



THEORETICAL AND TECHNOLOGICAL RESEARCH ESO FLEAD SLIME SULPHIDATION PROCESS

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ABSTRACT

The article presents the results of a study of the process of sulfidizing lead slimes. Thermodynamic and technological research are reported for the possibility of sulfidation lead compounds, osmium and rhenium.

Key words: Lead slimes, Process sulphidation, Extraction of osmium and rhenium.

INTRODUCTION

Increased consumption of rare metals requires the development of rare metals resource base and to develop effective technology for processing raw materials to obtain high-quality concentrates of rare metals. The small number of rare metals in the ore raw materials and their processing is unprofitable for the purpose of extraction, which should be involved in the processing of industrial raw materials, where the content of rare metals in several times in their content of the ore. These types of materials include lead slimes of copper production, where the content of osmium and rhenium reaches 50 g/t and 1500 g/t, respectively. Basis of lead sludge is the lead compound. Mass fraction of lead compounds in the slime are given on the Table 1.

Table 1: Mass fractions of lead and its compounds in the sludge in %

Pb_{total}	Pb (PbSO₄)	Pb (PbS)	Pb (PbO)	Pb (PbCO₃)
62.0	52.92	0.23	1.51	7.3

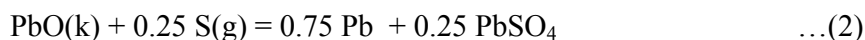
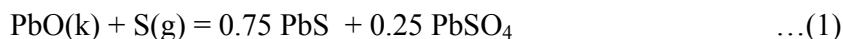
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Osmium and rhenium in the lead slime are oxide and sulfide form compounds. Methods for preparing concentrates, osmium and rhenium provide lead removal and concentration of rare metals in an insoluble residue. Under the sodium chloride leaching process lead compounds are easily passed into a solution from the slime^{1,2}. In such cases, approximately 80-100% of rhenium and 50% of osmium pass into the solution, which reduces their extraction to the concentrate. In this regard, a pre-sulfided carried reductively fired material transfer osmium and rhenium compounds in the form of sulphide. Earlier, we developed the technology receiving of osmium and rhenium concentrates with sulfiding slime in the presence of 20% sodium sulfate and 10% of the coke at 800-850°C³⁻⁵. Technology permits to receive the concentrates containing upto 0.4% osmium against its original content in the slime of 0.0025%. The results of physico-chemical studies showed the possibility of sulfidation and reduction of compounds of osmium and rhenium and the effectiveness of their concentration in the insoluble residue after leaching sulfide cake with sodium chloride in the presence of hydrochloric acid.

Therefore, the process of reductive sulphidation sintering requires further investigation in terms of testing and other types of sulphidation reducing agents. As a cheap and available sulphidation agent can be elemental sulfur- a by product of oil production. Opportunities sulphidation main components of lead slime predicted by thermodynamic calculations (Table 1). Sulphidation rare metals depends on the sulphidation degree of lead compounds in the slimes.

As a result of thermodynamic calculations settled that, in the system PbO-S in the charge of sulphur at a rate of 1.5 mol per 1 mol of lead oxide may practically complete its sulfidization (Reaction 1), as $\Delta G^{\circ T}$ has a negative value at low temperatures and is -291.7 kJ/mol at 400°C and -137.4 kJ/mol at 1100°C and the process is exothermic, as showed by the decrease in the equilibrium constant ($\ln K_p$) and is 52.2 and 12.0, respectively.

At a charge of 1 mole of sulfur per 1 mole of lead oxide in the system, the formation of sulfate 0.25 mol and 0.75 mol of lead sulfide, and the charge of sulfur in an amount of 0.25 mol insufficient for the formation of lead sulphide and the system can be expected to form of lead sulfate and lead metal.



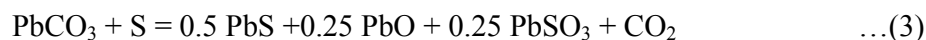
The system PbCO_3 -S interaction can be accompanied with the formation of lead

sulfate and sulfide, carbon dioxide, depending on the amount sulphidizer.

Table 2: Thermodynamic parameters of the chemical reactions in a wide temperature range

Thermodynamic parameters	Temperature (°C)							
	400	500	600	700	800	900	1000	1100
$\text{PbO (k)} + 1.5 \text{ S(g)} = \text{PbS} + 1.5 \text{ SO}_2$								
$\Delta G^0_{\text{T}} \text{kJ/mol}$	-291.7	-269.8	-247.8	-225.7	-203.6	-181.5	-159.4	-137.4
$\ln K_p$	52.2	42.0	34.1	27.9	22.8	18.6	15.1	12.0
$\text{PbCO}_3 + 1.5 \text{ S(g)} = \text{PbS} + 0.5 \text{ SO}_2 + \text{CO}_2$								
$\Delta G^0_{\text{T}} \text{kJ/mol}$	-315.2	-320.4	-324.4	-327.2	-328.8	-329.1	-328.1	-325.7
$\ln K_p$	56.4	49.8	44.7	40.5	36.9	33.8	31.0	28.5
$\text{PbSO}_4 + 2 \text{ S (g)} = \text{PbS} + 2 \text{ SO}_2$								
$\Delta G^0_{\text{T}} \text{kJ/mol}$	-163.6	-172.4	-180.8	-188.7	-196.2	-203.1	-209.4	-215.2
$\ln K_p$	29.2	26.8	24.9	23.3	21.9	20.8	19.8	18.9
$\text{PbCO}_3 + \text{PbO} + 3.5 \text{ S (g)} = 2 \text{ PbS} + 2.5 \text{ SO}_2 + \text{CO}_2$								
$\Delta G^0_{\text{T}} \text{kJ/mol}$	-460.0	-432.9	-405.1	-376.4	-346.8	-316.5	-285.3	-253.4
$\ln K_p$	82.2	67.4	55.8	46.5	38.9	32.4	26.9	22.2
$\text{PbSO}_4 + \text{PbO} + 4.5 \text{ S(g)} = \text{PbS} + 2 \text{ SO}_2$								
$\Delta G^0_{\text{T}} \text{kJ/mol}$	-466.0	-445.2	-423.7	-401.5	-378.6	-355.0	-330.8	-305.8
$\ln K_p$	83.3	69.3	58.4	49.6	42.5	36.4	31.3	26.8
$\text{PbCO}_3 + \text{PdSO}_4 + 3.5 \text{ S (g)} = 2 \text{ PbS} + 2.5 \text{ SO}_2 + \text{CO}_2$								
$\Delta G^0_{\text{T}} \text{kJ/mol}$	-321.2	-332.6	-343.0	-352.3	-360.6	-367.6	-373.5	-378.1
$\ln K_p$	57.4	51.8	47.3	43.6	40.4	37.7	35.3	33.1

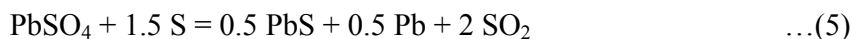
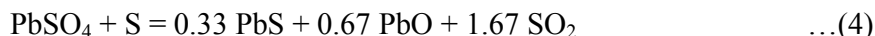
By decreasing the flow of sulfur charge that CO is a strong reducing agent, together with a sulfide, oxide formation is not excluded and lead sulfite by reaction:



When reducing the flow rate of sulfur upto 0.5 mol per 1 mol of lead carbonate in the system lead sulfide formed, since this is insufficient for the amount of sulfur is practically complete sulphidation lead carbonate.

To form lead sulfide in the system $PbCO_3-S$ must spend 1.5 moles of sulfur per 1 mol of lead carbonate from the reaction of 2 (Table 1). Negative values $\Delta G^{\circ}T$ increases with increasing temperature, and is -315.2 kJ/mol at 400°C and -325.7 kJ/mol at 1100°C, the equilibrium constant ($\ln K_p$) also decreases and is 56.4 and 28.5, respectively. The process is also exothermic. In $PbSO_4-S$ system for complete sulphidation lead sulfate requires 2 moles of sulfur per 1 mole of lead sulfate (reaction 3, Table 1), $\Delta G^{\circ}T$ has negative values with increasing temperature, and is -163.6 kJ/mol at 400°C and -215.2 kJ/mol at 1100°C, equilibrium constant ($\ln K_p$) also decreases and is 29.2 and 18.9, respectively an exothermic process.

When reducing sulfur to 1.5 mole, together with the lead sulfide formed metallic lead, and for reducing sulfur to 1 mol of lead oxide is formed, which is undesirable products sulphidation process:



Thus, as a result of thermodynamic calculations indicated that, in the systems $PbO-S$, $PbCO_3-S$, $PbSO_4-S$ occurs virtually complete sulfidization, $\Delta G^{\circ}T$ as lead sulfide formation has negative values at low temperatures, process is exothermic, with rising temperatures seen decrease the equilibrium constant ($\ln K_p$). The reaction takes place in the diffusion region after melting elemental sulfur above 112°C and as you move it to a gaseous state reaction is accelerated, which can be attributed to kinetic transition region.

Based on the results of thermodynamic calculations conducted exploratory research on sulphidation sludge with elemental sulfur.

EXPERIMENTAL

The process of reductive sintering sulphidation slimes were conducted in a muffle furnace grade Nabertherm (more than heat 30-3000°C) on temperatures 400, 600, 800°C. Carefully mixed batch placed in alundum crucible, and then placed in a muffle furnace heated to the desired temperature. Heating time are two hours. Chemical composition of the lead slime used in the experiments is given in Table 3.

Table 3: Chemical composition of the lead slime

S. No.	Elements	Content (%)	S. No.	Elements	Content (%)
1	Lead	62.12	15	Rhodium	0.0008
2	Copper	0.47	16	Palladium	<0.0001
3	Zinc	0.19	17	Tin	0.0024
4	Cadmium	0.068	18	Barium	0.0195
5	Selenium	0.184	19	Tungsten	<0.0001
6	Iron	0.116	20	Rhenium	0.0925
7	Arsenic	0.174	21	Osmium	0.0036
8	Nickel	0.0002	22	Iridium	<0.0001
9	Aluminium	0.0440	23	Platinum	<0.0001
10	Magnesium	0.0143	24	Gold	< 0.0001
11	Calcium	0.0290	25	Mercury	0.4270
12	Molibdenum	0.0008	26	Thallium	0.0020
13	Silver	0.0073	27	Bithmus	0.0370
14	Ruthenium	<0.0001			

As sulphidation agent used sulfur brand «chemical clean». Subjected to sintering batch of the following composition:

100 g lead slime : 10 g sulfur

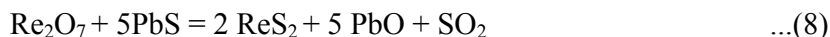
100 g lead slime : 30 g sulfur

100 g lead slime : 50 g sulfur

After the heat treatment obtained cake weighed, grinding and analyzed for rhenium and osmium. Quantitative analyzes of osmium were carried out according to the method^{6,7} of photometric determination of osmium complex thiourea. Analysis measurements were performed based on the method photocolorimetry perrhenate ion complexation with ammonium thiocyanate procedure⁸.

RESULTS AND DISCUSSION

Sulfidation reactions lead compounds, osmium and rhenium on following reactions occur:



Stoichiometric amounts of sulfur for the sulphidation of the slime components is 22% by weight of the slime. Tables 4 and 5 show the results of sintering slime with sulfur in an amount of 10, 30 and 50% by weight of the slime. 10% sulfur fuel is designed to assess the feasibility of sulfidation only osmium and rhenium.

Table 4: Phase composition of sinters obtained at different temperatures and composition of the batch

Slime: Sulfur	400°C		600°C		800°C	
	The content of lead compounds (%)					
	PbSO ₄	PbS	PbSO ₄	PbS	PbSO ₄	PbS
100 : 10	86.33	2.07	87.8	-	87.79	-
100 : 30	73.16	11.54	47.55	31.16	15.07	57.37
100 : 50	73.16	11.54	13.46	59.8	3.65	66.38

Chemical analyzes of the phase lead compounds have shown the possibility of sulfidation or recovery of lead sulfate at temperatures of 600-800°C and sulfur at a rate of 30-50% by weight of the slime. When 800°C basic mass of lead sulfate is converted to the sulfide form. At a rate of 30% sulfur and 50% of lead sulfide content in the sinter is upto 57.37% and 66.38%, respectively.

Our results obtained previously sulphidation slime with coke and sodium sulfate, showed a direct dependence of the degree of sulfidation osmium and rhenium sulfidation main component of slime-lead sulphate³⁻⁵. The same dependence is observed in the sulfidation processes with sulfur. The degree of extraction of osmium and rhenium in the cake increases with increasing content of lead sulfide in the receiving product.

Table 5: The recovery of rhenium and osmium (%) in the cake depending on the composition of the batch and temperature

Slime: Sulfur	400°C		600°C		800°C	
	Os	Re	Os	Re	Os	Re
100:10	52.3	79.3	50.6	63.2	50.0	60.2
100:30	65.8	80.0	98.5	100.0	99.7	100.0
100:50	78.2	85.3	100.0	100.0	100.0	100.0

Maximum extraction of osmium and rhenium in the cake is occurred at temperatures of 600-800°C and charge of sulfur 30-50% by weight of the slime. Low extraction of osmium and rhenium in the cake at 400°C explained their transfer into the gas phase due to the absence of the protective effects of lead sulfide and failure temperature for the formation of osmium and rhenium sulfide. The product yield was 85-87% of sulphidation of the slime.

CONCLUSION

The process of sulphidation lead slime with elemental sulfur is investigated. The possibility of producing sulfide cake suitable for further obtaining concentrates osmium and rhenium.

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