

# **REMOVAL OF IMPURITIES FROM COPPER SULFIDE MINERAL CONCENTRATES**

Bу

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# ABSTRACT

Certain Copper Sulfide mineral concentrates in certain parts of the world not only contain gold and silver but also varying levels of impurities. Additionally some halides and certain base metals can also be present. A process has been developed and tested that both addresses the simultaneous removal of these impurities and reduces the shipping mass to produce a "Super Concentrate" to Smelters.

Keywords: Copper Sulfide, Copper Concentrate Impurities Removal, Concentrate Upgrade, Process Development

## INTRODUCTION

The dominant copper-containing minerals in most copper sulfide deposits are chalcopyrite, bornite. chalcocite and covellite. In some cases cubanite, enargite and tennantite are also present. Pyrite and sometimes pyrrhotite are present as gangue sulfide minerals in copper sulfide deposits.

High-grade, copper sulfide concentrates, (typically greater than about 25% w/w Cu), are commonly treated via pyrometallurgical routes, while hydrometallurgical routes are typically favoured for lower grade or impurity bearing concentrates. The processing routes for the treatment of copper concentrates can also be influenced by the presence of minor valuable metals such as nickel, cobalt, silver, gold, palladium and platinum, as well as deleterious metals such as arsenic, lead, and uranium.

Most of the copper concentrates produced around the world contain some impurities. Depending on the type and level of impurities present in the copper concentrate, the price received for the copper concentrate can be penalised. Copper concentrate containing high levels of impurities is not acceptable to some smelters. This can render them unsaleable in some countries as in the case of the high arsenic containing concentrates from the Pacific Rim.

To permit treatment and to maximise the value of a copper concentrate, the levels of impurities in the concentrate need to be reduced below the limit sets by the smelters and in some cases the authorities in the producing and receiving countries. This paper presents a method of impurity removal for copper concentrates.

## IMPURITY TYPES AND TYPICAL LEVELS

Table 1 provides typical assays of the copper concentrates of a few producing plants.

Element	Boliden (1)	Hindustan (Khetri Concentrate)	Hindustan (Malanjkhand Concentrate)	Assarel- Medet <sup>(3)</sup>	Lumwana (Malundwe) (4) (5)	Lumwana (Chimiwungo) (4) (5)
		Note 1	Note 1			
Cu	21.7%	15-19%	25-28 %	20-26	41-45%	28-32%
S	31.8%	26-31%	28-32 %	34-38	26-29%	28-31%
Fe	24.8%	32-40%	27-31 %		19-22%	24-27%
Au		1.5-3 ppm	1-3 ppm	2-5 ppm	2-4 ppm	2-4 ppm
Ag		12-20 ppm	50-80 ppm	15-40 ppm	0-2 ppm	0 -2 ppm
As	0.34%		<100 ppm	<0.02%	10 ppm	10 ppm
Cd	0.018%			<0.01%	5 ppm	57 ppm
F					100 ppm	200 ppm
Hg			< 5 ppm	<0.3 ppm	0.18 ppm	0.100 ppm
Ni		200-300 ppm	<250 ppm	<0.008%	430 ppm	2150 ppm
Pb	5.6%	50-100 ppm	<400 ppm	<0.06%	34ppm	60 ppm
Sb	0.16%		<100 ppm	<0.01%	5 ppm	7 ppm
Se		8-15 ppm	<100 ppm		23 ppm	16 ppm
Te		5-8 ppm	<100 ppm	< 50 ppm	4.2 ppm	1.6 ppm
U					<130ppm <sup>(5)</sup>	<130ppm <sup>(5)</sup>
Zn	4.9%	200-400 ppm	<1000 ppm	<0.03 %	150 ppm	260 ppm

#### Table 1: Copper Concentrate Assays of Operating Plant

Note 1: on dry basis

# IMPACT OF IMPURITIES ON TRANSPORT, TREATMENT AND PROCESSING

The impurities in the copper concentrate can have a significant effect on transport requirements and downstream treatment.

Impurities in copper concentrate can<sup>(6)</sup>:

- Impact the occupational health and safety of the smelter and refinery employees,
- Increase the cost of waste disposal,
- Increase the overall operational cost,
- Increase the smelter-refinery capital cost, and
- Reduce the cathode quality and thereby the revenue stream.

Table 2 summarises the impact of different types of impurities on transport, treatment and processing of concentrate.

# Table 2: Summary of the Impact of Impurities in Copper Concentrate on Transport,Treatment and Processing<sup>(6)(7)</sup>

Impurities	Impacts
Arsenic	<ul> <li>Reduces conductivity of copper metal (0.1% in copper can reduce conductivity by 23%)</li> </ul>
	- Raise recrystallisation temperature of copper
	- Cause cracking at copper grain boundary
	- Arsenic is a known human carcinogen
	<ul> <li>As<sub>2</sub>O<sub>3</sub> in acidic conditions and in the presence of a reductant can form highly toxic arsine gas</li> </ul>
Antimony	- Reduces conductivity, annealability and drawability in copper metal
	- Sb <sub>2</sub> O <sub>3</sub> is a possible human carcinogen
Bismuth	- Causes rod cracking and poor drawability
Selenium	- Mainly report to the slimes. Causes cracking during wire drawing
Tellurium	- Mainly report to the slimes. Causes rod cracking and poor drawability
Lead	- Toxic heavy metal and carcinogen
	- Can cause anode passivation in refining at concentrations > 0.15%
Nickel	- Nickel compounds and metallic nickel is a known human carcinogen
	- High level of NiO promotes anode passivation and decrease the
	solubility of copper in the electrolyte
	- High nickel concentration in the electrolyte decreases its electrical
	conductivity
	- Nickel is required to be removed from the electrolyte
Cobalt	<ul> <li>Cobalt will follow nickel in the refinery and is required to be removed from the electrolyte</li> </ul>
Chlorine	<ul> <li>Causes corrosion in smelter flues, waste-heat boiler tubes, heat</li> </ul>
	exchanges and other places where it can condense as HCl
	<ul> <li>Can react with partially combusted hydrocarbons present in the smelter off gases to form dioxins and furans</li> </ul>
Fluorine	<ul> <li>Can react with water in the off-gas to form hydrofluoric acid</li> </ul>
	<ul> <li>Hydrofluoric acid can cause corrosion in the off-gas systems in smelter, cause catalyst degradation, attack on the silica in acid brick linings and corrosion of stainless steel components in the strong acid systems of acid plants</li> </ul>
Cadmium	- Cadmium is a toxic heavy metal and is a known human carcinogen
Mercury	- Mercury is highly toxic
	- Raises waste disposal costs
	- Fouls acid plant catalysts
	<ul> <li>Build up in the acid plant heat exchangers</li> </ul>
	- Can contaminate the smelter acid
	<ul> <li>Can report to the exhaust gases</li> </ul>

Impurities	Impacts
Uranium	<ul> <li>Uranium reports to slag and is lost from any potential revenue stream</li> <li>Slag is potentially problematic to manage with uranium deportment</li> <li>A radiation management and compliance system is potentially required</li> </ul>
Zinc	<ul> <li>Reports to the smelting furnace slag and can increase the slag viscosity, which can raise smelting costs and increase copper losses</li> <li>Can create fumes and increase the dust recycle load</li> </ul>
Silica	<ul> <li>Higher silica in concentrate results in higher treatment cost and freight cost per tonne of copper as the treatment costs is based on the mass of copper concentrate and not copper content</li> <li>Silica is normally not a problem as silica is normally added to the furnace feed to achieve the correct SiO<sub>2</sub>/Fe ratio. However, if the silica concentration is too high, the slag can have a higher melting point and higher viscosity</li> </ul>
Alumina and Magnesia	<ul> <li>Increase the melting point and viscosity of the slag if alumina and magnesia content rises beyond a certain percentage (typically 3-5%) As a result, higher operating temperatures will be required which increases the energy costs</li> <li>Higher operating temperatures can also lead to higher refractory losses and shorter furnace crucible life</li> </ul>
Gold and Silver	<ul> <li>Precious metals such as gold and silver are recovered as "slimes" in the electro refining cells</li> </ul>

As the cost of concentrate transportation has decreased and the cost of smelter emission controls has increased, an increasing number of mines are exporting concentrate to large custom smelters for treatment to produce copper cathodes and sulfuric acid<sup>(6)</sup>. The cost of emission controls and the overall operating cost environment of a smelter has made it prohibitive for small (<100,000 t/annum copper matte) smelters to remain in business.

Impurities impact established smelters differently depending on the quality of the primary feed, their location with respect to adjacent farming and human activities, recreational sites and national regulations. For example, the Japanese copper smelter impurities limits are shown in Table 3 and those for China in Table  $4^{(6)}$ .

Species	Charge (US\$t)	For each (%)	Exceeding (%)
As	2.5	0.1	0.2
Sb	0.50	0.01	0.1
Bi	0.30	0.01	0.05
CI	0.50	0.01	0.05
Pb	1.50	1.0	1.0
Zn	1.50	1.0	3.0
Ni + Co	0.30	0.1	0.5
$AI_2O_3 + MgO$	4.50	1.0	5.0
F	0.10	10ppm	330 ppm
Hg	0.20	1ppm	10 ppm

# Table 3: Japanese Copper Smelter Penalty Elements<sup>(6)</sup>

#### Table 4 : Upper Concentration Limits for Importing Copper Concentrates into China<sup>(6)</sup>

Species	Upper Limit (%)
Pb	≤ 6.0
As	≤ 0.5
F	≤ 0.1
Cd	≤ 0.05
Hg	≤ 0.01

#### MINERALOGY OF COPPER CONCENTRATES

OZ Minerals Pty Ltd provided two distinct concentrate samples for test work purposes with a focus on developing the impurity removal methodologies proposed by Orway Mineral Consultants (OMC) in this paper. These two concentrates were subsequently named concentrate A and B. The two copper sulfide concentrates supplied (and copper concentrates in general) can be loosely grouped into two categories, i.e. secondary and primary. Examples of these are given in Figure 1. The major elements of concentrate types A and B are given in Table 5.

Examples of the mineralogy of the copper concentrates are shown in Figure 1, with the corresponding elemental assays for each concentrate shown in Table 5. Dominant copper minerals in copper concentrate are typically chalcopyrite, chalcocite, covellite and bornite. In some cases cubanite, enargite and tennantite are also present.



Figure 1: Mineralogy of Copper Concentrate

Element	Units	Secondary Concentrate (A)	Primary Concentrate (B)
Cu	%	49.5	27.6
Fe	%	13.4	31.8
S	%	22.4	35.5
Au	ppm	23	9.2
Ag	ppm	110	109
Co	ppm	730	1400
Ni	ppm	110	215
Мо	ppm	290	95
Pb	ppm	287	241
Se	ppm	135	95
Те	ppm	44	29
Si	%	3.1	1.0
Th	ppm	6	6
U	ppm	<80	<80
CI	ppm	70	33
F	ppm	<600	68

Table 5: Typical Assay of Copper Concentrate

#### IMPURITY REMOVAL

## Approach

The objective of impurity removal is to produce a smeltable concentrate. Impurities are invariably locked within the valuable mineral particles. If not locked, they would typically be separated in the flotation process.

Any process to remove impurities locked within the value mineral has to "open" the minerals to allow extraction to occur. While this is occurring, the following objectives also need to be met;

- Copper losses need to be minimal,
- Sulfur levels in the feed concentrate need to be adequate for autogenous smelting and of a quality suited to sulfur dioxide production and ultimately captured as sulfuric acid, and
- The impurities removed from the concentrate should ideally be captured in a single phase and be readily immobilised quantitatively for landfill in a H-H (highly hazardous waste site) or equivalent mono-site.

To achieve these goals, OMC concluded that hydrometallurgical processes offered the best opportunities and within this broad category both anoxic alkaline and acidic leaching were seen to offer potential.

Anoxic Alkaline Leaching has been shown to demonstrate potential for impurities elements such as arsenic, antimony and mercury<sup>(8)</sup>.

While acid leach, involving a sulfate-chloride blend, offered the best opportunity to remove impurities such as:

- Iron,
- Cobalt,
- Nickel,
- Zinc,
- Lead,
- Bismuth,
- Thorium and its daughter products, and
- Uranium and its daughters products

This paper addresses the anoxic hydrometallurgical acid leach approach to the removal of the impurities listed above with the results as attained from concentrate A and B referenced to demonstrate some outcomes along with the broad outcomes possible from the technology.

#### **Mechanism Adopted**

Not all the impurities listed above were present in the concentrates and thus some were replaced with "proxies" that were laced into the concentrate. While not ideal, this method was adopted to understand impurity deportment in the anoxic acid leach that followed.

This early work was conducted in South Africa<sup>(9)</sup>. It was recognised at the time that the only way for a majority of the copper and sulfur to remain unleached was to adopt the classical metathesis and hydrothermal approach<sup>(10)(11)(12)</sup> employed in some Southern Africa autoclave systems.

The hydrothermal mechanism is kinetically slower than the more favoured metathesis and also requires a mild oxidant to be effective.

Metathesis is an electrochemical process in which the soluble cupric cation exchanges for a more electronegative element in the concentrate. The more electronegative element, for example iron, is solubilised while the copper cation is received into the concentrate matrix in a reduced form. These two mechanisms create pathways into the mineral structure for the impurities to escape.

Mineralogically, the mineral alteration commences as a "rimming" effect in which covellite (CuS) is formed (refer to Figure 2) and thereafter further sulfur depletion ensues in which chalcocite/digenite minerals are formed. Depending on the copper activity in the aqueous phase, sulfur depletion (oxidation) and hence final copper in concentrate grade can be influenced.



Figure 2: Metathetic Alteration of Chalcopyrite in Concentrate

An example of the alteration of the copper sulfide minerals in a hydrothermal process can be seen in Figure 3. This thin section of Chalcopyrite (Cp) and bornite (Bn) particle clearly shows a rimming alteration product of chalcocite and covellite (Ch/Cv) forming.



Figure 3: Hydrothermal Alteration of Bornite and Chalcopyrite in Concentrate

The metathesis process is pictorially shown in Figure 4 for the alteration of chalcopyrite (Cp) to covellite (Cv) and chalcocite (Ch). In this example, the release of locked "Fe" is as shown. The other locked impurities follow a similar pathway to iron.



Figure 4: Metathesis Alteration of Chalcopyrite to Covellite and Chalcocite

The use of a sulfate-chloride matrix is imminently suited for the mobilisation of impurities unlocked by the metathetic and hydrothermal alteration of the host value Cu-Fe-S mineral.

The hydrothermal alteration of chalcopyrite is thought to proceed in a different manner as shown in Figure  $5^{(12)}$ .



Figure 5: Hydrothermal Alteration of Chalcopyrite to Covellite and Chalcocite

The chalcocite (Ch) layer once nucleated in the hydrothermal process moves both outwardly and inwardly converting to chalcopyrite (Cp) and covellite (Cv). However, it is our experience that the total conversion to Ch may not be economic and consequently OMC have terminated the process with Cv being the dominant mineral in the alteration process.

## CHEMISTRY AND MINERALOGY

Copper concentrates are upgraded via the metathesis process in an autoclaving step called Nonox (a non oxidative high temperature environment). Copper in final concentrate can typically range from 50 to 60%. The reactions below are examples of metathesis in a "sulfate only" system for various copper minerals. As shown in the reactions of chalcopyrite and bornite, the iron in the copper minerals exchanges with the copper ion in solution and in the process upgraded the copper concentrate. The sulfate chemistry of the primary value minerals in the metathesis process is possibly explained by the following reactions:

#### **Primary Value Minerals**

 $\begin{array}{ll} Chalcopyrite: & 3CuFeS_{2}\left(s\right)+6CuSO_{4}\left(aq\right)+4H_{2}O\left(I\right)\rightarrow5Cu_{1.8}S(s)+3FeSO_{4}\left(aq\right)+4H_{2}SO_{4}\left(aq\right)\\ Bornite: Cu_{5}FeS_{4}(s)+2.06CuSO_{4}\left(aq\right)+1.42H_{2}O\left(I\right)\rightarrow3.64Cu_{1.94}S(s)+FeSO_{4}\left(aq\right)+1.42H_{2}SO_{4}\left(aq\right)\\ Covellite: 6CuS(s)+3CuSO_{4}\left(aq\right)+4H_{2}O\left(I\right)\rightarrow5Cu_{1.8}S(s)+4H_{2}SO_{4}\left(aq\right)\\ \end{array}$ 

Other gangue sulfide minerals, for example pyrite and carrolite are also altered in the metathesis, although the reactions appear to be kinetically slower than those of the copper-iron-sulfides. Galena is also altered in the metathesis process.

#### **Other Sulfides**

 $\begin{array}{l} \mbox{Pyrite: } FeS_2(s) + 2.8CuSO_4 \ (aq) + 2.4H_2O \ (l) \rightarrow 1.4Cu_2S \ (s) + FeSO_4 \ (aq) + 2.4H_2SO_4 \ (aq) \\ \mbox{Galena : } PbS \ (s) + CuSO_4 \ (aq) \rightarrow PbSO_4 \ (aq) + CuS \ (s) \\ \mbox{Carrolite : } 2CuCoS_4(s) + 7CuSO_4(s) + 4H_2O(l) \rightarrow 5Cu_{1.8}S \ (s) + 4CoSO_4(aq) + 4H_2SO_4(aq) + 2S^0(s) \\ \end{array}$ 

The possible chemical reactions for the alteration of other non-sulfides impurities in sulfate medium are described below.

#### **Other Non Sulfides**

 $\begin{array}{l} \text{Uraninite: } UO_2 \ (s) \ +2H_2SO_4(aq) \ + \ Fe_2(SO_4)_3(aq) \ \rightarrow \ H_4(UO_2)(SO_4)_3(aq) \ + \ 2FeSO_4 \ (aq) \\ \text{Thorium: } ThO_2 \ (s) \ + \ H_2SO_4 \ (aq) \ \rightarrow \ Th(OH)_2(SO_4) \ (aq) \\ \text{Fluoroapatite: } 2Ca_5(PO_4)_3F \ (s) \ + \ H_2SO_4 \ (aq) \ \rightarrow \ 3Ca_3(PO_4)_2 \ (s) \ + \ CaSO_4 \ (aq) \ + \ 2HF \ (aq) \\ \text{Chloroapatite: } 2Ca_5(PO_4)_3Cl \ (s) \ + \ H_2SO_4 \ (aq) \ \rightarrow \ 3Ca_3(PO_4)_2 \ (s) \ + \ CaSO_4 \ (aq) \ + \ 2HF \ (aq) \\ \text{Chloroapatite: } 2KAlSi_3O_8(s) \ + \ H_2SO_4(aq) \ \rightarrow \ K_2SO_4(aq) \ + \ Al_2(SO_4)_3(aq) \ + \ H_4SiO_4(aq) \ + \ 5SiO_2(aq) \ + \ 2H_2O(l) \\ \end{array}$ 

Residual impurity levels that have been achieved employing the sulfate-chloride matrix are as shown in Table 6.

Impurities	Residual Level of Impurities	
Fe	5-10%	
Со	0.06-0.08%	
Ni	0.01%	
Pb	<50ppm	
Th	<3ppm	
U	<20ppm	

# Table 6: Residual Levels of Impurities in Final Concentrate

# IMPACT OF THE PROCESS ON THE FINAL CONCENTRATE GRADE

Secondary Concentrate A and Primary Concentrate B in Figure 1 were subjected to an anoxic sulfate-chloride leach employing a temperature between 180 - 220°C and the mineral assemblage resulting from the leach is given in

Figure 6 and the corresponding elemental assay is shown in Table 7.



Mineral Type	Breakdown of Minor Minerals of Upgraded Concentrate A % Mass	Breakdown of Minor Minerals of Upgraded Concentrate B % Mass
Enargite/ Tennantite Group	0.100%	0.100%
Native Copper	0.180%	0.000%
Plagioclase/Feldspar / Mica/ Clay/ Chlorite	1.800%	0.060%
Carbonates	0.820%	0.080%
Uraninite	0.000%	0.000%
Coffinite	0.000%	0.000%
Brannerite	0.000%	0.000%
Apatite	0.000%	0.000%
Other Minerals	3.130%	1.010%
Total Minor Minerals	6.030%	1.250%

#### Figure 6: Mineral Composition of the Upgraded Concentrate

Element	Units	Upgraded Secondary Concentrate (A)	Upgraded Primary Concentrate (B)
Cu	%	57	60
Fe	%	9.1	6.0
s	%	23.3	24.2
Au	ppm	23	9.2
Ag	ppm	43	71
Co	ppm	590	750
Ni	ppm	80	105
Мо	ppm	350	35
Pb	ppm	35	11
Se	ppm	255	75
Те	ppm	42	16
Si	%	2.3	0.5
Th	ppm	4.7	1.8
U	ppm	14	3
CI	ppm	31 35	
F	ppm	300	30

#### Table 7: Elemental Assay of Upgraded Concentrate

Table 8 shows the concentration of copper, gold and silver in the Nonox autoclave discharge liquor for a typical Nonox autoclave slurry density of 20%w/w solids. The value metal losses are relatively minor and do not normally justify a recovery circuit.

# Table 8: Typical Concentration of Copper, Gold and Silver in Nonox Autoclave Discharge Liquor

Element	Units	Concentration in Solution
Cu	g/L	<0.5
Au	µg/L	<10
Ag	mg/L	1

#### **FLOWSHEET OPTIONS**

Two flowsheets will be discussed. These are;

- Sulfate lixiviant, and
- Sulfate-Chloride lixiviant.

The sulfate lixiviant described in  $patent^{(13)}$  employed an Upgrade autoclave (Figure 7) similar to those employed in Southern Africa<sup>(14)</sup>.

The Sulfate Lixiviant Process as shown in Figure 7 is capable of treating a high and low grade concentrate suite. The first step involves the leaching of lower grade copper concentrate (15-25% Cu) in a Copper Pressure autoclave to produce the copper sulfate lixiviant for the Upgrade autoclave. The second step considers the introduction of a higher grade Copper Concentrate into the Upgrade autoclave where sulfate soluble impurities such as iron, uranium, thorium and cobalt are removed.



Figure 7: Sulfate Lixiviant Flowsheet

The flowsheet in Figure 7 has additional embellishments such as:

- Uranium recovery, and
- Iron re-assignment from the Upgrade Leach autoclave to a Tailings Leach.

Non-sulfate soluble impurities such as bismuth, lead and some of the daughter products of uranium are not significantly removed in the Sulfate Lixiviant Process.

The Sulfate-Chloride Lixiviant Process Flowsheet – refer patent<sup>(15)</sup> and Figure 8 is similar to the Sulfate Lixiviant Process in Figure 7. The only differences are found in:

- Leach matrix now includes chlorides from site waters,
- Slightly higher preferred operating temperatures in the Upgrade autoclave (sometimes called Nonox autoclave), and
- A copper source generated from the internally produced upgraded concentrate

While not shown in Figure 8, the impurities can be processed to a value product or immobilised as a residues for impounding.



Figure 8: Sulfate-Chloride Lixiviant Process Flowsheet

The Copper Pressure Leach may not be required if an alternate source of aqueous copper is available, for example, a loaded strip from a contiguous copper solvent extraction circuit.

# PROCESS EQUIPMENT SELECTION AND OPTIONS

The autoclave process in the Upgrade step is not novel. Variants of this process have been in service for over 40 year <sup>(16)</sup>. In excess of 8 of these vessels are or have been in service in South Africa. Traditionally, these have been constructed with carbon steel shells, a chemical copper-lead homogenous liner and low iron aluminium silicate bricks. However, in cases where the oxidant requirements are small, it makes more sense to employ titanium clad to carbon steel.

The typical internals of an Upgrade or Nonox autoclave is shown in Figure 9.

**Figure 9: Nonox Autoclave Internals** 

The Upgrade Autoclave Flash Tank is no different to those employed in the general autoclaving industry (see

Figure 10).



Figure 10: Upgrade Autoclave Flash Tanks Internals

Filters employed in the separation of the Upgraded Concentrate from the process liquors can be various types. Considering the solution matrix composition, OMC are of the view that classical vertical chamber filter presses are best suited to this process (refer to Figure 11).



Figure 11: Vertical Chamber Filter Presses (Courtesy of Diemme Filtration)

The Copper Pressure Leach autoclave as shown in the flowsheet in Figure 8 is processing the concentrate from the Upgrade or Nonox autoclave. From Table 7, this concentrate is dominated by either covellite or sulfur depleted variants of covellite and as such is not a natural mineral and its response in leaching is quite different from the established Copper Concentrate Leach autoclaves operating in Zambia and Arizona for example. The Southern African matte leach autoclaves closely resemble the Copper Pressure Leach autoclave shown in Figure 8. Up until recently, these autoclaves employ a carbon steel shell, chemical lead corrosion barrier and an aluminium silicate brick lining. Figure 12 shows the first compartment internals of a copper leach autoclave.



Figure 12 : Copper Pressure Leach Autoclave Internals

The covellite and chalcocite/digenite rich concentrate in Table 7 does not necessary need to be pressure leached. There are cases where these minerals can be leached to yield copper sulfate at temperatures below boiling point and at atmospheric pressure.

Furthermore, the copper sulfate from an oxide or tailings leach process can be an alternate source of copper, thus avoiding the need to have a Copper Pressure Leach autoclave. The flowsheet in

Figure 13 is one possible variant of this.



Figure 13: Sulfate-Chloride Lixiviant Process with Oxide or Tails Leach

# **CAPEX AND OPEX DRIVERS**

## Capex

The following factors influence the capital cost of a flowsheet such as that in Figure 8:

- Vessel retention time, operating temperature and pressure, and
- Materials of construction.

The metathesis step employed in the Upgrade Nonox autoclave is extremely fast and is complete in less than 1 hour in the Figure 7 flowsheet. Similarly, the copper pressure leach of the Upgraded Concentrate is equally fast and again less than 1 hour is required.

When it comes to materials of construction, copper is a well known passivator of nickel based alloys which can be employed in the Copper Pressure Leach autoclave with remarkable confidence. Titanium, either Grade 2 (R 50400), Grade 12 (R 53400), Grade 5 (R 56400), Grade 17 (R 52252) can also be employed in Copper Leach within its pressure envelope with appropriate care.

The Upgrade autoclave (Nonox), which does not employ oxygen gas, can be constructed using either the above grades of titanium or a combination of titanium and certain grades of acid resistant brick.

For the copper pressure leach on concentrates derived from the Upgrade Leach autoclave, there would be a preference to employ acid resistant bricks for the working face of the vessel.

The above factors together with the simple flowsheet suggest the capital cost of the process is quite modest.

#### Opex

Again, referencing the flowsheet in Figure 8, it can be expected that reagents and utilities requirements will influence the operating cost more so than other consumables and power.

Oxygen consumption in the Copper Pressure Leach autoclave can vary between 0.15 and 0.4 tonnes/tonne of concentrate. Any sulfuric acid requirement in the Copper Pressure Leach is negligible and can be discounted.

The Copper Pressure Leach autoclave is autogenous and requires no base operating steam load.

The Upgrade autoclave is only mildly oxidative and its exotherm is inadequate to support the process operating temperature. Typically, the steam requirement in the Upgrade autoclave will vary

# between 0.8 and 0.9 tonnes/ tonne of concentrate depending on the concentrate mineralogy. **CONCLUSIONS**

The Upgrade (Nonox) autoclave process employing a combination of copper metathesis and hydrothermal leach mechanisms has demonstrated that:

- Impurities of the type such as iron, cobalt, nickel, zinc, lead, bismuth, thorium and its daughter products and uranium and its daughter products are removed from the upgraded concentrate,
- Copper iron sulfide concentrates of the type chalcopyrite, bornite and pyrite can be upgraded to chalcocite / digenite with a final copper-in-concentrate grade of 50 to 60% Cu,
- Minimal losses of copper are incurred,
- Gold follows the copper and remains in the upgraded concentrate,
- The process is relatively simple with the Upgrade autoclave serviced by a Copper Pressure Leach autoclave to provide the copper required in the upgrade step, and
- Reagent requirements are modest with oxygen being the principle input to the Copper Pressure Leach autoclave.

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## REFERENCES

- 1. Boliden Cu Concentrate Safety Data Sheet Version 2, 1/11/2012
- 2. Hindustan Copper Website : http://www.hindustancopper.com/CopperConcentrate.asp?lnk=4&plnk=1
- 3. Asarel website : http://www.asarel.com/en/Products.aspx
- 4. Technical Report on Lumwana Mine NI 43-101, 16/3/2012
- 5. Araya, R et.al., Necessity Driving Change and Improvement to the Cleaner Circuit at Lumwana Copper Concentrator, 46<sup>th</sup> Annual CMP Meeting, 2014
- 6. Fountain, C., The Whys and Wherefores of Penalty Elements in Copper Concentrates, Metallurgical Plant Design and Operating Strategies Metplant 2013, 2013
- 7. Davenport, W.G et. al., Extractive Metallurgy of Copper 4th Ed., Elsevier Science Ltd, 2002
- 8. Bartsch, P., et. al., Purification of Copper Concentrate by Removal of Arsenic and Antimony with Concomitant Regeneration and Recycle of Lixiviant, International Patent Application PCT/AU2015/000188, 2015
- 9. Private communications from GM Dunn, Hydromet Pty Ltd.
- Jang, J.H. and Wadsworth, M.E., Hydrothermal Conversion of Chalcopyrite Under Controlled EH and pH, The Paul E.Queneau International Symposium Extractive Metallurgy of Copper, Nickel, and Cobalt, Volume 1: Fundamental Aspect, The Minerals, Metals and Materials Society, 1993.
- 11. Vinals, J et. al., Transformation of Sphalerite Particles into Copper Sulfide Particles by Hydrothermal Treatment with Cu(II) Ions, Hydrometallurgy Volume 75, 2004
- 12. Peterson, R.D. and Wadsworth, M.E., Enrichment of Chalcopyrite at Elevated Temperatures, EPD Congress, 1994.

- 13. Dunn, G.M. et.al., Integrated Hydrometallurgical and Pyrometallurgical Processing of Base-Metal sulphides, US Patent US 2008/0173132 A1, 2008
- 14. Fugleberg, S., et. al., Development of the Hartley Platinum Leaching Process, Hydrometallurgy Volume 39, Issues 1-3, 1995.
- 15. Dunn, G.M. et.al., Truncated Hydrometallurgical Method for the Removal of Radionuclides from Radioactive Copper Concentrates, Australian Provisional Patent Application 2015904596, 2015
- 16. Plasket, R.P. and Romanchuk, S., Recovery of Nickel and Copper from High-Grade Matte at Impala Platinum by the Sherritt Process, Hydrometallurgy, 1978