

## **Hydrometallurgical processing of anode slime for recovery of valuable metals**

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### **ABSTRACT**

*The anode slime obtained from Indian Copper Complex, Ghatsila was used for the recovery studies with the aim of developing a hydrometallurgical processing route. The chemical analysis of the slime showed that it contained valuable metals like copper, nickel, selenium, tellurium, gold, silver and platinum group metals. Characterisation study by XRD analysis revealed the presence of various phases like NiO, CuSO<sub>4</sub>.5H<sub>2</sub>O, NiSe, α-CuSe, Cu<sub>4</sub>SeTe<sub>6</sub>, Cu<sub>2</sub>Te, (Cu<sub>0.2</sub>Ni<sub>0.8</sub>)O, Cu<sub>7</sub>Te<sub>5</sub>, AgCu<sub>7</sub>Te<sub>10</sub>, SiO<sub>2</sub> etc. in the slime. Presence of free moisture, combined moisture, selenium and tellurium were detected by TG/DTA studies. Preliminary leaching experiments of the anode slime in sulphuric and hydrochloric acid media at different conditions were carried out to recover copper, nickel and tellurium. Maximum copper recovery in sulphuric acid and hydrochloric acid leaching experiments at normal pressure was found to be about 55% and 77% respectively. In both the cases nickel and tellurium recoveries were poor. In the autoclave leaching copper and tellurium recoveries improved with increasing time and pressure. Maximum copper and tellurium recoveries to the tune of 85% and 71% respectively were achieved using 1% sulphuric acid as leachant. On increasing the sulphuric acid concentration to 20% in the pressure leaching, the recoveries of copper and nickel improved to 95% and 46% respectively.*

**Keywords** : Anode slime, Characterization of anode slime, Leaching, Recovery of valuable metals.

### **INTRODUCTION**

Anode slime is the insoluble product deposited at the bottom of the electrorefining tank at the time of electrorefining of copper. It contains valuable

metals like Cu, Ni, Se, Te, Au, Ag and platinum group metals (PGM) <sup>[1,2]</sup>. The slime is periodically collected from the electrorefining tank and is processed for the recovery of these metals. Depending upon the composition and morphology of the anode slime, a number of processes following pyro, pyro-hydro and hydrometallurgical routes have been developed. One of the well known pyrometallurgical processes is the slime smelting in Dore furnace with selenium recovery from the flue gases followed by soda-niter treatment for the recovery of precious metals <sup>[3,4]</sup>. However, this process suffers from various drawbacks which include potential environmentally abusive smelting emission, recycling of precious metals in the slag, large in-process inventories of precious metals, high energy consumption etc. <sup>[5]</sup>. Therefore, to overcome these problems pyro-hydrometallurgical routes were evolved. Some of the important pyro-hydrometallurgical processes are soda roasting followed by leaching <sup>[6]</sup>, sulphation roasting followed by leaching <sup>[7]</sup>, oxidation roasting followed by leaching <sup>[8]</sup> etc. Some of the process routes involve decopperization of the slime by atmospheric and pressure leaching methods prior to the smelting and fire refining operations <sup>[9,10]</sup>. However, all the roasting and smelting stages involved in the volatilization of selenium and sulphur require efficient scrubbers to convert them to selenious acid or sulphuric acid <sup>[11]</sup>. These processes also pose the problems like substantial inventories of precious metals and recycle of precious metals in slag which account for the major cost of the slime processing plant. To address these problems, evolution of pure hydrometallurgical process took place. So far only one complete hydrometallurgical process e.g. the wet chlorination process has been developed. However, this process requires special attention with respect to pollution problem and materials of construction to handle the chloride solution. The other hydrometallurgical approaches to slime treatment have not yet provided the complete flow-sheet for recovery and separation of various metals <sup>[12]</sup>.

In the present investigation, attempt have been made to develop a hydrometallurgical process to recover the valuable metals present in the anode slime obtained from Indian Copper Complex, Ghatsila. The detailed characterisation and analyses of the slime have been carried out. Since the anode slime of ICC, Ghatsila contains major amount of copper and nickel, extraction of these metals from the slime prior to the recovery of other metals have been examined through acid leaching tests and these have also been described in this paper.

## **MATERIALS AND METHODS**

The anode slime obtained from Indian Copper Complex, Ghatsila was used for the experiments. The sample was ground and mixed thoroughly. Representative samples were prepared by coning and quartering method for chemical analysis,

X-ray diffraction (XRD) and DTA/TG studies. Leaching experiments were carried out at normal pressure as well as super atmospheric pressures. The normal pressure leaching experiments were done with the help of a magnetic stirrer having the speed and temperature controlling devices. Leachants used were sulphuric acid and hydrochloric acid. The effects of various parameters such as period of leaching, acid concentration and temperature were studied. The scale of experiment was 10g and solid:liquid ratio of 1:10 was maintained in the experiments.

High pressure leaching was carried out in an autoclave (Model-4521M made by PARR, USA) in sulphuric acid medium on 50g scale. The solid:liquid ratio was maintained at 1:10. The parameters studied in the autoclave leaching were period of leaching, sulphuric acid concentration and pressure. All the chemical reagents used for the experiments were of A.R. grade. Chemical analyses of the head sample and leach solutions were carried out by atomic absorption spectrometer (AAS) as well as by conventional methods.

## RESULTS AND DISCUSSION

The chemical analyses of the anode slime is presented in Table 1. It shows that the major constituents in the slime are copper and nickel. The other metals present in significant amounts are selenium and tellurium along with minor amounts of silver, gold, platinum, lead, arsenic etc. Of particular importance to the slime treatment is a knowledge of various phases present in the slime, which has direct bearing on the processing steps and reagents to be used for attacking different phases [13,14]. Various phases present in the slime have been revealed by

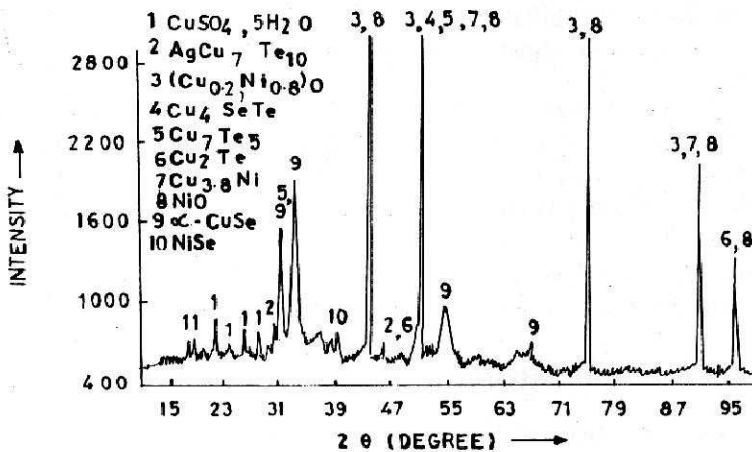


Fig. 1 : XRD pattern of anode slime.

Table 1 : Chemical composition of anode slime (wt.%)

Cu	=	12.29	Be	=	0.014
Ni	=	36.76	Sb	=	0.01
Se	=	10.50	As	=	0.036
Te	=	3.38	Pb	=	0.16
Ag	=	1.54	Fe	=	0.29
Au	=	0.0064	SiO <sub>2</sub>	=	4.0
Pt	=	0.015	Moisture	=	3.75
LOI	=	21.99			

XRD studies, as shown in Fig.1. It can be seen that the most common phases are CuSO<sub>4</sub>.5H<sub>2</sub>O and NiO. The other phases are copper selenide, nickel selenide, copper telluride, copper-selenium-telluride, silver-copper-telluride, silica etc. In the TG/DTA studies as shown in Fig.2, endothermic peaks observed at about 90°C and 350°C represent the removal of free moisture and combined moisture respectively. The weight loss observed in TG curve at higher temperatures indicate the removal of selenium and tellurium as they volatilize in the temperature range of 500° to 1000°C.

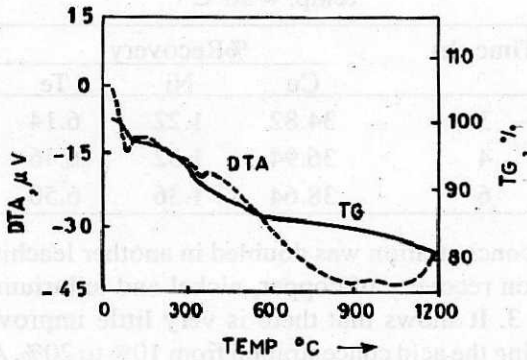


Fig. 2 : DTA/TG curves of anode slime.

### Acid Leaching

The characterisation of anode slime sample indicates that copper is mainly present in the forms of sulphate, telluride or selenide. Major amount of nickel is present as oxide as well as in selenide form. Although copper sulphate can be

dissolved easily in water but its telluride and selenide forms can be attacked only in acidic media. Therefore, acid leaching in presence of air has been carried out to recover copper along with the other metals present in the slime. The results of the sulphuric acid and hydrochloric acid leaching experiments in various conditions are presented below.

### Sulphuric Acid Leaching at Normal and High Pressures

The recoveries of metals in 10% sulphuric acid leaching at various durations of leaching are shown in Table 2. It can be seen that the copper recovery of about 35% has been achieved in 3 h leaching. There is very little improvement of copper recovery on increasing the time of leaching upto 6 h, which has been found to be about 39%. The dissolution of nickel and tellurium in these experiments is found to be poor. The results imply that most of the copper telluride and nickel bearing phases can not be leached by sulphuric acid at ambient conditions. The dissolved copper (39%) in the leached solution may account for the leaching of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  present in the slime.

Table 2 : Effect of time on recovery of metals

$\text{H}_2\text{SO}_4$  concentration = 10 V%

S:L = 1:10

Temp. = 30°C

Time (h)	%Recovery		
	Cu	Ni	Te
3	34.82	1.22	6.14
4	36.94	1.32	6.46
6	38.64	1.36	6.50

Sulphuric acid concentration was doubled in another leaching experiment to examine its effect on recovery of copper, nickel and tellurium. The results are presented in Table 3. It shows that there is very little improvement in copper recovery on increasing the acid concentration from 10% to 20%. Almost no change in the recovery of nickel and tellurium has been noted on increasing the acid concentration.

As the increase in acid concentration and leaching time could not improve the metal recovery much, the temperature of the leaching experiment was increased to examine its effect on leachability of copper, nickel and tellurium. The results are given in Table 4. It can be seen that the copper recovery increases from about 39% to 55% with the increase of temperature from 30°C to 70°C.

Table 3 : Effect of  $H_2SO_4$  concentration on recovery of metals

Time of Leaching : 4h

S:L = 1:10

Temperatures = 30°C

Conc. of $H_2SO_4$ (V%)	%Recovery		
	Cu	Ni	Te
10	36.94	1.32	6.46
20	38.56	1.32	5.24

However, nickel and tellurium recoveries are once again unsatisfactory. Although the copper recovery increases to 55% on increasing the temperature, copper telluride and copper selenide phases are presumably, not fully attacked even at higher temperatures.

In view of the above, high pressure leaching experiments were carried out at elevated temperature (125°C). Sulphuric acid concentration was fixed at low value (1%) in the preliminary experiments. The recovery pattern of copper, nickel and tellurium in pressure leaching at 1.8 kg/cm<sup>2</sup>, with increasing time has been shown in Fig.3. It can be seen that the recovery of copper and tellurium increase rapidly with time upto 1 h of leaching, after which the metals dissolution particularly copper slow down. It can be further noticed that although the copper recovery (56%) has not improved much compared to the atmospheric leaching (55%), there is a remarkable improvement in the tellurium recovery (about 68%) in the pressure leaching for 4 h. However, copper recovery has not improved to

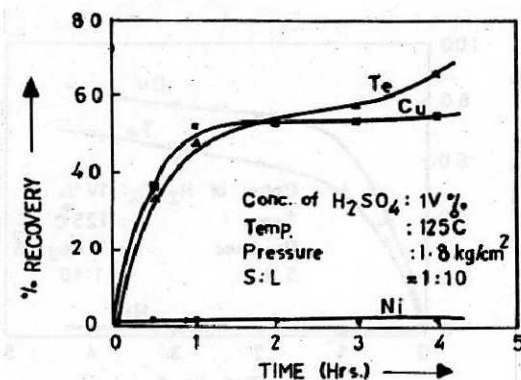


Fig. 3 : Effect of time on recovery of metals at low pressure.

Table 4 : Effect of temperature on recovery of metals

H<sub>2</sub>SO<sub>4</sub> concentration = 20 V%

S:L = 1:10

Time of Leaching = 4h

Temp. °C	%Recovery		
	Cu	Ni	Te
30	38.56	1.32	5.24
50	39.70	2.01	5.30
60	44.67	2.00	5.39
70	54.67	2.06	6.34

the extent as expected on dissolution of tellurium from copper telluride. This signifies that most of the copper is in the form of copper selenide, which is also evident from the high intensity peak of copper selenide in the XRD pattern (Fig. 1) of the anode slime. The chemical analysis of the slime also indicates that selenium content of the sample is higher than tellurium which further confirms that appreciable amount of copper dissolution can be achieved only by dissolution of the copper selenide. The poor recovery of nickel in this case may be attributed to the use of low concentration sulphuric acid.

Fig.4 shows the metal recovery values with increasing time at higher pressure (7.14 kg/cm<sup>2</sup>) autoclave leaching while keeping the temperature and acid concentration same at 125°C and 1% respectively as in the case of low pressure leaching. Here the copper recovery reaches to about 85% in 4 h leaching while tellurium recovery is almost same (about 71%) as it has been found in the case

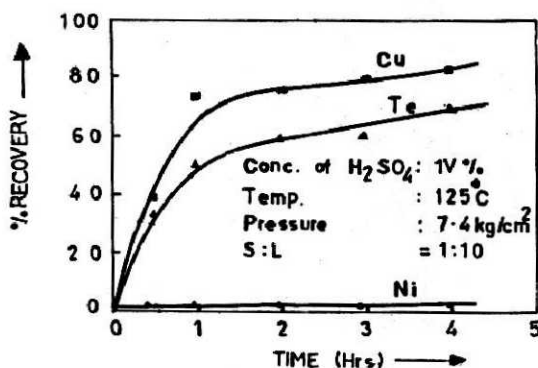


Fig. 4 : Effect of time on recovery of metals at high pressure.



of low pressure leaching. The high copper recovery in high pressure leaching may be attributed to the dissolution of copper from the copper selenide. However, selenium content in the leached solution has been found to be poor (0.82%) due to its low solubility in sulphuric acid medium. Nickel recovery is, once again, low in this case which has been found to be about 2%. This may be due to low acid concentration. In one experiment with 20% sulphuric acid at 125°C and at 28.5 kg/cm<sup>2</sup> pressure, the metal recovery values of 95% copper and 46% nickel have been achieved. This implies that nickel recovery can be further improved by increasing the acid concentration and pressure in autoclave leaching.

### Hydrochloric Acid Leaching at Normal Pressure

In the sulphuric acid leaching, nickel recovery was poor in general and copper recovery was also not satisfactory until copper selenide phase was attacked. Since the hydrochloric acid has reducing power and selenium can be made soluble in chloride medium, some hydrochloric acid leaching experiments were also performed. The results of the hydrochloric acid leaching are shown in Table-5. It can be seen that more copper recovery (55%) at 30°C has been achieved compared to the recovery value of 39% at same temperature in sulphuric acid medium (Table 4). Further, copper dissolution has been found to increase with the increase in temperature and it has reached to a value of about 77% at 80°C. This further confirms that the reason of improved copper recovery lies due to providing proper lixiviant such as chloride medium in this case, for the dissolution of copper selenide. However, nickel oxide present in slime could not be dissolved to an appreciable amount in hydrochloric acid medium also.

Table 5 : Effect of temperature on recovery of metals

HCl concentration = 20 V%

S:L = 1:10

Time of Leaching : 4h

Temp. °C	%Recovery	
	Cu	Ni
30	54.75	1.18
70	75.75	1.43
80	77.29	2.01

### CONCLUSION

The anode slime of ICC, Ghatsila contains major amount of nickel oxide, copper sulphate and copper selenide. The other metals present in the slime are tellurium, silver, gold and platinum group metals. Preliminary leaching experi-



ments in sulphuric acid medium show that copper and tellurium can be extracted in considerable amounts only at high pressures and temperatures. Hydrochloric acid leaching at normal pressure yields good recovery of copper. Nickel extraction is not good in either of the acidic mediums. However, nickel extraction may be improved by increasing the sulphuric acid concentration in pressure leaching experiments.

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