

# Simultaneous Extraction of Selenium from Intermediate Products of Extraction Reprocessing of Washing Acid of Copper Production

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## Abstract

**Background:** In pyroprocessing sulphide complex copper ores, considerable amount of selenium along with radio genic osmium and rhenium concentrated in the solid-phase products of acid wash is disappearing with waste chromium-containing solutions. **Methods:** Studying the peculiarities of selenium recovery in sulfuric acid chromium-containing medium is an important task, which will prevent channel losses of selenium with intermediates of sulphate production at complex processing of sulfide polymetallic raw materials and thereby increase up the production. On the basis of analysis of the literature and patent data as the most promising methods for the extraction of selenium and selenium from sulfuric acid solutions, recovery methods were chosen. **Results:** The thermodynamic evaluation of the possibility of extracting selenium from sulfuric acid solutions at the temperatures of 298-348 K, with the use of sulfur dioxide and sodium sulfite proved a high probability of recovering selenite-ions  $\text{SeO}_3^{2-}$  and to a lesser extent, selenate-ions  $\text{SeO}_4^{2-}$ . The experiment on precipitation of selenium were carried out on the basis of synthetic sulfuric solutions, containing, (g/l): 5-15 Se (IV), 5 Se (VI), 60 Cr (III), 5 Cr (VI), 100-250  $\text{H}_2\text{SO}_4$ . It has been found that the temperature increase adversely affects the process of recovering selenium with sulfur dioxide, which is caused by reduction of the solubility of sulfur dioxide. The selenium selection process using sodium sulfate is characterized by significantly higher recovery rate due to removal of the diffusion constraints associated with the dissolution of sulfur dioxide. By using all studied reducing agents in the optimum conditions, almost complete recovery of selenium is ensured, selenium is at that recovered with not more than 60%.

**Conclusion:** Taking into account high rates of extraction of selenium from sulphate chrome-bearing solutions, sulfur dioxide and sodium sulfite, choice of selenium recovery, largely determined by specific features of an enterprise.

**Keywords:** Chromium, Recovery, Selenium, Sulphide Copper Ores, Washing Acid

## 1. Introduction

Due to the usage expansion in the high-tech areas in the world market before long, the increase in demand for selenium is expected, which leads to the need of developing methods of selenium removal from intermediate products of metal manufacturing. Total selenium extraction at the metallurgical enterprises is determined by the degree of complexity of using raw materials. The largest Russian manufacturers of selenium are MMC "Norilsk Nickel" (~100 tons/year), Ural Mining and Metallurgical Company (80 tons/year) and Kyshtym Copper Smeltery

(5 tons/year)<sup>1</sup>. The development of intensive high-temperature technologies of processing copper and copper-nickel raw material is accompanied by an increase in the degree of transition of selenium into the gas phase and change in its distribution among the main products-concentrators - sludge of copper electrolysis, sulfuric sludge and washing sulphuric acid<sup>2</sup>. Occurring selenium accumulation in appreciable amounts in washing sulfuric acid<sup>3</sup> determines the appropriateness of its consideration as an independent source of selenium equally with the traditional products, first and foremost, with electrolyte slimes.

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During the processing of copper rhenium – containing ores of the Zhezkazgan deposit of Kazakhstan washing acid is the main source of extraction of rhenium and radioactive osmium, the preparation of which is occurred by processing the interfacial extraction precipitations, being generated in rhenium redistribution<sup>4</sup>. Hydro metallurgical technology of extracting radioactive osmium provides for oxidative opening of extraction precipitations (upto 5000 g/mOs) in sulfuric acid medium in the presence of hexavalent chromium as an oxidant. Selenium and rhenium are thus turned into sulphate solution, wherein the chromium concentration is at the level of 60-80 g/dm<sup>3</sup>. Thus about 80% of the total chromium is the compounds of trivalent chromium and the remainder is in the form of hexavalent chromium. Selenium concentration represented by its forms at higher oxidation level in the solution with their different ratio is 5-7 g/dm<sup>3</sup>, rhenium - 1 dm<sup>3</sup>. With consideration for their full transition from interphase precipitation in the mother liquor is concentrated to 5% of rhenium and the substantial amounts of selenium from the original content in ore. Reprocessing mother sulfuric acid solutions provides for the restoration of the original solution by sodium sulfite with subsequent sorption isolation of rhenium. Introduction of recovery operation of hexavalent chromium into the flow chart is mainly directed towards the prevention of its negative impact on the subsequent sorption of rhenium, but may be considered as a promising element of the channel of extraction and concentration of selenium.

There are a number of methods of processing of selenium-containing solutions, providing a sufficiently high recovery of selenium<sup>5</sup>. At the same time, non-traditional nature of selenium production of sulfuric acid solutions with a high ionic background of chrome requires a detailed study of applicability of the known technologies.

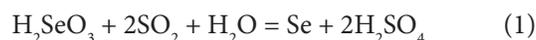
Considering that at the metallurgical enterprises the trend of transition from traditional pyrometallurgical technologies to SW-EX Technologies is observed, precluding the formation of the main sources of selenium production – anode slimes, the task of developing efficient technologies for the extraction of selenium from the solutions of different genesis is becoming increasingly important.

## 2. Working Methods

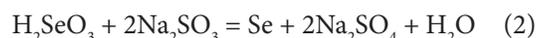
The experiments on precipitation of selenium were based on synthetic sulfuric acid solutions containing (g/l), selenium (IV) - 5-15, chromium (III) - 60. In separate

experiments, potassium dichromate based on the content of 5 g/l Cr (VI) and selenium acid based on the content of 5 g/l of Se (VI) were introduced into the solution. The sulfuric acid concentration varied from 100 to 250 g/l. The temperature change interval - 50-80° C. Sulfur dioxide and sodium sulfite were used as the reducing reagents.

For sulfur dioxide, the traditional method based on the interaction of concentrated sulfuric acid and sodium sulfite was used. Consumption of sulfur dioxide reached double excess of stoichiometry of reaction (1) and was controlled by the amount of consumed sulfuric acid.



The experiments with sodium sulfite were carried out with excess of reducing agents from 150 to 250% of the theoretically required according to the reaction (2):

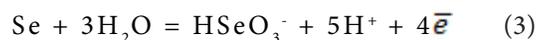


The control of red-ox-potential of the systems under study was carried out by means of platinum and saturated silver-chloride electrodes using pH millivoltmeter (pH-673). Selenium and chromium concentration in the solutions was determined by applying mass spectrometry with inductively coupled using the plasma spectrometer (ICAP-6300 Duo).

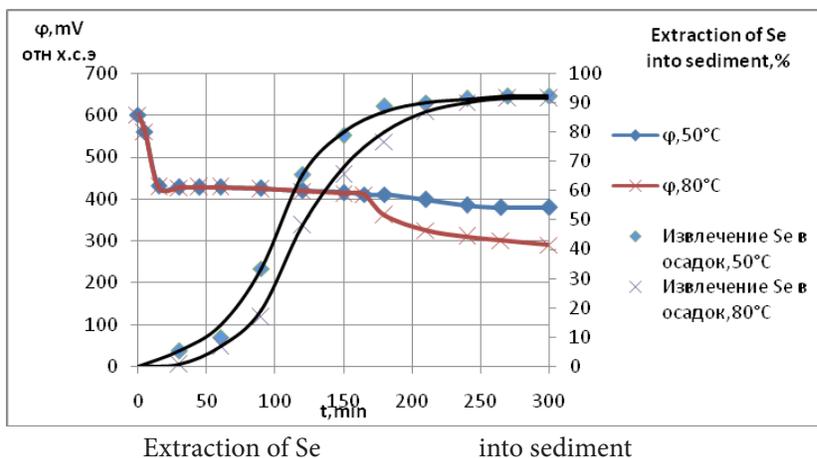
## 3. The Results of Investigation and their Discussion

The deposition of selenium (IV) with sulfur dioxide at a constant speed of its purge is accompanied by a decrease in red-ox-system potential (Figures 1, 2, 3 and 4). Considering that in the solution there are several coupled oxidation-reduction systems, the measured potentials are compromise.

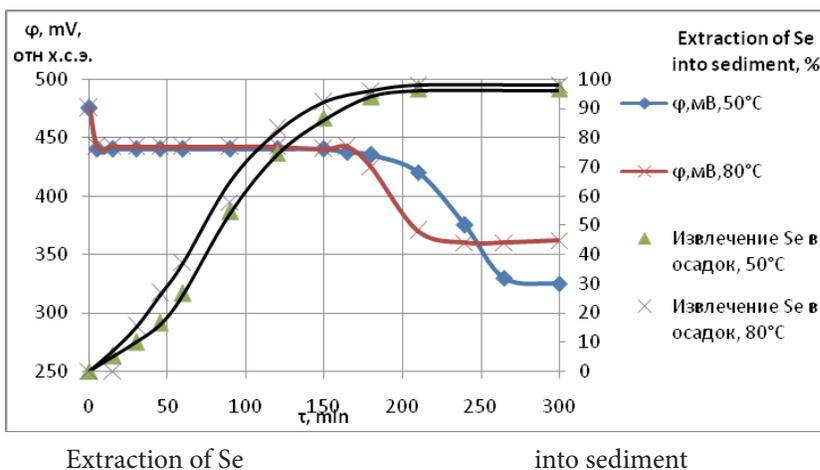
The fixed further horizontal section in the graphics dependency of potential on the time indicates further course of the process and at the same time, the fixed compromise potentials are determined by the presence in solution H<sub>2</sub>SeO<sub>3</sub> and are very close in value to the theoretically calculated ones for the given system (Table 1).



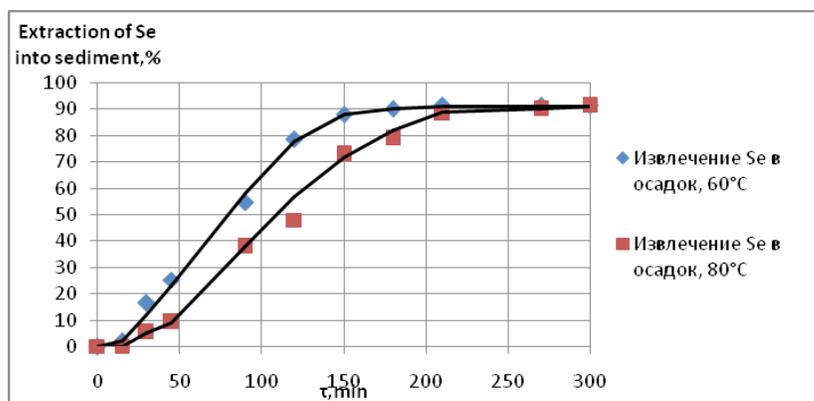
In calculating, the average value of ionic activity coefficients in sulfuric acid in a predetermined concentration, was taken constant and equal to 0.13, considering that, depending on the temperature and acid concentration it



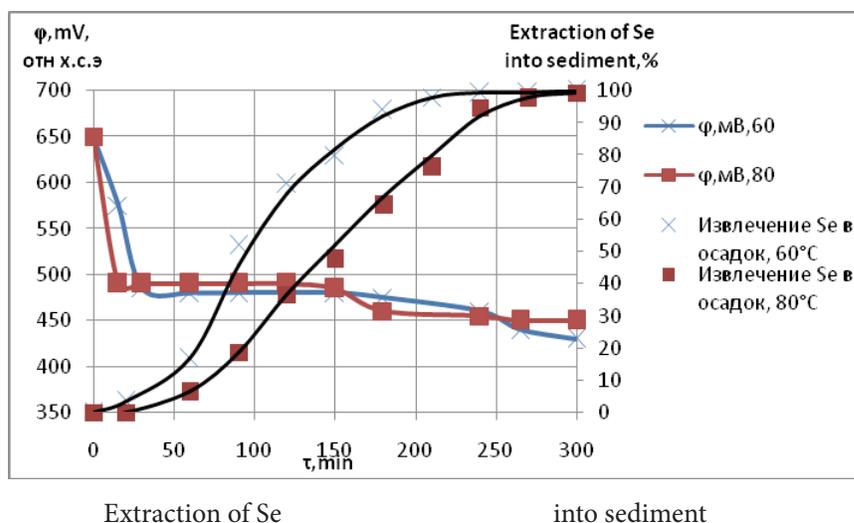
**Figure 1.** The kinetics of sedimentation of selenium (IV) with sulfur dioxide in the sulfuric acid solutions. Composition of the solution (g/l): Se (IV) -5, H<sub>2</sub>SO<sub>4</sub> -100, the experiment temperature – 50 and 80° C, the maximum sedimentation time - 5 hours.



**Figure 2.** The kinetics of sedimentation of selenium (IV) with sulfur dioxide in the sulfuric acid solutions. Composition of the solution (g/l): Se (IV) -5, H<sub>2</sub>SO<sub>4</sub> -150, the experiment temperature- 50 and 80° C, the maximum sedimentation time – 5 hours.



**Figure 3.** The kinetics of sedimentation of selenium (IV) with sulfur dioxide in the sulfuric acid solutions. Composition of the solution (g/l): Se (IV) -5, H<sub>2</sub>SO<sub>4</sub> -200, the experiment temperature 60 and 80° C, the maximum sedimentation time – 5 hours.

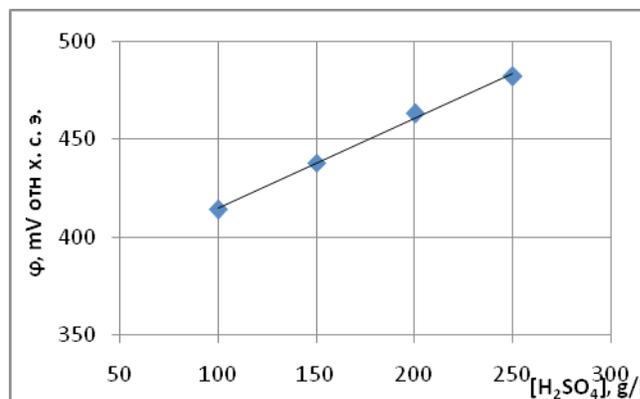


**Figure 4.** The kinetics of sedimentation of selenium (IV) with sulfur dioxide in the sulfuric acid solutions. Composition of the solution (g / l): Se (IV) -5, H<sub>2</sub>SO<sub>4</sub> -250, the experiment temperature 60 and 80 °C, the maximum sedimentation time – 5 hours.

**Table 1.** Comparison of experimental and calculated values of the red-ox potentials of the system (reaction 2)

№	Experiment conditions		φ <sub>т.р.</sub> , mV	φ <sub>эксп.</sub> , mV (rel. warter el.)
	Concentration H <sub>2</sub> SO <sub>4</sub> , g/l	Temperature, °C		
1	100	80	646	636
2	100	50	663	636
3	150	80	661	664
4	150	50	678	644
5	200	80	671	638
6	200	60	684	684
7	250	80	679	695
8	250	60	692	704

ranges within 0,086-0,151<sup>6</sup>. The calculations have shown that the potentials corresponding to the extraction of selenium (IV) from the solution are indicative of the very low content of sulfur dioxide (5 x 10<sup>-16</sup> g/l). Apparently, sulfur dioxide being added to the solution is immediately consumed to recover selenium (IV), which suggests limiting the rate of reduction process of selenium (IV) SO<sub>2</sub> with the dissolution rate. With increasing concentration H<sub>2</sub>SO<sub>4</sub>, the red-ox potential of the horizontal part of the curve increases (Figure 5), which corresponds to decrease in the quasi-stationary concentrations of sulfur dioxide and is consistent with the data<sup>7</sup>.



**Figure 5.** The dependence of the potential of reduction of selenium (IV) with sulfur dioxide on the concentration of sulfuric acid (80°C, the selenium concentration 7,5 g/l).

The second potential jump on the curves (Figures 1-4) corresponds to the end of the reduction of selenium (IV), when its concentration in the solution is close to zero. In this case, the oxidation-reduction potential of the systems being studied is determined by dissolving sulfur dioxide.

On the kinetic curves of deposition of selenium (IV) there are also initial horizontal sections, which correspond, in all probability, the formation of a new phase nucleus. With the content of sulfuric acid in the solution 100 g/l, the length of this section is maximum. Furthermore, with increasing concentrations of acid

(150-250 g/l), the time of nuclei formation remains practically unchanged.

The pieces of kinetic curves corresponding directly to a process reduction of selenium (IV) with sulfur dioxide are straight, i.e., the rate of reduction reaction is not dependent on the chalcogen concentration in the solution and the reaction (1) under the given conditions has zero order according to the selenium concentration. Thus, it has been confirmed that the limiting stage of the process (1) is the rate of dissolution of sulfur dioxide, which, in turn, is a function of many factors (temperature, concentration  $H_2SO_4$ ).

Calculation of the apparent activation energy of reduction process of selenium (IV) with sulfur dioxide with different concentration of sulfuric acid was done using the equation:

$$E^* = \frac{R \ln \frac{k_2}{k_1}}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (4)$$

Where R-gas constant, J/mol·K.

$k_2, k_1$  - Rate constants for reaction at different temperatures;

$T_2, T_1$  - Absolute temperature of the process, K.

After preliminary estimate the obtained negative values of the apparent activation energy of the process with different concentrations of sulfuric acid (-8.21, -15.22, -22.4 and -28.9 kJ/mol to 100, 150, 200 and 250 g/l  $H_2SO_4$ , respectively) indicate the complexity of the formal description of this process from the perspective of the traditional Arrhenius equation. By all appearances, a crucial role is played by the stage of absorption of sulphur dioxide with the solution, while the selenium recovery process occurs mainly in the external diffusion region.

The diffusion flux of sulfur dioxide, which characterizes the rate of external diffusion, is given in these cases by8:

$$j = \frac{D_g i C_s}{\delta} \quad (5)$$

Where  $D_g$  - Diffusion coefficient of gas in solution,  $m^{2/s}$

$C_s$  - Gas concentration in the saturated solution, g/l;

$\delta$  - Thickness of the diffusion layer at the liquid-gas boundary, microns.

Considering the reduced solubility of sulfur dioxide in sulfuric acid solutions with increasing the temperature<sup>9</sup>, it

is possible to mention reducing external gas diffusion rate in the reaction volume, which, in turn, reduces the rate of reaction (1).

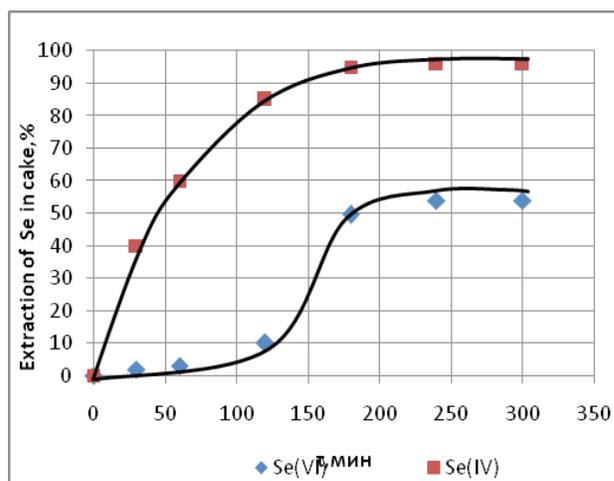
Consequently, negative values of apparent activation energy formally characterize the dependence of the rate of diffusion of sulfur dioxide on temperature.

The experiments have shown that the recovery process of selenium (IV) occurs almost completely for 3 hours at a flow rate of sulfur dioxide being equal to 150% of the theoretically required according to the reaction (1).

The ratio of forms of selenium of higher oxidation levels in chromium-containing sulfuric acid solutions of processing osmium intermediates is estimated by current parameters of oxidation process and according to analytical data on the composition of the solutions is within Se (IV): Se (VI) = 5:1÷1:1.

The results of experiments conducted with synthetic solutions at the ratio of concentrations  $C_{Se(IV)} : C_{Se(VI)} = 1:1$  show that significant precipitation of hexavalent selenium begins after isolation of the basic (about 80%) portion of Se (IV) and does not exceed 54% for 3 hours at total extracting selenium being not higher than 80% (Figure 6).

The concentration of chromium (III) in the synthetic solution is 60 g/l. In the solutions Cr (III) forms neutral, negatively and positively charged complexes with coor-

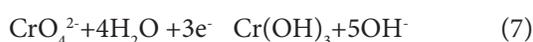
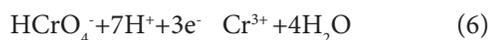


**Figure 6.** Isolation of selenium of the higher oxidation states from the chromium sulphate solution in the presence of sulfur dioxide.

Composition of the solution (g / l): Se (IV) - 5, Se (VI) - 5, Cr (III) - 60, sulfuric acid-200, the temperature is 50°C, the maximum sedimentation time - 5 hours, sulphur dioxide flow - 300% (reaction 1).

dination number 6 and octahedral configuration, the relative amounts of which depend on the composition of the solutions. The complex with an ions  $\text{SO}_4^{2-}$  refers to such complexes<sup>10</sup>. Visible influence of Cr (III) on the parameters of extraction from the sulfuric solution of Se (IV) has not been detected.

According to<sup>11</sup>, in acidic media the predominant form of chromium (VI) is  $\text{HCrO}_4^-$ . Recovery of  $\text{HCrO}_4^-$  in acid media is accompanied by absorption of  $\text{H}^+$  (6), however, the reduction of potential is influenced not only by reduction of chromium concentration but lowering acidity of medium.

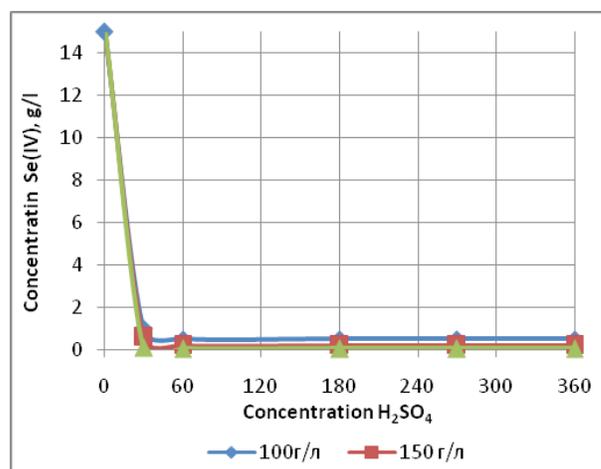


The presence of hexavalent chromium in solution in a relatively low concentration does not significantly alter the initial red-ox potential of the studied system (red-ox equilibrium potential varies in the range 550-620 mV relative to water el.). Sulfur dioxide purge of synthetic sulphate solution containing 60 g/l of Cr (III), 5 g/l of Cr (VI), 5 g/l of Se (IV) and 1 g/l of Se (VI) at the temperature of 50° C for 3 hours (total reductant consumption to 300%) provides the complete recovery of hexavalent chromium and selenium isolation to 90% in the form of prone to clumping black-gray deposits.

When using sodium sulfite regardless of acidity within the first 5-10 minutes a sharp reduction of the concentration of selenium (IV) in the synthetic solution from 15 g/l to 0.5-1.0g/l is observed. This indicates a significantly greater velocity of the process of selenium recovery with sodium sulfite as compared with sulfur dioxide (Figure 7).

Increasing the rate of reduction-oxidation reaction is conditioned by the removal of diffusion constraints associated with the dissolution of sulfur dioxide. Influence of the acidity of the medium affects the depth of discharge of selenium (IV) at low residual concentrations in the solution. The sulfuric acid concentration of 200 g/l is optimum, providing deposition of selenium to residual concentration of 0,05-0,03 g/l. One and a half excess of sulfite ensures high extraction of selenium (IV) into the crude product.

With the presence of chromium (VI) in the synthetic solution, high recovery of selenium into filter cake is stored under optimal parameters of reduction process. At the same time, the degree of reduction of hexavalent chromium to trivalent state reaches 95-97%<sup>12</sup>.



**Figure 7.** Sedimentation of selenium (IV) with sodium sulfite.

Composition of the solution (g/l): Se (IV) -5,  $\text{H}_2\text{SO}_4$  - 100, 150 and 200 g/l, the temperature is - 50° C, the maximum sedimentation time - 6 hours, sodium sulfite consumption - 150% of the theoretically required according to reaction 2.

The conducted experiments have shown in the reduction of selenium (IV) from synthetic sulphate solutions with sodium sulfite, the optimal process conditions must be considered the following: the concentration of sulfuric acid-200 g/l and above, the temperature - 50° C, duration -30 min, 1,5- fold reductant consumption<sup>13</sup>.

The use of sodium sulfite to process sulfuric acid solution under these conditions, obtained after hydrothermal distillation of tetraoxidaosmy with Chromium Oxide  $\text{CrO}_3$  from interfacial precipitate (0,91% Se, 5,6% Re, 5160 g/t Os), provides a quantitative recovery to 92, 5% of the tetravalent form of selenium and less than 48% Se (VI), as well as a full transfer of hexavalent chromium into trivalent state. The total selenium extraction from the mother liquor characterized by the ratio of selenium forms  $C_{\text{Se(IV)}} : C_{\text{Se(VI)}} = 5:1$  is 90-92%.

## 4. Summary

The main results of the conducted investigations are as follows:

- Extraction of selenium from the sulfate solutions of osmic redistribution is determined by the ratio Se (IV):Se (VI) which depends on the parameters of the process of oxidation of extraction precipitates and is within 5:1÷1:1.

- The use of sulfur dioxide allows to provide almost complete recovery of selenium (IV) from the sulfuric acid solution and about 55% of selenium (VI) at the temperature of 500 C, the sulfuric acid concentration of 150-200 g/l for 3 hours and reductant consumption being equal to 150-200% of the theoretically necessary.
- The negative effect of temperature on the process of reduction of selenium with sulfur dioxide is conditioned by a decrease of solubility of sulfur dioxide with an increase of temperature, 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 in the studied range of acidity) of recovery of selenium with sulfur dioxide formally characterize the dependence of the rate of diffusion of sulfur dioxide into the solution on the temperature of process.
- The process of separation of selenium using sodium sulfite is characterized by significantly higher recovery rate, which is due to the removal of diffusion constraints associated with the dissolution of sulfur dioxide. Within 30 min with the acidity of 200 g/l of H<sub>2</sub>SO<sub>4</sub>, at 50° C and 1,5 times consumption of the reducing agent it is ensured reduction to 92.5% of tetra-valent form of selenium and not at least 48% of Se (VI).
- High consumption of sulfur dioxide, the process duration and the need of hardware solutions to a certain extent may complicate the industrial implementation of this variant. The choice of reduction method will largely be determined by the specific features of the enterprise.

## 4. Conclusion

The research results allow us to recommend the use of deposition of selenium in elemental form of the sulfate solution with sulfur dioxide or sodium sulfite in the hydrometallurgical flow sheet of processing solid products of washing acid, which will prevent the permanent losses of chalcogene. The application of reduction methods will provide the level of extraction of selenium not less than 80%. The solution refined from selenium is advisable to send for the sorption selection of rhenium, the high extraction rate of which is determined by the absence of negative impact of preliminary derived macro admixtures - selenium and chromium.

## 5. References

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