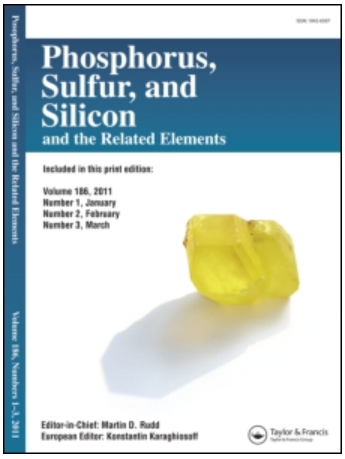

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Narinder Sing[a]; S. B. Mathur[a]
[a] Extraction Metallurgy Division, National Metallurgical Laboratory, Council of Scientific & Industrial Research, Jamshedpur, India

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STUDIES ON THE EXTRACTION OF SELENIUM AND TELLURIUM FROM COPPER ELECTROLYTIC SLIMES BY SUBLIMATION IN VACUUM

by

Narinder Singh and S. B. Mathur

Extraction Metallurgy Division, National Metallurgical Laboratory, Council of Scientific & Industrial Research, Jamshedpur, 831007 India

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ABSTRACT

Anode slimes obtained from the electrolytic refining of copper contain selenium and tellurium in the form of selenides and tellurides of metals, *e.g.*, copper and silver. The slimes were treated with sulfur under vacuum; selenides and tellurides decomposed to give selenium and tellurium in metallic form which condensed on a cooler zone. Various parameters studied were temperature, time, sulfur addition, briquetting pressure, and fineness of sulfur added. The X-ray diffraction studies carried out on treated and then on untreated slime proved the reaction of sulfur with selenide and telluride of copper to give copper sulfide, selenium, and tellurium. Sulfurization at around 475°C for 60 min gives optimum recoveries.

Introduction

Selenium and tellurium both occur rarely in the elemental state and are usually found as selenides and tellurides of heavy nonferrous and precious metals. They are, in fact, indispensable components in almost all of the sulfide ores of heavy nonferrous metals—copper, nickel and multimetallic ores. During the roasting and smelting of these ores some of the selenium and some of the tellurium volatilize and accumulate in dusts and sublimates; the remainder passes into the smelted crude metals. In subsequent refining of crude copper and nickel by electrolysis, selenium and tellurium settle in the bottom of the cell along with other insoluble metals and compounds as the anode slimes.[1,2,3]

In present day industry the main sources of raw selenium recovery are the anode slimes of electrolytic copper and nickel refineries. However, selenium is also present in the sludge of the gas-washing equipment of sulfuric acid and pulp and paper industry.

The copper anode slimes are mainly composed of:

a) Impurities insoluble in electrolyte; these impurities are either metallic or non-metallic.

i) Metallic impurities are gold, silver, platinum, selenium and tellurium;

ii) nonmetallic impurities are, Cu_2S, Cu_2Se, Cu_2Te, NiO, ZnO, SnO_2, SiO_2 and iron oxide.

b) Impurities precipitated by electrolyte due to:

i) Hydrolysis; As, Sb, Bi, Sn;

ii) formation of insoluble sulfates, Pb.

In addition to this some mechanically detached copper is also present.

The most probable forms in which the selenium and tellurium are present are Ag_2Se, Cu_2Se, Cu.AgSe, Se and Ag_2Te, $(AgAu)Te_2$ and Te respectively.[4,5,6]

The chemical composition of the slimes, however, depend upon the raw materials used in the production of copper.

The methods of treatment of copper anode slimes and other selenium and tellurium bearing materials are determined by the chemical and phase composition of materials and on the form in which these metals occur in them.[4,5,6]

The principal methods of selenium and tellurium extraction from raw materials are based mainly on the physico-chemical properties of the dioxide, the relatively high vapor pressure of selenium dioxide and volatilization in pyrometallurgical processes, solubility in water in the form of acids and salts, and the reduction to elemental state with the aid of sulfur dioxide.

In practice, there are three methods of preliminary high-temperature treatment; baking with soda ash in an oxidizing medium; sulfatization with strong sulfuric acid, and smelting with soda and nitre. These methods, as well as other recent methods, have been discussed in detail by the authors elsewhere.[6] The authors[7,8,9] have also made an extensive study of sulfatization of electrolytic copper slimes in which the slimes were digested and roasted with concentrated sulfuric acid. The selenium was recovered from the sublimed selenium dioxide by scrubbing with dilute sulfuric acid and reduction with sulfur dioxide gas.

Isakova and Nesterov[10] studied the extraction of selenium and tellurium, from electrolytic slimes, by sublimation in vacuum. They treated the copper anode slimes with 200% sulfur, by weight of slimes. The degree of sulfurization of selenides, at 0.15 mm mercury and 450°C, was 86.2% while that of telluride was 93%. Repeated, sulfurization, however, had no effect. Selenides and tellurides of copper decomposed completely after one hour at 450°C, but the corresponding silver compounds decomposed much less readily.

In the vacuum sublimation method, the problem of corrosion and pollution are not involved as in acid roasting, where the digester and roaster have a short life and must be replaced periodically. Also the gases given off may contain sulfur dioxides, selenium, or selenium dioxide, which, if not recovered fully, may pollute the atmosphere. Therefore, a systematic study was initiated at the National Metallurgical Laboratory to recover selenium and tellurium from copper anode slimes by vacuum sublimation with sulfur. This paper gives the results of this study.

Experimental Section

The anode slimes used for this study were obtained from the Indian Copper Complex Ghatsila (Hindustan Coppers Limited), India. The slimes were dried at 110 ± 10°C in an oven, crushed to −200 mesh size and analyzed spectrographically, followed by X-ray fluoroscent methods. Table I gives the chemical composition of two batches of slimes.

An X-ray diffraction study of the slime samples confirmed the assumption made in the literature,[5,6] that selenium and tellurium are present in the form of selenides and tellurides of copper, silver and gold. The details of the X-ray study are given at the end of the paper.

Selenium and tellurium can, therefore, be extracted from slimes, if selenides and tellurides are decomposed and freed selenium and tellurium are removed from the reaction zone.

By treating the slimes with elemental sulfur, the selenides and tellurides may be decomposed, to form base metal sulfides, thereby, releasing the elemental selenium and tellurium. The reactions occurring most probably are:

$$Cu_2Se + S \longrightarrow Cu_2S + Se \quad (1)$$

$$Cu_2Te + S \longrightarrow Cu_2S + Te \quad (2)$$

$$Ag_2Se + S \longrightarrow Ag_2S + Se \quad (3)$$

$$Ag_2Te + S \longrightarrow Ag_2S + Te \quad (4)$$

The free energy value of compounds involved in the above reactions were calculated at the reaction temperature of 475°C (748°K) and are given in Table II.

TABLE II

Free Energy Values as Calculated thermodynamically

Compound	ΔG_{748} k cal/degree/mole
Cu_2S	−25.8
Ag_2S	−14.79
Cu_2Se	−21.13
Ag_2Se	−9.135
Ag_2Te	−5.55
Cu_2Te	−25.05

Data for calculations taken from references 11 and 12.

It is clear from Table II that $-\Delta G$ value of Cu_2S, is higher than that of Cu_2Se and Cu_2Te and $-\Delta G$ value of Ag_2S is higher than that of Ag_2Se and Ag_2Te. This shows that copper sulfide and silver sulfide are more stable than the corresponding selenides and tellurides. Hence, the above reactions must proceed towards the right-hand side.

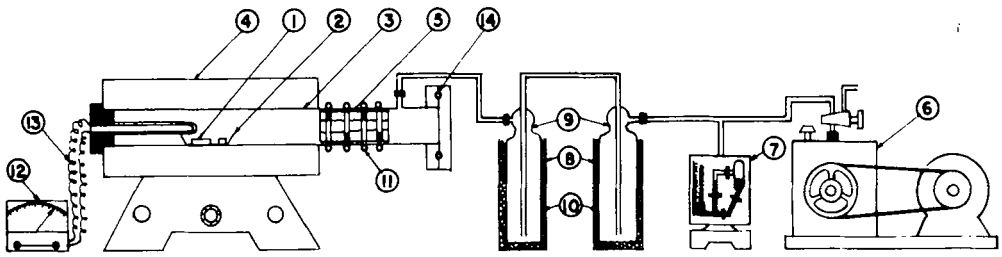
The schematic diagram of the experimental set up for vacuum sublimation of selenium is given in Figure I.

Powdered and dried slimes were mixed throughly with excess of pure sulfur powder and the briquettes (1) of one inch length and half an inch diameter were made, by hydraulic press, in a steel die. The briquettes were weighed and placed in a stainless steel boat (2) which was then introduced into a stainless steel retort (3), with one end closed and a flange fixed on the open end. The retort was placed horizontally in a

TABLE I

Chemical Analysis of Electrolytic Copper Slimes from Hindustan Copper Limited, Ghatsila (India)

	Se, %	Te, %	Cu, %	Ni, %	Ag, %	Au, %	As, %	Fe, %	SiO_2, %	S, %
Batch I	8.3	6.2	14.6	33.7	1.58	0.05	–	0.6	6.2	4.25
Batch II	8.15	6.2	10.9	38.1	1.60	0.1	5.44	0.5	6.6	3.87



1. SLIME SULPHUR BRIQUETTES
2. STAINLESS STEEL BOAT
3. STAINLESS STEEL RETORT
4. TUBE FURNACE
5. CONDENSER ASSEMBLY
6. VACUUM PUMP
7. VACUSTAT
8. THERMOS FLASKS
9. CONDENSING BOTTLES
10. ICE
11. COPPER TUBE FOR COOLING
12. TEMPERATURE INDICATOR
13. THERMO-COUPLE
14. NEOPRENE -O-RING

FIGURE I

Schematic diagram of set up of vacuum sublimation

tube furnace (4). A portion near the flange, approximately 10 cm, was water cooled by a copper coil soldered to the retort. After introducing the boat and pushing it to the sealed end of the retort, a condensor assembly (5) was introduced into the cooling zone. The condensor assembly consists of a number of perforated stainless steel circular discs, mounted parallel over a threaded stainless steel tube. The discs were adjusted in such a manner that the perforations, which were only on half of the disc, were not all in a straight line; this was to facilitate the deposition of sublimate on one disc and simultaneously allowing it to pass on to the next, through the holes of the first disc. The discs mounted on the threaded tube were enclosed in a pipe, cut in half along its axis. The flanged end of the retort was then closed. The outlet tube near the flange was connected to the vacuum pump (6) through a vacustat (7). Cooling devices (8–10) were placed in between the vacuum pump and the retort, to condense any residual sublimed material, which might not have condensed in the cooling zone.

A vacuum of 0.1 mm of mercury was created in the system by a rotary vacuum pump. On completion of the experiment the vacuum pump was stopped, the furnace turned off and the system was sealed. After the retort had cooled down the flange was opened and the condensing pack was removed. Selenium and sulfur were found condensed over the first few discs. The boat was removed and the residue was weighed, crushed and analyzed, to determine the extent of sulfurization of selenides and tellurides. The percentage recovery was based on the percentage of selenium and tellurium remaining in the residue.

Results and Discussions

The parameters studied in the sulfurization of slime in vacuum were as follows:

a) Effect of temperature.

b) Effect of duration of sulfurization.

c) Effect of amount of sulfur added.

d) Effect of briquetting pressure.

Effect of Temperature

To study the effect of temperature on the sulfurization of slimes, for the recovery of selenium and tellurium, the experiments were performed at temperatures within the range of 200° and 600°C, the duration being kept at 60 min. and 90 min. The briquetting pressure and amount of sulfur added were kept constant at 6 kg/sq mm and 40 times that theoretically required, respectively. The recovery of selenium and tellurium as a function of temperature is indicated in Figure II.

The recovery of selenium increases instantaneously at temperatures beyond 175°C up to about 250°C, after which the recovery is more or less uniform. The curve for 60 min and 120 min are more or less parallel.

The recovery at 120 min is a little more throughout the temperature range used. In the case of tellurium also the curves at 60 min and 120 min duration are more or less parallel. A peak is formed at 60 min and 120 min duration at 475°C. The downward trend beyond 475°C may be attributed to the loss of reactant sulfur by sublimation before it could react with tellurides. As far as selenium is concerned the maximum recovery can be obtained at 250°C at 60 min sulfurization, but tellurium recovery at this temperature is practically nil. At 475°C, though the recovery of selenium is reduced, that of tellurium is increased to about 80% for 120 min sulfurization.

Effects of Duration of Reaction

To study the effect of duration of reaction on the recovery of selenium and tellurium, the experiments were performed for various durations, 30, 60, 90, 120, 180, 210, and 240 min at 450°C and 475°C, while keeping the briquetting pressure and amount of sulfur added constant. The results are plotted in Figure III.

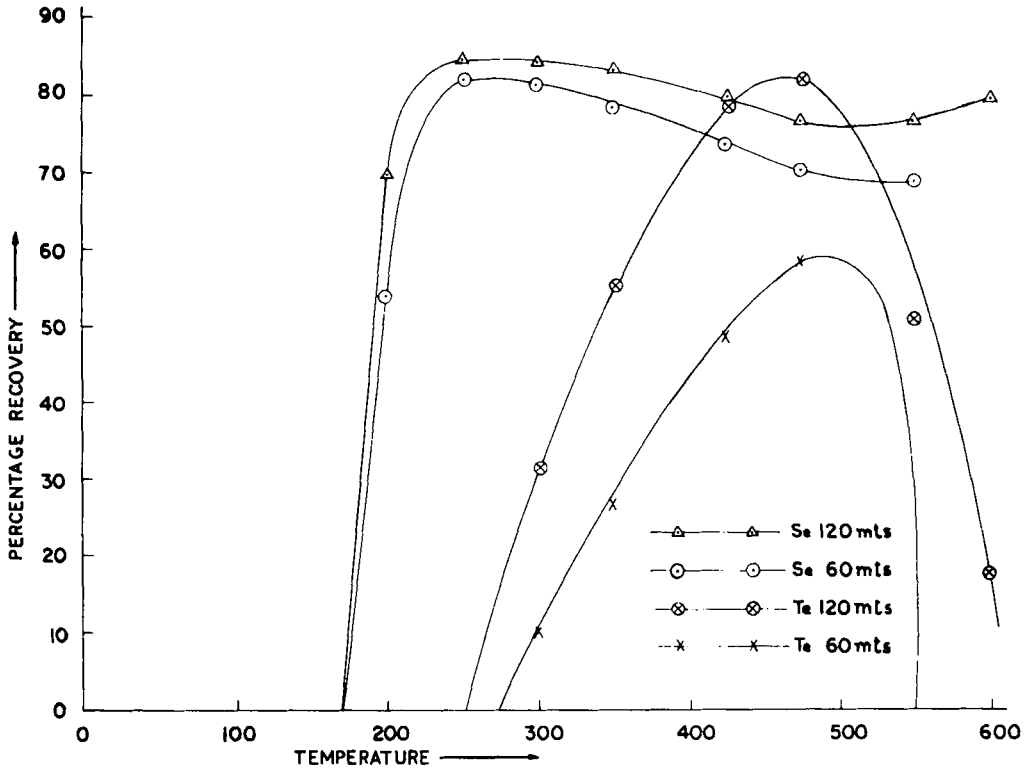


FIGURE II

Effect of temperature on recovery

The recovery of selenium sharply increases in the first 30 min at 450°C as well as at 475°C. At both temperatures, the rise in the next 60 min is less steep. The maximum recovery is observed at 120 min sulfurization; the increase from 60 to 120 min is less than 20%. The curves become horizontal on further sulfurization.

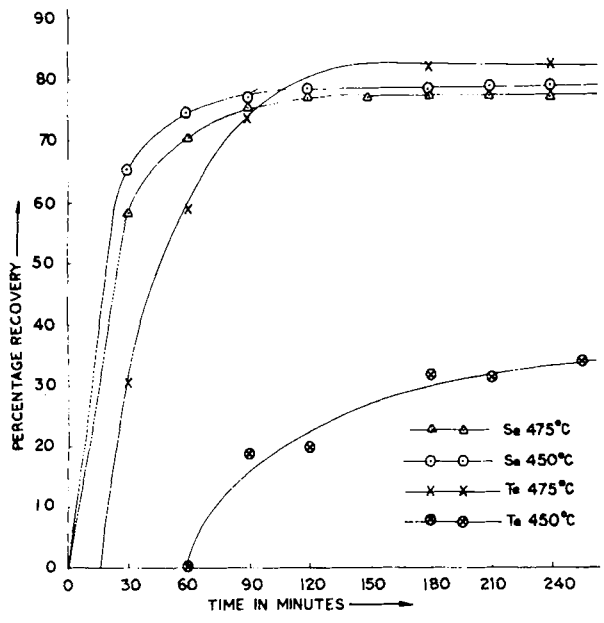


FIGURE III

Effect of duration of sulphurisation on recovery

The rise in tellurium recovery is not steep at 450°C, but at 475°C the curve rises steeply up to 120 min, after which it is horizontal. The curve at 450°C is almost parallel to that for 475°C, but the maximum recovery in the first case is about 40%. Less recovery at 450°C shows that sulfurization of tellurides is either not complete or tellurium produced is not completely evaporated below 475°C when evacuated.

Two hours sulfurization at 475°C gives maximum recoveries of about 75% selenium and 82% tellurium. These conditions can be taken as optimum.

Effect of Sulfur Addition

To study the effect of sulfur addition on the recovery of selenium and tellurium, experiments were performed with addition of various amounts of powdered sulfur. The principal reactions expected to take place are represented in eqs (1) and (4). The theoretical quantity of sulfur powder of −200 mesh size required for sulfurization was calculated from the above equations. As the briquettes were very small, the amount of selenium and tellurium present in each would be so small that the stochiometric quantity of sulfur added would be insufficient for its homogeneous distribution around the slime particles. Hence, excess of sulfur was added and experiments were performed at 0, 5, 10, 20, 30 and 40 times the amount of theoretically required sulfur. Other variables, like temperature, duration and

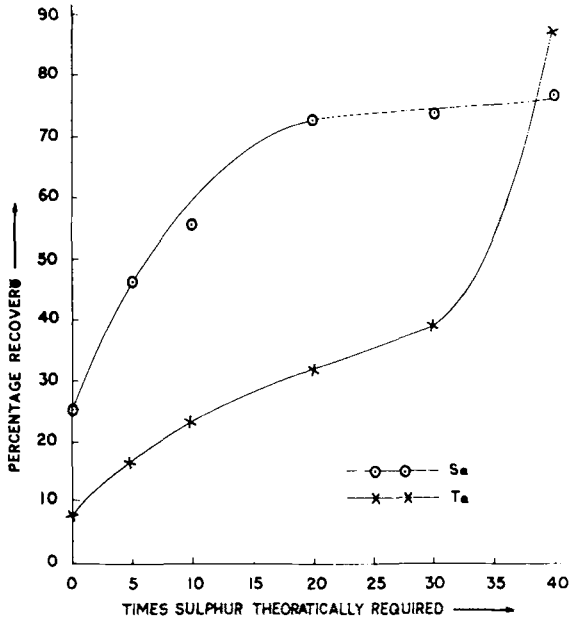


FIGURE IV

Effect of addition of sulphur on recovery

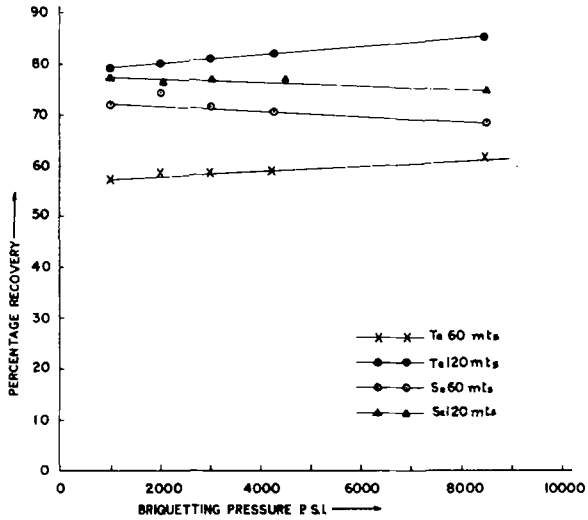


FIGURE V

Effect of briquetting pressure on recovery

briquetting pressure, were kept constant at 475°C, 120 min and 2.85 kg/sq mm respectively. The results are plotted in Figure IV. Without the addition of sulfur, the recovery of selenium and tellurium is very small. Selenium recovery is greater from 5 to 20 times sulfur, after which the increase is negligible, while in the case of tellurium the increase up to 30 times sulfur is small but shoots up beyond this, and at 40 times sulfur it is above 80%. This rise may be attributed to the fact that the sulfur may not be sufficient for complete decompositon of tellurides and might be subliming before the reaction is completely. When the quantity is increased, more sulfur may be available for reaction in the charge. In the present slime, 40 times sulfur was double the quantity of total slime added in the briquette. In other words, the ratio of slime and sulfur was 1 : 2 by weight which is in agreement with the findings of Isakova.[10] From the above figure, it can be concluded that for both selenium and tellurium best recovery was achieved when 40 times the amount of sulfur was added than that required theoretically.

Effect of Briquetting Pressure

Two sets of experiments were performed, at 60 min and 120 min duration, to study the effect of briquetting pressure on the recovery of selenium and tellurium. The briquetting pressures studied were 1.4, 2.8, 4.2, 5.6, and 11.2 kg/sq mm. The results are plotted in Figure V.

The briquetting pressure does not seem to have any effect on the recovery. The graphs for selenium and tellurium are almost horizontal. During heating, sulfur melts quite early and the briquettes crumble to a pasty mass, which flows inside the boat. The briquettes must stay in form till the sulfur melts. When the briquette crumbles before the sulfur melts the fine particles of sulfur and slime may choke the vacuum line. The briquetting pressure, therefore, does not seem to have any bearing on the recovery of selenium and tellurium.

Effect of Particle Size of Sulfur

As sulfur melts down at a much lower temperature than the temperature of the experiment and the whole briquette becomes a pasty mass, varying particle size of sulfur may not have any effect on the recovery of selenium and tellurium. It was, therefore, decided to keep the particle size of sulfur the same as that of the slime to ensure homogeneity of the reactants. Sulfur powder of −200 mesh size was, therefore, used for all the experiments.

X-ray Powder Diffraction Analysis

To prove the assumption that sulfur added to slime replaces selenium and tellurium from selenides and tellurides of copper and silver, X-ray powder diffraction analysis was carried out on two different samples of electrolytic copper slimes and also on the powders obtained after vacuum sublimation of each sample. The samples of slimes and their respective residues after experiments were ground to −100 mesh BSS and X-ray diffraction photographs were taken with a Debye-Scherrer Powder Camera of 5.7 cm diameter using Strauman's method of mounting. Exposure of

7 hr under CyKα and radiation using nickel filter to avoid Kβ rays was given. The rating was kept at 25 kV and 10 mA. From the X-ray diffraction photographs, the following phases were detected in the slime samples before and after treatment. First sample before treatment: copper selenide, silver telluride, copper telluride, nickel oxide (hydrated), lead palledium and platinum; after treatment; copper sulfide, silver telluride, silver-gold selenide and silver selenide. This indicates that most of the copper selenide had decomposed to form copper sulfide, whereas silver selenide and silver telluride does not seem to have been reacted and, thus, have become predominant. In the second sample the following phases were detected before and after treatment. Before treatment: copper selenide, silver selenide, copper telluride, tellurium, nickel oxide (hydrated) and selenium. After treatment the phases like copper sulfide, silver telluride and even free silver and gold were found, suggesting that copper selenide is reacted with sulfur completely while silver selenide and telluride are reacted partly. Silver sulfide is not detected, which may suggest, that free silver is formed but not silver sulfide.

The phases like platinum and nickel oxide were not detected in treated samples. May be, they were superimposed by more prominent phases.

Hence, the assumption that sulfur is decomposing the selenides and is taking the place of selenium is correct. Selenium is freed and is condensed on the perforated plates in the set up.

The product obtained contains selenium, tellurium and sulfur. Sulfur can be separated by dissolving in carbon disulfide and selenium and tellurium can be separated by the usual method.

Conclusion

1. Selenium and tellurium can be removed from electrolytic copper slimes by heating it with elemental sulfur under vacuum. Selenium, tellurium, and sulfur can be recovered by condensing their vapors in cooler zone.

2. Maximum recovery of selenium can be achieved around 250°C (82%) while tellurium recovery is maximum at 475°C.

3. At 250°C and 60 min sulfurization maximum selenium (82%) is recovered while tellurium recovery is nil. At 475°C and 120 min sulfurization maximum recovery of tellurium (82%) is achieved.

4. About 40 times of sulfur than theoretically required to decompose selenides and tellurides, gives maximum recovery of selenium and tellurium. In other words the ratio of slime and sulfur should be 2 : 1 by weight.

5. The briquetting pressure does not seem to be having any effect on the recovery.

6. Particle size of sulfur added has no effect on the recovery as it melts below the temperature of the reaction. The particle size of sulfur should almost be the same as that of slime which is −200 mesh BSS.

7. X-ray powder diffraction study showed that copper selenide is decomposed in preference to silver selenide and silver telluride to form copper sulfide and selenium. Silver selenide and telluride seem to be more stable than the selenide and telluride of copper.

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