

# **MINERAL PROCESSING and COPPER EXRACTIVE METALLURGY**

## **Complete Metal Recovery**

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### **ABSTRACT**

Processing and smelting of copper containing sulphide concentrates result in the accumulation of impurities into various process streams. All primary copper smelters and refineries around the world produce significant amounts of slag, dust, sludge, residues and others, which contain copper and precious metals. The recovery of these valuable metals is essential to the overall economics of the smelting process. Physical, chemical and mineralogical characterization of particular slag and Cottrell dusts from primary smelters and Doré furnace (TBRC) slag and Pressure Leached Anode slimes from a copper refinery have been carried out to understand the basic behind the recovery processes. Various process options have been evaluated and adapted for the treatment of slag from different smelting furnaces and Cottrell dusts as well as the intermediate products from copper refineries.

Besides the hydro- or pyro-metallurgical treatments, the above mentioned physical separation options such as magnetic, gravity separation, flotation and precipitation flotation processes have been successfully identified and adapted as the possible process options to produce a Cu-rich or precious metal-rich concentrates for in-house recycling and other valued by-product for further treatment. The results of laboratory, pilot plant and production operations are presented, and incorporation of several alternative flowsheet is discussed in this paper.

### **INTRODUCTION**

Processing and smelting of copper concentrates result in the accumulation of environmentally sensitive materials into various process streams. Significant quantities of lead, zinc, cadmium, arsenic, bismuth, etc. are often found in process intermediates, such as slag, flue dusts, sludge, residues and others, which also contain some copper and precious metals. Complete re-circulation of these process intermediates within the smelter is not always feasible, since the given impurity limits established by copper refineries for anode copper. The development of processes to separate intermediates into a copper and precious metal-rich fraction for recycle within the copper smelter / refinery, while rejecting environmentally harmless materials for proper disposal are required. In addition, the depletion of high-grade / low impurity ore deposits will necessitate processors to treat more complex concentrates, and hence will require more attention in the area of waste treatment and by-product recovery.

Different slags from different smelting furnaces (Reverberatory, Continuous smelting furnace and Converter) have quite unique characteristics, such as different mineralogical compositions and copper phases. Since smelter slags are the finally rejected material from the smelting operations, it is desired that the slags contain minimal values. Therefore, the value recovery techniques may have greater impact on overall smelting operation, and hence the

recovery process should have to be tailored to accommodate the particular slag treatment options. Recovering copper values from various slag has been practiced in a number of smelters around world, however, not much published information is available. A brief description of the process developed over the years is given.

In general, electro-static precipitators are used to clean the off-gases from the smelting furnaces to catch solids particles. Part of the dust catch in the precipitator, a lead-rich fraction, is shipped to a lead smelter for lead and silver recovery depending on the proximity of the lead smelter, while the copper-rich fractions are recycled within the copper smelter. Dust bleed at the copper smelter is essential for limiting the minor elements reporting to the anode copper, which in turn affects the quality of electro-refined copper cathode. The main objectives of bleeding and treating dust are to provide an exit for harmful impurities such as Pb, Bi, As and Sb, in the anode copper and maintain an environmentally acceptable work place. Recovering copper and precious metals-rich fractions from the dust for in-house recycle and shipping up-graded lead-rich fraction to the lead smelter would improve overall smelting operation. Furthermore, the reduced copper content in the lead-rich fraction shipped to the lead smelter would significantly simplify the dross furnace operation at the lead refinery as compared to materials of high copper content, and reduce the amount of copper/arsenic spieess production, which is not easily recyclable.

Number of pyro-metallurgical and hydrometallurgical processes have been proposed, tested or practiced to a certain extent. Hydrometallurgy includes the sulphuric acid leaching, pressure leaching as well as chloride and caustic leaching processes. However, each smelter seems to possess unique dusts characteristics reflecting the variable concentrations of impurities in copper concentrates being treated. This paper presents the results of development work carried out for a number of dusts. Also the feasibility of separating copper and lead by physical means, including flotation, classification (granulometric), gravity and precipitation / flotation, is presented.

Apart from the smelter operation, the treatment of intermediate products within the copper refinery may give a greater impact in the overall economics of smelter / refinery complex, since all or most of the intermediate products generated from the refinery are traditionally recycled back to the smelter, which takes the value return period of about 6 months. Therefore, cost-effective in-house recycling processes and simplification of the recovery operations are required to enhance the overall economics of the smelter-refinery complex. In this connection, the treatments of Doré furnace (TBRC) slag and Leached Anode Slimes have been developed. The plant practice of these operations is briefly discussed in this paper.

## DETAILS

### A. Slag

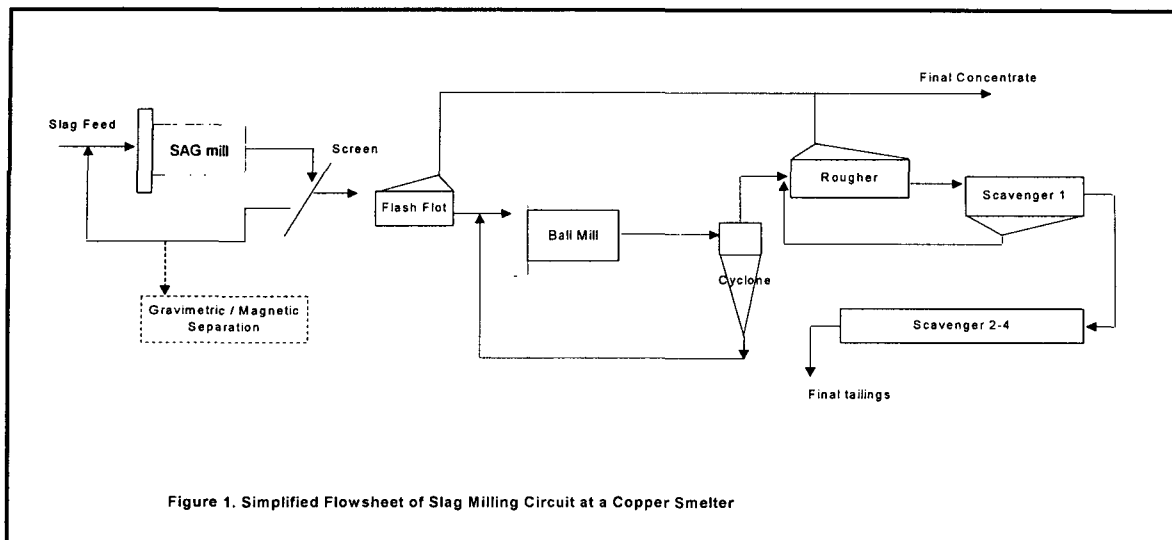
Different slags from different smelting furnaces (Reverberatory, Continuous smelting furnace and Converter) have unique mineralogical compositions and copper phases. Since smelter slags are the finally rejected material from the smelting operations, it is desired that the slags contain minimal values. Therefore, the value recovery techniques may have greater impact on overall smelting operation, and hence the recovery process should have to be tailored to accommodate the particular slag treatment options. Recovering copper values from various slag has been practiced in a number of smelters around world, however, not much published information is available. A brief discussion of the operation and process improvement over the years are given.

#### A.1 Process Audit (Circuit Survey)

The objectives of the work was to examine the slag milling operation at a copper smelter to identify metallurgical opportunities with regard to :

- concentrate grade improvement,
- simplifying / rationalizing the flotation circuit,
- copper recovery improvement,
- decreasing cost.

##### A.1.1 Methodology



The scope of the work is one of basic information/data gathering in order to understand the current circuit performance for a given feed material and flotation conditions. The variables include the mixing ratio of two slags (Reactor and Converter). Knowledge of the flotation behaviour of the various copper species in the circuit was a primary objective of this study. As an initial task, a circuit survey was carried out with a feed mixture of 80% Reactor slag and 20% Converter slag. The schematic diagram of the circuit is given in Figure 1. All samples were sized and analyzed for (1) sulphide copper,  $Cu_{Sul}$ , (2) total copper,  $Cu_{Tot}$ , (3) oxide copper,  $Cu_{Ox}$ , and (4) metallic copper,  $Cu_{Met}$ .

X-ray diffraction on selected samples of flotation products showed the presence of copper sulphide and metallic copper as the major copper bearing materials. No copper oxides phase was detected due to low concentration. The detected non-copper phases include major quantities of magnetite, minor quantities of fayalite and silicates. Several size fractions were mounted and polished for microscopic examination and image analysis at a later stage.

### A.1.2 Results

The results of chemical analysis shown in Tables 1 and II were used to balance the copper phases in each size fractions as well as in the circuit.

Table I. Grade/Recovery of copper phases on samples around Flash Flotation Cell.

Products	Grade, %				Recovery, %			
	Cu (t)	Cu(s)	Cu(ox)	Cu(m)	Cu (t)	Cu(s)	Cu(ox)	Cu(m)
Conc.	45.93	38.15	0.47	8.67	72	75	20	64
Tails	2.17	1.49	0.22	0.58	28	25	80	36
Feed	6.81	5.38	0.25	1.44	100	100	100	100

SEM of Flash flotation tails have shown the presence of large grains of free metallic copper (Plate A). It shows low recoveries of all copper species in the coarse fractions (+65 mesh, 210 microns) due to (i) poor liberation of the sulphide copper and/or (ii) difficulty in floating metallic copper (too larger particle sizes and flatness of their shape). The oxide copper content in the feed (<0.25%) is not high enough to affect the overall flotation recovery significantly. It should be noted that  $Cu_{Tot}$  is not the exact summation of  $Cu_{sul}$ ,  $Cu_{ox}$  and  $Cu_{Met}$ , since  $Cu_{tot}$  was analyzed independently.

As shown in Table II, the concentrate grade and recovery of total copper and sulphide copper in the rougher bank following regrinding are very high. The oxide copper recovery is only 37 %, as expected, since no provisions are in place for the specific flotation of oxide or oxidized copper species. The low metallic copper recovery may be the result of the surface tarnishing of the metallic copper during the extended retention time in the flotation circuit.

The circulating loads of sulphide and metallic copper species by size fraction are given in Table III. A significantly higher circulating load of metallic copper in the coarse fractions is evident as is that of higher circulating load of oxide copper in the very fine fractions. The metallic copper is slower floating than sulphide copper, as evidenced by significant quantities still being recovered in scavenger cells 2, 3 and 4.

The overall balancing of the slag milling circuit is given in Table IV. Total copper recovery is 92.8% while individual recoveries for sulphide, metallic and oxide are 95%, 73% and 44%, respectively. About 5% of the mill feed is circulated as scavenger concentrates from Cell 2, 3 and 4 containing 1.58% Cu(tot).

Table II. Grade/ Recovery of copper phases of circuit samples after regrind. (recovery based on Rougher feed)

Products	Grade, %				Recovery, %			
	Cu (t)	Cu(s)	Cu(ox)	Cu(m)	Cu (t)	Cu(s)	Cu(ox)	Cu(m)
Rgh Conc	44.0	34.1	1.73	2.97	85	91	37	63
Scav 1 Conc	5.89	2.45	1.25	2.02	6	3	14	17
Scav 2-4 Conc	1.58	0.77	0.49	0.38	7	3	16	9
Final Tails	0.28	0.13	0.11	0.09	15	9	63	37
Rgh Feed	1.87	1.36	0.17	0.23	100	100	100	100

Table III. Circulating load of copper species in size fractions. (weight % based on fresh feed to rougher Cell)

size	Rougher				Scavenger 1				Scavenger 2 - 4			
	Cu(s)	Cu(met)	Cu(ox)	Cu(tot)	Cu(s)	Cu(met)	Cu(ox)	Cu(tot)	Cu(s)	Cu(met)	Cu(ox)	Cu(tot)
+200	59	50	6	58	11	49	8	23	6	32	6	16
200/325	78	54	12	74	5	36	9	12	5	21	8	7
325/635	85	56	22	86	2	8	8	3	3	6	10	3
-635	95	51	32	88	3	4	16	4	6	5	12	4
total	91	53	30	85	4	17	14	6	5	9	11	5

The present recoveries of copper species and the impact of possible incremental recovery improvements on metallurgy are given in the Table IV below. The results suggest that efforts be primarily focused on improving metallic copper recovery

Table IV. Current Recoveries and possible recovery improvement.

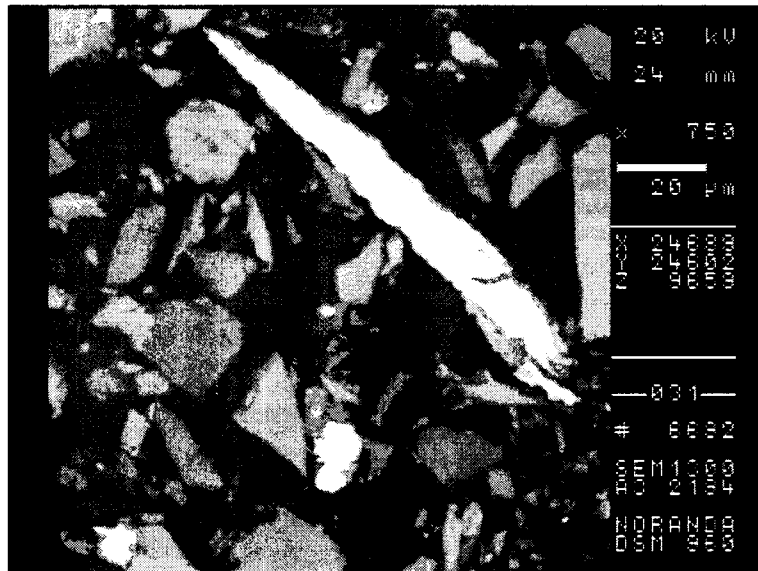
Copper species	Current Recovery, %	Reasonable Expectation of Possible Recovery Improvement, %	Impact on Overall Recovery, %
Sulphide	95.4	+1	+0.8
Metallic	72.9	+10	+2.1
Oxide	44.5	+20	+0.7

### A.1.3 Conclusions

1. Best payback is to focus effort on metallic copper recovery. Early recovery of metallic copper in the grinding/sizing operation would reduce the negative impact of coarse losses in down stream flotation circuit.
2. The analysis suggests two approaches,
  - Circuit simplification to reduce high circulating load in scavenger cells and to improve the poor recovery of coarse fractions
  - Use of a gravity unit to recover coarse metallic copper in the regrind cyclone U/F.
3. Copper sulphide (76%) and metallic copper (20%) are the main copper species in the circuit feed. Copper oxide represents only 4% of the copper in the feed, and its behaviour does not significantly impact overall circuit performance.
4. Flash flotation cell recovers about 72% of copper in the feed recovery, but recovery drops significantly for +100 mesh material mostly due to their shape and weight.
5. A high circulating load of coarse metallic and fine oxide copper exists in the scavenger cells and may be contributing to losses. Use of gravity or magnetic separation devices in the regrind cyclone U/F stream to recover metallic copper is strongly recommended.

Plate A. Scanning Electron Microscope Images of rougher tailings from Converter slag (metallic copper).

A : Total backscattered electron image





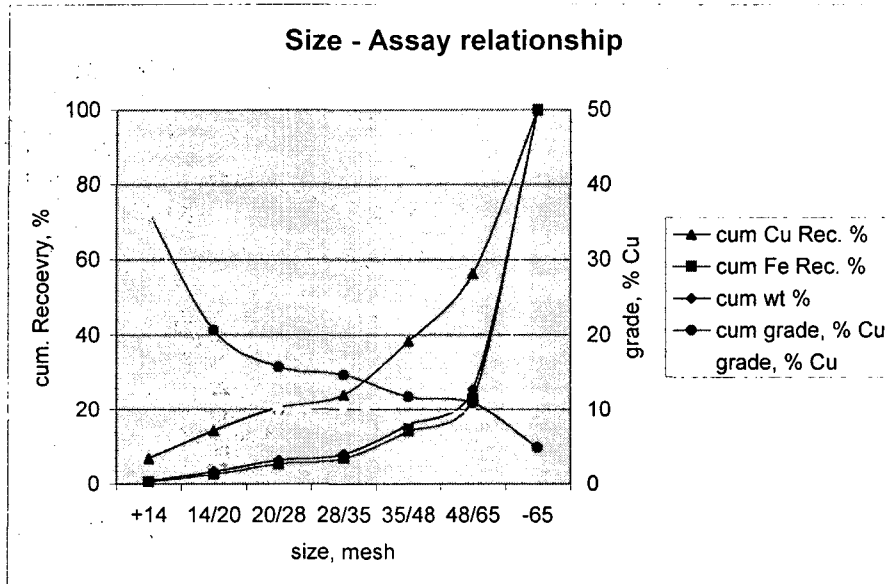


Figure 2. Grade recovery of size fractions.

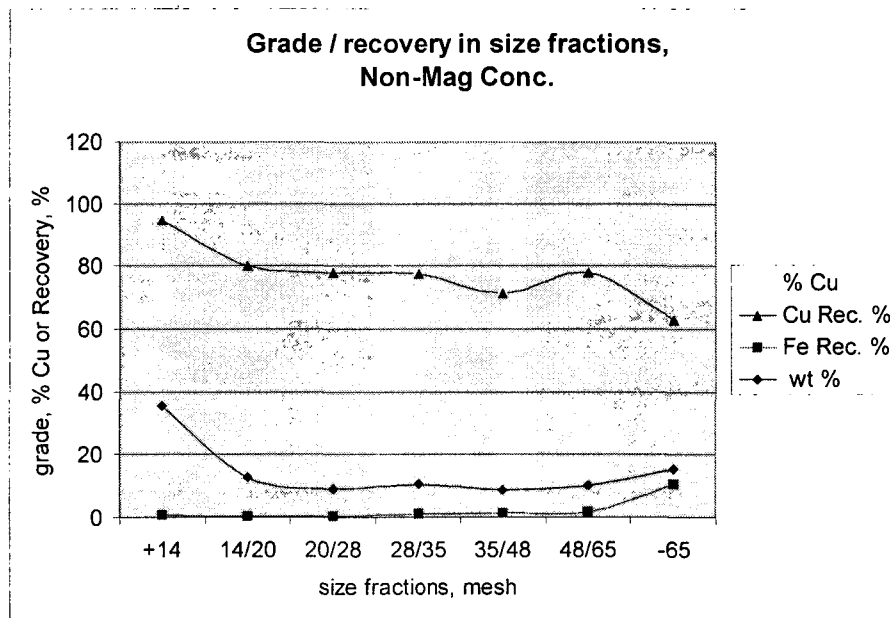


Figure 3. Grade / recovery of non-magnetic fractions of each size fractions.

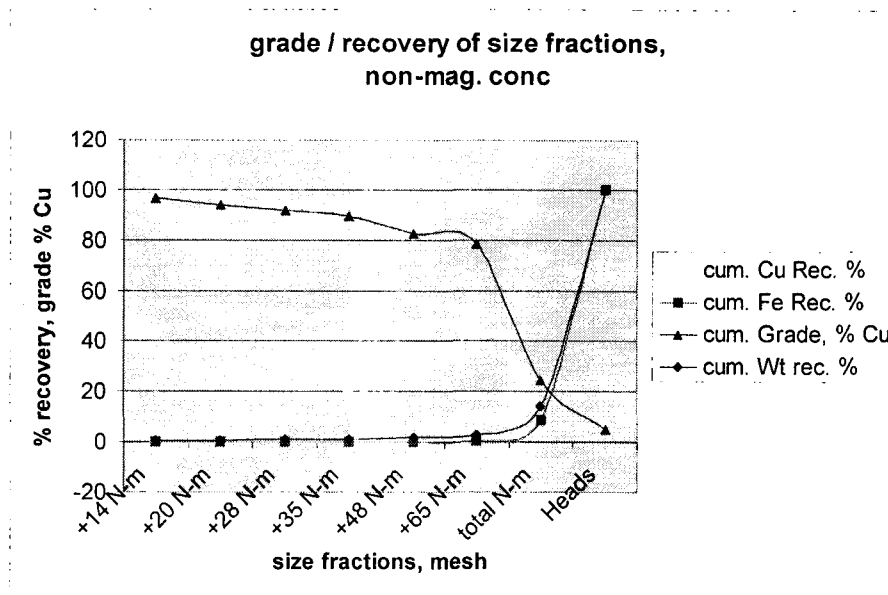


Figure 4. Cumulative grade / recovery of non-magnetic fractions of each size fractions.

## B. Dusts

Laboratory bench scale flotation and pilot plant scale classification using a cyclone and Multi-gravity separation (MGS) as a means of separating the copper value in dusts were carried out. Several different types of dust samples were used to define the variability dust samples and their metal content on the separation response in the production of a lead-rich material (low in copper) to be shipped to the lead smelter and copper-rich material for in-house recycling.

### B.1 Flotation

The results are given in Table V. The content of soluble species in the dusts varies widely, ranging 11-44%, depends on the particular operating characteristics of the furnaces, stages of smelting operations as well as the feed material composition. The once-cleaned copper concentrates assaying 49 - 65% Cu and 6-7% Pb were obtained from feed samples containing 4 - 13.8% Cu and about 30% Pb with copper recoveries of 45 - 60%. The lead rejections in the rougher tail were over 90%. The soluble copper and zinc contents vary significantly from one sample to another, which affects the copper recovery. Arsenic and bismuth behaved similar to lead giving 85-90% rejection in the tails. Un-dissolved zinc and cadmium did not respond to the flotation and remained in the rougher tails. Additional copper (5 - 20%) could be recovered by screening the rougher tail at 400 mesh, which may provide a supplementary process to the flotation operation.

### B.2 Gravity Separation

#### B.2.1 Hydro-Cyclone Separation

Although the cyclone operation was not optimized in the present work, there seems to be a clear separation. It should be noted that the dust slurry was scalped at 100 mesh (150 microns) prior to cycloning to remove extra large



particles. These particles were then composited to the final cyclone concentrate. The results are given in Table VI.

The sample No. 2 dust produced a better grade copper concentrate (42% Cu and 14% Pb) with recoveries of 75% for copper and 9% for lead from a feed assaying 10% Cu and 28.9% Pb. The overflow assaying 47% Pb and 3% Cu contained 13% of the copper and 72% of the lead in a weight of 45% of the feed. It should be noted that the samples tested in the present study contained very small proportion of soluble copper as compared to the other dusts used in the flotation tests (Sample No. 1).

### **B.2.1 Multi-gravity Separation**

A series of gravity separation tests using a pilot scale Multi-gravity separator (MGS) was carried out to scope out the possibility of recovering copper and silver values in the rejects. Cyclone classification (granulometric separation) tests were also carried out for comparison using two different dusts from same smelter. The results are given in Table VII.

The results of the above cyclone classification and multi-gravity separation tests clearly indicate that these processes could be applied alone or supplementing the flotation process for the separation of copper from lead.

## **B.3 Process Medium and Flowsheet Development**

### **B.3.1 Dissolution Tests**

A series of dissolution tests was performed with a particular converter dust sample to characterize the solubility of metals and their contents in the leach liquor. The results are given in Figure 5.

Low acid and water leaching reduced the solids weight by 44-47%. The acid content up to 30 g/L did not affect the dissolution of metals significantly. Water leach gave 55% copper dissolution. About 70% of the copper, over 90% of the zinc, 70% of the iron and 85% of the cadmium were dissolved in water or 30 g/L H<sub>2</sub>SO<sub>4</sub> solution.

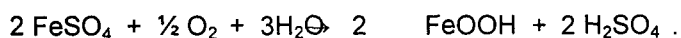
Bismuth and arsenic did not respond to a low acid leach. When the acid content in the leach solution was increased to 100 g/L (high acid leach), the rates of metals dissolution were also increased to 80% for Cu, 97% for Zn, 95% for Fe and 98% for Cd. Again, arsenic and bismuth were not affected appreciably. The leach liquors from the water and low acid leaching contained about 5 g/L Cu, 21 g/L Zn, 2 g/L Fe, <10 mg/L Bi, 30-100 mg/L As, and 1.5 g/L Cd.

From the above results, the copper phases present in this particular dust are estimated to be about 50% as sulphate, 5% as oxide, 15% as metal and 30% as copper sulphide. It is also estimated that about 85-90% of the zinc is present as sulphate and/or oxide, 7% as ferrite and very small amount as silicates. Almost all the lead is present as lead sulphate. Over 75% of the cadmium is present as sulphate, about 10% as oxide and 15% as sulphide or silicates. Water leaching process would be the best preliminary step for the separation of soluble metals from the lead. The most important findings from the above work are; (i) that most of the minor elements (As and Bi) presumably in the form of oxides are chemically/physically tied with lead, and hence they could be removed along with lead, and (ii) that the amount of soluble material (Cu, Zn and Cd) is highly variable depending on the source and furnace operation.

### **B.3.2 Process Medium and Separation of Copper by Pyrrhotite and Precipitates**

As shown above the metal content in the dust medium is highly variable, ranging 0.1 - 6 g/L Cu, 2 - 25 g/L Zn and 0.5 - 5 g/L Cd. It is unlikely that the concentration of dissolved metals can be increased sufficiently by increasing the pulp density to produce a solution suitable for shipping to zinc plant for Zn and Cd recovery. One option of treating the medium is to precipitate copper for recycle and treat the barren solution containing all other metals at a process water treatment plant.

Since large amount of copper is soluble in either water or in weak acidic media, the precipitation of the dissolved copper with sulphide minerals, such as pyrrhotite, was examined. Copper in the solution was then precipitated with the addition of pyrrhotite while adding SO<sub>2</sub> gas. The following chemical reactions should occur ;



The results of copper precipitation tests before and after pyrrhotite addition are given in Table VIII. As shown, all the copper in solution has been re-precipitated and remained with pyrrhotite. The solution still contained all the zinc, cadmium and arsenic. This arsenic-rich solution can be processed in the wastewater treatment plant. Scanning electron microscope images of pyrrhotite before and after the treatment have shown that very fine copper containing precipitates are present on the surface of pyrrhotite. It has been confirmed in separate tests that the flotation of copper-laden pyrrhotite is complete with over 95% copper and pyrrhotite recoveries.

### B.3.3 Flowsheet

From the batch and pilot-scale test results, a conceptual flowsheet incorporating flotation, cycloning and MGS processes for the treatment of a copper smelter dust had been developed, along with the dissolved copper precipitation. Since the objective of treating dusts is to recover values with minimum cost while rejecting as much environmentally safe materials as possible, the process itself is somewhat complex and many unit operations are involved.

As shown in Figure 6, this flowsheet is given to serve the complexity of the whole process. There are many unit operations involved, namely, pulping, flotation, gravity separations (cycloning or MGS), leaching, precipitation, thickening, solid/liquid separation, etc. This option starts first with leaching and precipitation followed by flotation and gravity separation for any values escaped in the flotation stage. This option has the less solid / liquid separation operations. Since the content of soluble material in the dust is highly variable, copper in solution is also recovered as precipitates. It is assumed that a total weight of about 1,000 tpm dust having assays of 8% Cu, 30% Pb, 10% Zn, 1% Cd, 1% As and 1% Bi would be treated. The treatment plant would operate 5 days/ week at a throughput of 50 tpd. The material balances are based on the tests results of a number of different dust samples. The copper concentrate would be recycled to the smelting furnace and the lead concentrate would be shipped to a lead smelter after thickening and filtration. Copper and lead recoveries in the final copper and lead products are 60% and 94%, respectively. The arsenic and bismuth rejections in the lead product would be over 90%. The envisaged flotation/gravity process would produce 120 tpm of copper concentrate (40% Cu, 10% Pb, 2% Zn, 0.4% Cd, 0.7% As and 0.7% Bi) and 650 tpm of lead concentrate (45% Pb, 2.5% Cu, 5% Zn, 0.5% Cd, 1.4% As and 1.4% Bi).

The dust feed would be slurried in water at 20% solids, and leached (natural or acidic pH ~1.5 with sulphuric acid) to dissolve most of the zinc and cadmium. Some oxidized copper would be dissolved as well. The dissolved copper is then precipitated using sulphide minerals such as pyrite or pyrrhotite and SO<sub>2</sub>, and floated using usual sulphide collectors (20-min. roughing and 10-min. cleaning operation). Additional copper will be recovered from the flotation tails by gravity separation using cycloning or MGS. The combined cleaner flotation concentrate and cyclone underflow (or MGS heavies) are sent to solid/liquid separation operation as final copper concentrate. The final cyclone overflow (or MGS lights), which is the lead product, is thickened prior to solid/liquid separation.

Above example is given to demonstrate the possibility of treating copper smelter dusts to recover the copper, precious metals, and dissolved copper are considered.

### B.3.4 Summary

Physical, chemical and mineralogical nature of copper smelter precipitator dust have been carried out using techniques of physical chemical, microscopic and microprobe analyses. A number of metal containing phases are identified, but the relative amount of the soluble materials in a particular dust is highly variable depending on the smelting furnace and its operation, impurity content of copper concentrate feed, among others. Laboratory batch and pilot scale tests have shown that the copper (associated PM) can be separated from the undissolved metals of Pb, Fe, As and Bi. It was confirmed that the dissolved copper can be recovered by the newly developed process. The lead-rich residue is more acceptable for a lead smelter than untreated dusts since it contains significantly less copper,

zinc and cadmium contents. Most of the arsenic in the dusts follows the liquid phase and can be fixed in the wastewater treatment plant as safely dischargeable compounds.

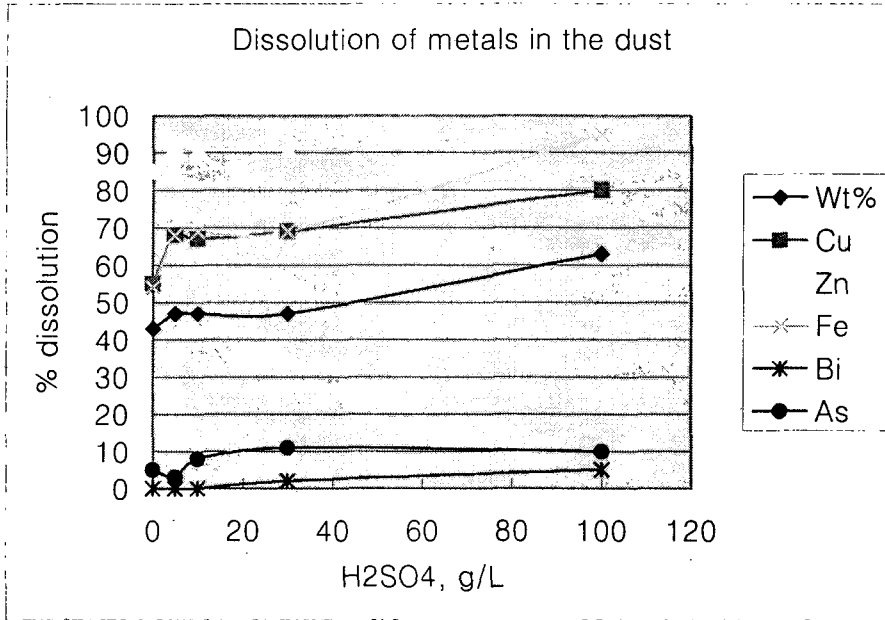


Figure 5 - Effects of acid concentration on metal extraction (20° C)

Table V - Results of Flotation in Water Medium.

Products	Wt. %	Grade, %				Recovery, %			
		Cu	Pb	Zn	As	Cu	Pb	Zn	As
Sample #1									
Rgh Conc	5.7	22.1	44.5	1.9	0.8	31.7	8.5	1.1	7.3
+400 mesh	2.3	9.3	45.7	2.1	1.0	5.3	3.5	0.5	3.2
combined	8.0	18.4	44.9	1.9	0.8	37.0	12.0	1.6	10.5
Tails, -400	48.2	0.9	54.7	2.2	1.0	10.6	88.0	10.5	85.9
medium	43.8	(5.9)	(0)	(25.1)	(0.1)	52.4	0.0	87.9	3.6
Heads	100.0	4.0	30.0	10.0	0.6	100.0	100.0	100.0	100.0
Sample #2									
Conc	12.6	64.8	6.1	1.7	-	59.3	2.7	1.4	-
mid	12.5	8.1	46.2	9.5	-	7.4	20.0	7.9	-
Tails, -400	51.7	8.8	43.5	9.3	-	33.1	77.3	31.7	-
medium	23.2	(0.1)	(0)	(15.0)	-	0.2	0.0	59.0	-
Heads	100.0	9.2	30.5	11.6	-	100.0	100.0	100.0	-

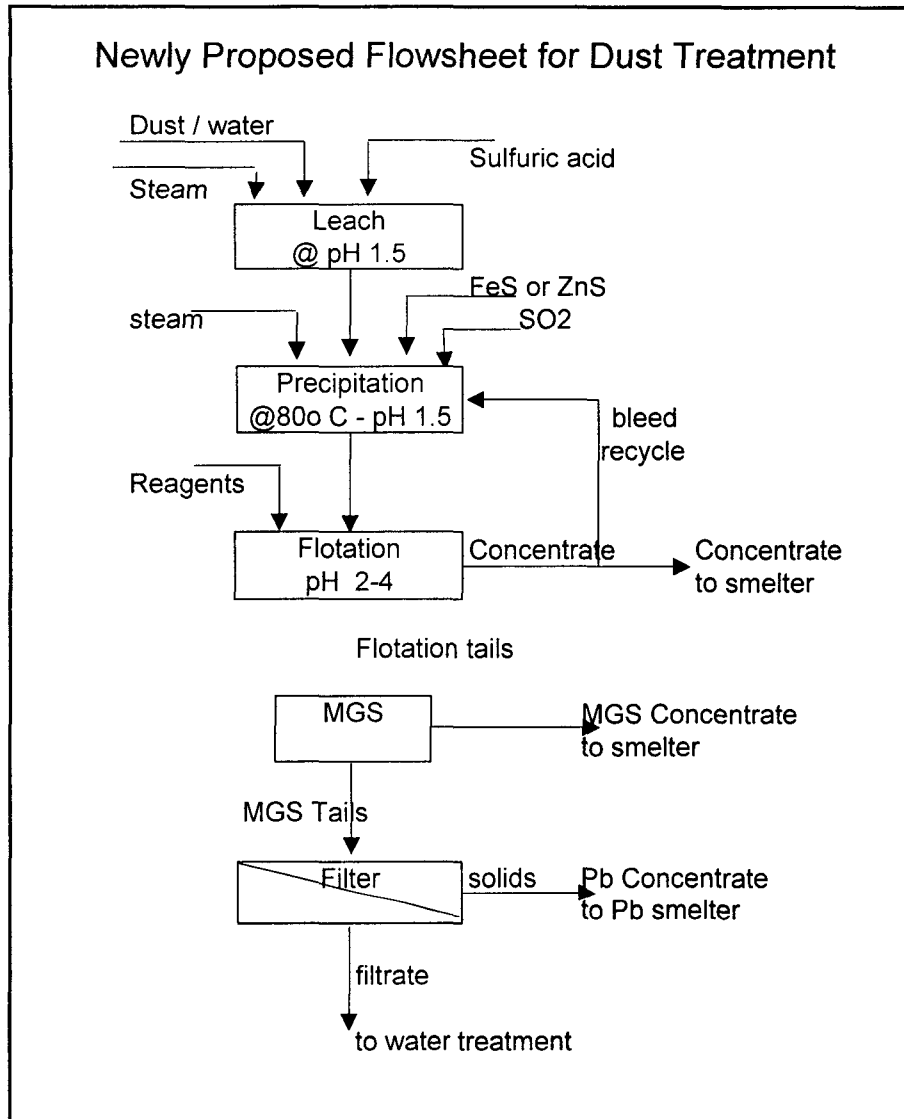


Figure 6. - Leaching-precipitation-flotation-gravity separation flowsheet.

Table VI - Results of Cyclone Tests in Water Medium

Products	Wt. %	Grade, %			Recovery, %		
		Cu	Pb	Zn	Cu	Pb	Zn
Sample #2							
U/flow	12.6	64.8	6.1	1.7	59.3	2.7	1.4
Cl Tails	12.5	8.1	46.2	9.5	7.4	20.0	7.9
O/flow	51.7	8.8	43.5	9.3	33.1	77.3	31.7
medium	23.2	(0.1)	(0)	(15.0)	0.2	0.0	59.0
Heads	100.0	9.2	30.5	10.0	100.0	100.0	100.0

Table VII. Results of MGS and Cycloning of two dusts samples from smelter "B".

Converter Dust from Smelter "B"

	MGS, Conc.		Cyclone U/F		Heads grade
	Grade	Recovery	Grade	Recovery	
Wt. %		32.8		49.7	
As	1.8	14.1	2.0	26.5	4.1
Bi	0.6	14.4	0.6	26.4	1.3
Cu	33.5	90.4	33.9	96.3	12.1
Sb	0.2	15.8	0.2	26.5	0.5
Pb	20.0	15.5	20.7	27.6	42.5
Ag, g/t	586	54.0	575	70.1	356
Au, g/t	15	87.8	16	94.3	6

Reverberatory Furnace Dust from Smelter "B"

	MGS Conc.		Cyclone U/F		Heads grade
	Grade	Recovery	Grade	Recovery	
Wt. %		4.3		21.3	
As	4.3	5.9	4.0	32.2	3.1
Bi	0.4	1.6	1.0	17.5	1.2
Cu	8.8	35.3	3.0	57.0	1.1
Sb	1.3	1.8	3.0	17.5	3.0
Pb	37.0	17.8	20.2	2.0	44.1
Ag, g/t	1,950	15.6	890	34.7	533
Au, g/t	16	13.0	8	31.4	5

Table VIII. Composition of solution before and after pyrrhotite precipitation.

	As	Cd	Cu	Fe	Zn
Solution initial (g/L)	7.4	5.3	3.4	0.1	4.5
Solution final (g/L)	7.2	5.7	0.001	3.7	4.7
Pyrrhotite initial (%)	n.a.	n.a.	0.14	47.1	0.03
Precipitates final (%)	0.02	0.02	5.67	31.2	0.03

Conditions : pH 2, 80°C, 50 ml/min SO<sub>2</sub>, ratio FeS/Cu : 6.