MesoTherm™ Bio-Oxidation Technology: A Simple Process Adjustment for African Copperbelt Mixed and Sulphide Ores

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Diminishing acid-leachable copper oxide resources, coupled today with an ever-increasing need to competitively beneficiate primary and secondary copper and cobalt sulphide ores has seen Outotec accelerate the development of its MesoTherm™ bio-oxidation technology for base metals. Initially developed for refractory gold ore applications of the well-established and commercialized BIOX® process, ongoing development of the technology has shown it to be effective on primary (chalcopyrite) and secondary (covellite) copper sulphides, yielding 98% copper dissolution for these minerals, while cobalt sulphide minerals (carrollite) yielded 97% cobalt dissolution. Outotec is in the unique position to bring this simple technology competitively to the market with its leading world-class equipment, providing the best of both process and mechanical performance guarantees in an optimized flowsheet to users. This is particularly relevant in the African Copperbelt where, through this relatively cost effective process adjustment, many existing oxide operations can now process mixed and or sulphide ores. Use of this technology offers the flexibility for expanded production, extended life of operations and/or to counter the effects of falling head grades.

INTRODUCTION

Gencor has pioneered the commercialization of the bio-oxidation of refractory gold ores since the 1980s. When the interests of Gencor and Gold Fields of South Africa were merged in 1998 to form the new Gold Fields, the BIOX® technology and its holding company BIOMIN Technologies Limited were transferred to the new company. On 19 April 2013, Gold Fields Limited and BIOMIN South Africa (Pty) Limited signed an agreement whereby BIOMIN acquired the full title and rights to the BIOX® technologies from Gold Fields. In November 2015, Outotec Oyj (Outotec) acquired BIOMIN South Africa (Pty) and the BIOX® technology and its holding company BIOMIN Technologies Limited were transferred to Outotec who are now the owners of the technology.

The BIOX® technology has been in commercial operation for over 25 years with thirteen BIOX® plants successfully designed and implemented in that time, with almost 23 million ounces of gold produced through utilization of the technology. With such an effective technology commercialized for refractory gold concentrates, application of the technology for base metal sulphide processing was the next logical step. The distinguishing feature between the two processes is metal recovery on subsequent cyanide leaching for the former process, while the latter would yield immediate metal solubilisation as the extent of sulphide oxidation proceeds.

In 1998, the Kasese Cobalt Company commissioned and operated the first commercial mesophile bio-oxidation facility in Uganda, treating a cobaltiferous pyrite concentrate through what were then the largest bio-oxidation reactors, viz. 1400 m^3. Traditional mesophile bioleaching, having its optimum operating temperature in the range 38 ^oC to 42 ^oC, is effective for the minerals bornite, covellite and chalcocite; it is, however, not suitable for the minerals chalcopyrite, enargite and carrollite, with only limited metal solubilisations possible.

For base metal bio-oxidation to be to be economical, very high extents of sulphide mineral oxidations with the concomitant high extents (>98%) of metal recoveries are required. Developmental work to enhance mineral bio-oxidation using higher temperature thermophile micro-organisms was looked at in 1996 by BHP Billiton precisely for this reason. This work proved to be very successful, showing that high extents of sulphide oxidation could be obtained at temperatures spanning the range 68^oC to 75 ^oC, with near-complete solubilisation of copper and cobalt from chalcopyrite and carrollite, respectively. Ongoing technology trialing eventually led to the successful operation of a thermophile demonstration circuit at the Codelco Chuquicamata processing facility in 2003.

In 2002, Outotec commenced work using high-temperature thermophile micro-organisms as well, but this work focused on a combination mesophile–thermophile bio-oxidation process, which showed huge potential in reducing the cyanide consumption when compared with conventional mesophile bio-oxidation residues. Moreover, Outotec started to investigate this technology for its efficacy on base metal sulphides and achieved results in line with previous investigators, reporting chalcopyrite, covellite and carrollite mineral solubilisations in excess of 97%.

This approach of utilizing mesophiles for the initial extent of sulphide oxidation is quite novel as it lowers the sulphide loading and duty for the subsequent thermophile stage, thus resulting in a less onerous mass transfer requirement at the higher thermophile temperatures. Furthermore, by considering inter-stage thickening between the two oxidative processes, the various metals (copper, iron, arsenic) and sulphates prevalent in the mesophile stage can be decanted off, thus simplifying the operation of the thermophile stage, hence maintaining high levels of activity.

This paper provides some laboratory results obtained by using this combination mesophile–thermophile bio-oxidation processing stage, describes some of the large-scale testing currently ongoing to validate certain engineering scale-up parameters and intends to provide a novel hydrometallurgical and economical process route to effectively treat mixed or sulphide ores.

OUTOTEC'S TRADITIONAL BIOX® PROCESS

The Outotec BIOX® process for the treatment of refractory gold concentrates has been in commercial operation for 30 years, with 13 successful BIOX® plants commissioned worldwide. To date, over 23 million ounces of gold have been produced through BIOX®. The BIOX® process is especially suitable for remote locations by virtue of the simplicity of operation and scalability of the technology using a modular design. Commercial BIOX® plants operate at treatment capacity within the range of 20 to 2137 tons per day of flotation concentrate. Figure 1 shows the typical flowsheet.

Table I shows the 13 Outotec BIOX® plants commissioned to date and Figure 2 shows photographs of three of the thirteen plants, viz. Suzdal, Fosterville and Kokpotas, while Figure 3 shows a view of the decommissioned Kasese and BHP Billiton bio-oxidation plants.

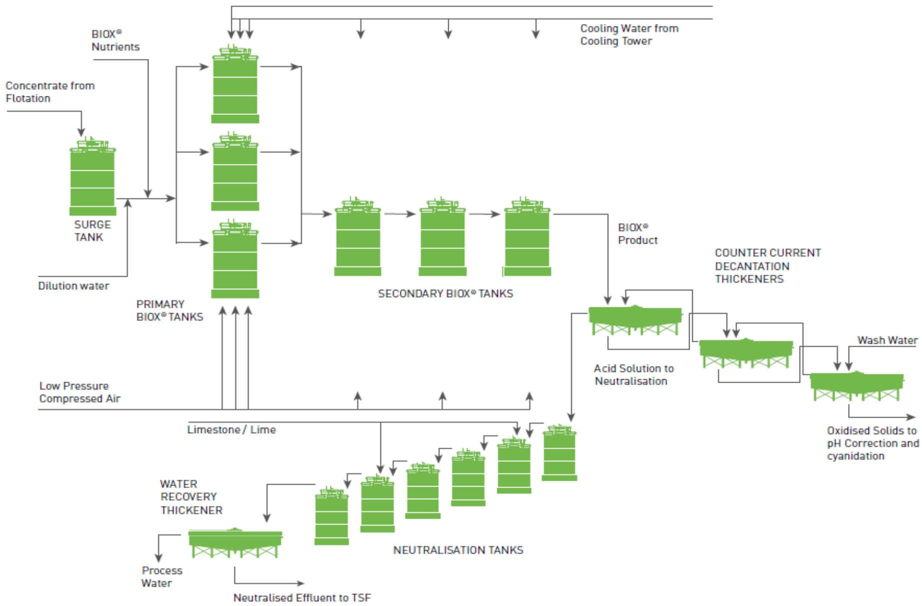

Figure 1: Outotec BIOX® circuit for gold schematic.

Table I: Summary of commercial BIOX® operations.

Country	Mine	Capacity	Reactor (m³)	Commissioned
South Africa	Fairview	62	340	1986
Brazil	Sao Bento	150	550	1990
Australia	Harbour Lights	40	160	1991
Australia	Wiluna	158	480	1993
Ghana	Ashanti	960	900	1994
Peru	Coricancha	60	262	1998
Australia	Fosterville	211	900	2005
Kazakhstan	Suzdal	520	650	2005 / 2010
Ghana	Bogoso	820	1500	2007
China	Jinfeng	790	1000	2007
Uzbekistan	Kokpotas	2138	900	2009 / 2011
South Africa	Agnes	20	60	2010
Philippines	Runruno	404	1300	2016

Figure 2: Photographs of the Suzdal, Fosterville and Kokpotas Outotec BIOX® plants.

Figure 3: Photographs of the mesophile Kasese cobalt and the thermophile BHP Billiton copper plants.

OUTOTEC'S MESOTHERM™ BIOX® PROCESS

Outotec is currently trialing its MesoTherm™ technology—a hybrid bio-oxidation process using mesophiles to realise the primary-stage oxidation and a thermophile culture to realise the near-complete final sulphide oxidation. The commercial demonstration of the thermophile technology is not new and BHP Billiton operated a commercial-scale facility using thermophiles with their BioCOP™ technology at the Chuquicamata mine in Chile with a design production rate of 20 000 tons of copper cathode per annum. This process utilized thermophilic micro-organisms operating at temperatures in the range 70^{o}C to 77^{o}C with bio-oxidation reactor volumes of 1200 m^3.

Combining the best of both technologies and almost identical to the BIOX® process, Outotec's MesoTherm™ technology comprises contacting the sulphide ore or concentrate with a strain of the thermophile mixed culture post the conventional BIOX® primary stage processing. The thermophiles therefore continue catalysing the oxidation of the sulphide minerals, which in the case of gold recovery, results in high dissolutions and significantly reduced cyanide consumption, while in the case for base metals results in much improved metal solubilisation (particularly for chalcopyrite and carrollite).

The oxidation reactions of various sulphide minerals are identical for the two stage bio-oxidation applications and some principal reactions are summarized as follows:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad [1]$$

$$2FeAsS + 7O_2 + H_2SO_4 + 2H_2O \rightarrow 2H_3AsO_4 + Fe_2(SO_4)_3 \quad [2]$$

$$Cu_5FeS_4 + 6O_2 + 4H_2SO_4 \rightarrow FeSO_4 + 5CuSO_4 + 2So + H_2O \quad [3]$$

$$2CuFeS_2 + 8.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2CuSO_4 + H_2O \quad [4]$$

$$Cu_2S + 2.5O_2 + H_2SO_4 \rightarrow 2CuSO_4 + 2H_2O \quad [5]$$

$$2Cu_3AsS_4 + 17.5O_2 + 5H_2O \rightarrow 2H_3AsO_4 + 6CuSO_4 + 2H_2SO_4 \quad [6]$$

$$CuCo_2S_4 + 6O_2 \rightarrow CuSO_4 + 2CoSO_4 + S^0 \quad [7]$$

Figure 4 shows photographs of the typical Outotec mesophile and thermophile community structures, while Figure 5 shows the MesoTherm™ flowsheet schematic.

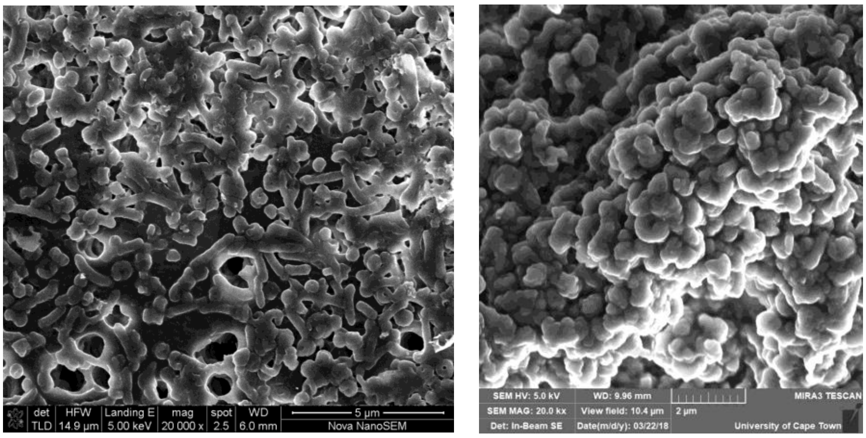

Figure 4: Photos of the Outotec mesophile and thermophile cultures.

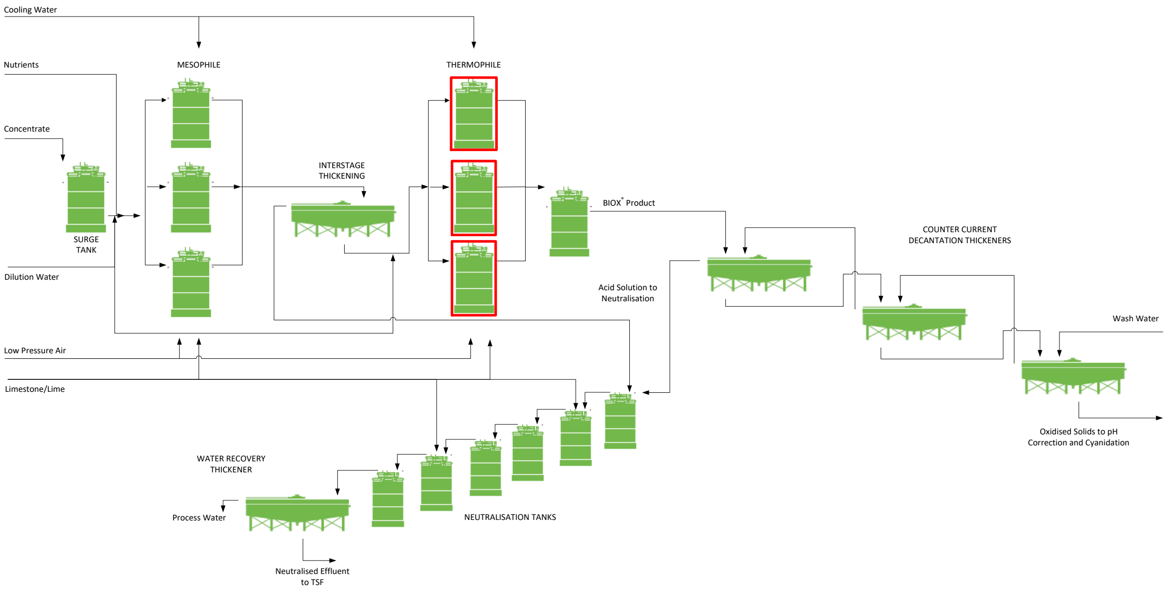

Figure 5: Outotec MesoTherm™ BIOX® circuit for gold schematic.

MESOTHERM™ BIOX® LEACHING OF COPPER SULPHIDE CONCENTRATES

Batch laboratory test campaigns simulating a mesophile bio-oxidation stage followed by a thermophile bio-oxidation stage were conducted on two copper–cobalt sulphide concentrates sourced in Zambia. Prior to conducting the test work, the respective cultures were first adapted to copper and cobalt concentrations using the corresponding salts. These salts were frequently added with a clean pyrite–arsenopyrite concentrate. The concentrates used in the batch experiments had varying degrees of primary and secondary copper sulphides, and also varying amounts of carrollite. On average, Sample 1 had an average particle size distribution of 90% passing 75 µm and a top size of 100% passing 150 µm, while Sample 2 had an average particle size distribution of 66% passing 75 µm and a top size of 90% passing 150 µm. The basic mineralogical composition of the two concentrates, as well as the respective bio-oxidation stage results, are shown in Tables II and III, respectively.

The results show that the mesophile stage bio-oxidation is effective in achieving a high extent of copper dissolution, which can be attributed to the secondary sulphide mineral oxidation. The residual copper content of the mesophile residues shown in the tables, although not quantified in these test campaigns, can most likely be attributed to chalcopyrite copper. A limited extent of carrollite dissolution was achieved, viz. only 65% for Sample 1 and 40% for Sample 2. Completing the mineral oxidation using thermophiles yielded copper and cobalt dissolutions of 96% and 97%, and 99% and 93% for Samples 1 and 2, respectively. Sulphide oxidations for the two samples reached 88% and 92%, respectively, for Samples 1 and 2. These results are consistent with results from previous investigators (Dew *et al., 1999*) who developed similar final extents of mineral oxidation for mesophile stage bio-oxidation in continuous pilot trials, as well as batch thermophile tests. Figure 6 and Table IV show these results.

Table II: Summary of batch MesoTherm™ results for a Zambian sample (Sample 1).

Mineral	Mineral content / sulphide (%)	Metal distribution (%)		Metal content (%)		Mesophile residue (%)			Metal dissolution (%)		S^{2-} oxidation (%)
		Cu	Co	Cu	Co	S^{2-}	Cu	Co	Cu	Co	
Carrollite	1.77	0.92	100.00	0.36	0.67						
Secondary Cu S^{2-}	34.09	69.36	–	27.19	–						
Chalcopyrite	33.82	29.72	–	11.65	–						
Pyrite	2.19	–	–	–	–						
Sulphide	20.64	–	–	–	–						
		100.00	100.00	39.20	0.67	8.20	6.30	0.23	84	65	60
						Thermophile residue (%)			Metal dissolution (%)		S^{2-} oxidation (%)
						S^{2-}	Cu	Co	Cu	Co	
						2.40	1.40	0.02	96	97	88

Table III: Summary of batch MesoTherm™ results for a Zambian sample (Sample 2).

Mineral	Mineral content / sulphide (%)	Metal distribution (%)		Metal content (%)		Mesophile residue (%)			Metal dissolution (%)		S^{2-} oxidation (%)
		Cu	Co	Cu	Co	S^{2-}	Cu	Co	Cu	Co	
Carrollite	5.28	4.76	100.00	1.08	2.01						
Secondary Cu S^{2-}	19.16	67.62	–	15.28	–						
Chalcopyrite	18.12	27.62	–	6.24	–						
Pyrite	8.08	–	–	–	–						
Sulphide	16.72	–	–	–	–						
		100.00	100.00	22.60	2.01	6.10	2.31	1.20	90	40	64
						Thermophile residue (%)			Metal dissolution (%)		S^{2-} oxidation (%)
						S^{2-}	Cu	Co	Cu	Co	
						1.34	0.33	0.15	99	93	92

Table IV. Summary of batch thermophile results for various samples.

Concentrate	Chalcopyrite (%)	Secondary copper sulphides (%)	Culture (°C)	Copper dissolution (%)
Chile	4.3	14.2	68	96
Zambia A	23	41	78	97
Zambia B	11	30	68	95
Australia	55		68	96

While no detailed mineral speciation of the samples shown in Table IV is available, the overall MesoTherm™ results achieved for copper and shown in Tables II and III compare well with the results shown in Table IV.

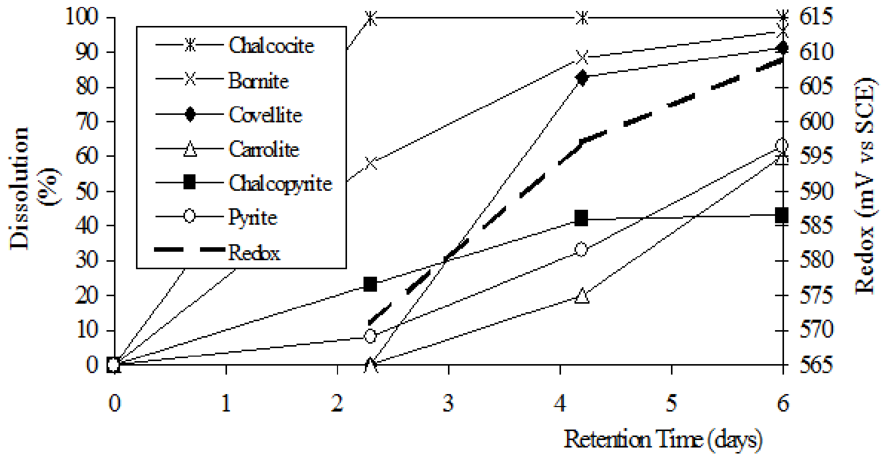

Figure 6: Continuous bioleaching of a Zambian concentrate with a mesophile culture at 40°C.

The case study discussed here considers that Co occurs as carrollite, which leaches in the oxidative conditions prevailing during bioleaching. The occurrence of Co in heterogenite and other Co(III) minerals will require reductive leaching. Reductive leaching to recover cobalt present in such minerals may need to be considered in some African Copperbelt orebodies. It is worth noting that the reductive leach step is often included in the oxide ore leach circuits on existing plants and may be considered for inclusion in the integrated flowsheet.

MESOTHERM™ BIOX® FLOWSHEET CONSIDERATIONS FOR BASE METAL SULPHIDES

As noted earlier, the use of bio-oxidation for base metals has been commercialized before at the Kasese cobalt operation in Uganda, which used a mesophile culture, and the Chuquicamata facility in Chile, which used a thermophile culture. The Outotec MesoTherm™ bio-oxidation flowsheet follows on from these previous applications, with variances introduced owing to the nature of the feed concentrate chemical and mineralogical characteristics.

For the easily leachable secondary copper sulphides, such as covellite, chalcocite and bornite, a simple straight-through mesophile bio-oxidation circuit can be applied and high copper solubilisations and sulphide oxidations can be expected. Usually, when the copper concentrations are expected to exceed 30 g/L, a pre-leach stage is considered, which limits the copper tenor in the subsequent bio-oxidation circuit. A further advantage of having a pre-leach stage for secondary copper sulphide minerals, particularly for high chalcocite contents, is that a significant degree of chemical leaching can be obtained in this stage, which will result in higher oxidizing conditions in the bio-oxidation circuit, which will be more favorable for improved covellite and bornite mineral oxidation. This was also described by Dew *et al.* (1999), as shown in Figure 6. The mesophile secondary copper sulphide circuit can be schematically described as shown in Figure 7.

While the flowsheet shown in Figure 7 will be effective for secondary copper sulphide mineral oxidation, it is not expected to yield economical metal recoveries from chalcopyrite and carrollite dominated minerals. To this end, a more effective flowsheet is the Outotec MesoTherm™ circuit, which is conceptualized in Figure 8.

Figures 7 and 8 depict the bio-oxidation circuits as stand-alone operations, yet most likely, any consideration for utilizing the technology will be as bio-oxidation circuits integrated into existing facilities where mining is progressing from oxide, through transitional material, and eventually into sulphide material. The integration of this hydrometallurgical technology is quite simple and ultimately considers a series of aerated reactors and counter-current decantation thickeners configured to treat the corresponding sulphide material with pregnant liquor reporting to an existing metal recovery area. While potential applications will need to be assessed on individual merits, it may be also be a fair assumption that existing leach operations may have redundant equipment that may mitigate considerable capital expenditure equipment.

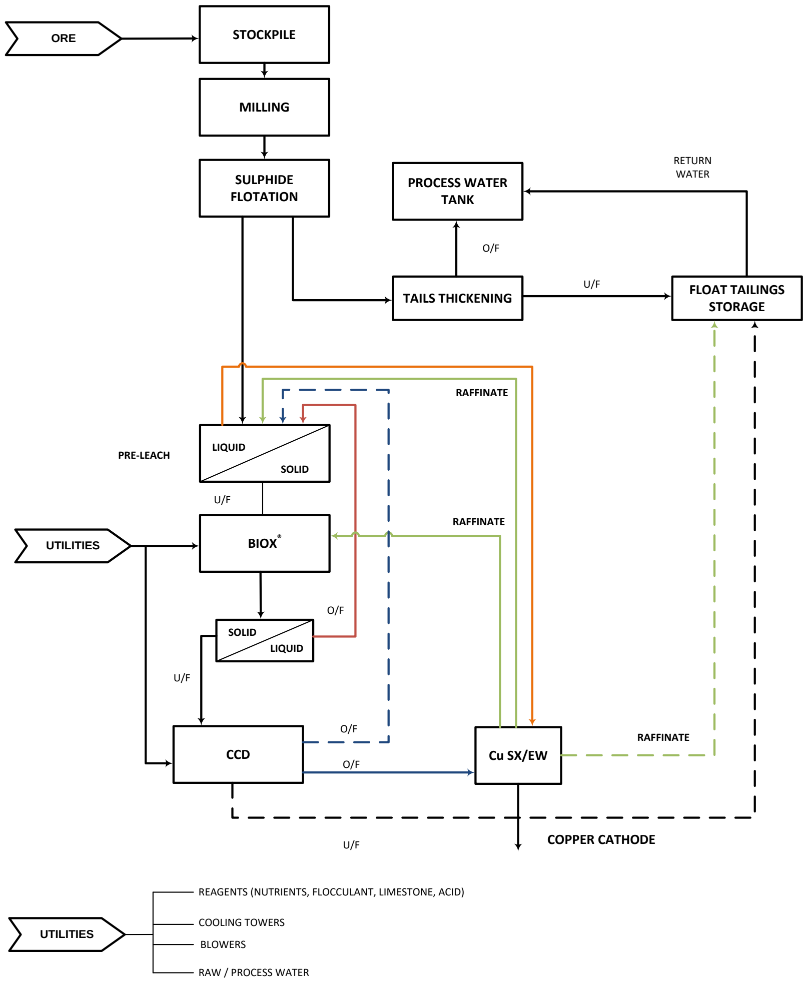

Figure 7: Conceptual Outotec BIOX® flowsheet for secondary copper sulphides (40°C)

Table V provides a high level capital cost (±30%) estimation considered for a 2017 Zambian project evaluating the treatment of a mixed copper sulphide (primary and secondary) and carrollite concentrate. The capital costs were determined by concluding a preliminary design on the envisaged feed characteristics and thereafter costing the principal capital cost items. The intended bio-oxidation circuit proposed was a MesoTherm™ circuit targeting copper and cobalt dissolutions exceeding 97%. This evaluation considered integration of the bio-oxidation circuit only with subsequent metal recovery achievable in the existing circuit. The circuit is therefore premised on the flowsheet depicted schematically in Figure 8. The estimated capital breakdown is shown in Figure 9.

Note that the bio-oxidation circuit costs shown consider new equipment and the reactor material of construction as a duplex steel (SAF 2205). It can be expected that the capital costs may be lower should existing site equipment be retrofitted in to a bio-oxidation circuit.

Table V: High-level MesoTherm™ capital cost estimation for a Zambian study.

Description	Units	Value

Feed rate (design)	tpd	250
Sulphur	%	13
Copper	%	22
Cobalt	%	2
Total retention time	days	5.5
Number of primary reactors (mesophile)		3
Number of primary reactors (thermophile)		3
Number of secondary reactors (thermophile)		1
Total number of reactors		7
Live volume per reactor	m^3	945
Total mechanical equipment supply	USD million	8.3

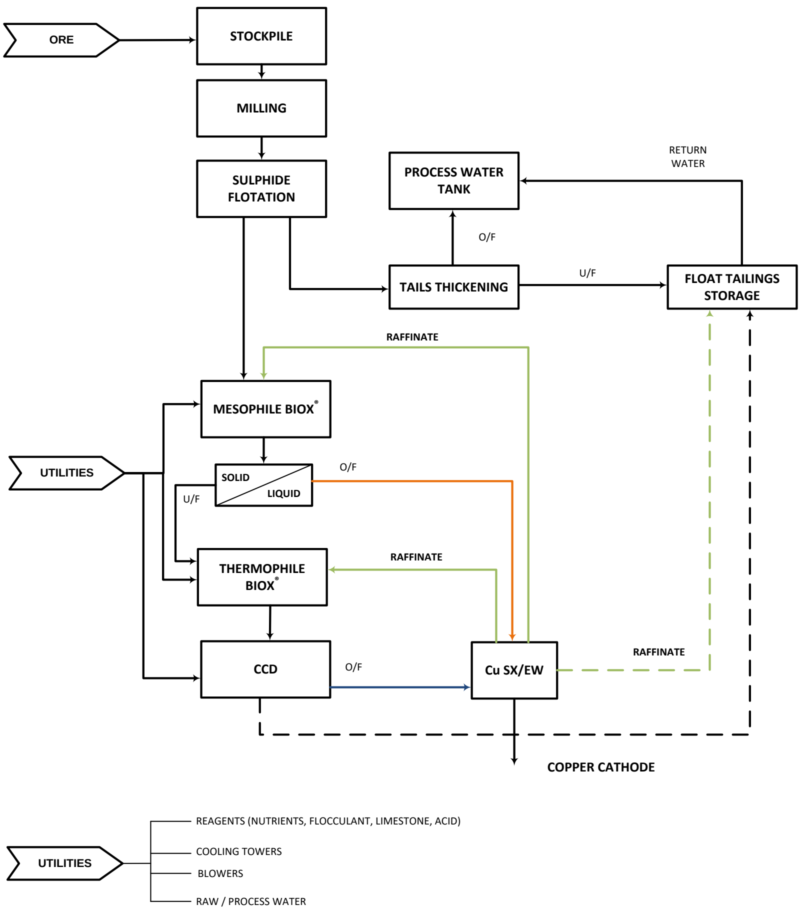

Figure 8: Conceptual Outotec MesoTherm™ BIOX® flowsheet for primary copper sulphide (40°C to 68°C).

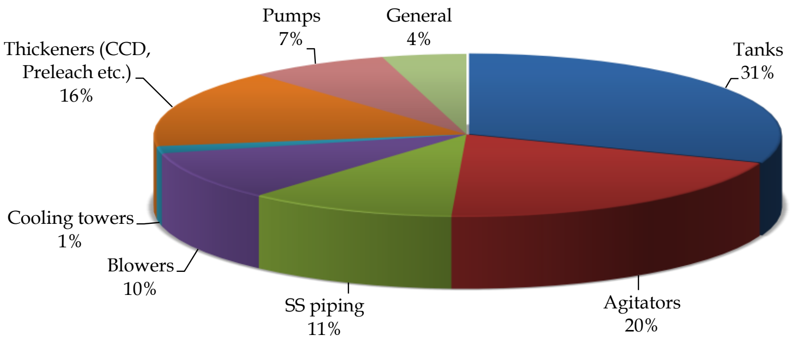

Figure 9: High level cost estimate for a 250 tpd MesoTherm™ BIOX® circuit (40°C to 68°C).

MESOTHERM™ BIOX® ENGINEERING SCALE-UP AND VALIDATION

Outotec are currently concluding a large-scale engineering validation in a 21 m^3 test reactor at the Fairview BIOX® plant in Mpumalanga. While laboratory batch tests have shown the feasibility of the thermophile culture to achieve high metal solubilisations and sulphide oxidations, the purpose of the larger scale-up stage is to:

- evaluate the robustness of the thermophile culture by exposing it to varying feed (pyrite and arsenopyrite) blends and operating the reactor in situ as a "production reactor";
- determine the tolerance of the reactor to varying solids concentrations and total dissolved solids;
- study the energy generation (W/m^3) potential of different sulphide feeds to keep the reactor auto-thermal;
- evaluate the actual mass transfer rates achievable at temperatures ranging from 65°C to 68°C by measuring aqueous dissolved oxygen concentrations, oxygen off-gas analyses and relating these to sulphide oxidations. One attractive prospect of the MesoTherm™ technology is the use of low-pressure blower air and, while the solubility of oxygen decreases at higher temperatures, the lower sulphide duty to perform on the partially oxidized material mitigates the use of oxygen-enriched air (lower costs).

Figure 10 shows views of the 21 m^3 demonstration reactor being utilized for these investigations.

CONCLUSIONS

The bio-oxidation of primary and secondary copper sulphide concentrates, as well as carrollite, using mesophile and thermophile cultures has shown that high metal dissolutions can be achieved.

Outotec is currently developing its MesoTherm™ bio-oxidation technology for base metals. Initially developed for refractory gold ore applications from the well-established and commercialized BIOX® process, ongoing development of the technology has shown it to be effective on primary (chalcopyrite) and secondary (covellite) copper sulphides, yielding 98% copper dissolution for these minerals while cobalt sulphide minerals (carrollite) yielded 97% cobalt dissolution.

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Figure 10: 21 m³ Thermophile validation and scale-up reactor (65–68°C).

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