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REGULARITIES OF SELENIUM AND CHROMIUM BEHAVIOR IN REDOX PROCESSES DURING HYDROMETALLURGIC TREATMENT OF SOLID PHASE PRODUCTS OF RHENIUM EXTRACTION

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The main source of selenium is copper anode slime. But during the pyrometallurgical treatment of sulphide polymetallic ores significant amount of selenium along with radiogenic osmium and rhenium is concentrated in the solid-phase products of acid wash extraction and cannot be extracted, as gets lost with discharged chromium-containing solutions of osmium stage.

The paper presents results of research into selenium reduction in the chromium-containing sulfuric acid medium by sulfurous gas and sodium sulphite. The use of the above reducers in optimum conditions leads to almost complete recovery of selenium (VI) while selenium (IV) extraction rate is not exceeding 60 %. The chrome (III) present in solutions has no impact on the selenium extraction rate. Chrome (VI) is almost completely reduced to a trivalent state, thus its negative impact on subsequent rhenium sorption from solutions purified from selenium is excluded. In view of a high rate of selenium extraction from chromium-containing sulfuric acid solutions formed in the process of radiogenic osmium production using sulfurous gas and sodium sulphite, choice of a method for selenium reduction is to a great extent dependent on the company's profile.

Kew words: selenium, washing acid, reduction, chromium, sulphide copper ores.

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Introduction Extensive penetration of knowledge-intensive industries into the global market will in the near future drive up the demand for selenium, highlighting a need for developing efficient methods for selenium extraction from intermediate products of metallurgical plants. Selenium extraction at metallurgical plants depends on how complex is the use of raw materials there. The largest Russian producers of selenium include Norilsk Nickel MMC (~ 100 tons per year), Ural Mining and Metallurgical Company (80 tons per year) and Kyshtym Copper Plant (5 tons per year) [10, 20].

Development of intensive high-temperature technologies for processing of copper and copper-nickel raw materials is coupled with increased conversion of selenium to gaseous state and changes in its distribution between the major concentrators + copper electrolysis slimes [16, 19], sulfuric acid slimes and washing sulfuric acid. Selenium high concentration in washing sulfuric acid makes it expedient to review it as an independent source of selenium along with traditional products such as first of all the electrolytical ones.

During processing of rhenium-containing copper ores of Kazakhstan Zhezkazgan field the washing acid is the main source of rhenium and radiogenic osmium, produced through processing of interfacial extraction precipitation, occurring at a rhenium stage [1, 5, 9, 11, 14, 15].

Hydrometallurgical technology for radiogenic osmium extraction implies oxidizing loosening of extraction precipitation (5,000 g/t Os) in sulfuric acid medium with the hexavalent chromium acting as an oxidant. Thereupon selenium and rhenium migrate to sulfuric acid solution with chromium concentration of 60-80 g/dm^3. About 80 % of total chromium content is trivalent chromium and the rest is the hexavalent chromium. Selenium is present in solution in its higher oxidation states with different proportions in concentration of 5-7 g/dm^3, rhenium concentration may reach 1 dm^3. In view of their full conversion from interphase precipitation the concentration of rhenium in the mother solution may reach 5 % and the amount of selenium as compared to its original content in the ore can be quite considerable. Processing of mother sulfuric acid solutions implies original solution restoring by sodium sulfite with subsequent rhenium sorption. The main reason why hexavalent chromium recovery operation is introduced in the technological sequence is the prevention of its negative impact on the subsequent sorption of rhenium, but it can also be considered as a potential channel for selenium extraction and concentration [7, 12].

There are several processing methods for selenium-containing solutions providing quite high selenium yields [2-4, 8, 18]. At the same time non-traditional for selenium producers nature of sulfuric acid

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solutions with high ionic strength of chromium need thorough investigation with regard to applicability of known technologies.

As metallurgical enterprises tend to move away from traditional pyrometallurgical technologies towards SX-EW technologies, which do not assume the production of anode slimes being the primary source of selenium, a task of developing efficient technologies for selenium extraction from solutions of different genesis is becoming ever more urgent.

Research Procedure. Experiments to precipitate selenium were carried out in sulfuric acid solutions, g/l: selenium (IV) – 5-15, chromium (III) – 60. In some experiments potassium dichromate containing 5 g / l of Cr (VI) and selenium acid containing 5 g/l of Se (VI) were added to the solution. Concentration of sulphur acid changed in a range between 100 and 250 g/l. The temperature range was 50-80 °C. The reducing reagents were sulfurous gas and sodium sulphite. Experiments were conducted in a laboratory thermostated reactor with mechanical stirring of pulp (stirrer speed – 500 rpm). Sulfurous gas was fed into the space under reactor's impeller to ensure maximum dispergation of sulphurous gas when in liquid state.

Sulfurous gas was produced using a traditional method based on reaction between concentrated sulfuric acid and sodium sulfite. Sulfurous gas consumption reached double stoichiometry and was controlled through consumption of sulfuric acid using the following reaction

$$H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4. \quad (1)$$

Experiments with sodium sulphite were carried out with the reducer in excess of theoretically required amount by 150-250 % using the following reaction

$$H_2SeO_3 + 2Na_2SO_3 = Se + 2Na_2SO_4 + H_2O. \quad (2)$$

Redox potential of the systems studied was controlled using a platinum electrode and a saturated silver-chloride electrode by means of pH millivoltmeter (pH = 673). Selenium and chromium concentrations in solutions were measured by means of mass spectrometry with inductively coupled plasma using spectrometer (ICAP-6300Duo).

Research Findings and Discussion. Selenium (IV) precipitation by sulfurous gas at constant gas blowing speed is occurring concurrently with reduction in the redox potential of the system (Fig.1). Given that solution included several coupled oxidation-reduction systems, the measured potentials are compromise-based.

The process of selenious acid reduction to selenium was preceded by the first jump in the redox potential (Fig.1). After this we see a horizontal part of the curve on the graph representing changes in potential over time, which is showing how process moved on, the compromise potentials registered at that time can be explained by the presence of H_2SeO_3 in the solution and their values are quite close to the theoretical estimates made for this system (please see table).

$$Se + 3H_2O = HSeO_3^- + 5H^+ + 4\bar{e}\,. \quad (3)$$

Comparison between experimental and theoretical values of the system redox potentials (3)

Experiment conditions		φ_{theor}, mV	$\varphi_{experim}$, mV (respective to aqueous element)
H_2SO_4 concentration, g/l	Temperature, °C		
100	80	646	636
100	50	663	636
150	80	661	664
150	50	678	644
200	80	671	638
200	60	684	684
250	80	679	695
250	60	692	704

For calculation purposes the average activity factor of ions in sulfuric acid of a certain concentration was assumed to be constant and equal to 0.13, while bearing in mind that depending on temperature and acid concentration it may vary in the range between 0.086-0.151 [15]. The undertaken calculations have shown that potentials characterizing selenium (IV) extraction from the solution are indicative of quite

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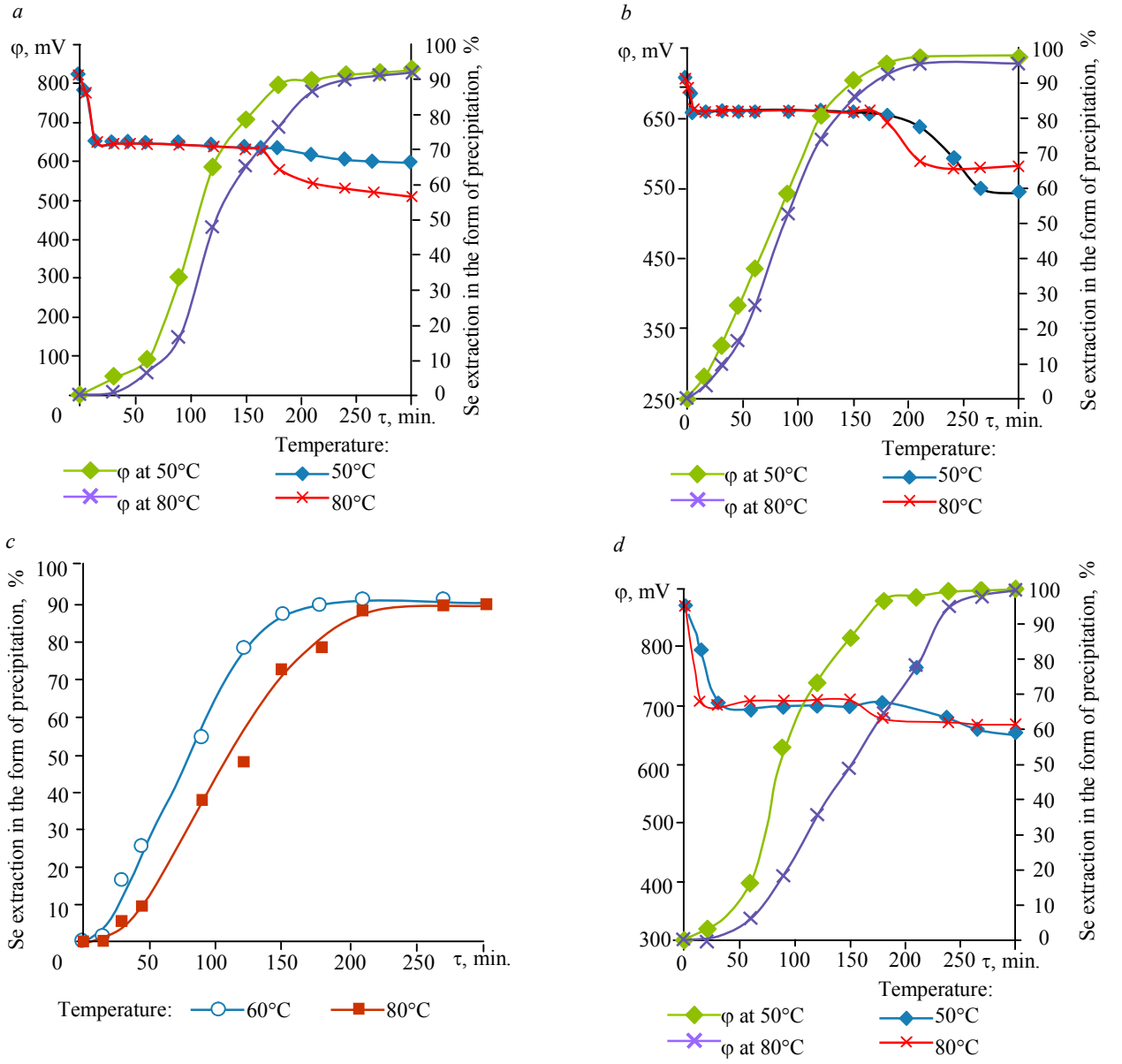

Fig.1. Kinetics of selenium (IV) sulfuric acid precipitation by sulfurous gas in sulfuric acid solutions

Solution composition, g/l: *a* – Se(IV) – 5; H_2SO_4 – 100; *b* – Se(IV) – 5, H_2SO_4 – 150; *c* – Se(IV) – 5, H_2SO_4 – 200; *d* – Se(IV) – 5, H_2SO_4 – 250

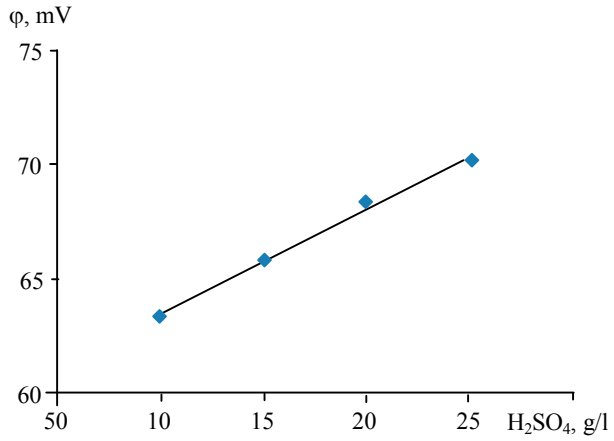

Fig.2. Dependence of potential of selenium (IV) reduction with sulfurous gas on concentration of sulfuric acid (temperature 80 °C, selenium concentration 7.5 g/l)

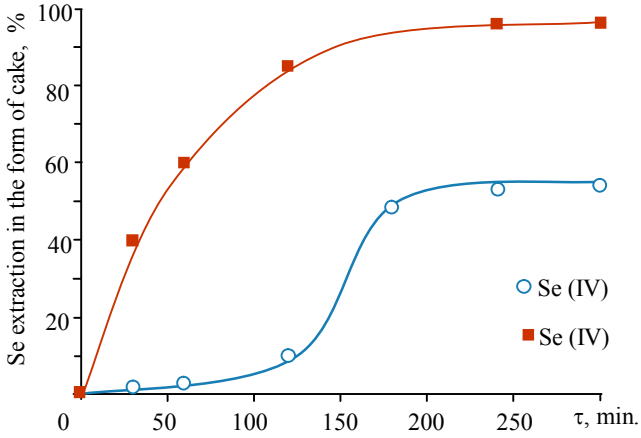

Fig.3. Extraction of selenium with highest oxidation rates from sulfuric acid chromium-containing solution in the presence of sulfurous gas

Solution composition, g/l: Se (IV) – 5, Se (VI) – 5, Cr(III) – 60, sulfuric acid – 200. Temperature – 50 °C, maximum precipitation time – 5 h, sulfurous gas consumption – 300 % (Reaction 1)

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low concentration of sulfurous gas therein ($5 \cdot 10^{-16}$ g/l). As it appears the sulfurous gas getting into the solution is immediately consumed for selenium (IV) reduction, which gives grounds to assume that the rate of selenium (IV) reduction is limited by the rate of SO_2 dissolution. The increase in H_2SO_4 concentration leads to higher redox potential of the curve's horizontal part (Fig.2), which corresponds to a decrease in quasi-stationary concentration of sulfurous gas.

The second jump of potential as demonstrated by the curve (see Fig.1) corresponds to the final stage of selenium (IV) reduction, when its concentration in the solution is close to zero. In this case redox potential of studied systems is determined by the sulfurous gas dissolution.

The kinetic curves of selenium (IV) precipitation also have horizontal parts at the curve beginnings, which apparently correspond to new phase nucleating. When sulfuric acid concentration in the solution is 100 g/l, the length of this part is the longest (Fig.1, *a*). Then with increase in acid concentration (150-250 g/l) the nucleating time remains almost unchanged (Fig.1, *b-d*).

Parts of the curves, corresponding to the selenium (IV) reduction by sulfurous gas are straight, i.e. the reduction rate does not depend on the chalcogen concentration in solution, and reaction (1) with this selenium concentration is equal to zero. Thus it is proved than the limiting stage of the process (1) is the sulfurous gas dissolution rate, which in its turn is a function of many factors (temperature, H_2SO_4 concentration and others).

Negative values of the apparent process activation energy at different concentrations of sulfuric acid (–8.21, –15.22, –22.4 and –28.9 kJ/mol for 100, 150, 200 and 250 g/l H_2SO_4 respectively) based on preliminary assessment are indicative of the complexity of formal description of this process using traditional Arrhenius equation. As it appears decisive is the stage of sulfurous gas absorption by the solution, with the selenium reduction process occurring predominantly in the external diffusion region.

Reduction in the solubility of the sulfurous gas in sulfuric acid solutions with the temperature increase is indicative of reduction in the speed of gas external diffusion to reaction volume, which in its turn slows down the reaction (1). Therefore negative values of apparent process activation energy formally characterize dependence of the rate of diffusion of sulfurous gas on temperature.

The conducted experiments have shown that selenium (IV) is almost completely reduced in 3 hours with consumption of sulfurous gas equal to 150 % of the amount theoretically required for reaction (1).

Proportion of the selenium higher oxidation forms in sulfuric acid chromium-containing solution of osmium intermediate products' processing is determined by the current parameters of oxidation process and analytical data on composition of Se (IV) solutions: Se (VI) = 5:1-1:1.

Results of experiments on synthetic solutions with concentration ratio $C_{Se(IV)} : C_{Se(VI)} = 1:1$, attest to noticeable precipitation of hexavalent selenium, which starts after extraction of the main part (about 80 %) of Se (IV) and does not exceed 54 % in 3 hours with a total extraction of selenium not exceeding 80 % (Fig.3).

Chromium (III) concentration in synthetic solution is 60 g/l. In solutions Cr (III) forms neutral, negatively and positively charged complexes with coordination number of 6 and octahedral configuration, the relative quantity of which depends on the solution composition. Such complexes include complex of Cr (III) with SO_4^{2-} anions. In acidic medium the predominant form of chromium (VI) is $HCrO_4^-$. $HCrO_4^-$ reduction in acidic media is coupled with absorption of H^+:

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr_3 + 4H_2O\,. \qquad (4)$$

That's why reduction in potential can be attributable not only to reduced chromium concentration, but also to lower acidity of medium [17].

No prominent impact of Cr (III) on Se (IV) extraction from sulfuric acid solution has been detected. The presence of hexavalent chromium in solution in a relatively low concentration does not significantly alter the initial redox potential of a studied system (equilibrium redox-potential varies in the range between 550-620 mV relative to aqueous element). The sulfurous gas blowdown through sulfuric acid solution, containing, g/l: Cr (III)-60, Cr (VI) – 5, Se (IV) – 5, and Se (VI) – 1 g/l at a temperature of 50°C for 3 hours (total reducer consumption equal to 300 % of theoretical amount required for the reaction (1)) ensures complete reduction of hexavalent chromium and extraction of up to 90 % of selenium in the form of greyish black deposit prone to pelletizing.

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When sodium hydrosulphide is used irrespective of the medium acidity in the first 5-10 minutes selenium (IV) concentration in a synthetic solution sharply drops down from 15 to 0.5-1.0 g/l, implying a much faster selenium reduction by sodium sulphite than by sulfurous gas. Selenium precipitation rate does not depend on the acid concentration and the depth of precipitation increases with the acidity increase (Fig.4).

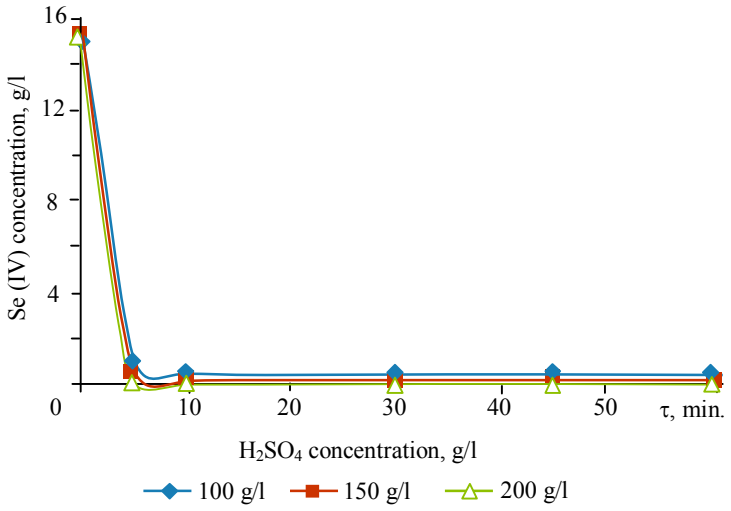

Fig. 4. Selenium (IV) precipitation by sodium sulfite

Solution composition, g/l: Se(IV) – 5, H_2SO_4 – 100, 150 and 200 g/l. Temperature - 50°C, maximum precipitation time - 6 hours , sodium sulphite consumption - 150 % of the amount theoretically required for reaction (2)

Increased speed of redox reaction can be explained by elimination of diffusion limitations associated with dissolution of sulfurous gas. The medium acidity impacts the depth of selenium (IV) precipitation when its residual concentration in solution is minor. Sulfuric acid concentration of 200 g/l is optimal and sufficient for selenium precipitation to the residual concentration of 0.05-0.03 g/l. Sulphite excess by a factor of 1.5 guarantees a high selenium (IV) extraction in the form of crude product.

When chromium (VI) is present in the synthetic solution high extraction of selenium in the form of cake is maintained at optimal reduction process parameters. Therewith the reduction of hexavalent chromium to trivalent chromium reaches 95-97 % [13].

The pursued experiments have shown that when selenium (IV) is reduced from synthetic sulfuric acid solutions by sodium sulphite the optimal process parameters shall be as follows: sulfuric acid concentration – 200 g/l; temperature – 50 °C; duration – 30 minutes; reducer consumption in excess by a factor of 1.5.

Use of sodium sulfite for processing under such conditions of the sulfuric acid solution produced after hydrothermal stripping of osmium tetroxide in the presence of chromium oxide CrO_3 from interfacial precipitate (0.91 % Se, 5.6 % Re, 5,160 g/t Os) leads to a quantitative reduction of selenium tetravalent form up to 92.5 % and less than 48 % reduction of Se (VI), along with complete conversion of hexavalent chromium into the trivalent state. Total extraction of selenium from the mother solution with the following proportion of selenium forms $C_{Se(IV)} : C_{Se(VI)} = 5:1$, comprises 90-92 %.

Conclusions

1. Extraction of selenium from sulfate solutions of osmium stage is influenced by proportion Se (IV):Se (VI), which depends on parameters of extraction precipitate oxidation process and may range from 5:1 to 1: 1.

2. The use of sulfurous gas helps to achieve almost complete selenium (IV) reduction and about 55 % selenium (VI) reduction at temperature 50 °C, with sulfuric acid concentration 150-200 g/l, in 3 hours and with reducer consumption equal to 150-200 % of amount theoretically required.

3. The negative effect of temperature on the selenium reduction by sulfurous gas is attributable to the lower solubility of this gas with the temperature increase, which is a limiting factor in the reaction. The calculated negative values of the apparent activation energy (–8.21, –15.22, –22.4 and –28.9 kJ/mol within the studied acidity range) of selenium reduction by sulfurous gas formally demonstrate dependence of the rate of sulfurous gas diffusion into the solution on the process temperature.

4. Selenium reduction process using sodium sulfite has a considerably higher reduction rate due to elimination of diffusion constraints associated with the dissolution of sulfurous gas. Within 30 minutes with the acidity of 200 g/l H_2SO_4, temperature 50 °C and 1.5-fold reducer consumption tetravalent selenium is reduced to 92.5 % and Se (VI) is reduced to at least 48 %.

5. Choice of a method for selenium reduction is to a great extent dependent on the company's profile. Reduction by sodium sulphite (sulfurous gas) occurs with intensive foaming of sulfuric acid solution, and generation of a fine-dispersed selenium. High consumption of sulfurous gas and long process time may also to some extent complicate the industrial feasibility of this option.

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