EXTRACTION OF RHENIUM FROM AMMONIACAL LEACHING SOLUTIONS OF COPPER SMELTING SLAG AND MODEL SOLUTIONS

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ABSTRACT. It is known that copper ores and waste of copper production often contain rhenium. In some deposits or dumps, its quantity is sufficient to recognize this raw material as profitable for obtaining rhenium in various forms. Rhenium has the status of a strategic raw material; it is used in the creation of refractory alloys and catalysts of the oil refining industry. At the moment rhenium is not produced in the Russian Federation. One of the options for obtaining rhenium is its extraction from leaching solutions of metallurgical slags. The most rational method of extraction is sorption on the ion exchange sorbent perrenate-ion. This process can significantly increase the profitability of copper slag processing. In the course of the work, the effect of various components of the solution on sorption of perrhenate-ion on an ion-exchange sorbent AV-17-8 was studied.

Keywords: perrhenate-ion, sorption, rhenium, hydrometallurgy

ЕКСТРАКЦИЯ НА РЕНИУМ ОТ АМОНЯЧНИ ИЗЛУЖВАЩИ РАЗТВОРИ НА РАЗТОПЕНА МЕДНА ШЛАКА И МОДЕЛИ НА РЕШЕНИЯ
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РЕЗЮМЕ. Известно е, че медните руди и отпадъците от производството на мед често съдържат рений. В някои находища или сметища неговото количество е достатъчно, за да се приеме тази суровина като рентабилна за получаване на рений в различни форми. Реният има статут на стратегическа суровина; използва се при създаването на огнеупорни сплави и катализатори в нефтопреработвателната промишленост. В момента рений не се произвежда в Руската федерация. Една от възможностите за получаване на рений е извличането му от разтворите за излужване на металургични шлаки. Най-рационалният метод за екстракция е сорбция на йонообменния сорбент перренат-йон. Този процес може значително да повиши рентабилността на обработката на медната шлака.В хода на работата е изследвано въздействието на различни компоненти на разтвора върху сорбцията на перренат-йон върху йонообменния сорбент AV-17-8.

Ключови думи: перренат-йон, сорбция, рений, хидрометалургия

Introduction

In recent decades, the abundance of natural resources has been significantly depleted. In addition, dumps and "waste" deposits are a long-term source of environmental pollution due to the spontaneous leaching of metals from them. Therefore, to solve these problems, many copper smelters aim at the introduction of technology for processing of copper smelting slurries. The main advanced technology is hydrometallurgical processing, namely the leaching of sludge. In addition to the main component – copper, it can extract by-products such as rhenium, which is found in the composition of copper-molybdenum ores (Luganov, 2004).

Rhenium is a typical dispersed element that does not form independent minerals. Mostly, rhenium is found in molybdenum and copper-molybdenum ores, which are currently its main sources.

The reserves of Russian rhenium are estimated at 310 tons, this is the 3rd place in the reserves worldwide. However, according to some data, there is no mass production of rhenium at the moment in the Russian Federation. This makes the issue of creating and implementing a cost-effective technology for its production even more acute, since rhenium is a strategic raw material. Rhenium is currently in demand in the industry. A significant step in the production of rhenium is the production of ammonium perrenate by sorption-elution processes with further cleaning. In the future, ammonium perrenate is converted in the form of metallic rhenium. Metal rhenium is a strategically important raw material. 83.3% of the produced rhenium is used to create heat-resistant alloys and super-alloys used in the manufacture of rocket engine nozzles and rotating parts of aircraft engines, as well as in energy. 9.3% of the produced rhenium is used in the production of Pt-Re catalysts for oil refining processes, for example, the production of high-octane gasoline, hydro desulphurisation processes. Rhenium is used in the production of thermocouples, heating elements, electrodes, electrical connectors, electromagnets, as well as in organic synthesis, catalysis and medicine. The main forms of rhenium used are rhenium, rhenium perrenate and renic acid.

Due to the fact that rhenium is a concomitant element, methods for obtaining rhenium as a by-product are now in demand since this can significantly increase the profitability of obtaining waste elements such as copper.

The accumulated volumes of copper-containing technogenic mineral resources in Russia practically correspond to the volumes of minerals put on the balance of deposits. Only in the metallurgical industry more than 95 million tons of slag are produced from them annually, more than 10% are in the copper metallurgy. In this situation, it is necessary to find ways to develop the copper raw material base with the involvement of man-made mineral resources, primarily through the improvement of existing technologies for their enrichment.

One of the most accessible resources for copper is slag of copper smelting metallurgical enterprises in the Urals. The Ural region is called the "copper belt" of Russia and it has accumulated a significant number of them over a long period. The predominant factors of the involvement of slag in processing are economic benefits, which are determined by the possible profit of the enterprise and environmental feasibility, which is expressed in terms of environmental performance. In total, the Ural region has accumulated more than 110 million tons of copper slag.

One of the most promising technologies for the associated extraction of rhenium is the ion exchange sorption, as it is effective for the extraction of dispersed components. In addition, sorption processes can have high selectivity, and can be easily integrated into the process cycle. To create the technology and select the sorbent, it is necessary to determine the thermodynamic and kinetic parameters of the ionite.

Review and selection of the analysis method

For the development of technologies related to the recovery of rhenium from the leaching solution a methodology is necessary to determine its content in the samples. It should be noted that the content of rhenium in raw materials is extremely low. What causes the choice of those techniques that are able to provide high accuracy?

Spectrophotometry, gravimetry, kinetic, electrochemical, extraction-fluorimetric methods as well as X-ray fluorescence analysis are used as the main methods for the determination of rhenium.

The main problems of most methods for the determination of rhenium are their lack of sensitivity, reproducibility of the results, and the interfering influence of accompanying elements of the sample. In modern analytical chemistry, methods such as inductively coupled plasma atomic emission spectroscopy (ICP AES), inductively coupled plasma mass spectrometry (ICP MS), as well as a number of electrochemical methods are used to determine rhenium.

However, the main problem that a researcher encounters when using these methods is the influence of incidental sample components. In view of this, the question of concentrating rhenium and separating it from the matrix is extremely important.

Spectrophotometric methods make it possible to determine the content of rhenium in a sample up to 10^{-2}–10^{-5} wt. %. The

advantage of these techniques lies in the simplicity, availability of equipment and relatively high sensitivity. Spectrophotometric techniques are based on the formation of coloured complex compounds of rhenium with appropriate reagents. The distributed methods use rodanide and thiocyanate ions, thiourea. The disadvantage is the need for preliminary separation of rhenium from interfering with the determination of impurities (Mo, W, Cu). This is carried out by concentrating the perrhenate ions by sorption or extraction.

Atomic emission spectroscopy with inductively coupled plasma (AES-ICP) is used to determine rhenium in mineral raw materials and metallurgical products. The advantage of AES-ICP is high stability and reproducibility of results, a wide linear range of concentrations. The method allows to determine up to 10^{-4} wt. % rhenium. However, the correctness of the results of analysis in atomic emission spectrometry with inductively coupled plasma depends on many factors, for example, related to the physical properties of the solutions — their viscosity, surface tension, etc.; with chemical interaction of the sample components; with the superposition of the spectral lines of the sample components and with the negative effect of plasma ionisation. The determination of rhenium by AES-ICP in complex objects, for example, products of metallurgical production, is a difficult task, since the emission lines of rhenium are not very sensitive, moreover, they partially overlap with the lines of accompanying elements.

Nowadays, ICP-MS allows rhenium to be determined at the ng/g level. However, when using ICP-MS, a number of problems arise associated with the influence of various factors on the formation of an analytical signal. The accuracy of the method is affected by the matrix, signal drift, saline background, and isobar overlays.

Over the past decade, the X-ray fluorescence method (XRF) has not lost its relevance for the determination of rhenium. It is fast and often used for mass analysis in industry. However, the method is not without flaws: firstly, the detection limit of rhenium by XRF is low and is only 0.05–0.1 wt.%, Secondly, there is a problem associated with interfering influence from the associated sample components. The use of concentration allows not only to lower the detection limit in the X-ray phase analysis method, but at the same time to reduce the influence of interfering elements on the rhenium signal. For the concentration of rhenium the XRF methods often use sorption of rhenium in the form of perrhenate ions.

A significant place in the analytical chemistry of rhenium is occupied by the electrochemical methods, in particular, inverse voltammetry. This method can determine up to 10^{-6}–10^{-5} wt.% rhenium. The first stage of the inversion voltammetry method is the electrochemical reduction of perrhenate ions on the surface of a graphite electrode, which takes place in two stages, while rhenium is deposited in two forms - in the form of ReO_2 and Re_0. Then, the precipitate concentrated on a graphite electrode is subjected to anodic dissolution, while on the voltammograms there are two anodic oxidation peaks, the peak currents and the areas under the peaks are proportional to the concentration in the analysed solution. In the determination of rhenium by the method of inversion voltammetry, metal ions, which occupy a position higher on the scale of standard potentials than the perrhenate ion, interfere. (Lakernik, 1957; Evdokimova, 2012)

Table 1. *The composition of the solution after leaching the slag with an aqueous solution of 3M ammonia*

C, g/l			C, mg/l			
Cu	Zn	SO_4^{2-}	Fe	Pb	Re	Ag
17.4	2.3	61.8	<0.1	<0.1	1.0	23.7

Table 1 shows the main components of the leaching solution, as well as their concentration. This composition allows the use of photometric analysis methods for the solution after the extraction of copper extraction. In addition, this method is an affordable and effective option for the analysis of model solutions.

For the selected method, the results were consistent with the ICP MS results.

Dynamics of perrhenate sorption with the sorbent AV-17-8

At this stage, a study was made of the dynamics of sorption on the AB-17-8 anion exchange resin on model solutions with varying composition of model solutions:
1) Model ammonium perrhenate solution.
2) Model solution of ammonium perrhenate in the environment of ammonium hydroxide 3M.
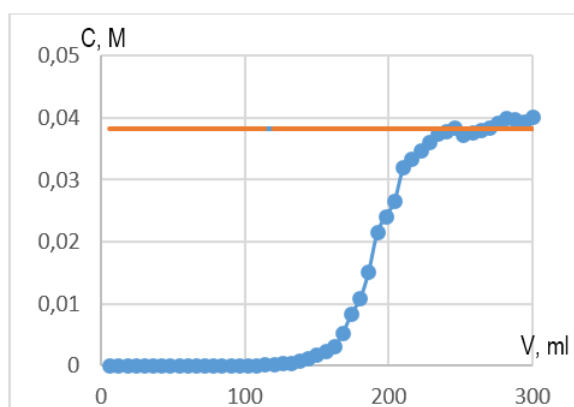3) Model solution of ammonium perrhenate in the environment of ammonium hydroxide 1.2 M and ammonium sulphate 0.9 M.

Fig. 1. Output sorption curve of solution N1

Anion exchanger AV-17-8 is a strongly basic ion-exchange resin with gel structure. It is used in the technology for softening and water desalination. AV-17-8 is pre-converted to chloride form. The experiment was carried out in a thermostated unit: T = 20°C sampling every V = 6 ml. The full exchange capacity according to the regulations is: FEC_{theory}=1.15 mol/l.

As we can see, in the presence of sulphate ions, FDEC remains at the same level. In addition, it was found that for perrhenate ion the capacity of this ion exchange resin exceeds the capacity declared by the manufacturer. This allows to consider this resin for use not only in water treatment, but also for extracting valuable components like rhenium. Also, a series of trial experiments allows us to supplement this conclusion with the fact that the ion exchange technology allows one to selectively extract the perrhenate from the technological leaching solution.
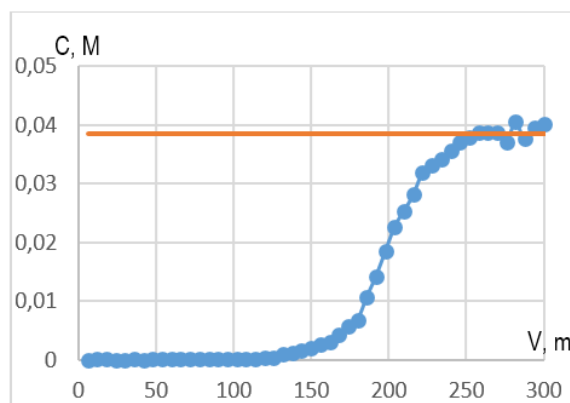

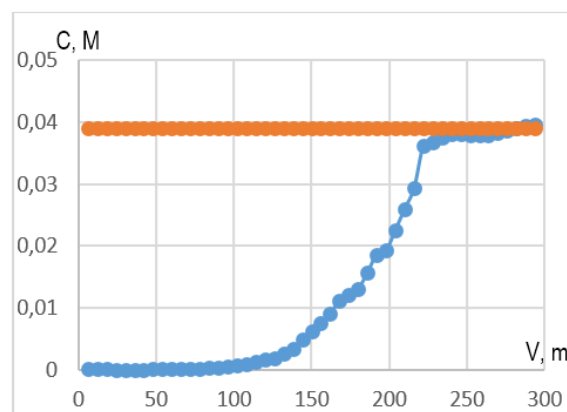**Fig. 2. Output sorption curve of solution N2**

Fig. 3. Output sorption curve of solution N3

Figure 1-3 shows the results of sorption. Based on these data, the values of full dynamic exchange capacity were obtained. These data are presented in table 2.

Table 2. *Full dynamic exchange capacity for different compositions of the solution*

	ReO_4^-	ReO_4^- + C(NH$_4$OH)=3M	ReO_4^- + C(NH$_4$OH)=1,2M C((NH$_4$)$_2$SO$_4$)=0,9M
FDEC, mol/l	1.91	1.78	1.91

The obtained data will allow further comparison with other ion exchange resins and calculate the technological installation for the associated extraction of rhenium.

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