

# Development of an Oxidizing-Distillation Technology for the Extraction of Tellurium from a Tellurium-Containing Middling

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**Abstract** - In this paper, the results of studying aimed at tellurium extraction from its compound with copper in the form of oxides by the pyrometallurgical method are presented. Technical copper telluride of Kazakhmys Corporation LLP containing crystalline phases, %:  $\text{Cu}_7\text{Te}_4$  – 36.5;  $\text{Cu}_5\text{Te}_3$  – 28.5;  $\text{Cu}_2\text{Te}$  – 12.9;  $\text{Cu}_{2.5}\text{SO}_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$  – 16.2 and  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$  – 6.0 was used as an object of research. As a result of the physical and chemical research and technological experiments, the fundamental possibility of processing technical copper telluride by oxidative distillation roasting with the extraction of tellurium into a separate product has been shown. Air oxygen was used as an oxidant. It has been established that a pressure decrease at the same temperature entails an increase in the degree of tellurium extraction. However, from a technological point of view, the value of the degree of tellurium extraction (93.0–98.0 %) at all pressures (within 1 hour) is achieved at a temperature of 1100 °C. Increasing the exposure to 3 hours has a minor beneficial effect. The derived condensate is a free-flowing mixture of crystalline phases of tellurium dioxide and tellurium oxysulfate. This condensate is a middling product for further production of elemental tellurium.

**Keywords:** tellurium, copper, distillation, roasting, oxides

## 1. Introduction

By now, the main raw material source intended to obtain tellurium is slime from the copper electrolysis production which is a multi-component material containing, wt. %: copper – from 1 to 50, silver – from 0 to 29, gold – from 0 to 2.18, selenium – from 2 to 15, tellurium – from 0 to 22. As a rule, copper in slime is in elemental form, selenium and tellurium are in the form of selenides and tellurides of copper and noble metals. There is quite a wide range of methods intended to process copper electrolyte sludge determined by the variety of their chemical and phase composition, with the use of both hydro- and pyrometallurgical and combined methods [1-3].

One of the valuable copper refining products is its telluride containing phases of both stoichiometric ( $\text{Cu}_2\text{Te}$ ) and non-stoichiometric compositions ( $\text{Cu}_{2-x}\text{Te}$ ) [4-7]. Analysis of the developed industrial copper telluride processing schemes showed that most of them refer to hydrometallurgical methods characterized by imperfection and multiple stages.

Pyrometallurgical methods well combined with the superpure element production schemes are the most preferable but it has not found both applications in practice and development of research in this area due to the high temperatures for the process to be performed. An effective way to reduce the process temperature by 100-200 °C is to conduct the process at reduced pressure. Besides the use of vacuum also contributes to the improvement of the staff's working conditions because the process is carried out in a sealed and compact apparatus.

However, receipt of metallic tellurium by  $\text{Cu}_2\text{Te}$  decomposition in real conditions with the use of the vacuum-thermal method is not possible because the dissociation pressure of liquid copper telluride is very low – 0.7 kPa at 1780 °C.

The study was performed in this regard to extract tellurium by pyrometallurgical method at reduced pressure in the oxide form that can be processed to obtain metallic tellurium without any technological and technical difficulties.

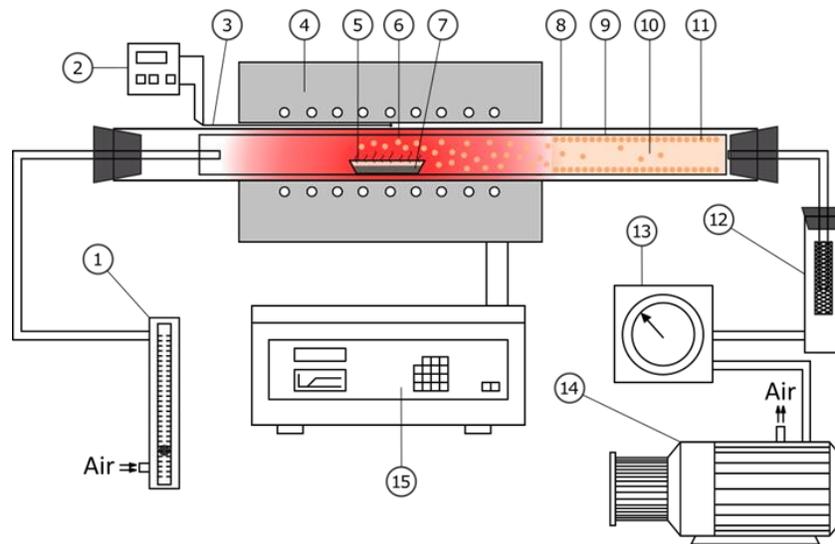
## 2. Materials and methods

Technological studies intended to determine the possibility to extract tellurium from industrial copper telluride by the oxidation-distillation method under reduced pressure were performed with a sample of precious metal production middling received from Kazakhmys Corporation LLC (Republic of Kazakhstan). The middling was a loose dark grey material of different grain sizes with green inclusions. Air oxygen was used as an oxidizer.

When the phase structure of the tested material was studied, it was determined that the material was mainly in the amorphous state. The crystalline phases included copper tellurides, wt. %:  $\text{Cu}_7\text{Te}_4$  – 36.5;  $\text{Cu}_5\text{Te}_3$  – 28.5;  $\text{Cu}_2\text{Te}$  – 12.9; and copper hydrosulfates, %: strandbergite ( $\text{Cu}_{2.5}\text{SO}_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ ) – 16.2 and antlerite ( $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$ ) – 6.0 %.

The presence of Cu – 47.19; Te – 31.22; Se – 0.05; O – 18.88; S – 2.09, and others – 0.57 (in wt. %) were found under X-ray fluorescence analysis in a dry copper telluride sample.

Technological experiments were performed at 500-1100 °C and a reactor pressure of 0.67-80 kPa on a horizontal laboratory unit (Fig. 1). The reactor was a hollow quartz tube with an alundum split condenser placed in it. The airflow rate was chosen to be constant and maximum at  $2.2 \cdot 10^{-2} \text{ m}^3/\text{m}^2 \times \text{s}$  based on the capacity of the evacuation vacuum system ensuring a pressure in the reactor of 5 mm Hg. The telluride sample oxidation process in all cases had a duration of 1 h. An increase in the exposure up to 3 h slightly raised the tellurium extraction degree.



1 – rotameter; 2 – temperature controller in the reaction zone; 3 – control thermocouple; 4 – tubular electric furnace; 5 – tank; 6 – isothermal zone; 7 – sample; 8 – reactor; 9 – alundum split condenser; 10 – condensation zone; 11 – condensate; 12 – filter; 13 – aneroid barometer; 14 – vacuum pump; 15 – furnace controller

Fig. 1: Horizontal laboratory unit

### 3. Discussion

It was found that lowering the pressure at the same temperature results in an increase in the degree of tellurium extraction into the condensate expectedly due to the dissociation pressure of the formed copper tellurate. However, a tellurium extraction degree acceptable from the technological point of view, i.e. 93.0-98.0 % at all pressures, was achieved (within 1 h) at 1100 °C.

X-ray phase analysis of cinders obtained at 1000 °C allowed us to trace the change in the number of phases and their ratio depending on the technological pressure (Fig. 2). A decrease in copper oxides content within the pressure range of 0.67-40 kPa and an increase in copper tellurite phase ( $\text{Cu}_3\text{TeO}_6$ ) content were noted under the quantitative analysis results for phase content. The marked decrease in the amount of cuprite was found due to a lack of oxidant with a subsequent increase in the rarefaction, and a sharp increase in the amount of monovalent copper oxide. The latter was  $\text{Cu}_2\text{O}$  summation contribution from the decomposition of  $\text{Cu}_3\text{TeO}_6$  because the increase in the amount of the latter at pressures of 20-40 kPa slowed down, and it dropped sharply below 13.3 kPa due to evaporation of the resulting tellurium oxides. The ratio of  $\text{CuO}/\text{Cu}_2\text{O}$  in the cinder dropped sharply at pressures below 13.3 kPa,

indicating the predominant sum of  $\text{Cu}_3\text{TeO}_6$  formation and decomposition reactions. Diffractometric studies of the cinder obtained at  $1100\text{ }^\circ\text{C}$  determined that it was represented practically by a monophas of copper (I) oxide with a small content of cuprite.

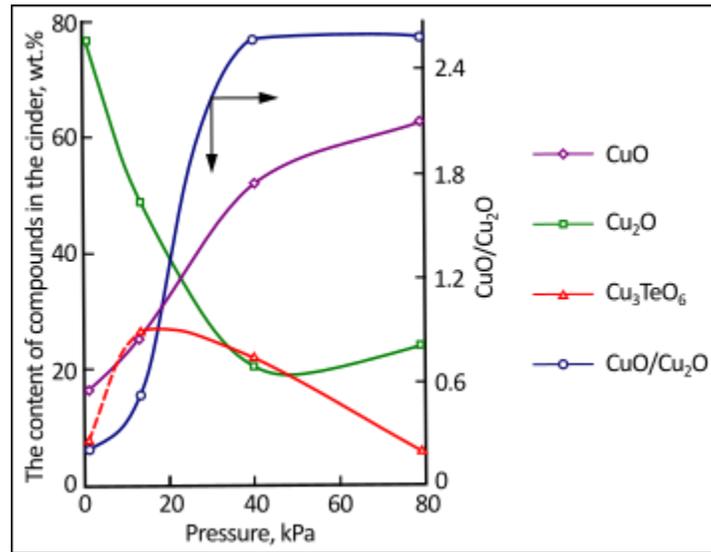


Fig. 2: Dependence of the amount of compounds in the cinder after oxidation at  $1000\text{ }^\circ\text{C}$

A series of experiments at  $500\text{-}1000\text{ }^\circ\text{C}$  (firing duration – 5-90 min, pressure –  $0.67\text{ kPa}$ , oxidizer feed rate –  $2.2 \cdot 10^{-2}\text{ m}^3/\text{m}^2 \times \text{s}$ ) was performed to study the phase transformations accompanying the oxidation process of tellurium-containing middling at different temperatures.

Dehydration of copper hydroxosulfate forms and formation of copper oxides ( $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ) and tellurium ( $\text{Te}_2\text{O}_5$ ,  $\text{Te}_4\text{O}_9$ ) were observed at  $500\text{ }^\circ\text{C}$  during the first 10 min. Tellurite phases of copper were not found, perhaps due to the disordered structure of the material, as evidenced by the presence of an amorphous halo on the diffractograms of the samples. The dehydration process of copper hydroxosulfates continued with a further increase in the exposure time. The formation of only copper orthotellurate ( $\text{Cu}_3\text{TeO}_6$ ) was also observed within the time interval of 15-90 minutes, which may be a secondary oxidation product of copper tellurites as well as an interactive product of the initial copper and tellurium oxides.

The complete decomposition of copper hydroxosulfates occurred within the first 15 minutes at  $700\text{ }^\circ\text{C}$ . The phases of orthotellurate  $\text{Cu}_3\text{TeO}_6$  (stable up to  $810\text{-}840\text{ }^\circ\text{C}$ ), metatellurite  $\text{CuTeO}_4$ , tellurite  $\text{CuTeO}_3$ , and tellurite  $\text{Te}_3\text{Cu}_2\text{O}_7$ , as well as crystals of telluric and telluric acids, were found in the cinders. At the same time, the orthotellurate formation was quite intensive: its content reached 40 wt. % at 5-minute processing, and 93-95 wt. % at 60-90-minute processing.

The X-ray phase analysis results of cinders obtained at 900 and  $1000\text{ }^\circ\text{C}$  showed that the complete decomposition of copper hydroxosulfates and oxidation of copper tellurides of variable composition occurred within the first 10 minutes. Then the process was accompanied by the decomposition of copper orthotellurate and tenorite to cuprite. The cinders obtained at  $1000\text{ }^\circ\text{C}$  within the interval of 10-90 minutes were mainly represented by phases of copper oxides.

An increase in the oxidation-distillation process temperature up to  $900\text{-}1000\text{ }^\circ\text{C}$  had a positive effect on the tellurium extraction rate: the extraction rate reached  $\sim 70\%$  at  $900\text{ }^\circ\text{C}$ , and  $\sim 90\%$  at  $1000\text{ }^\circ\text{C}$ . A sharp rise in the tellurium extraction rate curve was observed within the first 15 minutes. An increase in the process time over 60 minutes had little effect on the tellurium extraction degree.

Tellurium extracted in the form of its oxides precipitated on the condenser and was a crystalline powder of white color, well separating from the condenser surface (Fig. 3). The presence of tellurium dioxide  $\text{TeO}_2$  phases in an amount of

67.7 % and tellurium oxysulfate  $\text{Te}_2\text{O}_3(\text{SO}_4)$  phases – 32.3 % was found in the condensate by diffractometric analysis. The presence of tellurium oxysulfate can be explained by a violation of the technological process of technical copper telluride washing from sulfuric acid solution in the hydrometallurgical production scheme.

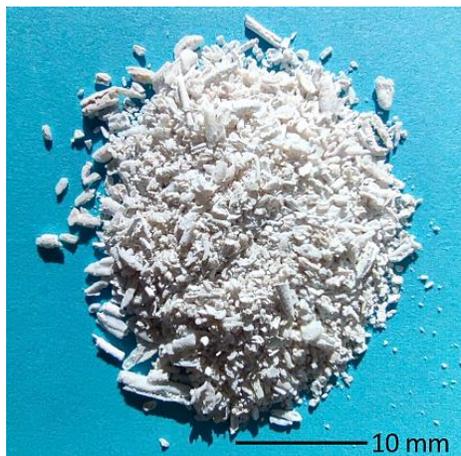


Fig. 3: Condensate from the roasting of industrial copper telluride

#### 4. Conclusion

Thus, the possibility to extract tellurium by the pyrometallurgical method was determined during the research on oxidation-distillation roasting of technical copper telluride supplied by Kazakhmys Corporation LLP (Kazakhstan). In this case, the process temperature was more than 1000 °C, the operation duration should be chosen based on the process design and extensive tests, process rarefaction was acceptable in the range of 0.67-80 kPa, and the oxidant flow where air oxygen was used should be maximum based on the pumping vacuum system capacity but not less than  $2.2 \cdot 10^{-2} \text{ m}^3/\text{m}^2 \cdot \text{s}$  per reaction space cross-section.

#### Acknowledgements

This work was supported by Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan (Grant AP08052016)

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