A Comparison of Hydrometallurgical Routes for Treating Copper Sulfide Concentrates

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Much progress has been made recently on recovery of copper by hydrometallurgical routes. Four routes for treatment of a copper concentrate are bioleaching, ultra-fine grinding followed by atmospheric leaching, medium-temperature pressure leaching and total pressure oxidation. In this paper, these four options for hydrometallurgical treatment of a typical smelter-grade copper concentrate are reviewed. The options are compared in terms of technology, degree of development and process economics.

INTRODUCTION

Chalcopyrite is the major source of copper, and there has been a concerted effort over the last four decades to develop a hydrometallurgical route for the production of copper from either concentrates or ore containing chalcopyrite. There are several contenders for such a hydrometallurgical process. The treatment of a copper-containing pregnant leach solution (PLS) using solvent-extraction and electrowinning (SX–EW) technology is now well-established. The difference then between these different contenders is in the proposed leaching technology.

The aim of this work is to compare four options for leaching of chalcopyrite:

(i) Bioleaching;
(ii) Ultra-fine grinding followed by atmospheric leaching;
(iii) Medium-temperature pressure leaching;
(iv) Total pressure oxidation.

The options are compared in terms of technology status, operability, and capital and operating costs. These four options are described in the next section, and are compared in the section that follows.

PROCESS DESCRIPTIONS

Bioleaching

Billiton, based in South Africa, and subsequently BHP Billiton, expended a significant amount of effort in the development of a bioleaching option for copper concentrates. The resulting process, known as BioCOP®, was commercially demonstrated by the Alliance Copper joint venture between BHP Billiton and Codelco (Batty & Rorke, 2006; Dreisinger, 2006).

In the version of this technology proposed in this study, the concentrate is ground in a vertical stirred mill to a P_{80} of about 25 µm in preparation for bioleaching. The key step, bioleaching, employs thermophilic micro-organisms at temperatures between 70 and 78°C with oxygen as the primary

oxidant. The leaching efficiency with respect to copper is between 90 and 95%. The leached slurry is then neutralised to remove iron from solution, and a clarified PLS is produced by counter-current decantation (CCD). Copper in the PLS is purified using SX, and the final product is produced in electrowinning cells from the purified solution.

A possible implementation of this flowsheet is shown in Figure 1.

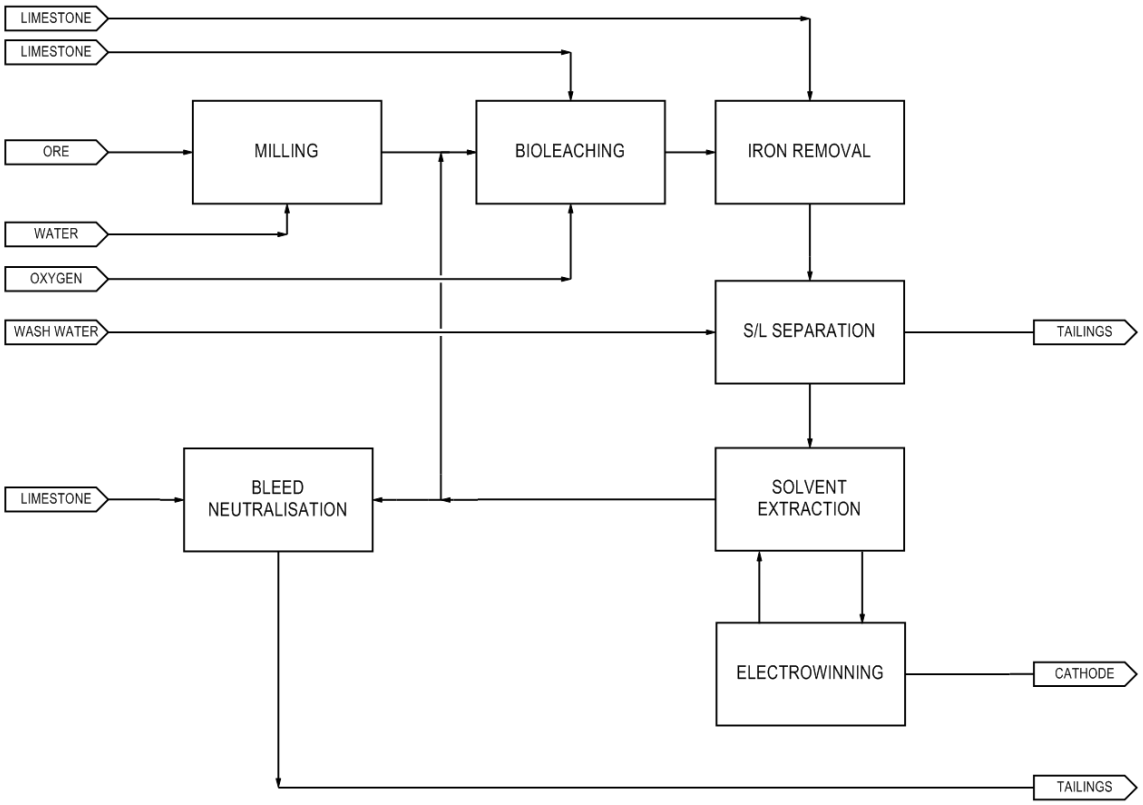

Figure 1. Block-flow diagram for the bioleaching of a chalcopyrite-containing concentrate.

Ultra-fine Grinding, Followed by Atmospheric Leaching

Ultra-fine grinding takes advantage of the increased surface area available for dissolution. The concentrate is ground in stirred mills to a P_{80} that is between 5 and 10 µm. The ground concentrate is leached at temperatures between 90 and 95°C and at atmospheric pressure, using oxygen as the primary oxidant. The leaching slurry is then neutralised to remove excess iron from solution, after which the slurry is fed to a solid–liquid separation circuit. Copper is then purified and upgraded from the PLS by SX. Finally, copper cathode is produced by EW from this upgraded copper solution.

A possible implementation of this flowsheet is shown in Figure 2.

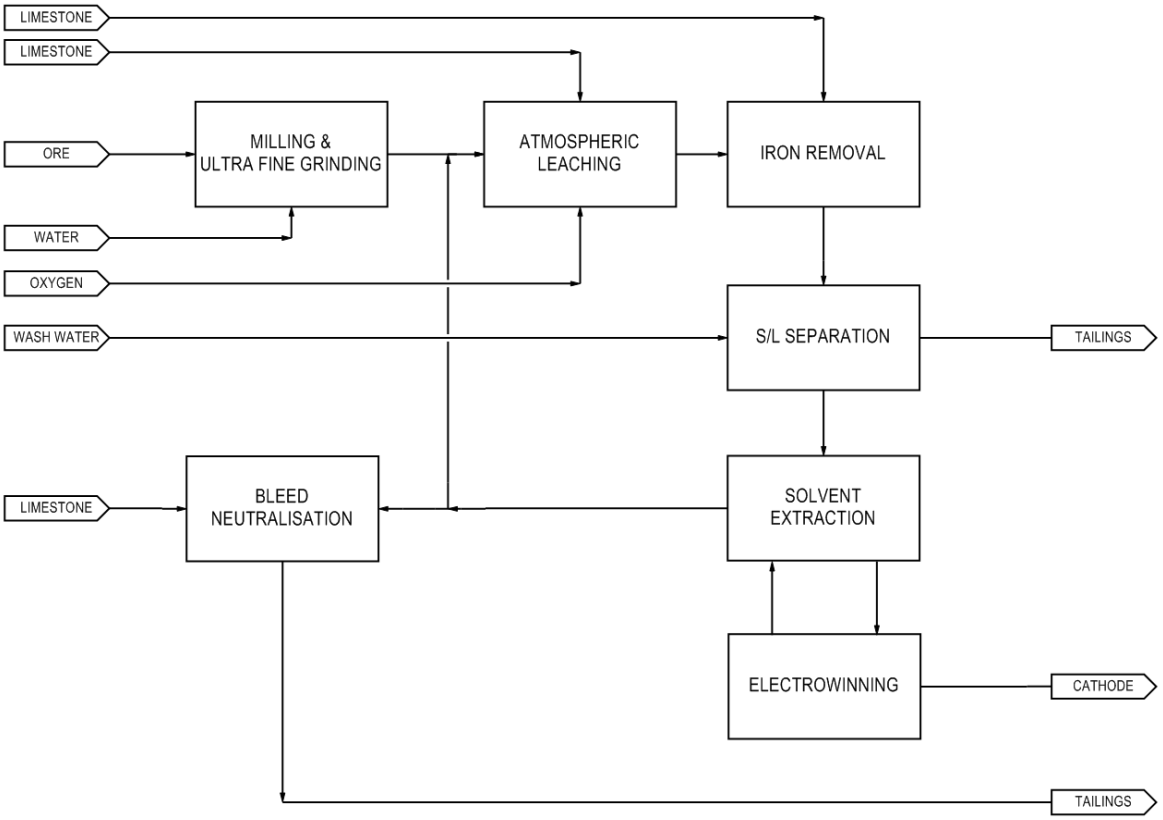

Figure 2. Block-flow diagram for the ultra-fine grinding/atmospheric leaching of a chalcopyrite-containing concentrate.

Medium-Temperature Pressure Leaching

This option balances temperature and the concentration of acid to take advantage of unique chemistry. As a result, sulfur is produced as elemental sulfur, which has the advantage of reducing the oxygen consumption. The concentration of iron in solution is dependent on the pH; therefore, by selecting the conditions judiciously, iron can be precipitated as hematite almost quantitatively. Copper also precipitates under these conditions as basic copper sulfate, which is solubilized in a subsequent step. Thus, the circuit is as follows: the concentrate is fed to the pressure oxidation step, where it is oxidized at a temperature of 150°C and 7 bar overpressure. The leaching slurry is fed to an atmospheric leaching stage where the basic copper sulfate is dissolved. The resulting PLS is treated by SX and EW.

A possible implementation of this flowsheet is shown in Figure 3.

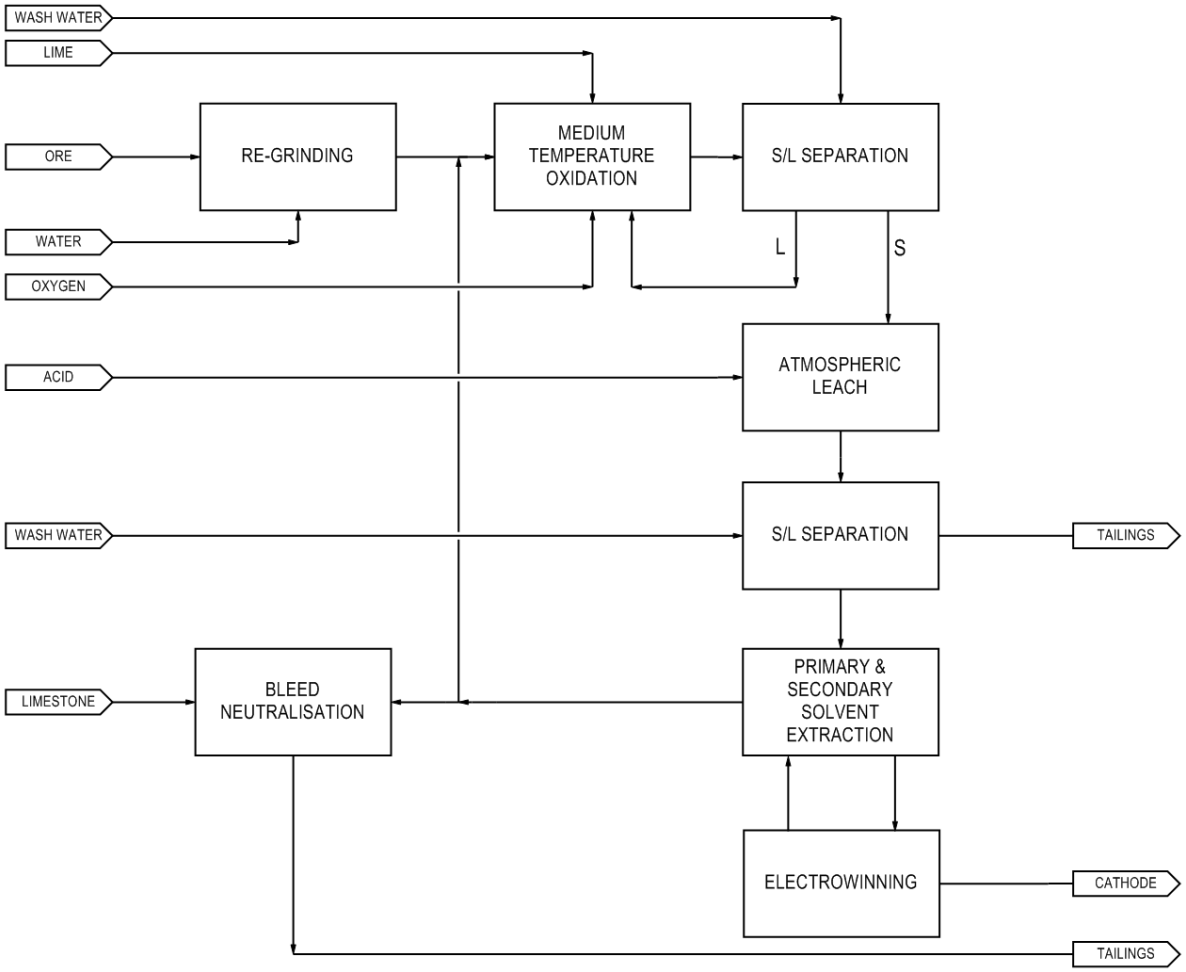

Figure 3. Block-flow diagram for the medium-temperature pressure leaching of a chalcopyrite-containing concentrate.

Total Pressure Oxidation

Total pressure oxidation aims to completely dissolve the chalcopyrite. The sulfide in the concentrate is oxidized by oxygen to sulfate ions. Depending on the conditions used, a significant amount of iron will precipitate as hematite. The autoclave operates at 200°C and 7 bar overpressure. The leaching slurry is further treated in an iron-removal stage, and the resulting PLS is processed in a split-circuit SX configuration and copper is produced by EW.

A possible implementation of this flowsheet is shown in Figure 4.

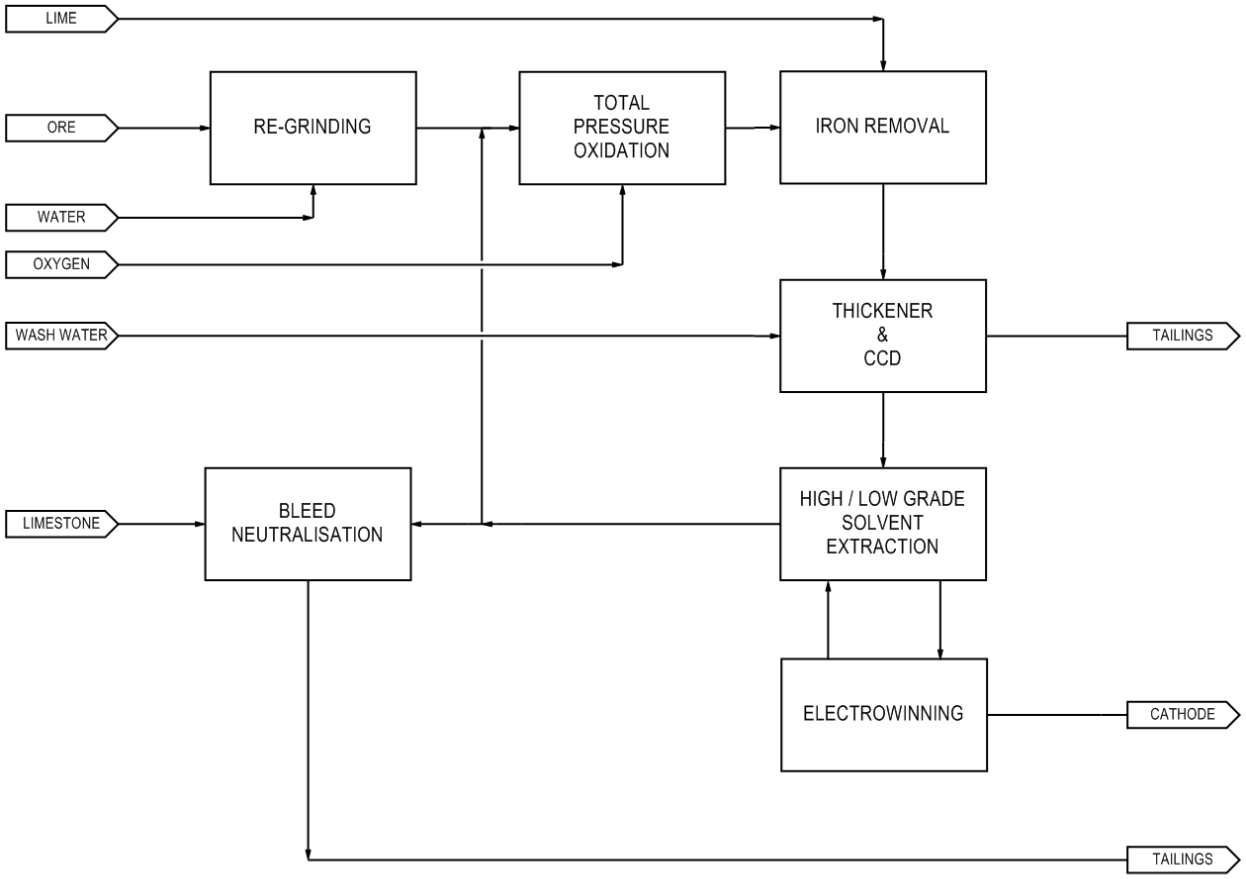

Figure 4. Block-flow diagram for the high temperature pressure leaching of a chalcopyrite-containing concentrate.

STATUS OF THE VARIOUS PROCESSES

The four processes discussed in this paper are at various stages of development. The status of these technologies is shown in Table I.

Bioleaching has been tested at large scale in a demonstration plant by Alliance Copper (Batty & Rorke, 2006; Dreisinger, 2006). Mintek and Bactech ran a bioleaching plant in Mexico (Gericke et al., 2009). Both these plants have subsequently ceased to operate because the end of the trial period was reached.

The option of ultra-fine grinding followed by atmospheric leaching has been tested at pilot-plant scale. It should be noted that atmospheric leaching of chalcocite concentrates has been implemented at three operations (Mount Gordon, Sepon and Cobre Los Cruces) (Baxter et al., 2003; Schlesinger et al., 2011; Smalley & Davis, 2000). However, it should be borne in mind that the leaching of chalcocite is considerably easier than that of chalcopyrite.

As mentioned earlier, the CESL implementation (Barr et al., 2004; Defreyne et al., 2004; Defreyne et al., 2006) of the medium-temperature process is a departure from the obvious chemistry of dissolution to a chemistry involving precipitation and selective redissolution. This chemistry seems to offer advantages, but is unproven at commercial scale, and may be difficult to achieve at full scale over prolonged periods.

Table I. Summary of the current status of hydrometallurgical options for treating chalcopyrite concentrates.

Process category	Technology name (provider)	Description	Capacity	Operation	Status
Bioleaching	BioCOP™ (Alliance Copper, and BHP Billiton and Codelco JV)	Leaching with thermophilic bacteria (70°C)	20,000 t Cu/a equivalent to 3.4 t Cu/h	Bioleaching plant built in 2002 in Chile	Demonstration plant closed – no commercial implementation
	Mintek/Bactech	Leaching with mesophilic bacteria and fine grinding	2.7 t conc/d equivalent to 0.024 t Cu/h	2.7 t conc/d built in 2001 at Monterrey, Mexico for Peñoles	No commercial or semi-commercial implementation
Ultra-fine grinding and atmospheric leaching	Albion (Xstrata)	Leaching after ultrafine grinding		Pilot plant	No commercial or semi-commercial implementation
	Activox (Norilsk)	Leaching after ultrafine grinding		Pilot plant to Tati Nickel – project terminated after sale of Lionore to Norilsk	No commercial implementation
Medium-temperature pressure leaching	CESL (Teck)	Leaching with chlorides and high pH to produce S and low iron in solution	1.2 t Cu/h	Semi-commercial plant – two year trial at UHC Sossego, Brazil	No commercial implementation
Total pressure oxidation	Freeport McMoran	Fine grind, followed by leaching at 160°C	1.8 t Cu/h	Semi-commercial – operated at Morenci, Arizona since third quarter 2007	Place on care and maintenance in 2009, due to restart in 2015
	First Quantum	Pressure leaching at 220°C	3.4 t Cu/h	Start-up of semi-commercial operations March 2007 at Kansanshi, Zambia	Operating continuously since startup
	Freeport McMoran	Pressure leaching at 220°C		Pilot plant – operated at Bagdad, Arizona and at Hazen	Close due to end of trial

The total pressure oxidation option has been semi-commercially proven over the last seven years at Kansanshi, Zambia (First Quantum) and Morenci, Arizona (Freeport McMoran) (Dreisinger et al., 2011). In the case of Kansanshi, the pressure oxidation step is part of a larger complex, and the ore contains a combination of chalcopyrite and chalcocite. In the case of Morenci, the PLS is fed to a direct electrowinning plant, and the spent electrolyte is combined with PLS from other sources and treated by SX–EW. In spite of the fact that Kansanshi is remote, on a distant extension of the African/Zambian Copperbelt, the plant has achieved acceptable levels of mechanical availability with local operating and support staff.

COMPARISON OF PROCESSES

Leaching Conditions

The leaching conditions can be compared using the Leaching Number, defined as (Crundwell, 2005):

$$N_L = \frac{r(T,C)\,\bar{t}}{L} \qquad [1]$$

where $r(T,C)$ represents the intrinsic leaching rate in m/s, $\bar{t}$ represents the residence time in s, and L represents the mean particle size in the reactor feed in m.

Since the reaction rate is exponentially dependent on temperature, it is temperature that primarily determines the rate. Therefore, the leaching conditions can be compared for the various processes in terms of temperature, residence time and mean particle size in the feed. Crundwell (2005) argued that these three variables are adjusted by the different processes in order to keep the leaching number roughly the same.

The comparison of these three parameters for the four process options is given in Table II, illustrating how temperature, particle size and residence time are balanced in the manner given by Equation 1.

Table II. Comparison of leaching conditions for the four process options.

Process category	Temperature (°C)	Particle size (μm)	Residence time (h)
Bioleaching	70	35	192
Ultra-fine grinding and atmospheric leaching	90–95	5–10	96–144
Medium-temperature pressure leaching	150	30–40	3–6
Total pressure oxidation	200	30–40	1–2

Leaching Products or Residues

The various leaching options do not all produce the same products, which are given in Table III. Most of the processes produce copper and sulfate ions in solution, except for the CESL process in which copper precipitates as basic copper sulfate and iron precipitates as hematite. The main difference between the processes is the form of iron remaining in the leaching residue. The iron deports as jarosite at lower temperatures, goethite in the middle of the temperature range, and as hematite towards the higher temperatures.

Table III. Leaching products for the four process options.

Process category	Copper product	Iron product	Sulphur product
Bioleaching	Cu^{2+} (aq)	Jarosite	SO_4^{2-}
Atmospheric leaching	Cu^{2+} (aq)	Jarosite/goethite	SO_4^{2-}
Medium-temperature pressure leaching	Basic copper sulfate	Hematite/basic ferric sulfate	Elemental sulfur
Total pressure oxidation	Cu^{2+} (aq)	Hematite/goethite	SO_4^{2-}

Copper Recovery
The copper recovery is relatively high for all the processes. Even for bioleaching, which one would expect to have lower recoveries, laboratory tests have produced copper recoveries consistently above 95%. Thus for this study, it was assumed that the copper recovery was between 95 and 98% for all of the options.

Capital Cost
The capital cost is estimated based on a plant in South Africa producing 50,000 tpa of copper cathode. The results of the equipment selection and costing exercise are shown in Table IV. The method of calculating the costs is based on determining the costs for the major equipment, and using factors to get an estimate of the direct field costs. The indirect field costs are estimated as a factor of the direct field costs.

The results of these calculations of capital costs indicate that the average cost of these four plants is $364 million. Interestingly, the Ultra-fine grinding process is potentially the lowest cost operation, and as a result may warrant further investigation. It should be borne in mind that at the level of accuracy of this study, it is not clear that this difference is statistically significant.

Table IV. Comparison of estimated capital costs in US$ (±50%).

	Bioleaching	Ultrafine grinding atmospheric leaching	Medium-temperature pressure leaching	Total pressure oxidation
Plant section:				
Concentrate receipt	270 000	270 000	270 000	270 000
Milling	30 000 000	40 000 000	11 000 000	11 000 000
Repulp	350 000	380 000	265 000	350 000
Leaching	170 000 000	97 000 000	175 000 000	172 000 000
Iron removal	2 000 000	2 400 000	0	1 700 000
Counter-current decantation	5 500 000	4 200 000	4 200 000	6 600 000
Solvent extraction	18 000 000	18 000 000	25 000 000	25 000 000
Electrowinning	25 000 000	25 000 000	25 000 000	25 000 000
Bleed neutralisation	1 000 000	1 000 000	2 500 000	0
Tailings treatment	25 000 000	25 000 000	22 000 000	30 000 000
Limestone plant	3 000 000	3 000 000	2 600 000	3 900 000
Oxygen plant	45 000 000	45 000 000	32 000 000	45 000 000
Total direct field cost	**280 120 000**	**216 250 000**	**267 835 000**	**275 820 000**
Indirect field costs	112 048 000	86 500 000	107 134 000	110 328 000
Total plant cost	**392 168 000**	**302 750 000**	**374 969 000**	**386 148 000**

Operating Cost
The operating cost estimates are given in Table V. These costs include power, labour, reagents, and maintenance.

Table V. Total operating costs for the four options.

	Bioleaching	Ultrafine grinding atmospheric leaching	Medium-temperature pressure leaching	Total pressure oxidation
Total operating cost ($ US million)	41	36.5	45	40

Assessment of Risk
Six criteria were used to rank the different options:

(i) **technology**, which refers to the maturity of the option, the accumulated knowledge for design and option, the availability of a number of suppliers to assist;
(ii) **risk**, which refers to an assessment of the relative chance of the process operating to design specification;
(iii) **operability**, which refers to ease of operating the process once installed;
(iv) **capital costs**, which refers the estimate within a range of +/- 50%, of the capital required to install the process;
(v) **operational costs**, which refers to the initial estimate of the operating costs of producing copper;
(vi) **health, safety and environment**, which refers to an assessment of the relative health, safety and environmental concerns for each of the process options.

The six criteria were ranked on a scale of 1 to 7, with 1 being the lowest and 7 being the highest. The results of this assessment are given in Table VI.

Table VI. Ranking of the four process options using the selection matrix.

Key evaluation criterion	Bioleaching	Ultrafine grinding atmospheric leaching	Medium-temperature pressure leaching	Total pressure oxidation
Technology maturity	3	2	5	6
Risk	3	2	5	6
Operability	5	5	4	4
Capital costs	5	6	4	4
Operational costs	4	4	3	4
Health, safety & environment	5	5	5	5
Overall score	4.17	4.00	4.33	4.83

The results of the analysis using the selection matrix suggest that the total pressure oxidation option has the greatest chance of success.

CONCLUSIONS

The capital and operating costs suggest that there is little different between the four options, and that these values are all within the error of cost estimation used. The ultrafine grinding and atmospheric leaching option does seem to offer the possibility of reduced capital costs, but more detailed design, combined with experimental verification, is required. Based on the track record of the Morenci plant and the Kansanshi operation, the total pressure oxidation poses the least risk and smallest plant footprint, and is therefore the recommended option.

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