

## The Solubilities of Zn, Sb and Se Found in Anode Slime

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The purposes of the study were to examine the methods used for recovering the precious metals from the anode slime formed as a by-product during the production of high purity copper by electrolytic means, and to investigate the products obtained. The characteristics of the electrolysed copper dictate the type and the amounts of Cu, Se, Te, Zn, Pb, Fe, Ni, Ag, Au and Pt group of metals present in the slime. Since the anode slime has a very low ratio of zinc by virtue, obtaining zinc from its ore is the best and most convenient way. The solubilities of Zn, Sb and Se present in an anode slime were examined by using sulphuric acid for the effects of the concentration of solvent, temperature and time. The increase in temperature and time (at 210°C) increased the solubility of Se only and 80% of Se passed into the solution.

### INTRODUCTION

Approximately, 90% of the world's copper originates from sulphide ores present in the earth's crust mainly in the form of chalcopyrite ( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ). Most of Au, Ag, Pt and the part of Se, Te present in sulphide ores concentrate in blister copper during the pyrometallurgical treatment. Copper is produced in high purity by fire refining and then electrolytical refining of blister copper. During electrolytic refining, the insoluble impurities from the anode accumulate as undissolved slimes at the bottom of the electrolytic cells. The compositions of these slimes, the by-products of various refineries, are most variable<sup>1,2</sup>.

Turkey has mainly three electrolytic copper refineries, namely, Rabak, Sarkuysan and Bakirsan.

The physical properties and chemical composition of anode slime depends upon the characteristics of the copper ore. The properties of anode slime have extensively been studied by Hennig and Pawlek<sup>3</sup>. The insoluble metals and compounds settling at the bottom of the tanks during the electrolytic cycle were screened and used in recovering the precious metals and by-products. Most of the silver and copper was found to combine with the sulphur, selenium or tellurium. A portion of the copper, gold and platinum group metals was in the elemental form. Some of the gold was found as silver alloy or as telluride<sup>4</sup>.

The compositions of anode slimes of copper refineries show differences. Anode slime contains 11–67% copper, 0.5–5% silver, 0.02–0.70% gold, 0.50–24% lead, 2–8% antimony, 1.5–6% arsenic, 0.20–8% bismuth, 0.1–1.5% iron, 3–28% selenium, 0.10–8% tellurium and 0.50–12%  $\text{SO}_3$ .<sup>5</sup> Several methods are available for treating the anode slimes depending upon the composition of the slime and the concentration of the impurities<sup>6</sup>.

The most favoured procedure is the removal of copper, selenium and tellurium prior to the removal of the precious metals<sup>7, 8</sup>.

Copper can be removed as water-soluble sulphate, and then, if necessary, the sulphate solution is treated directly to produce metallic copper. Any of the commercial methods such as oxidizing roasting, sulphatizing roasting or leaching in dilute sulphuric acid may be utilised for copper recovery. In the first two pyrometallurgical methods, it is not possible to avoid volatilization of some compounds, especially Se as  $\text{SeO}_2$ .<sup>9</sup>

Selenium and tellurium in the slime are generally in the form of  $\text{Cu}_2\text{Se}$ ,  $\text{Cu}_2\text{Te}$ ,  $\text{Cu}(\text{Te}, \text{Se})_2$ ,  $\text{Cu Ag Se}$ ,  $\text{Ag}_2\text{Te}$ ,  $\text{Ag}_2\text{Se}$ .<sup>10</sup> The main purpose of treating the copper refinery slimes is the recovery and separation of precious metals, selenium and tellurium. The most preferred procedure is to remove copper and then the removal of selenium and tellurium prior to the removal of precious metals<sup>11</sup>. Copper is removed mainly as a water-soluble sulphate. This sulphate solution, if necessary, is purified or treated directly to obtain metallic copper<sup>12</sup>.

Selenium and tellurium in the anode slime are recovered as dioxides or in the elemental states. The usual methods of slime treatment for recovering selenium and tellurium are oxidizing roasting, sulphatizing roasting, soda roasting or smelting, caustic pressure leaching. The pyrometallurgical methods have some disadvantages due to losses caused by volatilization and air pollution<sup>13, 14</sup>.

This study considers the dissolution of precious metals in concentrated sulphuric acid using copper anode slime rich in both selenium and antimony. The effects of acid concentration, temperature and time were investigated.

## EXPERIMENTAL

*Anode slime sample:* The slime samples used in the study were obtained from Sarkuysan, Turkey. The copper dissolution studies were conducted on the original slime while the selenium solubilities were studied using the decopperized slime.

*Procedure:* First, sulphuric acid was placed in the reactor and heat was applied. When the desired temperature was reached 10 g sample was added and the reaction was started. The mixture was heated and stirred during the reaction. In the dissolving phase the mixture was suspended in the acid solution by the stirrer.

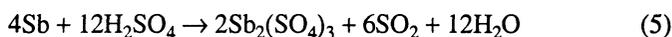
The reaction was violent and exothermic at the start. When the reaction was terminated the solution was filtered through a glass-filter. The mixture was washed with concentrated  $\text{H}_2\text{SO}_4$  during the solid phase and dissolved at  $70^\circ\text{C}$  for 1 h. The residue was dried at  $105^\circ\text{C}$  for 2 h. The samples were analysed for elemental compositions.

*Methods of analysis:* Analytical grade sulphuric acid was used as the dissolving reagent. The chemical analyses of the original anode slime samples were done by two different methods. All elements were analysed by wet analytical methods<sup>5, 15</sup> with the exception of Au, Sb, Se and Te analysis; the results of wet methods were checked by the atomic absorption spectrometry (Perkin-Elmer, model 370).

The changes in the weights of wet and dry slimes against time were determined at  $400^\circ\text{C}$ . The slime was mixed for 10 min during the operations. All experiments were performed on duplicate samples for consistent results.

## RESULTS AND DISCUSSION

The copper recovery was studied by leaching the slime into the sulphuric acid solution. The reactions between the acid and the slime are as follows:



The sulphate formed is undissolved in concentrated sulphuric acid; thus the whole copper remains as precipitate in the residue while  $\text{SeSO}_3$  can be dissolved.

The results of experimental analyses of elements are given in Table-1.

TABLE-1  
THE CHEMICAL COMPOSITION OF ANODE SLIME

Element % (by weight)	Cu	Sb	Te	Se	Pb	Fe	Zn	Ni	Ag	Au
By wet analytical method	18.56	2.32	1.12	4.48	7.00	0.18	0.02	0.93	0.73	0.12
By atomic absorp. spect. (AAS) method	19.00	*	*	*	6.98	0.20	0.03	0.94	0.74	*

\*Not determined due to unavailability of hollow cathode lamps.

TABLE-2  
THE WEIGHT CHANGE OF ANODE SLIME (AS DRY BASIS)

Experiment	Heating time (min.)	Weight changes, % (by weight)
1	30	15.15
2	60	17.52
3	90	18.23
4	120	19.47
5	150	19.57

The weight changes of wet and dry anode slimes against time at  $400^\circ\text{C}$  were determined by mixing for 10 min. The results are given in Tables 2 and 3. It is clear from the tables that the dry anode slime reached constant weight in about 2.5 h, whereas it took 4 h for the dry slime to come into constant weight. For both slimes 19–20% increase in weight was observed. Ziyadanoğullari *et al.*,<sup>6</sup> reported in a previous study that a convenient temperature for the oxidation of

selenides to selenites and tellurides to tellurites is 400°C. Therefore, the anode slime undergoes roasting at this temperature.

The effects of various concentrations of sulphuric acid on the amount of metal dissolved for Zn, Sb and Se are shown in Fig. 1. The experiments were carried out such that mixing was followed by immediate filtering and the reaction times of 15 and 30 min at 120°C were used. The amount of Se dissolved in 30 min was constant after 20 mL of acid addition. The solubilities of zinc and antimony increased continuously for different periods of time used.

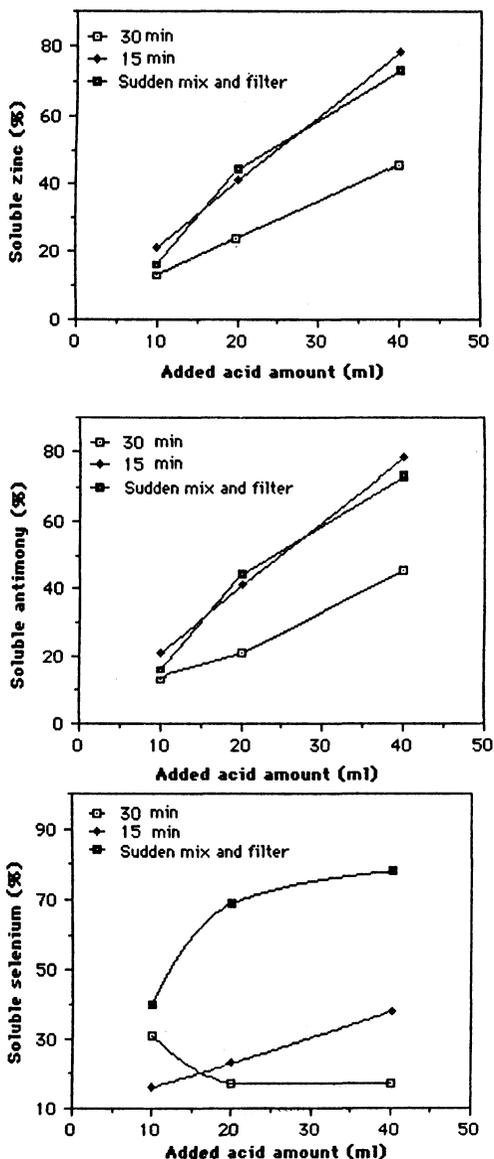


Fig. 1 The effect of acid amount on solubility of metals.

The solubility of selenium under the conditions of added acid quantity, sudden mixing and filtering and 15 min of solubility time appears to be increasing. The reason for this increase is probably the reaction of the selenium particles formed in the beginning of the reaction and escaped from the filter holes. Therefore, the experiments were performed using constant parameters of 20 mL of acid and 30 min of time.

The effects of temperature on the solubilities of Zn, Sb and Se are illustrated in Fig. 2. The solubilities of these elements were determined at 80, 120, 145 and 175°C.

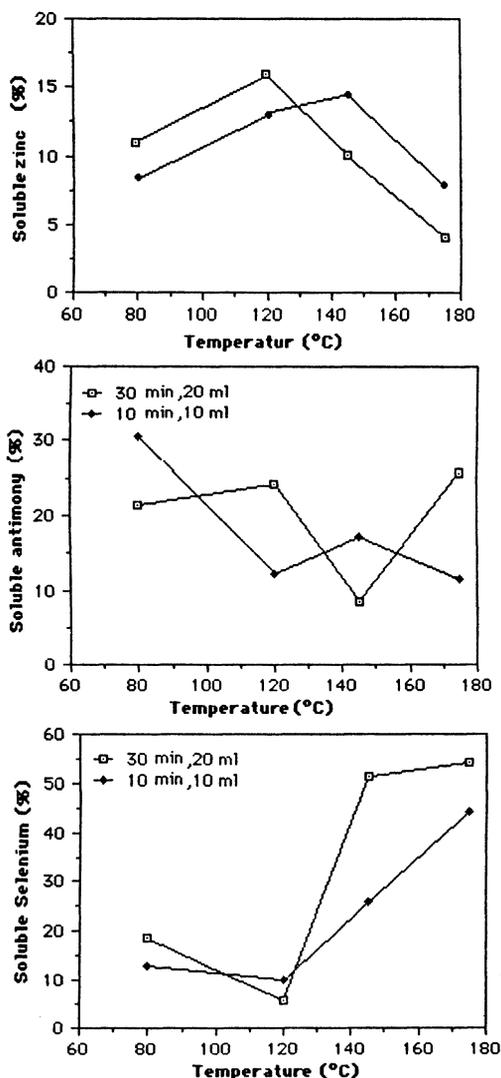


Fig. 2 The effects of temperature on solubility of metals.

The solubility of selenium increased with an increasing temperature after 120°C. This conclusion is in accord with the results given by Yildirim<sup>1</sup>. The variation in the temperature did not seriously affect the solubilities of zinc and antimony, probably due to the fact that zinc and antimony react very rapidly.

The variations in the solubilities of zinc, antimony and selenium in acid against time are presented in Fig. 3. The solubility of selenium at 120°C decreases by time and eventually remains constant. It increases by time at 210°C. The solubility of antimony increases at 120°C, later has a decrease and at 210°C decreases continuously. Increase in the solubility of zinc at 120°C requires an addition of

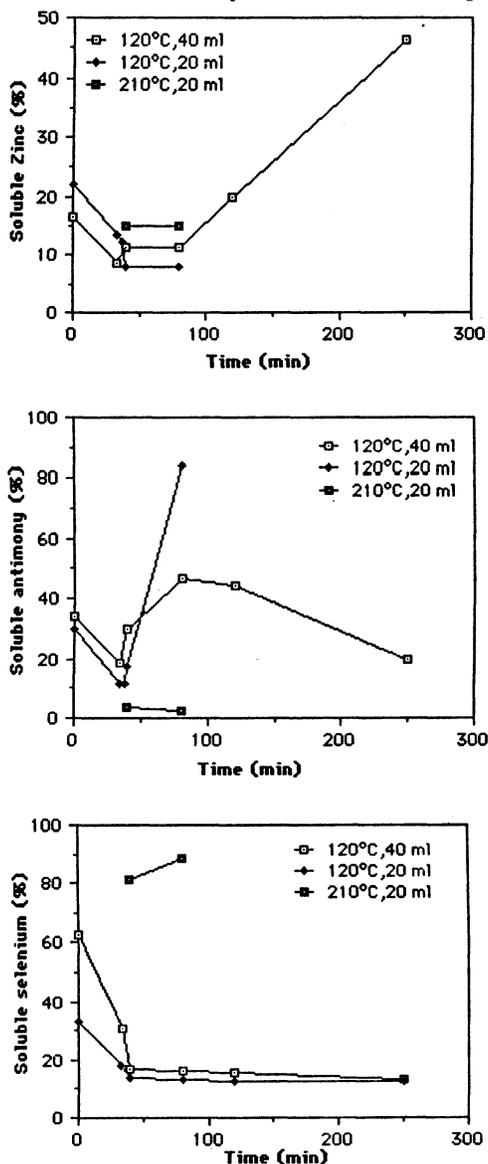


Fig. 3 The effects of time on solubility of metals.

40 mL acid while the solubility is constant by time at 210°C. Upon 20 mL acid addition the solubility of zinc at 120°C starts to decrease and eventually remains constant. These results confirm to the values reported in the literature<sup>1</sup>.

TABLE-3  
THE WEIGHT CHANGE OF ANODE SLIME (AS WET BASIS)

Experiment	Heating time* (min.)	Weight changes, % (by weight)
1	30	10.96
2	60	15.59
3	90	16.77
4	120	17.70
5	150	18.42
6	180	18.86
7	210	18.96
8	240	19.01

\*0.5 mL water was added to the mixture every 30 min.

## Conclusion

Copper can be removed from the anode slime by dissolving it in dilute sulphuric acid. Anode slime obtained as a by-product in the electrolytic refining of blister copper is a source of valuable metals such as Te, Ni, Se, Sb, Ag and Au. These leachates could yield valuable metals while achieving a residue removal. The first part of this study was for Fe, Pb, Ni, Te and Ag.<sup>7</sup>

The solubilities of zinc and antimony increase continuously at each of the three time periods tested with various quantities of sulphuric acid. An increase in the amount of selenium dissolved is observed with an increase in time and heat at 210°C and approximately 80% of selenium passes into solution. Yildirim<sup>1</sup> reports that 97% of selenium and silver passes together into solution with the increase in heat and time at 210°C.

The anode slime has low content of zinc, obtaining zinc from its ores is preferable to the slime.

In conclusion, some of the precious metals can be recovered from the anode slime which is a waste in copper refining plants.

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