

PROCESSING OF RARE METALS CONTAINING WASTE OF COPPER PRODUCTION

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Preliminary Note – Prethodno priopćenje

The article presents the research results processing rare metal-containing waste to produce osmium, rhenium concentrate using technical sulfur. Installed, the optimum leaching conditions sulfided waste. Presented results of microstructural analysis of electron-rhenium-osmium concentrate.

Key words: copper production, waste, leaching, rhenium/osmium, sulfur.

INTRODUCTION

The development of rare metals industry possible involvement in the production of technogenic deposits and mineral formations with the organization of individual production of rare metals. Since the volume of accumulated and current technological waste can provide production of rare metals.

Equally important is this problem in theoretical terms, as the work on the study of the behavior of rhenium and osmium in a sulfidation rare metal containing raw gray are not available. Most important is the translation of all the components of the feedstock into a single sulfide form, as sulfide compounds of heavy, non-ferrous and rare metals differ in their physicochemical properties further they are easily separated into individual concentrates.

We offer sulfided rare metal containing technogenic wastes with sulfur, then conduct a two-stage leaching.

EXPERIMENTAL AND DISCUSSION

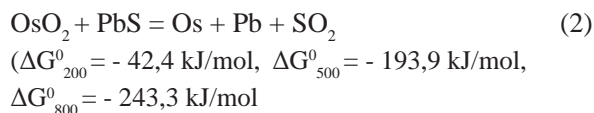
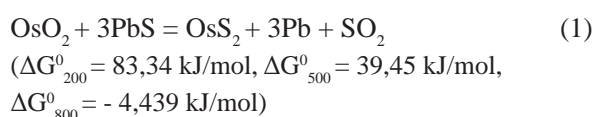
The main component of rare metal containing technogenic raw materials is lead to 60 % of osmium content 0,0020 - 0,0050 % rhenium 0,0600 - 0,12 %. Sludge basis is the lead sulfate (PbSO_4), and together with a sulfate the cake also contains lead carbonate PbCO_3 , prevails in dust is lead oxide [1].

In the systems $\text{PbO} - \text{S}$, $\text{PbCO}_3 - \text{S}$, $\text{PbSO}_4 - \text{S}$ sulphidation occurs almost complete as lead sulfide formation Gibbs energy (ΔG_T^0) has negative values at low tem-

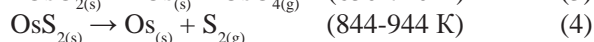
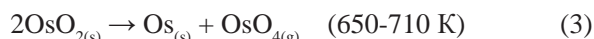
peratures, the process is exothermic, the temperature rise seen with reduction equilibrium constant ($\ln K_p$) [2]. As a result of thermodynamic calculations and thermal studies of model systems $\text{PbO} - \text{S}$, $\text{PbCO}_3 - \text{S}$, $\text{PbSO}_4 - \text{S}$ concluded feasibility of elemental sulfur for the sulphidation of lead slime (cakes) and dusts to recover osmium and rhenium. With abundance of sulfur in all mixtures of solid product is a single compound - lead sulfide.

Listed in the table sulfidation reaction and recovery osmium compounds in the presence of elemental sulfur is characterized by a negative Gibbs energy, i.e., possible occurrence of all these reactions.

The values of the ΔG_T^0 reacting compounds of osmium with lead sulfide shows that the formation of sulphides of osmium little characteristic, since the values of these processes ΔG_T^0 positive than the processes of formation of metallic osmium:



Even in the case of formation of sulfide and osmium dioxide they decompose to form the metal osmium [3]:



The largest negative value of the Gibbs energy of reaction have joint sulphidation of lead oxides and sulfur with osmium tetroxide and oxide of lead sulfate.

Features sulphidation higher rhenium oxide in the presence of lead oxide more than the capacity of sulphidation osmium oxide as the Gibbs energy of the reaction at 600 °C is - 2 522,8 kJ / mol:



A.K.Serikbayeva, (e-mail: akm_rgp@mail.ru) Caspian State University of Technologies and Engineering named after Sh. Esenov, Aktau, Kazakhstan.

F.A. Berdikulova, (e-mail: pheruza_b@mail.ru) National Center for Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan, Almaty.

K.K. Mamyrbayeva (e-mail: gulzira70@mail.ru), Sh.K. Akilbekova (e-mail: cadikova74@mail.ru), Kazakh National Research Technical University named K.I. Satpayev, Almaty, Kazakhstan.

For rhenium compounds in this system, it is more likely the formation of disulfide.

Based on thermodynamic analysis of possible reactions can be assumed that during the sulfiding with sulfur slurry sintering metal formed osmium and rhenium disulfide. This study is in good agreement with experimental studies.

The influence of temperature and duration of the process sulphidation on the behavior osmium and rhenium.

Effect of temperature on the behavior of the metals during sulfiding is shown in Figures 1, 2.

Sulfidation at 400 °C results in a decrease in the degree of extraction of osmium in cake and to increase its 800 °C

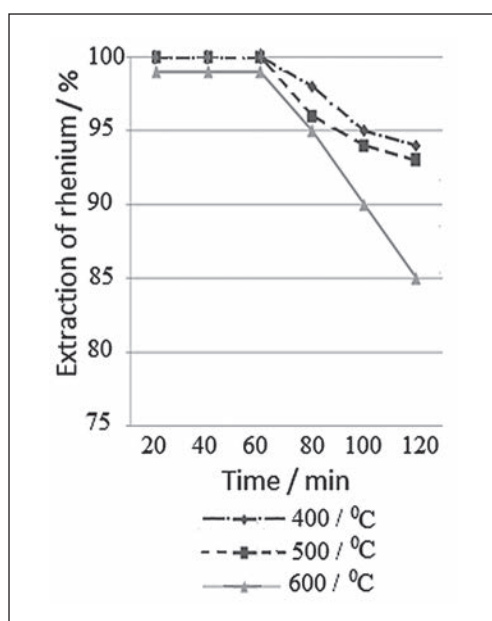


Figure 1 Effect of temperature and duration of the degree of extraction of osmium in cake / %

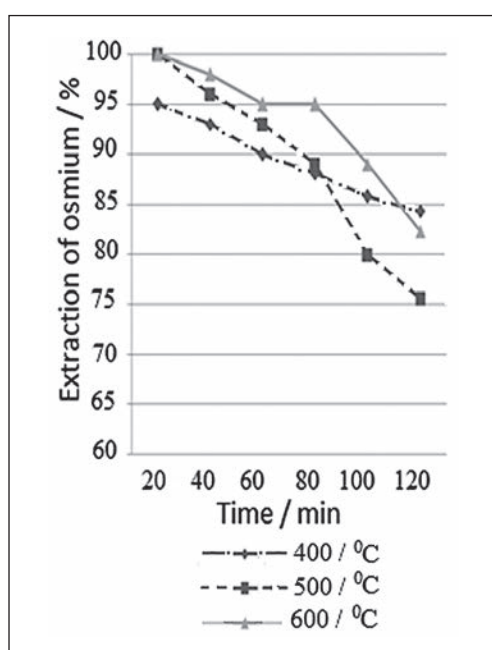


Figure 2 Effect of temperature and duration of the degree of extraction of rhenium in the cake / %

also reduces the degree of extraction of rhenium and osmium sulfidation cake due to volatilization of the higher oxides in the form of a gaseous phase. Is optimal 500 – 600 °C where achieved 95 - 99 % recovery of rare metals in the cake.

This is due to volatilization of some amount of osmium with increasing temperature and duration of sulphidation. Under optimal conditions obtained cake, a yield of 75 % by weight of the slime containing 0,0053 % osmium and rhenium 0,11 %.

Subsequently, the obtained cake was subjected to leaching with sodium chloride solution for presenting the feasibility of sulfidation process in order to obtain concentrates osmium and rhenium.

The obtained cake in the optimal conditions for osmium and rhenium-containing concentrate is subjected to two-stage leaching [4]:

- leaching water to remove water-soluble compounds of the cake;
- leaching of sodium chloride solution to remove the lead compounds - the main component of the slime to obtain the insoluble residue containing osmium and rhenium.

The distribution of elements in the recycling products in the optimum leaching conditions are shown in Table 1.

Table 1 Distribution of the elements in the acid leaching of the cake

Elements	Products of leaching				Chemical composition PbCl ₂ / %
	Leaching solution		Concentrate		
	Contents / %	Degree of extraction / %	Contents / %	Degree of extraction / %	
Pb	0,2210	98,9	0,60	-	60,850
Cu	< 0,0015	97,5	2,40	3,6	< 0,0010
Zn	0,0130	98,8	0,02	-	0,0002
Fe	1,3200	93,2	0,07	-	0,0002
Bi	0,0003	13,3	2,08	32	0,0001
As	0,0021	88,6	0,07	-	0,0007
Se	0,0015	10,2	18,2	90	0,0002
Re	< 0,0001	2,39	2,5	97	< 0,0001
Os	-	-	0,123	100	-

When leaching cake with hydrochloric acid solution of sodium chloride in addition lead pass into the solution 99 % Zn, 93 % Fe, 25 - 95 % Cu.

Thus, in the leaching aqueous solution, and the cake, followed by leaching with hydrochloric acid solution of sodium chloride lead almost completely into solution, osmium and rhenium compound is accumulated in the insoluble residue. Sulphidation process slime elemental sulfur allows you to get the above results. To compare the efficiency of the process for sulfidation osmium and rhenium concentrates shown in Table 2 in comparison with the results of the initial leach slime.

The data in Table shows that the sulfidation slime concentrate obtained containing 0,12 % to 2,5 % osmium

Table 2 **Comparative results of leaching lead slime and slimesulphidated sodium chloride solution**

Initial dates			Results of leaching				
Materials	Contents / %		Concentrate output / %	Contents / %		Extraction / %	
	Os	Re		Os	Re	Os	Re
Lead slime	0,0042	0,084	12	0,03	0,35	85	50
Lead cake	0,0053	0,11	4,3	0,123	2,5	100	98

and rhenium with the degree of extracting rare metals 98 - 100 %.

If the leaching of lead slime without sulphidization osmium recovery rate does not exceed 85 %, and because of the large output of the concentrate, low content of osmium, which reduces the quality of the concentrate. The degree of extraction of rhenium in the concentrate in these cases does not exceed 50 %. Half of rhenium passes into solution from which its extraction does not seem viable.

Osmium and rhenium-containing resulting concentrate is analyzed for electron probe microanalyzer brand Superprob 733 company JEOL, Japan (Figure 3).

Analysis of the elemental composition and photography in secondary electrons was performed using energy dispersive spectrometer INCA ENERGY company OXFORD INSTRUMENTS, England, mounted on the electron probe microanalyzer Superprob 733 at an accelerating voltage of 25 kV and a current probe 25nA.

In the structure of the concentrate revealed four phase whose chemical composition is shown in Table 3.

Table 3 **Distribution of the elements in the particles of concentrate**

Elements	Contents of the elements in the particles of concentrate/ %			
	№1	№ 2	№ 3	№ 4
Pb	74,05	27,79	83,60	39,27
Cu	-	25,57	1,94	18,81
Zn	-	0,74	-	0,04
Fe	-	4,03	-	2,82
Si	-	4,64	-	3,62
Se	-	-	1,11	-
Cl	25,95	2,31	-	1,58
S	-	16,56	13,35	16,6
O	-	13,96	-	12,91
Re	-	2,86	-	3,40

The first phase consists of lead chloride in the form of inclusion to the main phase - lead sulfide. The crystals of lead chloride, disseminated to lead sulfide crystals is clearly seen in Figure 3 (d). The main phase is composed of lead sulfide (a, b, c).

Rhenium is present in the phase of lead sulfide in the sulfide form. That is, the compound completely sulfidated rhenium during sulphidation that in turn provides the completeness of rhenium in the concentrate. Contents osmium could not be determined because of the low content of osmium (below detection limit), but its content in the concentrate is determined by chemical analysis methods. Present largely elemental sulfur, sulfide enveloping phase. Perhaps, the presence of elemental

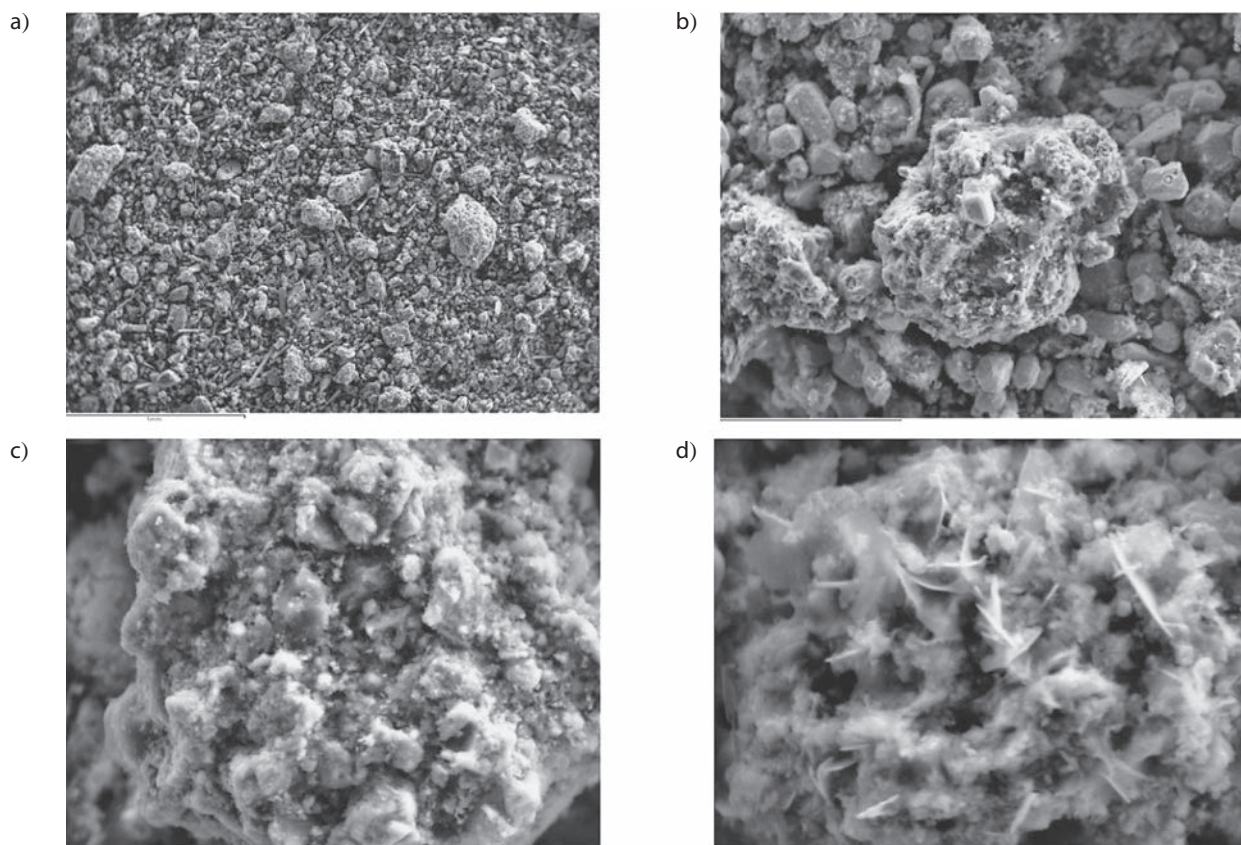


Figure 3 The micrographs of osmium and rhenium concentrate

sulfur as the film allows the concentration of osmium and rhenium in the insoluble residue.

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CONCLUSIONS

- The optimum parameters of a technogenic waste sulphidation with sulfur: 500 – 600 °C, 60 min.
- Reached the complete removal of lead compounds in solution to obtain a concentrate containing 0,123 % - 2,5 % osmium and rhenium extraction with a degree of 95 – 98 % of the initial lead content of the slime;

- The results of experimental studies showing the feasibility of the sulphidation of lead slime for further processing to produce concentrates, osmium and rhenium with a high degree of extraction.

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Note: The responsible for English language is the lecture from University named after Sh. Esenov.