UDC 669.849 Complex use of mineral resources. № 4. 2017.

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BALKHASH COPPER-SMELTING PLANT SULFURIC ACID WORKSHOP'S SLIME COMPOSITION

Abstract: The production of copper from the charge at the Balkhash copper smelting plant is carried out according to the following scheme: melting in a molten bath → matte conversion → copper refining. In this case a number of technogenic formations (slags, dust, gases, solutions and slimes from flushing gases, copper electrolytic slimes) are obtained, wherein contained in the charge various elements are concentrated. Separate formations either are already raw materials for the extraction of certain elements, or they are considered as raw materials for other elements. Now from copper electrolytic slime the plant produces Au, Ag, Se, from the gases - H_2SO_4. The device for Re extraction from solutions of flushing gases is designed. The solutions contains in addition to Re also the elemental Se of red modification. The project covers cleaning the solution from solid suspensions and Se (slime). This slime can be considered as a raw material for Se extraction. Now there is no technology for obtaining Se from such slimes. As a rule the development of any technology for the extraction of metals begins from study of raw materials. The purpose of this work is to study the chemical, phase and granulometric composition of the slime formed during flushing of the gases. Studies were carried out on a sample of slime separated from industrial solutions. Slime was studied by various methods of analysis: X-ray fluorescence (XRF); chemical; X-ray phase diffraction (XRPhD); infrared spectroscopy (IRS); sieve. In the slime were found 18 elements (Pb, Se, Re, Al, Si, S, Ca, Fe, Cu, Zn, Sr, Cd, I, Hg, Ni, Br, Bi, As), which content varies in a wide range. The slime-forming element is Pb (57.87 % by weight), the content of other elements interesting for their possible recovery as follow, % by weight: 4.6 Se, 0.14 Re, 0.33 I, 0.57 Hg. According to the XRPhD data in the slime basic compound is $PbSO_4$ (92.8 %), there are selenium compounds: $PbSeO_4$ (4.8 %) and very small amounts of elemental selenium of three modifications (0.4, 0.9 and 1.1 %). The presence of $PbSO_4$ and $PbSeO_4$ compounds is confirmed also by IRS method. But in addition to the named compounds, in the slime there are other compounds that contain groups SeO_3^{2-}, CH_2, CH_3, C=O (of yet unidentified compounds). The granulometric composition of the slime is represented approximately 48.4 % by particles smaller than 0.4 mm, into which 47.84 % of Pb, 47.45 % of Se, 55.31 % of Re are recovered. The results obtained will be used to substantiate the method for selenium recovery from the slime into the solution, taking into account the properties of its compounds. Nevertheless, studies on the specification of the substantial composition of Se contained in the slime must continue. It was not possible to determine all the selenium-containing compounds because of its insignificant content in the slime compared to lead.

Key words: solutions, slime, elemental, quantitative, substantial, granulometric composition, selenium, lead, rhenium

Introduction. In Kazakhstan, at the copper smelters of the Corporation Kazakhmys: (Balkhash - BCSP and Zhezkazgan - ZhCSP), ore is being processed from various deposits containing along with copper, Re, Os^{187}, Se, Au, Ag, Zn, Cd, TI and other elements. When pyrometallurgical processing of copper charge and matte, electrolytic production of commodity copper from rough sulfur and some metals are concentrated in different technogenic formations: in solutions of washing off metallurgical gases (industrial terminology: washing sulfuric acid), dusts, copper electrolytic slimes and slime of sulfuric acid workshop (SAW). In particular, Re and Os^{187} concentrates mainly in washing solutions, Se, Au, Ag - in copper electrolytic slimes. At present, NH_4ReO_4, Os^{187}, H_2SO_4 (ZhCSP), Au, Se, Ag and H_2SO_4 (BCSP) are obtained from these technogenic formations at the plants. From the dust and slime of sulfuric acid workshop no metals are recovered: the slimes are dumped, the dust is periodically stored, and is sent to China.

It should be noted that the processing of copper charge on the target metal and the washing of metallurgical gases of BCS significantly differ from the ZhCSP. First, the charge melts in Vanyukov's furnaces, and secondly, the preparation of metallurgical gases to produce sulfuric acid from them is conducted without circulation of washing solutions and their sedimentation from the slime. According to BCSP data, up to 1400 m^3 of washing solutions are daily discharged to the treatment plant (hereinafter: solutions of the sulfuric acid workshop BCSP - SAW BCSP), with which 2-3 tons of rhenium are lost per year (ZhCSP dumps 100 m^3 of solution per day). Employees of the Institute of Metallurgy and Benefication developed and tested on a semi-industrial scale a technology for extracting rhenium from solutions of SAW BCSP with the production of ammonium perrhenate and rhenium acid. [1] The technology provides for the purification of solutions from slime, the content of which varies from 0.0805 to 0.5998 g/dm^3. The developers of the technology in the process of carrying out rhenium work have established the presence of selenium in solutions and slimes, with which about 20 tons of metal are lost per year. "Corporation Kazakhmys" carries out the design of the site at BCSP to extract only rhenium from the SAW solutions to produce ammonium perrhenate. The question of extracting selenium did not stand. Consequently, a significant amount of it, already extracted from mineral raw materials, will be discharged to treatment facilities, as does rhenium from 2006.

Considering that in the technology of rhenium extraction from SAW BCSP solutions, the slime containing selenium is provided for, and the production of selenium from copper-electrolyte slimes BCSP and ZhCSP exists at the plant; expansion of its use in various industries [2, 3] involvement in the production of selenium-containing sediment of SAW in a timely manner.

But as of today, according to the analysis of available publications [2-10], the existing technologies for extracting selenium from slimes of the SAW of copper plants are absent, research works on their development are very insignificant [11-14]. In the world practice, up to 90 % of selenium is obtained from copper electrolytic slime, 10 % from slurries of pulp and paper and sulfuric acid production of the chemical industry [2-5]. The transfer of technologies for the extraction of selenium from copper electrolytic slime to the slime of SAW copper plants is not possible because of their different qualitative and quantitative compositions. Probably, and the material composition of selenium. In the scientific and technical literature there is sufficient information mainly on the chemical and material composition of copper electrolytic slimes [4-9]. In [6], the real composition of selenium contained in these slimes is also given. Concerning the slime of the SAW of non-ferrous metallurgy plants, the information is very limited. Data are mainly given on the content of the basic elements, for which either technologies are developed for their extraction, or payment is made by the consumer plant to the supplier plant. In particular, this applies to lead. The data on the forms of selenium in the slimes of the SAW of copper plants in the periodicals available to us, technical and educational literature were not found. The material compositions of the SAW slime and selenium contained therein, taking into account the chemical properties of the compounds, are necessary for a rational choice of the method and reagents for the recovery of selenium from the slime and the production of metal.

The purpose of the work - determination of the qualitative, quantitative, granulometric and substantial composition of the slime contained in wash solutions of SAW BCSP (SAW BCSP slime, sometimes sediment).

Experimental part. *Materials:* SAW BCSP solutions and slimes extracted from them.

Analysis technique. X-ray fluorescence (XRF) (spectrometer with wave dispersion Venus 200 PANalyticalB.V.), chemical (atomic emission spectrometer Optima 2000 DV, USA, PerkinElmer), X-ray phase diffraction - XRPhD (diffractometer D8 Advance, BRUKER), infrared spectroscopy (IRS) (Thrillo Nicolet Avatar 370 FTIR Spectrometer FT-IR spectrometer), sieve. All devices passed the State verification. The identification of compounds and their groupings was carried out according to data from directories and books [15-20].

Experiment procedure. The SAW BCSP solutions were selected before being dropped onto the treatment plant from the Venturi scrubber cone. To conduct a visual analysis of 1 dm^3 of the average daily solution (the solution was taken hourly), it was kept for 30 days (720 h) in a glass container without stirring.

Due to the notable absence of sediment (0.0805 to 0.5998 g/dm^3) in solutions, the studies were carried out on a sample obtained during semi-industrial tests of sorption technology of rhenium extraction. [1]. Fresh solutions for processing were monthly released with an interval of 10 days. From each batch of the solution, a precipitate was filtered off, which was washed with water to pH = 6 on the filter, dried to constant weight at 105 °C. The dry precipitates were combined, thoroughly mixed, averaged by quartation [21].

Results and discussion. Figure 1 demonstrates the images of SAW BCSP solution at the time of selection (Figure 1a), after settling for 2 h (Figure 1b) and 720 h (Figure 1c). As appears from the figure the initial solution is cloudy, white-pink, these characteristics gradually changed in time due to precipitation. In such a manner, after 2 hours of sedimentation, the solution became much lighter with the predominance of pink color (Figure 1b); in the clarified solution fixed a light suspension of red color. The sediment is represented by layers and impregnations of different colors and densities. Color of the layers: mostly light and dark reddish; white - minor blotches, black - single blotches. Bluish hue - background surface. The bottom layer of the sediment is compact, above it - loose. After 720 hours (30 days), the solution is clear, colorless (Figure 1c), the compact is not uniform, the lower layer is white, the upper layer is red, there are insignificant inclusions of black color. Taking into account the available information, it can be stated a priori that layered precipitation from solutions and their different colors are due to the presence of lead red sulphate and elemental selenium in the red modification [5, 7].

a – at the time of selection

b – after 2 hours of sedimentation

c – after 30 days of sedimentation

Figure 1 – External view of the solution

The ruddy color of the combined sediment obtained from different batches of solution changed to black after drying. The sediment is soft, crumbly.

However, at preparing the sediment for analysis by XRF method, it was observed that the consistency of the sediment changed during grinding: it became viscous, which did not allow us to conduct the analysis. In this regard, it was first washed with alcohol, then with water and again dried at 105 °C. The color of the alcohol filtrate is dark brown, the colorants are colorless. After removing the alcohol from the filtrate evaporated in a water bath, droplets of a viscous brown liquid formed (Figure 2), which after cooling to room temperature was transformed into a tar-like mass.

Figure 2 – The remaining phase after removing alcohol from the filtrate from slime washing

An effort of determining its phase composition of IRS was unsuccessful: in electronic libraries of spectra, a similar connection was not found. Nevertheless, group-structure analysis revealed the presence of groups characteristic of aliphatic hydrocarbons (stretching vibrations ν CH_2, CH_3 – 2956, 2925, 2855 cm^{-1}, deformation vibrations δ CH_2, CH_3 1466, 1378 cm^{-1}, ρ CH_2 – 723 cm^{-1} [16]); C═O (1710 $см^{-1}$[16]); SO_4^{2-} (1244,1202, 1087, 1051, 624, 587 cm^{-1} [17]); ReO_4^- (919 cm^{-1}); SeO_3^{2-} (805 cm^{-1} [17]), SeO_4^{2-} (910-805 cm^{-1} for the $PbSeO_4$ compound) [18].

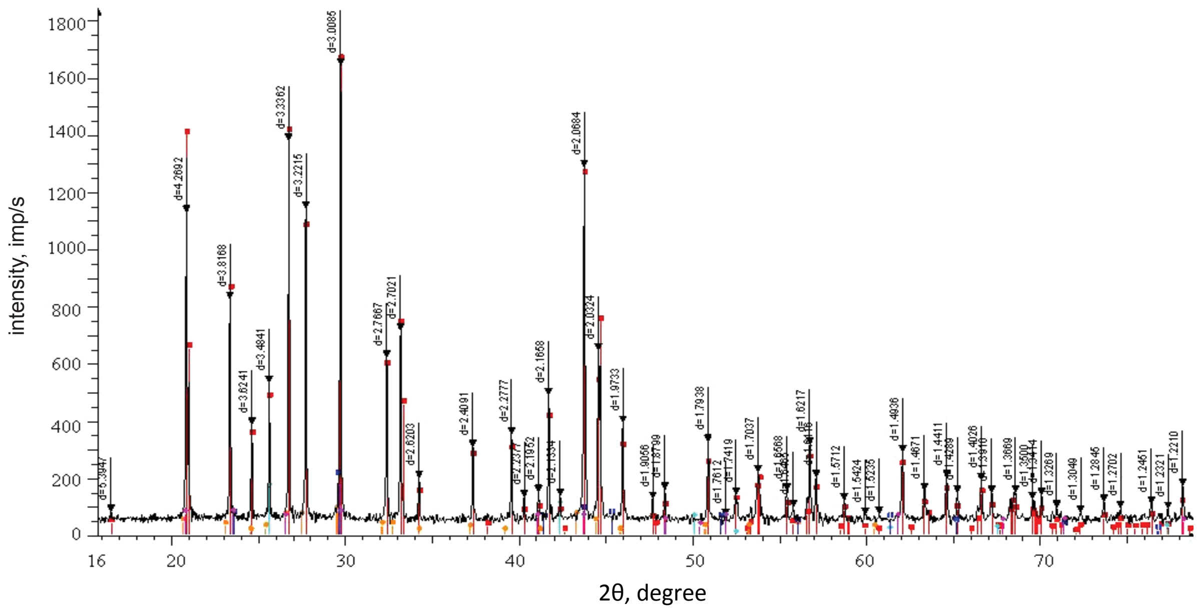
The washed sediment was analyzed by the methods: XRF and chemical only on the elements of interest (Table 1); XRPhD and IRS (Figures 3, 4).

Table 1 – Chemical composition of the slime extracted from the SAW BCSP solution

Content of elements, wt. %	X-ray fluorescence analysis	Chemical analysis
Pb	57.87	56.40
Se	4.60	4.60
Re	0.14	0.12
Al	0.03	
Si	0.23	0.60
S	7.78	9.91
Ca	0.34	0.44
Fe	0.08	
Cu	0.28	0.30
Zn	0.35	0.30
Sr	0.08	
Cd	0.15	0.09
I	0.33	
Hg	0.57	
Ni	0.02	
Br	0.01	
Bi	0.32	
As	0.15	

According to the XRF analysis data, 18 elements with widely varying content were found in the slime. The slime-forming element is Pb (57.87 wt %), the Se content is 4.6 wt %. The content of other elements in terms of their possible recovery is, mass. %: 0.14 Re, 0.33 I, 0.57 Hg. The observed scatter of the numerical contents of elements detected by both methods is probably a consequence of the human factor and the precision of the methods.

As appears from XRPhD data (Figure 3), two lead compounds are contained in the slime: $PbSO_4$ (92.8 %), $PbSeO_4$ (4.8 %); three modifications of selenium in very small quantities (0.9 %, 1.1 %, 0.4 %).



Slime diffractogram – black; diffraction reflexes: red – $PbSO_4$, yellow – $PbSeO_4$, turquoise, blue, pink - elemental selenium of different modifications

Figure 3 – Diffractogram of washed dry slime

The IRS method (Figure 4) confirmed the presence of $PbSO_4$ (1175, 1057, 968, 632, 599 cm^{-1}) in the slime [17]; $PbSeO_4$ (vibrations ν_3 910-805 cm^{-1} [18]); revealed the presence of the group SeO_3^{2-} (801 cm^{-1}, the values of the vibrations ν_1 and ν_3 of this are close and are manifested by one band [17]); groups of aliphatic hydrocarbons: stretching vibrations ν CH_2, CH_3 - 2954, 2924, 2854 cm^{-1}, deformation vibrations δ $CH_2 \bullet CH_3$ - 1456 cm^{-1} [16]; C═O (1732 cm^{-1}). The carbonyl group band falls within the absorption range of di-α-halogen-substituted aliphatic acids, saturated aliphatic aldehydes, ketones [19, 20], β-lactams of monocyclic, γ-lactams of cyclic condensed [19]. The presence of a carbonyl complex with bridging carbonyl groups bound simultaneously with two metal atoms is possible [19].

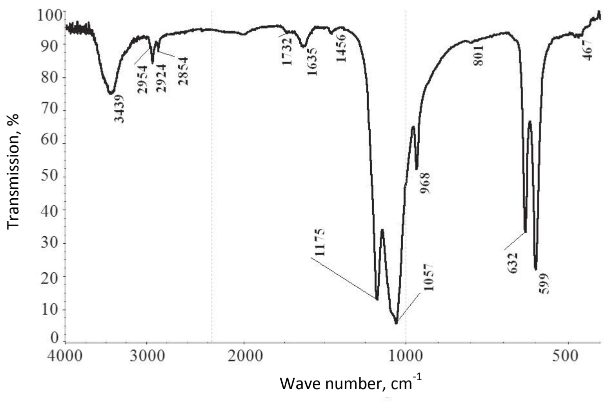


Figure 4 - IRS of washed dry slime

A comparison of the spectra of the organic phase separated from the slime by washing it with alcohol and washed slime showed the presence of identical groups: SeO_4^{2-}, SeO_3^{2-}, CH_2, CH_3, SiO_2. Unfortunately, it is impossible to identify which compounds (with the exception of $PbSeO_4$) due to the absence of spectra in electronic libraries, as mentioned above, spectra similar to the slime. It can only be stated that there are organic compounds in the slime. And they and $PbSeO_4$ are poorly soluble in alcohol. Obviously, the amount of alcohol was insufficient to wash out certain organic compounds and $PbSeO_4$ from the slime, so some of them passed into the alcohol filtrate, some remained in the slime. The compounds with the groups SO_4^{2-} and ReO_4^- from the slime were washed. Since there is iodine in the slime, it can be assumed that there are iodized aliphatic acids in the slime.

The granulometric composition of the slime was determined according to GOST 12536-2014 by the method of dry sieve analysis. A sample of slime (300 g) was sieved through a standard set of sieves. In each class, determine the content of Pb, Se and Re. The results are shown in Figure 5 and Table 2.

As appears from the histogram (Figure 5a) the granulometric composition of the slime is represented by particles of the particle size class from +0.16 to -0.4 + 0 mm. But the prevalence (48.4 %) is mostly particles of the class of size -0.4 + 0 mm. The concave curve of the total yield of classes of size confirms the significant predominance of small particles in the slime. The content of the controlled elements in classes of different sizes is almost identical: Pb (56.7 - 58.1 wt. %), Se (4.00 - 4.51 wt. %), Re (0.10 - 0.16 wt. %) (table 2). 47.84 % of Pb, 47.45 % of Se, 55.31 % of Re are extracted into the smallest class of size.

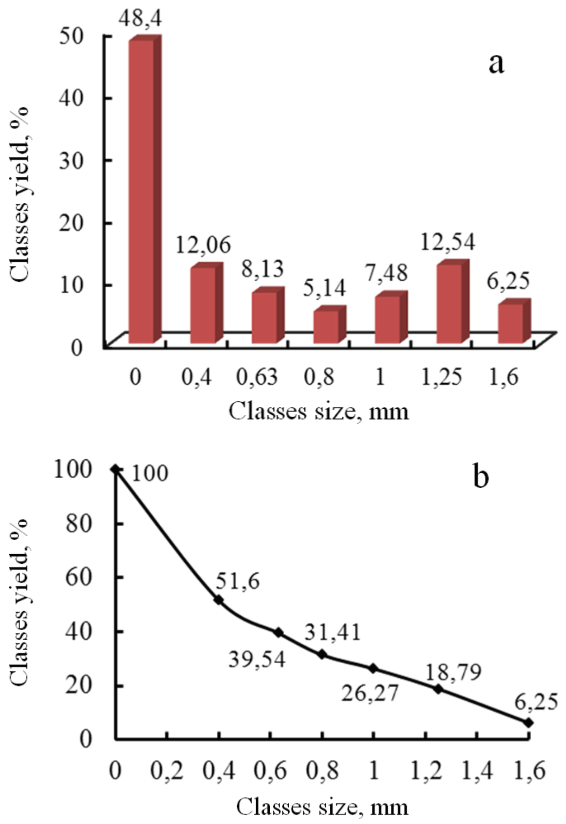


Figure 5 - The partial (a) and total (b) yield of grades of slime size

Table 2 - Content of Pb, Se and Re and their distribution according to the slime size classes

(Content in the original slime, wt. %: 57.87 Pb, 4.60 Se, 0.14 Re)

Size classes, mm	Content of elements, wt. %			Distribution of elements by the size classes, %		
	Pb	Se	Re	Pb	Se	Re
+1.6	57.40	4.30	0.14	6.20	5.84	6.25
-1.6+1.25	58.10	4.11	0.10	12.59	11.20	8.96
-1.25+1	57.50	4.15	0.14	7.43	6.75	7.48
-1+0.8	57.70	4.00	0.14	5.12	4.47	5.14
-0.8+0.63	57.40	4.05	0.15	8.06	7.16	8.71
-0.63+0.4	56.70	4.09	0.14	11.82	10.72	12.06
-0.4+0	57.20	4.51	0.16	47.84	47.45	55.31
Итого:				98.76	93.59	103.91

Conclusions. 18 elements (Pb, Se, Re, Al, Si, S, Ca, Fe, Cu, Zn, Sr, Cd, I, Hg, Ni, Br, Bi, As) were found in the slime of the sulfuric acid workshop of the Balkhash copper smelting plant, varies in a wide range. The slime-forming element is Pb (57.87 % by weight), the content of other elements of interest in terms of their possible recovery is, %: 4.6 Se, 0.14 Re, 0.33 I, 0.57 Hg.

The presence of two lead compounds in the slime of $PbSO_4$ (92.8 %) and $PbSeO_4$ (4.8 %) was established by XRPhD and IRS methods.

Selenium in the slime can be found in the elemental state of various modifications as well, but in insignificant amounts (0.4, 0.9 and 1.1 %, XRPhD); and in the form of some kind of compound, in the composition of which there is SeO_3^{2-} (IRS).

Organic compounds of the class of aliphatic acids (IRS) are also found in the slime.

Slime by 48.4 % is represented by particles of the size class -0.4 + 0 mm, into which 47.84 % of Pb, 47.45 % of Se, 55.31 % of Re were recovered.

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ТҮЙІНДЕМЕ

Балқаш мыс балқыту зауытында шихтадан мыс алу: сұйық ваннада → штейнды конвертлеу → мыс тазалау сызба бойынша жүзеге асады. Бұл жағдайда шихта құрамында бар әртүрлі элементтермен байытылатын техногендік түзілімдер (шлактар, шаңдар газдар, мен ерітінділер) алынады. Жеке түзілімдер кейбір элементтерді өндіруге шикізат түрінде қарастырылады. Қазіргі кезде зауытта мысэлектролиттік шламнан Au, Ag, Se, H_2SO_4– газдардан өндіреді. Газдар шайылған ерітіндіден Re өндіру қондырғысы жобаланады. Ерітіндіде Re басқа элементтік Se қызыл модификациясы бар. Жобада ерітіндіні қатты қоспа мен Se (шлам) тазалау қарастырылған. Бұл шламды Se өндіру үшін шикізат түрінде қарастыруға болады. Бүгінде осындай шламнан Se өндіру технологиясы жоқ. Ереже бойынша, металдарды өндірудің кез келген технологиясын жасау шикізатты зерттеуден басталады. Жұмыс мақсаты – газды шаю кезінде түзілетін шламның химиялық, фазалық және гранулометриялық құрамын зерттеу. Зерттеу өндірістік ертітінділерден бөлінген шлам үлгісінде жүргізілді. Шламға сараптама әрүрлі әдістермен: рентгендік флуоресценттік, химиялық, рентгендік фазалық, инфрақызыл спектроскопиялық және елеу жүргізілді. Шламда мөлшері кең ауқымда өзгеретін18 элемент бар екені анықталған. Шлам түзетін элемент Pb (57,87 мас. %) болып табылады, оларды өндіру мүмкіншілігі жағынан қызығушылық танытатын басқа элементтер мөлшері мас. %: 4,6 Se, 0,14 Re, 0,33I, 0,57 Hg құрайды. Рентгендік фазалық сараптама бойынша шламның негізін $PbSO_4$ (92,8 %) қосылысы құрайды; және де селен қосылысы: $PbSeO_4$ (4,8 %) мен аз мөлшерде элементтік селеннің үш модификациясы (0,4; 0,9 и 1,1 %) бар. $PbSO_4$ мен $PbSeO_4$ қосылыстарының бар екендігі инфрақызыл спектроскопиямен де дәлелденген. 47,84 % Pb, 47,45 % Se, 55,31 % Re өндірілетін, шламның гранулометриялық құрамы 48,4 %-ы мөлшері 0,4 мм кем емес бөлшектерден тұрады

Түйінді сөздер: ерітінділер, шлам: элементтік, құрамы, сандық, заттық, гранулометриялық

РЕЗЮМЕ

На Балхашском медеплавильном заводе получение меди из шихты осуществляется по схеме: плавка в жидкой ванне → конвертирование штейна → рафинирование меди. При этом получается ряд техногенных образований (шлаки, пыли, газы, растворы и шламы от промывки газов, медеэлектролитные шламы), в которых концентрируются различные элементы, содержащиеся в шихте. Отдельные образования либо уже являются сырьем для извлечения некоторых элементов, либо они рассматриваются в качестве сырья для других элементов. В настоящее время на заводе из медеэлектролитных шламов получают Au, Ag, Se, из газов – H_2SO_4. Проектируется установка по извлечению Re из растворов от промывки газов. В растворах кроме Re содержится и элементный Se красной модификации. В проекте предусмотрена очистка раствора от твердых взвесей и Se (шлам). Этот шлам можно рассматривать как сырье для извлечения Se. На сегодняшний день технологии получения Se из таких шламов нет. Как правило, разработка любой технологии извлечения металлов начинается с изучения сырья. Цель настоящей работы – изучение химического, фазового и гранулометрического составов шлама, образующегося при промывке газов. Исследования проводили на образце шлама, выделенного из производственных растворов. Шлам изучали различными методами анализа: рентгенофлуоресцентным; химическим; ренгенофазовым (РФА); инфракрасной спектроскопии (ИКС); ситовым. В шламе обнаружено 18 элементов (Pb, Se,Re,Al, Si, S, Ca, Fe, Cu, Zn, Sr, Cd, I, Hg, Ni, Br, Bi, As), содержание которых колеблется в широком диапазоне. Шламообразующим элементом является Pb (57,87 мас. %), содержание других элементов, представляющих интерес с точки зрения их возможного извлечения, составляет, мас. %: 4,6 Se; 0,14 Re; 0,33 I; 0,57 Hg. По данным РФА в шламе основным соединением является $PbSO_4$ (92,8 %); есть соединения селена: $PbSeO_4$ (4,8 %) и элементный селен трех модификаций в очень незначительных количествах (0,4; 0,9 и 1,1 %). Наличие соединений $PbSO_4$ и $PbSeO_4$ подтверждено и методом ИКС. Но кроме названных соединений в шламе есть другие соединения, содержащие группы SeO_3^{2-}, CH_2, CH_3, C═O (пока неустановленных соединений). Гранулометрический состав шлама примерно на 48,4 % представлен частицами размером менее 0,4 мм, в которые извлекается 47,84 % Pb, 47,45 % Se, 55,31 % Re. Полученные результаты будут использованы для обоснования способа извлечения селена из шлама в раствор с учетом свойств его соединений. Тем не менее, исследования по уточнению вещественного состава Se, содержащегося в шламе, необходимо продолжить. Из-за незначительного его содержания в шламе по сравнению со свинцом установить все селенсодержащие соединения не получилось.

Ключевые слова: растворы, шлам, состав элементный, количественный, вещественный, гранулометрический, селен, свинец, рений

Received 18.11.2017.