

## CURRENT OPERATIONS IN SMM'S SLIME TREATMENT

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### Abstract

SMM operates an original slime treatment process for recovering precious metals and other metals (Te,Se,Sb,Bi) from the copper and the lead anode tankhouse slimes. In recent years, the amount of slimes has increased and the pyrometallurgical processing units capacity became the bottleneck of the entire plants. For the expansion of the plant, new pyrometallurgical facilities, incorporating a BBOC, was commissioned in 1992 and has now been successfully operated. In addition, unit operations were optimized to increase recovery and reduce operating cost. The results of modifications made in the plant are discussed in this paper.

## Introduction

Niihama Copper Refinery of Sumitomo Metal Mining Co., Ltd. which commenced the operation in 1919 is one of the Japan's custom copper and precious metal refineries with a capacity to refine 130,000 tonnes of copper per year. Copper anodes are transported to the refinery by trucks from SMM Toyo Smelter which is located near the refinery. The precious metals plant which treats 1,200 tonnes per year of slime from both in-house and Toyo copper refinery and 400 tonnes per year of lead refinery slime generated at Harima ISP lead refining plant, produces 200,000kg of silver, 22,000kg of gold, 1,500 kg of palladium, 300 kg of platinum and 40 kg of rhodium as well as 60 tonnes selenium, 9 tonnes tellurium, 50 tonnes bismuth and 150 tonnes antimony alloy annually.

During the latest decade the production of gold has increased about twice because of increasing copper concentrate smelting and processing silicate ores averaging 80g gold per tonne at Toyo Smelter. The gold ores are received from SMM's Hishikari gold Mines. Reduction of gold inventory has, therefore, always been an important factor in the operation of the Niihama refinery.

The existing slime treatment plant was completely reconstructed in 1969 and through the years expanded its precious metals and by-products production. However as the throughput slimes increased, the pyrometallurgical facilities had difficulties in meeting production requirements. In 1990, the company has adopted the extension of a Girod type electric furnace bulk and the introduce of a new type Doré furnace.

The electric furnace was extended in 1991 and a Bottom blown oxygen cupel (BBOC) (1) developed by Britannia Refined Metals Ltd. replaced the old reverberatory type Doré furnace in October 1992. The accelerated oxidation capacity of the BBOC was recognized and then a modified process operation on extension of this furnace to chloridizing duty was carried out in 1994.

## Slime treatment process

The former process as it existed in 1991 is shown schematically in Figure 1 with typical analysis of the slimes treated being shown in Table I.

Table I. Typical analysis of slimes

Element (weight %)	Copper tankhouse slime	Lead tankhouse slime
Au	1.8	0.04
Ag	10.5	16.0
Cu	13.1	6.7
S	7.4	0.2
Ni	1.1	-
Pb	25.5	6.8
Se	5.2	-
Sb	4.3	35.0
Bi	2.5	15.0
Te	1.4	-

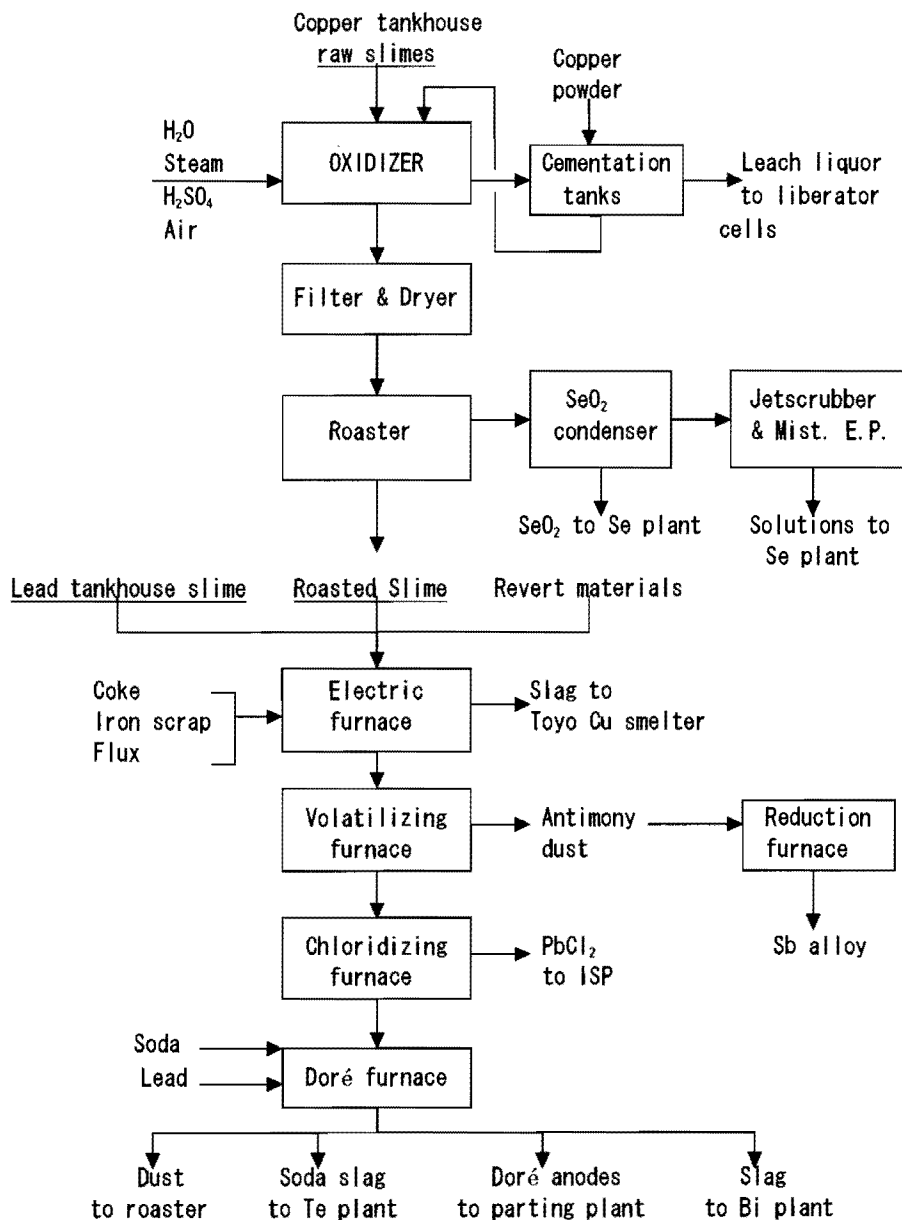


Figure 1 - Existing slimes treatment flow sheet at SMM

### Copper and selenium elimination process

Slimes from the in-house electrolytic cells are settled and the supernatant electrolyte is returned to the tankhouse. The thickened slimes are pumped into two centrifugal separator to decrease the moisture content up to 20%. The dehydrated slimes are discharged into a brick lined oxidizer to which sulfuric acid are added to obtain 1,000 g/l  $\text{H}_2\text{SO}_4$ . The mixture is heated to 90°C with direct steam. Compressed air is blown through the tank to oxidize and dissolve the copper. Blowing is continued until the free acid content of the liquor becomes constant. The decopper slimes solution is pumped to the leaching tank to which deselenium solutions from a jet scrubber and mist electrostatic precipitator are added to obtain 200g/l  $\text{H}_2\text{SO}_4$ . The leached slimes are filtered by means of a semi automatic filter press and dried by a band dryer, and then charged to two rotary kilns to separate the selenium. After leaching and roasting, the slimes contain only 0.5-1.5 % copper and selenium.

### Pyrometallurgical treatment of the roasted slime

Generally, the roasted slimes are charged to the Doré furnace for refining to metal for Moebius-cell parting. But in our treatment plant process, an electric furnace, two volatilizing furnace and a chloridizing furnace were used before the Doré furnace for the following reasons.

- 1) Minimizing precious metals content in the revert materials to the smelter
- 2) Recovery of Antimony
- 3) Good separation of lead as lead chloride
- 4) Successful separation of bismuth and tellurium, as well as a more effective operation of Doré furnace

### Electric furnace

Feeds consist mainly of the roasted slimes and lead tankhouse slimes. However, there are other feeds which are materials recycled from the volatilizing furnaces and Doré furnace, precious metals refining plant residues and by-products plant residues. These are blended with coke, iron scrap and flux and charged into the 700kVA Girode type electric furnace. A charge is melted and reduced in this furnace for 4 hours. The electric furnace produces molten metal containing 15-17% precious metals, iron silicate slag and dust. The molten metal is charged into a hot volatilizing furnace. The crushed slag is sent to the Cu smelter. The dust is returned to this furnace.

To cope with increasing the treated slimes, this furnace was extended from 0.64 m<sup>3</sup> to 1.32 m<sup>3</sup> working volume without enlargement of transformer capacity. The comparison of typical operating data between the previous and present furnace is shown Table II.

Table II Operating data of electric furnace

Item	Unit	Previous	Present
Charge	t/batch	3.2	4.9
Power Consumption	kWh/batch	1,700	1,960
Surface area of slag	m <sup>2</sup>	1.43	1.43
Secondary voltage	V	64	73
Secondary current	A	8,220	7,230

Volatilizing furnace ( Antimony recovery )

The volatilizing furnace consists of two 1.8m diameter by 3.3m long rotary vessels fitted with oil burners. The vessel is periodically rotated through 110° at 1 rpm to agitate the metal. Two electric furnace charges are transferred a vessel: 4 tonnes molten metal. Oxygen partial pressure in the furnace is maintained about in the range of 0.10-0.15 atm. Antimony in the metal is volatilized. The deantimonized molten metal contains 18-20% precious metals and 5-10% antimony. The dust at 70-75% antimony is recovered in bag filters and then is reduced to produce Sb alloy.

Chloridizing furnace

Chlorination to remove a large portion of the lead from the deantimonized molten metal was carried out in an insulation castable refractory lined cast iron kettle installed in a refractory lined furnace. Chlorine gas was blown into molten metal and lead chloride was generated on the metal. The deleadized metal contained about 10% lead. This metal was cast as 20Kg bullion with the help of a casting machine. After casting, matte was formed on the bullion and easily separated.

Doré furnace

Prior to 1992, the Doré furnace was an oil-fired reverberatory which consisted of an easily exchangeable hearth and an arched roof. Operation of the Doré furnace was carried out on a 3 day cycle. The basic operating procedure was as follows:

- 1) A hundred bullion ingots (about 2 tonnes) were charged.
- 2) The charge was melted using an oil burner.
- 3) Compress air was blown on the surface of molten metal through three steel lancing pipes with clay lining.
- 4) Slag was poured and several ingots charged.
- 5) Steps 3-4 were repeated until a 6.5 t charge was complete.
- 6) Soda ash flux was added.
- 7) Soda slag was poured.
- 8) Lead ingots were added.
- 9) Litharge was poured.
- 10) Doré metal was cleaned with Portland cement.
- 11) Doré metal was cast out.

The Doré metal was cast into Doré anodes of about 22 kg/piece and was treated for separation of silver and gold in the parting plant. The slag is crushed and sent to the bismuth recovery plant. The soda slag is ground into powder and sent to the tellurium recovery plant. Typical analyses of Doré furnace charges and products are shown in Table III.

Table III. Typical analyses of Doré furnace charges and products

		Composition, wt%					
		Au+Ag	Sb	Pb	Bi	Te	Cu
Charge	Bullion	34.0	16.0	8.2	24.0	5.1	4.1
	Matte	22.2	0.8	15.0	1.0	11.4	29.0
Product	Doré anode	98.0	tr.	0.3	0.1	tr.	0.7
	Slag	3.9	10.6	12.5	36.6	1.8	8.7
	Soda slag	4.1	5.6	9.4	20.5	15.6	12.4
	Dust	8.6	29.2	13.9	5.2	9.5	0.2

tr.: < 0.01

This furnace had served SMM's slime treatment plant well and operation had been stable. But, drawbacks of pyrometallurgical process in addition to that of capacity include:

- 1) high manpower and low fuel efficiency
- 2) high waste gas volume
- 3) low reaction speed

These drawbacks had to be considered in the selection of new cupel.

#### Process selection

Over the last decade, two types of new furnace which are the top-blown rotary converter (TBRC)(2) and the BBOC have been developed for the Doré furnace. The BBOC appeared attractive in the SMM's process on account of a easy control of the bath temperature, oxygen efficiency of around 100% and simple maintenance etc. Visit was made to Britannia Refined Metals Ltd. and confirmed that production scale furnace had operated successfully.

#### Present Operation

The BBOC with a capacity of 3.5 tonnes was built and commissioned in October 1992. To fit the flow scheme for the expanded plant, it was planned that BBOC was sized to take 3.5t of feed bullion for each cycle, with each cycle being completed within 24 hours. But in order to meet the parting plant operation cycle, present operating cycle time is 44 hours. No principal changes of Doré furnace operation procedures are introduced, although reaction gas use oxygen. The unit weight of bullion which is charged by overhead crane has increased from 20Kg to 500Kg. Typical operation data is shown in Table IV.

Table IV. Operating data of Doré furnace

Item	Unit	BBOC	Old Cupel
Charge ; Bullion + Matte	t/batch	11.0	6.5
Product ; Doré	t/batch	1.8	1.6
Operational time	hrs./batch	44	72
Oxygen utilization efficiency	%	92	8
Fuel Consumption	GJ/t-Doré	7	93
Exhausted Gases	Nm <sup>3</sup> /min	120	800

### Process control technology

There is a requirement to determine the end-point of each step of Doré furnace process in order to:

- 1) maximize oxygen efficiency
- 2) produce Doré of high quality
- 3) optimize soda ash and lead addition costs.

To achieve this objective, the relations between equilibrium oxygen pressure and Doré contents of bullion were investigated in Doré furnace(3). In Figure 2, Doré contents in bullion are plotted against oxygen pressures in several oxidation and refining steps. Doré contents increases with oxygen pressures. Using oxygen sensors based on stabilized zirconia with a reference electrode of Fe/FeO achieves prompt and appropriate end-point control and maintains the optimum composition of Doré.

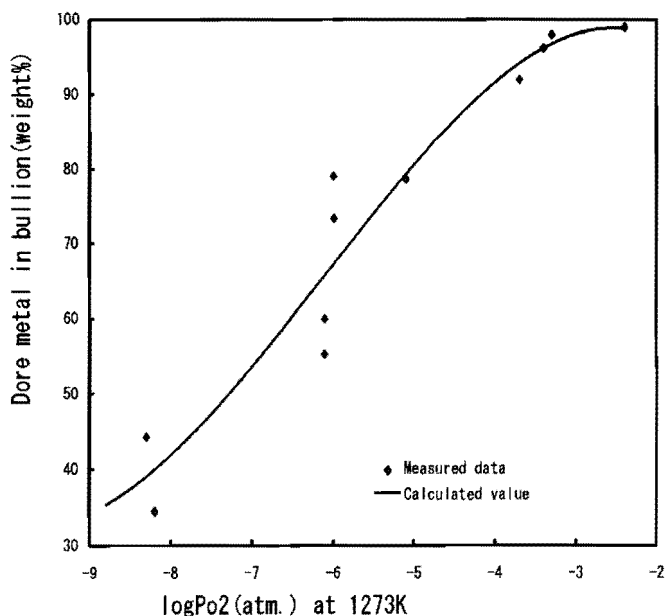


Figure 2 - Oxygen pressure change during oxidation and refining stages

Initially on start-up of BBOC, the impurity contents of Doré anodes were rather high. The purity of anode has been improved significantly with the introduction of oxygen pressure measurement and operation schedule based on mass balance model, in addition to conventional sensual inspection of a sample button. In the case of BBOC, the oxygen utilization efficiency is extremely high and the metallurgical balance is easily developed and available.

### Modification of pyrometallurgical treatment

The object of a modified process is to reduce in the working inventory of gold and elimination of chloridizing furnace. A modified process is shown on Figure 3 that consists of the following stages.

Charge 1 : Roasted slimes treatment with the reverts that contain less than 15% Sb and Bi.

- 1) Smelting and reduction in the electric furnace
- 2) Oxidation and refining in the BBOC to produce Doré (high gold)

Charge 2 : Lead tankhouse slimes treatment with reverts that contain more than 15% Sb and Bi.

- 1) Smelting and reduction in the electric furnace
- 2) Sb separation in the volatilizing furnace
- 3) Oxidation and refining in the BBOC to produce Doré (low gold)

Charge 1 treatment has priority over Charge 2. Several test operations were carried out in 1993 to find out optimum process parameters and technical practicability was confirmed for the process. The new process have been operating since February 1994 and giving very good results.

### Summary

Copper tankhouse slime treatment has been modified to process the electric furnace bullion directly to Doré anode in one process step, thereby releasing gold values quickly. The capacity and the productivity of slime treatment have been increased with the BBOC technology.

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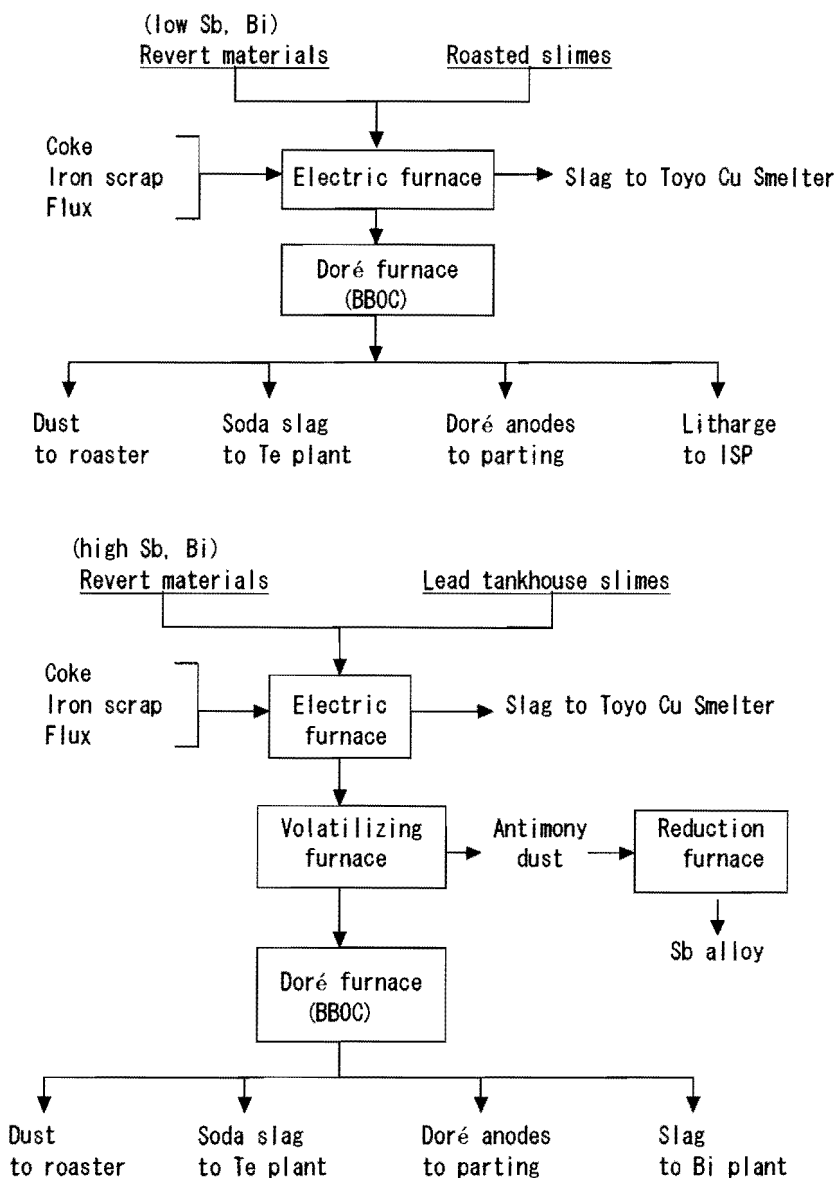


Figure 3 - Modified slime treatment flow sheet

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