in akaganeite. As the bromide ion is only slightly larger than the chloride ion (1.96 vs 1.81 Å), it may perform a very similar function within the akaganeite matrix. Direct analysis of sample DP showed 0.3per cent chloride and 0.045 per cent bromide, meaning that the sample was slightly enhanced in bromide over chloride compared to their solution mass ratios (280 g/L NaCl:28 g/L NaBr).

However, the bromide forms stronger complexes with the iron species in solution, with thermodynamic speciation calculations indicating that while chloride forms positive complexes in an acid environment (eg $FeCl_2^+$), bromide forms the neutral $FeBr_3$ complex. This complex does not hydrolyse until above pH5 which may favour the reverse reaction in Equation 3 more than in Equation 2, which would hinder the formation and stabilisation of akaganeite, indirectly favouring the formation of the more-stable hematite. At this stage it is difficult to predict the effect of the bromide.

As can be seen in the various analyses described above, the primary iron phases precipitated from ferric chloride are akaganeite and hematite. According to the literature, a number of factors can influence the balance between the competing precipitation mechanisms, most of which appear to favour the formation of hematite:

- **Temperature**: As the solution temperature rises, the formation of hematite is favoured. Cornell *et al* (1989) note that temperatures above 80°C also favour the direct formation of hematite over polynuclear species.

- **pH**: Lower pH favours the formation of hematite over akaganeite. As seen from Equation 3, higher acid concentrations hinder both hematite and akaganeite precipitation by le Chetalier's principle, but akaganeite is more vulnerable to acid attack than hematite. This would favour the dissolution/reprecipitation mechanism for conversion of akaganeite to hematite, resulting in more pure hematite mixtures. This effect would be particularly marked in the final leach stage, where the pH falls below 0.5.

- **Reaction time**: As hematite is the more thermodynamically stable iron oxide, reaction times at the elevated temperatures of the Intec Copper Process leach favour hematite formation. In atmospheric pressure experiments examining competitive akaganeite/hematite precipitation, Dutrizac and Riveros (1999) found that almost pure hematite was recovered after sixteen hours in the absence of seed, with no akaganeite found after three hours in tests utilising 15 g/L of hematite seed.

- **Seeding**: The presence of even small amounts of seed can have a marked difference on the overall reaction product, overwhelmingly favouring the formation of hematite (eg Atkinson *et al*, 1977; Dutrizac and Riveros, 1999; Herbert, 1996; Rose and Ghazi, 1998). Dutrizac and Riveros (1999, pg 995) report that '…the precipitation of more-stable hematite from the solution, a process accelerated by the presence of Fe_2O_3 seed, displaces the akaganeite equilibrium and promotes the dissolution of more of the akaganeite. The presence of Fe_2O_3 seed also favours the direct precipitation of hematite over that of akaganeite."'

The authors believe that this factor represents the critical difference between the batch laboratory tests and the continuously running Demonstration Plant which resulted in the differences between sample Lab and sample DP.

In a continuous circuit, slurry and liquor flows are calculated on average residence times per unit operation. Since continuously stirred tanks have a profile of residence times for individual molecules, the leach stages are each divided into a minimum of three tanks. Within each tank, some molecules or particles will spend only brief periods before short-circuiting to the next tank. Others will stay within the tanks for much longer than the average residence time. It is the latter type of hematite particles which are critical to this discussion.

Aqueous iron levels in Leach Stage 1 are low, typically <0.5 g/L, and the low redox potential of the solution means that the iron that is in solution will be an equilibrium mixture of ferrous and ferric. Overall, little precipitate will be formed in this stage. By proportion, then, the long-term particles (which should be hematite by virtue of their long residence time at high temperatures) should be sufficient to ensure that precipitation occurs as hematite, which then acts as seed for hematite for the subsequent leach stages. Any akaganeite that does form would be preferentially dissolved as the pH drops in Leach Stage 3, reprecipitating onto the seed hematite.

Additionally, given that the hematite particles in the SEM micrographs are smaller than 1 micron in diameter, it is possible that small particles remain suspended during the solid/liquid separation between Leach Stages 1 and 2, and that they return with the liquid phase to Stage 1 (rather than passing with the thickener underflow to Stage 2), where they act as seed for further hematite growth.

This explanation offers a plausible mechanism for the observation that the Demonstration Plant leach residues were *always* brick-red, while laboratory residues may report as either brick-red or yellow-brown. While the temperature, electrolyte composition, reaction time and pH, as measured variables, are comparable between the laboratory and the Demonstration Plant, the batch laboratory tests start without any residue in the solids,

unlike the continuous operation. The precipitate outcome, then, is strongly affected by minor differences that determine which iron oxide first precipitates, which as seed appears to then determine which precipitation mechanism goes on to dominate.

This theory was tested in a laboratory trial by repeating a previous experiment using a concentrate that had resulted in a yellow-brown (presumably dominated by akaganeite) residue. The test was run under identical conditions but with the addition of 20 g/L of recycled residue (equating to ~7 g/L hematite recycle). The residue resulting from the test was brick red and XRD analysis indicated only hematite as the iron phase, as predicted.

Electrolyte Composition: The precipitation of hematite is favoured over that of akaganeite by high ionic strengths in the electrolyte (Cornell *et al*, 1989), possibly because high ionic strengths raise the activity of H^+ ions, resulting in increasing preferential dissolution of any akaganeite formed, and possibly also because higher ligand strengths bond iron more strongly into solution, moving the equilibrium in Equation 2 to the left.

Provided that the ionic strength is maintained, the effects of specific electrolytes appear to be disputable. Dutrizac and Riveros (1999) report that the ferric chloride concentration affected the amount of precipitate formed in their experiments, but not the species formed, while the concentrations of $CaCl_2$ or NaCl did not affect the composition of the precipitates formed. However, Cornell *et al* (1989, pg 125) indicate that '…the majority of additives retard the crystallisation of ferrihydrite and frequently lead to an increase in the amount of α-Fe_2O_3 [hematite] relative to α-FeO(OH) [goethite] in the product.'

In summary, it may be seen that the generic conditions of the leach section of the Intec Copper Process – temperature >80°C, pH dropping from ~2 to ~0, residence time >10 hours, and the presence of hematite seed in continuous operations – all theoretically favour the formation of hematite over akaganeite. By incorporating the theory on seeding, a full explanation can be derived for the observed characteristics of both the laboratory and Demonstration plant samples.

LIFE CYCLE ANALYSIS OF THE INTEC COPPER PROCESS

In addition to the residue characterisation studies, Intec has also commissioned a Life Cycle Analysis (LCA) of the Intec Copper Process in comparison to competing copper processing technologies. This study was conducted by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) using published data and information provided by Intec Ltd. Given the relevance of the CSIRO LCA study, an overview is provided below, but readers are encouraged to view the complete report (Norgate, 2001), which is available at http://www.intec.com.au.

The base case of the CSIRO LCA compared the Intec Copper Process with flash smelting, four pressure oxidation hydrometallurgical processes, and two biohydrometallurgical processes. Using a system boundary incorporating mining, concentrate production and metal production and refining, the boundary for all processes was an equivalent 'cradle-to-gate'. The production of a 25 per cent copper concentrate (30 per cent S, 100 g/t Ag, 10 g/t Au) was assumed, with the electricity used by the processes being generated from black coal at 35 per cent efficiency.

As an Intec Copper Process plant would most likely be located at a mine site to optimise the advantages associated with the Process' flexibility of scale, improved ore-to-metal recoveries through the production of lower grade concentrates at the mill, and improved economics through avoiding smelter charges and penalties, it was assumed that no transport would be required for the Intec Copper Process. The same was assumed for the other hydrometallurgical processes. Given that approximately half of

the world's copper production occurs at integrated smelters (Brook Hunt, 2000), presumably involving minimal transport of concentrate, while the other half is traded on the custom market, and would presumably involve longer transport distances including road or rail and possibly ship, a conservative assumption of 500 km transport by rail was assumed for smelting in the base case.

After collating all process information from the published data, the figures were sent to the appropriate companies for review, and comments or changes incorporated where applicable. Within the context of the assumptions used for the LCA, then, the seven processes were compared for Total Energy Consumption (TEC, MJ/kg-Cu), Global Warming Potential (GWP, kg-CO_2(eq)/kg-Cu) and Acidification Potential (AP, kg-SO_2(eq)/kg-Cu).

The cradle-to-gate system boundary applied encountered one problem in that the Intec Copper Process produces LME Grade A copper in dendritic form, while the other hydrometallurgical and smelting processes considered produce copper in pure cathode form. It is unlikely that the Intec Copper Process product would be cast into ingot without any form of value-adding. Rather, the product would most likely be melted and cast into product forms from the molten state. Either way, this leaves a disparity between the products being compared. As no resolution for this was possible, the conservative assumption that the Intec Copper Process product would be melted and cast into ingot was used.

As shown in Figure 10, the base case conclusion from the CSIRO LCA was that the total energy requirement for the Intec Copper Process is 36 per cent lower than the average for pressure oxidation hydrometallurgical processes and 41 per cent lower than the average for biological processes, but 5.9 per cent higher than that for smelting. The differences are even more marked for Global Warming Potential (Figure 11).
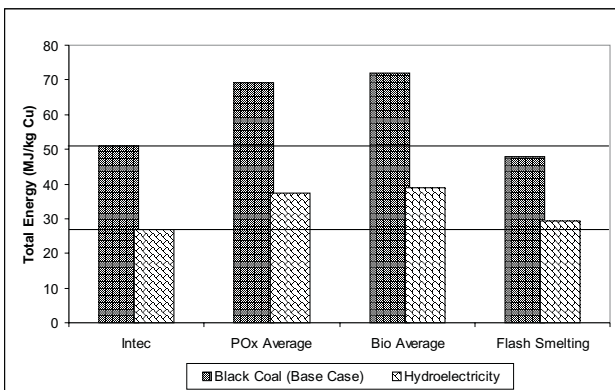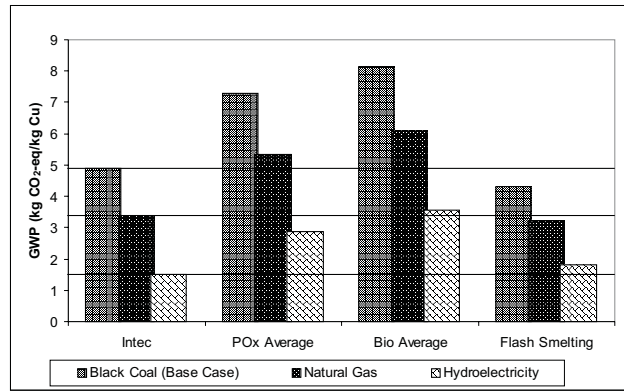

FIG 11 - CSIRO LCA Global Warming Potential (GWP) results: Base case, natural gas and hydroelectric power cases.

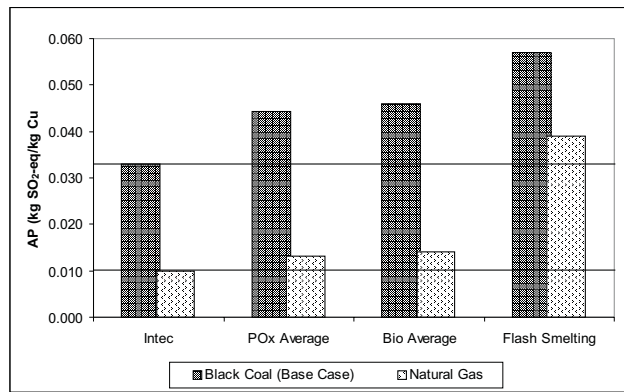FIG 12 - CSIRO LCA Acidification Potential (AP) results: Base case and natural gas power case.

FIG 10 - CSIRO LCA Total energy results: Base case and hydro-electric power case.

With respect to the differences between the Intec Copper Process and flash smelting, the result is similar to expectations due to the fact that a significant proportion of the energy obtained in smelting is obtained from the exothermic oxidation of sulphur minerals to produce sulphur dioxide. Even incorporating smelter gas controls, the production of this sulphur dioxide is the reason for the marked advantage for the Intec Copper Process for Acidification Potential (Figure 12). Effectively, smelters trade one form of environmental impact (GWP) for another (AP).

While both processes use electricity, the largest single source of electricity consumption associated with all hydrometallurgical processes is the electrowinning of metals from solution. As may be seen in Figures 10 and 11, the effect of changing the fuel used for power generation changes the ratios for Total Energy

Consumption and GWP. Using either natural gas or hydroelectricity instead of black coal, the Intec Copper Process maintains and extends its advantages over pressure oxidation and biological hydrometallurgical processes, while reducing the impact versus flash smelting. Using hydroelectric power, the Intec Copper Process offers the lowest impacts for Total Energy Consumption, Global Warming Potential and Acidification Potential under the set of assumptions employed by the CSIRO LCA.

The advantages of the Intec Copper Process over smelting become even more pronounced when lower concentrate grades are considered. Noting that flash smelting may not even be economic at lower grades, the total energy consumption associated with Intec Copper Process and flash smelting treating a 20 per cent concentrate was calculated to be almost identical at 51.4 MJ/kg-Cu and 51.5 MJ/kg-Cu, respectively. At 15 per cent copper in the concentrate, where no smelter could operate economically, the results were 52.1 and 58.5 MJ/kg-Cu, respectively. These results include the melting of the Intec Copper Product and casting as ingot, and the use of black coal power generation.

Given that higher metal recoveries may often be obtained at the mill by the production of lower grade concentrates, and given the greater flexibility of scale offered by the Intec Copper Process, the Process offers several notable advantages over smelting to the miner:

- Lower TEC, GWP and AP than smelting when using either lower grade concentrates or alternate fuel sources to black coal for power generation.

- Fewer environmental impacts associated with the loss of copper minerals to the mill tailings.

- Greater project returns associated with higher ore-metal recoveries.

- Greater resource utilisation associated with the ability to lower the ore cutoff grades feeding the mill. This contributes to resource conservation by delaying the need to open new mines.

- Similarly, greater utilisation of a resource may extend the mine life. This also extends the period of benefit to the local community.

- By operating at the mine site, the Intec Copper Process offers smaller mines the opportunity to contain the value associated with metal production from concentrate within the mine gate, rather than passing it on to smelters.

CONCLUSIONS

The environmental impacts of the Intec Copper Process have been studied extensively, both from the point of view of the solid residues from the process, and through a Life Cycle Assessment of the total energy consumption, Global Warming Potential, and Acidification Potential of the process. The LCA also considered the impacts of competing processes.

The solid residues from the process consist primarily of crystalline hematite, elemental sulphur, gypsum and quartz. Through a range of empirical studies and theoretical support, these have been demonstrated to be stable. Explanations have also been offered to demonstrate why hematite is always produced as the primary crystalline phase from continuous leaching operations.

The LCA found that the Intec Copper Process has lower impacts than the pressure oxidation and biological hydrometallurgical processes studies, and lower than smelting when either hydroelectric power generation or low head grade concentrates are used.

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