Determination of the sorption characteristics of ammonium perrenate ions on anion exchange resin AV-17-8

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Abstract. The article considers one of the aspects of the processing of copper waste, containing in addition to a significant amount of copper several dispersed elements, one of the most interesting for extraction is rhenium. The dynamic and full dynamic sorption capacity of the sorbent AV-17-in case of perrhenate ions from ammonia solutions of leaching of copper smelting was determined.

1. Introduction
The accumulated volumes of copper-containing technogenic mineral resources in Russia practically correspond to the volumes of minerals on the balance of deposits. In the metallurgical industry, more than 95 million tons of slag is produced annually, of which more than 10% is in copper production. Thus, in the current situation, there is a problem to develop ways of raw material base processing with the involvement of technogenic mineral resources.

Metallic rhenium is a strategically important raw material. More than 83% of the rhenium is used to create heat-resistant alloys and super-alloys used in the manufacture of rocket and aircraft engines. About 9% of the rhenium is used in the production of Pt-Re catalysts for oil refining processes, for example, the production of high-octane gasolines, hydrodesulfurization processes. Rhenium is used in the manufacture of thermocouples, heating elements, electrodes, electrical connectors, electromagnets, as well as in organic synthesis, catalysis and medicine. The low content and dispersion of rhenium in the earth's crust is $7 \cdot 10^{-8}\%$, of which not more than 25% are referred as recoverable [1].

In Russia, unconventional sources containing rhenium as an associated component include copper-pyrite deposits, copper-nickel deposits, uranium-noble metal-vanadium deposits, carbonaceous rocks, fumarole gases and near-ore rocks. The total reserves of rhenium in unconventional sources of raw materials in the Russian Federation are estimated at more than 350 tons. The most promising of which are copper-nickel deposits, which account for 55% of the estimated unconventional sources of raw materials. Many modern copper smelters are developing technologies for the integrated processing of technogenic waste, including copper sludge. The most promising processing technology is the hydrometallurgical method, namely, leaching of sludge, with further sorption extraction [2 - 9].

The solution obtained after leaching of copper sludge is sent to the stage of purification and separation of pure rhenium, most often in the form of ammonium perrenate. Subsequently, ammonium perrhenate is converted into the form of metallic rhenium. One of the most promising technologies for the associated extraction of rhenium in the form of a perrenate ion is ion-exchange sorption, since rhenium is a dispersed element, and sorption is actively used for the selective extraction of low-
concentration components. To develop effective industrial technology, it is necessary to determine the thermodynamic, kinetic and technological parameters of the ion-exchange process [9-12].

2. Research methods
In the work, the process of sorption of perrenate ions from model and technological solutions for the processing of slag from copper smelting was studied. The industrial anion exchange resin AV-17-8 was chosen as the most promising for the extraction of anion exchange resin from a multicomponent solution of ammonia leaching of copper smelting slags. Before studying the characteristics of ion exchange, anion exchange resin was converted to the chloride form. The setup for studying ion-exchange sorption consisted of a Liebig refrigerator with a diameter of 8 mm with a fiberglass filter installed at the base. The height of the ion exchanger layer was 10 cm. The solution was supplied from above through hoses from a thermostatically controlled vessel, forming a system of communicating vessels with a column. The solution was pumped using a re-static pump mounted on the outlet hose. The rotational speed was 0.9 rpm, which created a linear solution transmission rate of 2 ml · min⁻¹ in this system. The extraction column and the container with the working solution were thermostated using a Huber thermostat operating along the external circuit. After passing through the column, the solution was taken into 10 ml volumetric cylinders. The volume of the sample taken was 6 ml, which made it possible to make a guaranteed selection of a 5 ml aliquot for analysis with a Mohr pipette. Further analysis of the content of perrenate ions in the sample was carried out by photometry with antimony chloride and potassium thiocyanate. For the slip, the rhenium content in the solution at the column exit was 10% of the initial rhenium content [4,5].

3. Research results
During the experiment, experimental data on the sorption of perrenate ions from model and technical solutions of ammonia leaching of copper slag on anionite AV-17-8 were obtained. The sorption process was carried out under thermostatic conditions at a constant temperature of 20°C. the concentration of impurity sulfate ions interfering with the sorption of perrenate from technological solutions was changed in the model solutions. Sorption dependences obtained as a result of the experiment are shown in figure 1.

The dynamic exchange capacity (D) in moles per cubic meter was calculated by the formula:

$$D = \frac{V_f \cdot C \cdot 1000}{V_i}$$

where

- $V_f$ is the total volume of the filtrate passed through the ionite until the ions of the working solution appear, cm$^3$;
- $C$ - concentration of the working solution, mol · dm$^{-3}$;
- $V_i$ - volume of ionite, cm$^3$.

The full dynamic exchange capacity ($D_p$) in moles per cubic meter was calculated by the formula:

$$D_p = \frac{(V_f \cdot C - V_p \cdot C_p) \cdot 1000}{V_i}$$

where

- $V_f$ is the total volume of the filtrate passed through the ionite to equalize the concentrations of the filtrate and the working solution, cm$^3$;
- $C$ - concentration of the working solution, mol · dm$^{-3}$;
- $V_p$ - the volume of the filtrate portion after the appearance of ions of the working solution, cm$^3$;
- $C_p$ is the concentration of the solution in a portion of the filtrate after the appearance of ions of the working solution, mol · dm$^{-3}$;
- $V_i$ - volume of ionite, cm$^3$. 
Figure 1. Ion-exchange isotherms the process of adsorption of perrhenate ions by anion exchanger AV-17-8 in the environment of the hydroxide and ammonium sulphate: 1 - \([\text{ReO}_4^-] = 0.039 \text{ M}; [\text{NH}_4\text{OH}] = 0 \text{ M}; [(\text{NH}_4)_2\text{SO}_4] = 0 \text{ M}\); 2 - \([\text{ReO}_4^-] = 0.039 \text{ M}; [\text{NH}_4\text{OH}] = 3.000 \text{ M}; [(\text{NH}_4)_2\text{SO}_4] = 0 \text{ M}\); 3 - \([\text{ReO}_4^-] = 0.039 \text{ M}; [\text{NH}_4\text{OH}] = 1.200 \text{ M}; [(\text{NH}_4)_2\text{SO}_4] = 0.900 \text{ M}\).

The obtained values of dynamic and total dynamic sorption capacity are presented in table 1.

| Solution composition          | Dynamic exchange capacity \((D)\), g \cdot mol \cdot m^{-3} | Full dynamic exchange capacity \((D_F)\), g \cdot mol \cdot m^{-3} |
|-------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
| \([\text{ReO}_4^-] = 0.039 \text{ M}; [\text{NH}_4\text{OH}] = 0 \text{ M}; [(\text{NH}_4)_2\text{SO}_4] = 0 \text{ M}\) | 1431.46                                                       | 2524.52                                                       |
| \([\text{ReO}_4^-] = 0.039 \text{ M}; [\text{NH}_4\text{OH}] = 3 \text{ M}; [(\text{NH}_4)_2\text{SO}_4] = 0 \text{ M}\) | 1161.97                                                       | 2354.92                                                       |
| \([\text{ReO}_4^-] = 0.039 \text{ M}; [\text{NH}_4\text{OH}] = 1.2 \text{ M}; [(\text{NH}_4)_2\text{SO}_4] = 0.9 \text{ M}\) | 991.78                                                        | 3018.22                                                       |

Table 1 shows that the addition of ammonium sulfate significantly affects the total capacity of the ion-exchange sorbent, but significantly reduces the dynamic exchange capacity. The addition of ammonium sulfate within 0.9 mol \cdot l^{-1} reduces the dynamic exchange capacity from 1431 g \cdot mol \cdot m^{-3} to 991 g \cdot mol \cdot m^{-3}. This sorbent has a high selectivity to ions perrhenate, which allows you to use it to highlight Rennie from solutions obtained by leaching the slag of copper smelting production.

4. Conclusions
The dynamic and full dynamic sorption capacity of the sorbent AV-17-8 with respect to perrenate ions from ammonia solutions in the presence of sulfate anions were determined. It is established that the dynamic sorption capacity of perrenate ion dropped from $1431 \text{ g \cdot mol} \cdot \text{m}^{-3}$ to $991 \text{ g \cdot mol} \cdot \text{m}^{-3}$ after adding to solution ammonium sulfate to a concentration of $0.9 \text{ mol} \cdot \text{l}^{-1}$. It is established that the sorbent AV-17-8 is capable of effectively removing ammonium perrenate ions from solutions of complex salt composition containing up to $0.9 \text{ mol} \cdot \text{l}^{-1}$ of ammonium sulfate.

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