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Total value recovery in the copper smelting and refining operations

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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.

1. 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 spiess 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. Processing of Smelter Slags

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 2 were used to balance the copper phases in each size fractions as well as in the circuit.

Table 1. 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 2, 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 3. 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 4. 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).

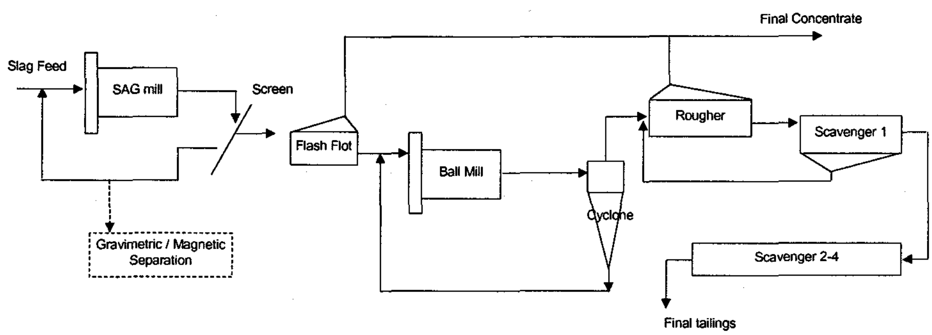


Figure 1. Simplified Flowsheet of Slag Milling Circuit at a Copper Smelter

Table 2. 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 Con	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 3. 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)	u(met)	Cu(ox)	Cu(tot)	Cu(s)	u(met)	Cu(ox)	Cu(tot)	Cu(s)	u(met)	Cu(ox)	Cu(tot)
+200	59	50	6	58	11	49	8	23	6	32	6	16
200/32	78	54	12	74	5	36	9	12	5	21	8	7
325/63	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 4 below. The results suggest that efforts be primarily focused on improving metallic copper recovery

Table 4. 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.2 Process Improvement (Magnetic Separation)

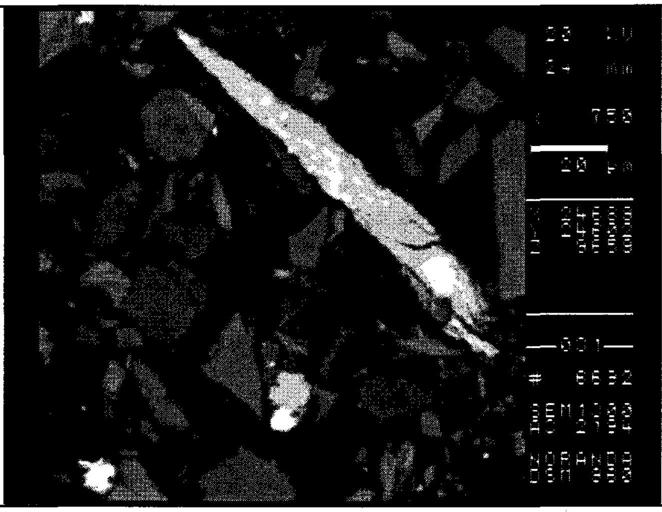
Ball mill cyclone underflow sample was used for sizing and magnetic separation to check the occurrence of metallic copper and possible means of recovering it as suggested in the above study. The results are given in Figures 2 – 4 below. As shown in Figure 2, the plus 14 mesh fraction assayed 36.2 % Cu while most of the other size fractions coarser than 65 mesh contained 9.4 – 14.7 % Cu. The plus 65 mesh as a whole contained over 55% of the copper in the feed at a cumulative grade of 10.9 % Cu. The feed assayed to contain 4.91 % Cu. The iron followed closely to the weight distribution.

The results of magnetic separation are shown in Figures 3 for each size fractions and 4 for cumulative data, respectively. The non-magnetic material from the each size fractions contains mainly metallic copper. The copper assay for these non-magnetic materials ranged 71.5 – 97 % Cu. The copper recoveries of the non-magnetics in each size fractions were around 80%. Almost all of the copper is present as metallic copper. The non-magnetic fraction from the minus 65 mesh assayed to contain 11.8 % Cu. The majority of the non-magnetic fraction is the silicate slag. The non-magnetic fractions of each size group are about 10% of the feed weight, except the plus 14 mesh and minus 65 mesh fractions. The copper remained in the magnetic fractions is mainly present as in the forms of unliberated matte or very small blebs of metallic copper. The iron recovery is negligible.

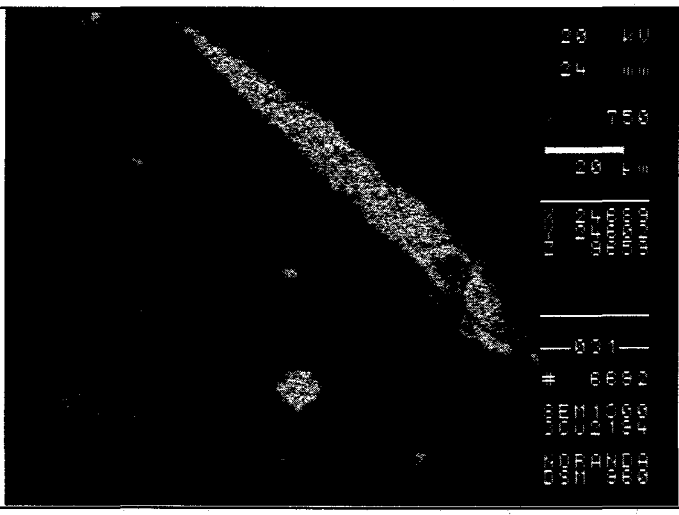
The cumulative grade and recovery relationships are shown in Figure 4. The particles coarser than 65 mesh gave copper concentrate containing about 80% Cu with about 45% recovery. The results showed that an application of classification and magnetic separation would produce a directly recyclable copper concentrate. The provision of removing metallic copper in the early stage of grinding and flotation should improve the overall copper metallurgy. According to the results of the present study, a magnetic separation unit was installed to treat the cyclone under flow. This configuration reduced the circulating load within circuit significantly. The coarse metallic copper (shapes, weight and particle size) and surface oxidation of these material had caused the metal losses in the flotation circuit due to the loss of floatability (only ~50% recovery).

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

A : Total backscattered electron image



B : Cu x-ray image.



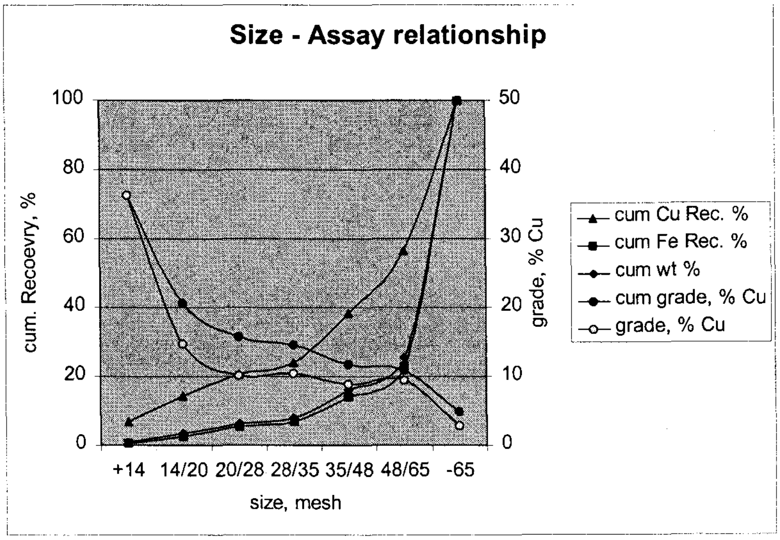


Figure 2. Grade recovery of size fractions.

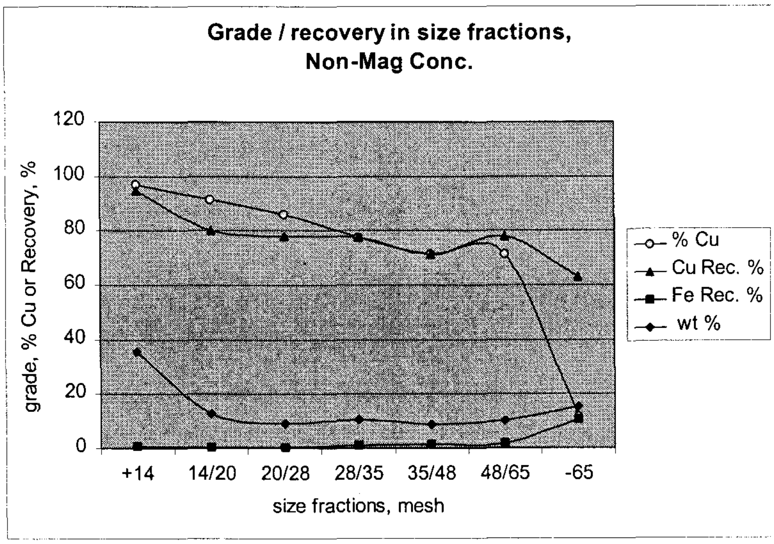


Figure 3. Grade / recovery of non-magnetic fractions of each size fractions.

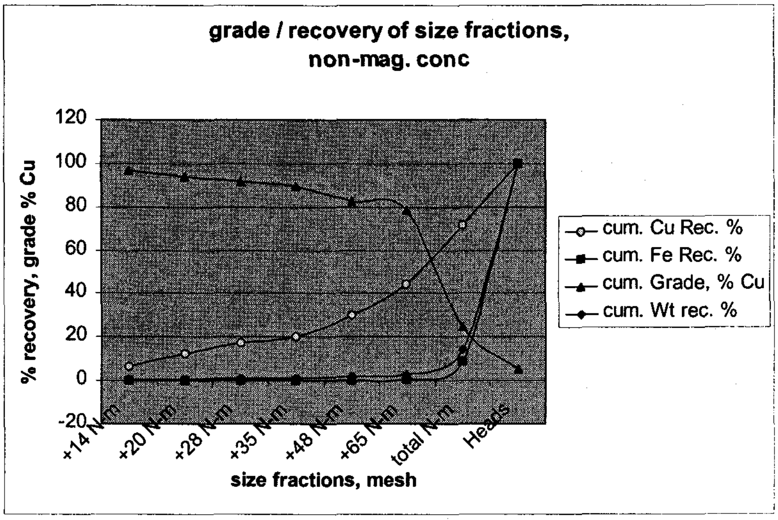


Figure 4. Cumulative grade / recovery of non-magnetic fractions of each size fractions.

A.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 grind classification U/F stream to recover metallic copper has been applied.

B. Treatment of Electrostatic Precipitator Dusts

Laboratory bench scale flotation and pilot plant scale classification / gravity separation using cyclones and Multi-gravity separator (MGS) as a means of separating the copper value in the dusts were carried out to define the range of applicability of the unit operations. Several different types of dust samples were used to examine the variability of the dust 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.

Due to the limitation in the space, a brief presentation will be made under the following subjects.

B.1 Flotation

B.2 Gravity Separation

B.2.1 Hydro-Cyclone Separation

B.2.1 Multi-gravity Separation

B.3 Process Medium and Flowsheet Development

B.3.1 Dissolution Characteristics

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

B.3.3 Flowsheet

C. Processing of Copper Refinery Intermediate Products.

Two samples of industrial flotation application in the copper refining operation are given below along with the process development and operational results.

C.1 Flotation of Doré Furnace(TBRC) Slag

C.2 Flotation of De-Copperized Anode Slimes