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ISSN 0543-5846
METABK 52(4) 515-517 (2013)
UDC – UDK 669.2/.8/669.054.8=111

RECOVERY OF VALUABLE METALS FROM INDUSTRIAL WASTES

Received – Prispjelo: 2012-12-06
Accepted – Prihvaćeno: 2013-03-15
Preliminary Note – Prethodno priopćenje

Recovery of valuable metals as osmium and rhenium from a industrial wastes are an actual problem. A wastes of copper production treat slime and cake. The content of rhenium in them makes 600 – 2 000 g/t, osmium to 50 g/t. In article results of research of a form of finding of osmium and rhenium in such waste and influence phase transformation of the main components on their extraction when processing are stated. The probable reactions, proceeding in this system are provided. The way of receiving enriched with osmium and rhenium of concentrates from a waste is offered.

Key words: osmium, rhenium, industrial waste, cupper production

INTRODUCTION

Kazakhstan is one of the major regions of the world with large reserves and the prospects for expansion of mineral resources of rare and noble metals. Rare metals are becoming increasingly important. It is hard to say the area of new technology, which does not use rare metals, alloys or different compounds. Nuclear energy, electronics, aircraft and missile technology, engineering, instrumentation, chemical and medical industry, light industrial materials, special types of steel alloys, composite materials used continuously expanding range of rare metals. These are rhenium and osmium, which are concentrated in industrial wastes of copper production.

Unique physical and chemical properties of rhenium and osmium and their alloys cause the growing consumption in all major industries. The main part of rhenium (over 70 %) is used in the production of ovenproof alloys, approximately 5 % is used in petrochemical, 5 % - in electronics and 20 % - in other areas. Therefore, in the past, special attention is paid to the completeness of rhenium extraction of mineral raw materials.

Despite the high degree of rhenium extraction from the leaching of sulfuric acid (over 99 %), the degree of rhenium extraction from the source of the copper concentrate market product is only 34 - 35 % [1]. During the pyrometallurgical processing of copper concentrate rhenium and osmium turn into technological middling (lead dust, slime, cake, etc.). To increase the production of these metals must be involved in the sphere of production man-made products, where the content is much higher than in the original concentrate. These products include lead slime (cake) of copper production. Rhenium content in them is 600 – 2 000 g/t, osmium till 50 g/t and requires developing an effective technological processing scheme.

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EXPERIMENTAL AND DISCUSSION

Physic-chemical studies of copper production slime showed the complexity of their thermal behavior and composition. The slime is a single phase of lead sulfate, where as cake contains 15 – 30 % lead carbonate and 5 – 15 % organic, which complicates the processing of these materials [2].

Due to the low content of osmium and rhenium in the slime it is not possible to find them by XRD, but the chemical phase analysis performed by the known method gives some possibility to find forms of rhenium compounds in the slime (Table 1).

Table 1 **Forms of compounds of rhenium in slime**

Compounds of rhenium in slime	Mass fraction / %
Water-soluble connections (rhenium acid, perenat)	25,6
Rhenium sulfides	43,6
Low-valency oxides of rhenium	30,8

It is known that osmium in sulfuric acid solutions forms sulfite complexes [3], and osmium can beas sulfites in the sulfuric acid-lead slime. To confirm this assumption, we conducted experimental studies on the dissolution of slime in different solutions (Table 2). Passed into solution osmium determined by a known procedure [4] which has refined by us. When the slime leaches in hydrochloric acid solution of sodium chloride, 50 % of osmium moves into solution (Table 2).

By leaching with sodium chloride solution according to the method, it was not observed the transition of osmium in solution without addition of hydrochloric acid.

Table 2 **Osmium distribution at a leaching of slime**

Leaching conditions			Exitof cake / %	The content of osmium in cake / %	Extent of extraction of osmium in solution / %
NaCl / g/l	HCl / mol/l	F:L			
300	3	1 : 12	3,74	0,0524	48,99
300	-	1 : 15	23,2	0,017	-

Apparently, about 50 % of osmium in the slime is in the sulfite form.

The diversity of lead, osmium and rhenium compounds finding forms in the lead technogenic raw of copper production with different operating characteristics, a close relationship them with the main raw components causes the necessity of developing combined schemes incorporating pyrometallurgical and hydrometallurgical processes.

We have proposed techniques, including low-temperature sulfiding sintering and hydrometallurgical processing of the material to produce a concentrate containing osmium and rhenium [5].

It was studied the effect of the lead compounds phase transformation to sulfiding sintering slime in the presence of sodium sulfate and coke extraction of osmium and rhenium to a sinter and final concentrate.

Phase changes of lead compounds approved by the results of chemical and X-ray analysis Figures 1, 2.

The Figures shows that the formation of lead sulphide accelerates with increasing temperature, if temperature is 800 °C then the degree of formation will be 80 %, then the 850 °C – 98 %. The exiting process of lead sulfide decreases by increasing sintering duration, there is a significant amount of lead oxide in the sinter Figure 1(a, b).

The resulting products of sulfiding sintering were analyzed for osmium and rhenium by known colorimetric method of analysis (Table 3).

Sulfiding sinter to remove the main phase, which is represented by lead compounds, was subjected to hydrometallurgical processing.

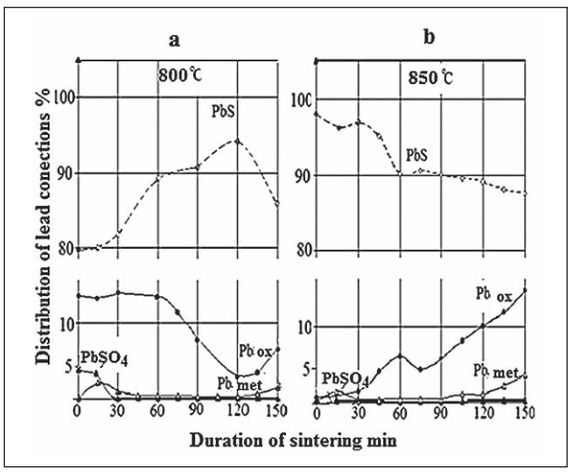

Figure 1 Phase transformation of lead connections in products of sulfiding at temperatures of 800 - 850 °C

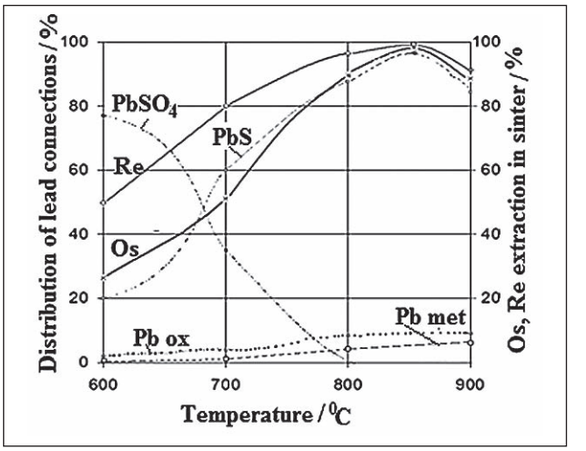

Figure 2 Osmium and rhenium extraction in sinter depending on phase transformations of lead

The cake obtained after the two-stage leaching has also been studied by physical and chemical methods of analysis.

The results of the study found that an increase of a lead sulfide formation degree, depending on the temperature, increases the extraction degree of osmium and rhenium in the sinter, as non-ferrous metal sulfides inhibit oxidation of their compounds:

$OsO_4 + MeS \rightarrow Os + MeSO_4$ (Me-Pb, Cu, Zn, Fe) (1)

$OsO_2 + MeS \rightarrow Os + Me + SO_2$ (Me-Pb, Cu, Zn, Fe) (2)

During the metallic lead formation, which occurs at 850 °C if the sintering duration is 150 minutes, the osmium extraction reduces as it is partially converted into metallic lead (Table 3).

Table 3 **Osmium and rhenium extraction in sulfiding sinter**

№	τ / min	800 °C			850 °C		
		PbS / %	α_{Os} / %	α_{Re} / %	PbS / %	α_{Os} / %	α_{Re} / %
	15	80,0	98,1	98,0	92,1	99,0	98,6
1	30	82,1	98,5	98,7	95,2	97,6	96,9
2	60	89,3	96,3	80,9	90,1	96,2	91,0
3	90	91,8	96,0	75,0	90,0	96,0	80,8
4	120	92,8	95,6	63,8	87,9	93,7	76,2
5	150	85,2	92,6	60,5	85,8	90,3	70,3

Reduction of rhenium extraction by reducing of lead sulfide number in the sinter (Table 3), probably associated with the formation of lead oxides (Figure 1), as the following reactions proceeds:

	ΔG^0_{500} kJ/mol	ΔG^0_{800} kJ/mol	$\Delta G^0_{1\,000}$ kJ/mol	
$2ReO_3+PbO \rightarrow Re_2O_7+Pb$	-600,8	-776,5	-899,7	(3)
$2ReO_2+3PbO \rightarrow Re_2O_7+3Pb$	-463,8	-406,0	-362,2	(4)

By increasing the extraction level of lead sulfide reduces the yield of the final concentrate (Table 4).

This is due to the fact that lead is completely removed during the two-stage sinter leaching. Then the

Table 4 **Influence of the content of sulfide of lead in sinter on an exit of a concentrate and osmium and rhenium extraction**

PbS / %	Exit of a concentrate / %	the Contents / %		Extraction from sinter /%		Concentrating «n»	
		Os	Re	Os	Re	Os	Re
20	4,0	0,0225	0,65	90,1	75,3	6	9
60	3,6	0,054	1,24	95,8	80,0	14	18
82	1,8	0,20	3,17	97,9	85,4	50	45
85	1,5	0,23	3,70	99,0	85,2	55	52

concentration degree of the «n» and extraction of osmium and rhenium to the concentrate increases. Low lead sulfide formation shows incomplete sulfidation system, then the osmium and rhenium compounds stay at unstable form, which transitions to the gas phase and to the solution during leaching.

CONCLUSIONS

1. Studying the effect of lead phase transformations with the behavior of osmium and rhenium determined that the fullness of lead sulfide formation at 800 - 850 °C, increases the extraction degree of osmium and rhenium in the sinter.
2. Revealed that the rhenium compounds are oxidized during the formation in the lead oxide system there by extraction in the sinter reduces.
3. During the formation of metal lead the osmium extraction in the sinter reduces due to its distribution to the metal lead.
4. It is shown that with increasing lead sulfide content increases «n» concentration degree of osmium and rhenium in concentrate by reducing concentrate's output.
5. The obtained concentrate is enriched by osmium 100 - 120 and 60 - 100 times by rhenium. Concentrate's output from the original slime is 0,8 - 1,5 %; osmium content in the concentrate is 0,40 - 0,59 % and rhenium is 5,0 – 8,16 %.

REFERENCES

[1] Complex processing the mineral raw materials of Kazakhstan. Condition, problems, decisions, Astana: Foliant, (2008), 500.

[2] A. K. Serikbayeva, A. Zharmenov, A. Sydykov., 15th conference on Environment and Mineral Processing, Czech Republic, (2011), 193-197.

[3] N. M. Bondar, O. I. Ostanin, T. M. Buslaev, Non-ferrous metals, 7 (2005), 66-69.

[4] Ginzburg A. D., Ezersky N. A., Analytical chemistry of platinum metals, M: Science, (1972), 613.

[5] Patent RK No. 13564. Zharmenov A. A., Sydykov A. O., Serikbayeva A. K., publ. 14.04.2006, bulletin No. 4

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