

## The Recovery of Tellurium from Copper Anode Slimes by Hydrometallurgical Processes

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### ABSTRACT

The recovery of tellurium from Te-cement obtained during the processing of copper anode slimes was carried out by a series of hydrometallurgical processes, i.e. leaching Te-cement in NaOH solution, precipitation of impurities with the addition of Na<sub>2</sub>S followed by direct electrowinning of tellurium in NaOH solution. The optimum conditions for each process were determined and discussed in terms of various parameters associated with each step to maximize the recovery and purity of tellurium. The final purity of tellurium from electrowinning in alkaline solution was found to be more than 99.9%.

### 1. Introduction

Tellurium has been used<sup>1)</sup> mainly in metallurgical area (70~80%) to improve the free machining quality of low carbon steel, in chemical area (~15%) as catalysts, curing and accelerating agents in rubber formulation, and in electronics area (~10%) as an alloying element with selenium in xerography and fabrication of thermoelectric power generating devices.

Te is a rare element of estimated crystal abundance of 10 ppb, and is recovered almost as byproducts from copper refinery with selenium. For instance, about 9 tons of Te can be recovered based on the production of 150,000 tons/yr of electric copper. However, it is generally considered as a nuisance metal and should be eliminated from anode slimes before recovering the precious metals. Slimes recovered from the tankhouse usually contain 30% Cu which has to be reclaimed. Sulfuric acid pressure leaching with oxygen is employed so that all of the copper may be removed and part of the tellurium is leached. This resulting solution is treated by copper scrap to recover the tellurium as copper telluride. Shibasaki *et al.*,<sup>2)</sup> suggested the use of fixed bed type reactor in cementation step to improve the tellurium recovery by decreasing the reaction time. Also it can be troublesome in lead smelting and detellurized as slag using NaOH to make Na<sub>2</sub>Te<sup>3)</sup>.

Recovery of tellurium from copper anode slimes has been practiced using various processes, and reviewed by Hoffmann.<sup>4)</sup> Soda ash roasting followed by reduction, alkaline pressure

leaching and wet chlorination process have been tested. However, each process has drawbacks in high oxygen and reagent consumption as well as difficulties in the separation of selenium. Hoffman recommended the chlorination process by hydrochloric acid with chlorine gas which had many advantages in rapid reaction, easy control and fast turnover of the precious metals in the slimes. Still, the problem accompanied with using the corrosive media should be solved in the process. Among those, alkaline leaching of Te-cement gives high selectivity over copper and tellurium metal can be recovered directly by electrowinning of leach liquor after the removal of minor impurities. If caustic soda is recycled, the minimization of NaOH consumption can be achieved which can be more economical.

Tellurium can be also recovered from thin-film photovoltaic device scrap using dilute sulfuric acid leaching in the presence of hydrogen peroxide.<sup>5)</sup> And the recycling of the tellurium from the other sources may play an important role in the near future.

In this study, a series of hydrometallurgical processes involving alkaline leaching and impurities removal with Na<sub>2</sub>S addition followed by electrowinning have been applied to produce high quality tellurium from the cemented tellurium. Leaching efficiency has been investigated in terms of pulp density, concentration of NaOH, temperature and also impurities behavior during the precipitation with an addition of Na<sub>2</sub>S has been examined. Electrowinning of tellurium from purified leach liquor was carried out to obtain high purity and recovery in terms of applied voltage

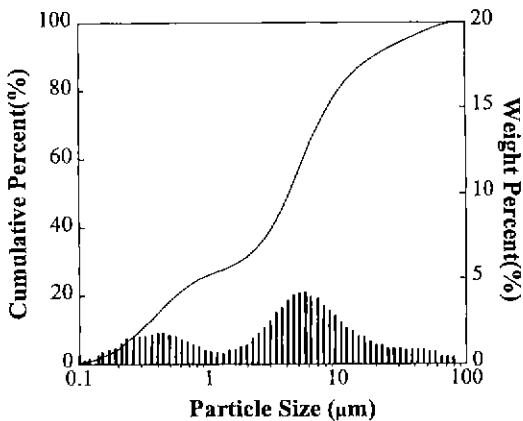


Fig. 1. Particle size distribution of Te-cement.

## 2. Experimental

Te-cement was ground in a ball mill and dried in oven at 60°C for 48 hours. The particle size distribution of the sample is shown in Fig. 1. and average particle size is approximately 2.5 μm (Malvern Instruments).

Leaching tests of Te-cement in NaOH solution were performed in 2 l reactor placed in a large vessel to control the reaction temperature, and preliminary studies showed that the leaching temperature had to be kept above 80°C for efficient extraction of tellurium. Also air was supplied through fritted glass gas dispersing device using air compressor at a rate of 0.5 l/min throughout the leaching.

Concentrations of various metal ions were measured with atomic absorption spectroscopy (Perkin-Elmer M3100). After solid-liquid separation, solid samples were analyzed with X-ray diffractometer (McScience Co.) Leach liquor was purified with an addition of Na<sub>2</sub>S for two hours at 80°C to remove the impurities such as Pb, Fe and Cu followed by the electrowinning of Te for 6 hours in electrolyzer at 25°C using power supplier. Cu plate was used as a cathode and graphite electrode was used as an anode. Also potentiodynamic polarizations were carried out using three-electrode system, i.e. Cu working electrode (rotating disk electrode), graphite counter electrode and Hg/HgO reference electrode, with a potentiostat (EG & G 273 A) at room temperature.

## 3. Results and Discussion

The chemical composition of Te-cement is shown in Table 1. Oxygen was analyzed with Leco TC436. X-ray dif-

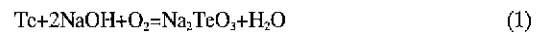
Table 1. Chemical analysis of Te-cement

Element	Content (%)	Element	Content (%)
Te	21.7	Zn	0.29
Se	0.59	Cu	32.9
As	1.30	Sb	1.28
Pb	0.55	Mg	0.10
Fe	2.15	Bt	0.52
S	6.51	O	26.8

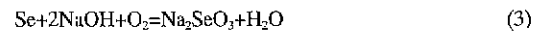
fraction data showed that the sample was composed of mainly oxidized copper tellurides and some other compounds.

### 3.1. Leaching of Te-cement

Leaching chemistry of major components in Te-cement with O<sub>2</sub> (air) in NaOH solution can be expressed as



Some of the minor components can be dissolved or precipitated as follows



and other elements such as Pb, Fe, As and Sb were also precipitated as oxides under leaching condition. Part of the precipitated CuO and PbO<sub>2</sub> can be redissolved in leach liquor as



The soluble species of Cu depends on Cu concentration.

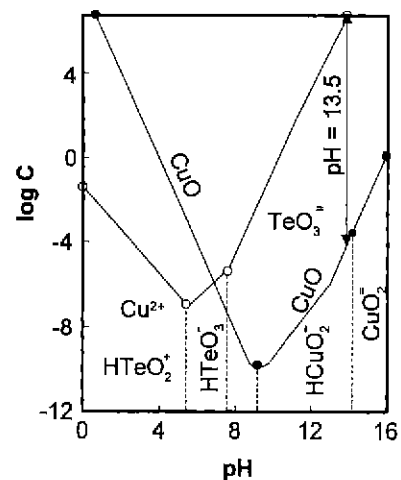


Fig. 2. The influence of pH on the Te and Cu species.

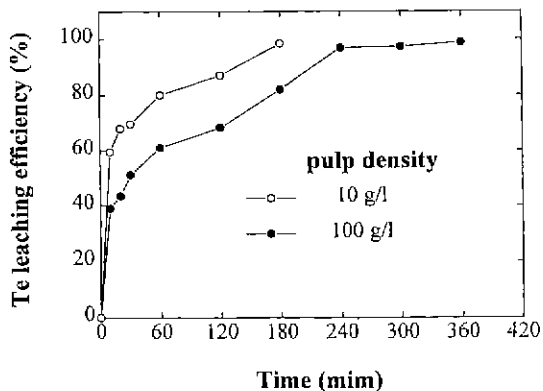


Fig. 3. Leaching efficiency of Te with the variation of pulp density (100 g/l NaOH, 80°C).

The influence of pH on the solubilities of Te and Cu species were calculated based on the data given by Pourbaix,<sup>6)</sup> and illustrated in Fig. 2. As shown in the Fig, the large difference in concentration of dissolved Te and Cu species is favorable to separate Cu from Te during leaching in high alkaline solution, e.g.  $\log(C_{Te}/C_{Cu})=11$  at a pH 13.5.

Fig. 3 illustrates the leaching efficiency in 100 g/l of NaOH solution (pH 13.5) with a pulp density of 10 g/l and 100 g/l at 80°C. Leaching efficiency of Te approached 98% after 3 hours for the case of pulp density 10 g/l and 6 hours for 100 g/l of pulp density, respectively.

The variations of Cu concentration with time in solution is shown in Fig. 4. Cu concentration was slightly increasing with time due to the reaction (4) and was approximately in the range of 250-400 ppm during leaching.

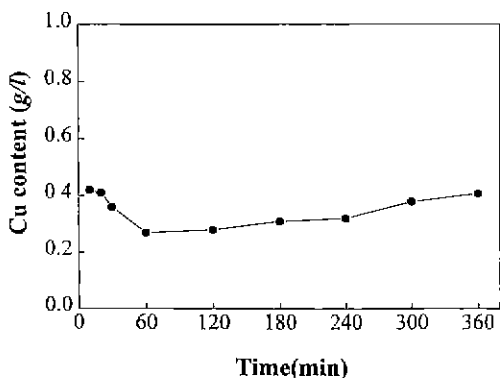


Fig. 4. Variation of Cu content in the leachate with time (100 g/l pulp density, 100 g/l NaOH, 80°C)

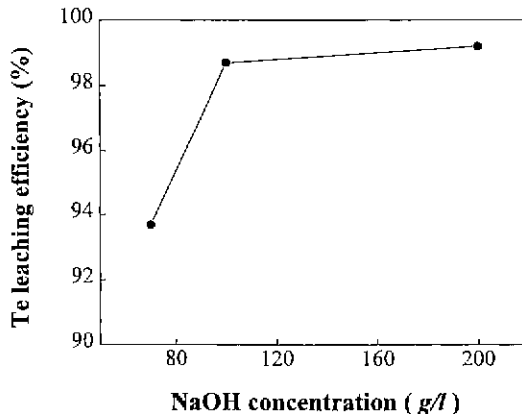


Fig. 5. Leaching efficiency of Te with the variation of NaOH concentration (100 g/l pulp density, 80°C)

As far as the effect of NaOH concentration on the leaching efficiency was concerned, it was increasing with NaOH concentration and reached a steady value approximately above 100 g/l of NaOH as shown in Fig. 5. For the case of 200 g/l of NaOH, the efficiency was over 99% but the filtration became difficult due to the increase of viscosity of solution. After solid-liquid separation, solid sample was analyzed with X-ray diffractometer and found to be mainly CuO and PbO<sub>2</sub>.

### 3.2. Removal of impurities with Na<sub>2</sub>S

Na<sub>2</sub>S was added into the leach liquor to remove the dissolved impurities such as Cu, Fe, Pb, etc in the form of sulfides. For 4 g addition of Na<sub>2</sub>S, the concentration of various metal ions is presented in Table 2 before and after reaction for 2 hours at 80°C. The concentration of Cu was approximately 400 ppm after leaching and was reduced less than 1 ppm after 4 g of Na<sub>2</sub>S addition.

Some of Se was deposited during electrowinning. The con-

Table 2. Various metal ion concentration before and after the addition of Na<sub>2</sub>S together with 6 hours of electrowinning

Element	After leaching (ppm)	After 4 g of Na <sub>2</sub> S addition (ppm)	After Electrowinning	
			3 V(ppm)	4 V(ppm)
Pb	153.4	0.35	0.60	0.60
Cu	260	~0.1	~0.1	~0.1
Se	427	420	407	403
Bi	3.35	0.85	1.60	0.88
Zn	16.2	13.0	16.2	13.8
Fe	4.25	0.96	0.95	0.92

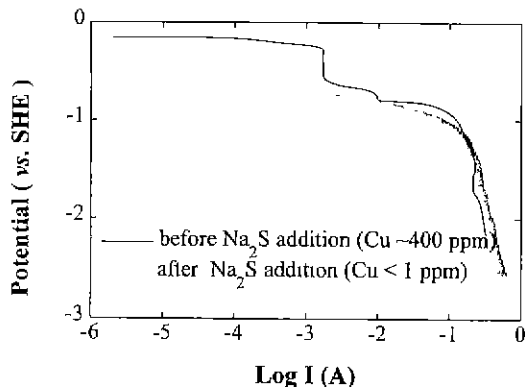
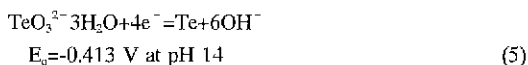


Fig. 6. Polarization curves of leach liquor on Cu electrode (10 mV/s scan rate, 300 rpm rotation speed).

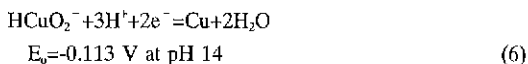
centration of Zn was approximately 13–16 ppm before the addition of  $\text{Na}_2\text{S}$ , and remains constant even after the addition of  $\text{Na}_2\text{S}$ . But it did not affect the purity of Te significantly as shown in Table 2 since the potential to be electrodeposited is much lower than that of Te. Other elements such as Fe and Bi were eliminated with the addition of  $\text{Na}_2\text{S}$  and their concentrations remained fairly constant during electrowinning step.

### 3.3. Electrowinning of tellurium

Fig. 6 shows the comparison of cathodic polarization curves for two different solutions. Reduction reaction of Te during electrowinning can be expressed as



where  $E_0$  is the equilibrium potential values.



As shown in the Fig, biciprite ion was deposited first which would affect the purity of Te and showed limiting current of 1 mA, and tellurium was reduced near -0.6 V (vs. SHE) with or without  $\text{Na}_2\text{S}$  treatment. After removal of Cu with  $\text{Na}_2\text{S}$  addition, only reduction of Te was observed.

Electrowinning of Te was carried out using parallel electrode type cell at constant applied voltage and stirring was provided with magnetic stirrer. The anodic reaction during electrowinning would be

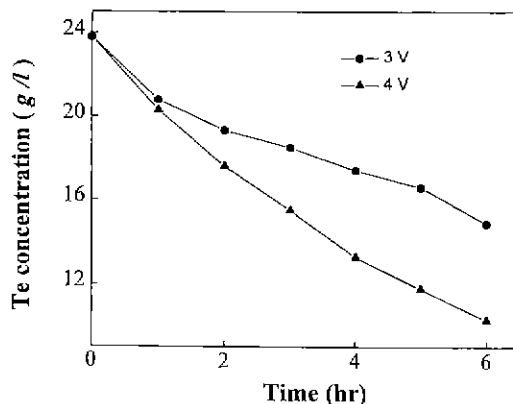


Fig. 7. Variation of Te concentration during electrowinning at different applied voltages

The variations of Te concentration during electrowinning is presented in Fig 7 at different applied voltages. Te metal can be obtained up to 80% within 6 hours under the condition of 4 V and 24 g/l initial Te concentration. The current efficiency was close to 100% based on the reaction chemistry given in reaction (6). The purity of Te electrowon was more than 99.9%. Major impurities was found to be selenium (~0.06%) and arsenic (~60 ppm), and other elements such as Bi, Pb, Fe, Sb, Mg, Zn and Sn were in the range between 5 ppm and 40 ppm. Further purification of Te can be achieved by multiple distillation method to obtain the high quality Te which can be used for single crystal material by Bridgman and Chochralski techniques.<sup>7)</sup>

## 4. Conclusions

The recovery of Te from Te-cement known to be a by-product of copper refinery was carried out by a series of hydrometallurgical processes. The following conclusions were made;

1. Tellurium in Te-cement was completely leached within 6 hours under the condition of 100 g/l NaOH, 80°C and 100 g/l pulp density. Other impurities such as Fe, Pb, As and Zn except Se precipitated in alkaline leaching. The resulting solution contained major impurities of 300 ppm Cu, 153 ppm Pb, 427 ppm Se.
2. Impurities in the leaching solution except Se and As were removed by adding 4 g of  $\text{Na}_2\text{S}$  based on one liter of Te leaching solution. Most of Pb, Fe and Cu sulfides have low solubility and the concentration of these ions were less than 1 ppm level.

3. Te metal can be obtained up to 80% within 6 hours under the condition of 4 V and 24 g/l initial Te concentration. It was interesting to note that Se showing the same chemical similarity was hardly electrowon under 3 to 4 applied voltage. The purity of tellurium electrowon was more than 99.9% while major impurities such as Se and As were found to be in the range of several hundreds and others were between 5 and 40 ppm.

### References

1. E. Hoffmann, "Selenium and Tellurium-Rare but Ubiquitous", JOM, **41**(7), 32 (1989).
2. T. Shibasaki, K. Abe, and H. Takeuchi, "Recovery of Tellurium from Decopperizing Leach Solution of Copper Refinery Slime by a Fixed Bed Reactor". Hydrometallurgy, **29**, 399 (1992).
3. C. DiMartini and R.F Lambert, Lead-Zinc-Tin '80, Ed. J. M Cigan, T. S. Machay, and T. J. O'Keefe, TMS-AIME, Warrendale, Pa (1979).
4. J.E. Hoffmann, "Recovering Selenium and Tellurium from Copper Refinery Slimes", JOM, **41**(7), 33 (1989)
5. W. Trolley and R. Swarup, "Recovering Cadmium and Tellurium from Thin-film Photovoltaic Device Scrap", EPD Congress 1995, Ed G.W. Warren, TMS-AIME, Warrendale, Pa (1995).
6. M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", 2nd Ed. NACE, Houston Tx. 384-392, 56057 (1974).
7. B. Wedlock, "Purification of Tellurium by Distillation", J. Electrochem. Soc., **109**, 318 (1962).

## 광 고

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