

Research Article

Extraction of Rhenium from Lead Sludge of Copper Production

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The article presents the results of oxidative leaching of lead sludge from copper production in order to extract rhenium into solution. The optimum regimes for product leaching man-made product in the presence of sodium peroxocarbonate $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ has been established: Experimental work was carried out under the following conditions: oxidant consumption 5% by weight of the raw material, leaching temperature 70°C, duration 30–60 minutes, stirring speed 200 rpm, and the ratio of liquid to solid $S:L = 1:3$. The degree of extraction of rhenium into the solution is 95–97%, and the content reaches 500–520 mg/L Re.

1. Introduction

Rhenium is an extremely rare refractory metal (melting point: 3185°C) and is one of the most sought-after metals in the world. Unique properties of rhenium combining high melting point and plasticity are used to create superalloys for the aircraft and missile industries. Rhenium is an indispensable component superalloy. Increasing the content of rhenium in superalloys and sharply increasing demand in the past determine its demand [1]. World production of rhenium is focused on copper-molybdenum and copper ores; in processes of oxidative roasting of concentrates, rhenium is converted to subsoil and captured in wet gas systems. 80% of sources of rhenium raw materials are molybdenum and copper sulfide concentrates, produced by Chile, Kazakhstan, France, Germany, Russia, the U.S., China, Great Britain, the Netherlands, and Poland [2]. In recent decades, nickel-based monocrystalline superalloys have been used for gas turbine blades and jet engines, which require thermal efficiency, oxidation resistance, and mechanical strength [3].

From acidic solutions of gas-collecting systems, rhenium is extracted by extraction-reextraction or sorption-

desorption methods in the form of commercial salt [4]. In the process of processing of ore mass and concentrates, rhenium is also distributed between intermediate production products (dusts, sludge, mother and circulating solutions, and interphase sediments) [5–7]. Due to significant content of rhenium in them, they are promising industrial sources.

The last stage of rhenium extraction involves sorption, extraction, or precipitation from solutions of perrhenate anion (ReO_4^-) in the form of ammonium or potassium perrhenate [8]. In this regard, the extraction of rhenium from solid technogenic waste should consider the oxidation of rhenium into higher oxides and their transfer into productive solutions. In technogenic dust and sludge, rhenium can be in the form of lower oxides and sulfides (ReO_2 , ReO_3 , ReS_2 , Re_2S_7) [9] and also in the form of higher oxides or perrhenate compounds of non-ferrous metals passing into dust and sludge as a result of chemisorption or absorption due to the developed surface of solid waste [10]. The proposed methods of rhenium extraction from technogenic industrial products include oxidizing roasting for transferring rhenium into the gas phase in the form of higher

TABLE 1: The chemical composition of lead sludge.

Element	Pb	Cu	Zn	Hg	As	Se	Fe	Cd	I	Re	Organics
Composition (%)	56.27	0.37	0.11	0.23	0.11	0.33	0.27	0.07	0.03	0.16	5.54

oxide Re_2O_7 or leaching in the presence of oxidizing agents to obtain productive solutions of rhenium. Potassium permanganate, manganese concentrate, calcium and sodium hypochlorite, hydrogen peroxide, and other oxidants are used as oxidants [11–14].

Oxidizing roasting is carried out at temperatures of 500–800°C, acid or water leaching is carried out at 50–100°C, and the oxidizer consumption varies from 5 to 50% depending on the content of rhenium and mineralogical composition of raw materials. The degree of extraction of rhenium in the target products is 80–99.5%.

The purpose of this article is to study the process of oxidative leaching of lead sludge from copper production in order to effectively extract rhenium into the solution. Lead sludge contains 600–1200 g/t of rhenium and is considered to be an additional source of the rare metal; besides, lead sludge contains 3–15% of organic substances that complicate interactions of the oxidizer with low-valent compounds of rhenium. Also, during the oxidation of sludge by hydrogen peroxide solutions, abundant foaming is observed that complicates the management of the process [15].

The novelty of the study is the study of the extraction of rhenium from lead slurry containing complex organic compounds in order to transfer it into solution. Also, a leaching process in the presence of sodium peroxocarbonate $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$. Sodium peroxocarbonate is known in applications for oxidation and decomposition of organic substances. Since the recovery of rhenium from lead sludge primarily involves the removal of organic matter, treatment of raw materials with this type of oxidizer is considered appropriate. The removal of organics from the waste is usually solved successfully by calcination or roasting of the raw material, but this method requires efficient gas purification systems when roasting lead sludge due to the transfer of significant amounts of CO_2 , mercury, and arsenic to the gas phase.

2. Experimental

Lead sludge was taken for research work. The chemical composition of lead sludge is shown in Table 1.

Oxidative leaching of sludge was carried out with sodium peroxocarbonate solution of various concentrations of 5–20% $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2$, temperature range of 50–90°C, ratio of T : L = 1 : 3–5, and stirring speed of 50–300 revolutions per minute.

The experimental work was carried out in the following order: 100 grams of lead sludge was placed in a 500 ml flask, then the required amount of sodium peroxocarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2$) solution of various concentrations was added, the flask was heated with a laboratory heating plate PL-1818 to the desired temperature, and stirring the reaction mixture was performed with a stirring device PE-830. After completion of the leaching process, the suspension was

filtered, and the solution and the leach cake were analyzed for the content of rhenium and other elements. Then, rhenium was extracted from solution by recrystallization in the form of ammonium perrhenate. Sorption-desorption was performed on anion-exchange resin MTA-170 of porous structure.

X-ray phase analysis of lead sludge showed that its basis is lead sulfate—82.7% and a small amount of lead carbonate—17.3% as shown in Figure 1. The organic inclusions in sludge are presented by oil fraction $\text{C}_8\text{-C}_{13}$ in Figure 2 and Table 2.

The chemical composition of the sludge, except for rhenium and osmium, was carried out on an atomic absorption spectrometer (AAS, Agilent 240AA, USA).

X-ray phase analyses of the initial slurry and cake after leaching were carried out on an automated diffractometer DRON-3 with CuCa-radiation, β -filter. Diffractogram operating conditions: $U = 35 \text{ kV}$; $I = 20 \text{ mA}$; $\theta\text{-}2\theta$; detector 2 deg/min. X-ray phase analysis on a semi-quantitative basis was performed on powder sample diffractograms using the method of equal weights and artificial mixtures. Quantitative ratios of crystalline phases were determined. The interpretation of diffractograms was carried out using data from the ICDD: Powder Diffraction File (PDF2) of impurity-free powder diffraction minerals.

The organic component of the slurry was analyzed by gas chromatography with mass spectrometric detection (Agilent 6890N/5973N, Agilent Technologies, Inc., 2850 Centerville Road Wilmington, DE 19808-1610, USA). A slurry sample weighing 2 g was placed in a 20 mL roll. The preincubation time was 30 min. Extraction of volatile organic compounds was performed with a divinylbenzene/carboxin/polydimethylsiloxane (DVB/CAR/PDMS) coated solid-phase microextraction fiber, with an extraction time of 15 min and an extraction temperature of 50°C. Fibers were desorbed in the sample introduction apparatus of a gas chromatograph in the mode without flow splitting at an evaporator temperature of 240°C. Separation of analytes was performed on a DB-WAXETR capillary chromatography column (Agilent, USA). Carrier gas rate (helium) 1 mL/min, column thermostat temperature: 40°C (exposure time 10 min), heating to 240°C at a rate of 10°C/min (exposure time 10 min). The total chromatography time was 40 min. The interface, quadrupole, and MSD ion source temperatures were 250, 150, and 230°C, respectively. The detection mode was ion monitoring in the m/Z 10–550 range.

Elemental analysis was performed using energy dispersive X-ray fluorescence spectroscopy on an INCA Energy 450 energy dispersive microanalytical system mounted on a JSM 6610 LV scanning electron microscope, JEOL, Japan. Determination error was 0.01%.

IR spectroscopy of rhenium-saturated anionite was performed on a Nicolet IS5 Thermo Scientific IR-Fourier

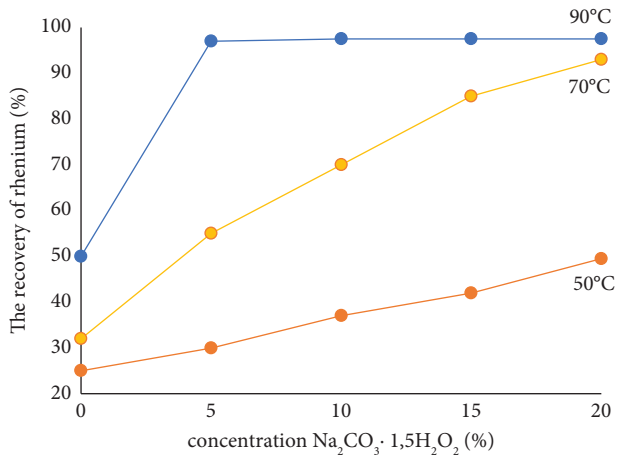


FIGURE 3: Influence of sodium peroxocarbonate concentration and temperature on the degree of rhenium extraction into solution ($S:L = 1:3$, process duration: 30 minutes, and stirring speed: 200 rpm).

ammonia solution. Temperature of ammonia solution was at least 40°C.

3. Results and Discussion

The results of experiments performed at $S:L = 1:3$ and stirring speed of 200 rpm at different temperatures and concentrations of oxidant are shown in Figure 3.

To find out the quantity of soluble rhenium, we carried out experiments on slurry leaching with only water without oxidizer at $S:L = 1:3$, and the degree of rhenium extraction into aqueous solution at 50, 70, and 90°C was 24.8%, 32.3%, and 49.2%, respectively. The obtained solutions contained 132–270 mg/L of rhenium. At low temperatures (50°C), poor wetting of the slurry was observed due to the hydrophobicity of the raw material and due to the presence of organic compounds, which prevented the dissolution of rhenium compounds. Increasing the temperature leads to an increase in the extraction of rhenium into solution, but the maximum transfer of rhenium into solution is 50%. Also, the obtained solution under these conditions contains dissolved organics of 3 mg/L. Further sorption extraction of rhenium from solutions containing dissolved organics is not recommended to avoid contamination of porous structures of anion-exchange resins.

The leaching of lead sludge with 5% sodium peroxocarbonate solution at 90°C allows 97% rhenium extraction in 30 minutes; when the leaching temperature is decreased to 70°C, only 55% rhenium extraction is achieved, but at the same temperature, by increasing the concentration of oxidizer to 20%, 95% rhenium can be extracted into solution as shown in Figure 3.

Experimental results show that an important factor influencing the degree of rhenium extraction is *temperature*. Increasing the temperature leads to a sharp increase in the degree of rhenium extraction in aqueous leaching without oxidizer. Increasing the concentration of sodium peroxocarbonate also exhibits a direct linear relationship for the

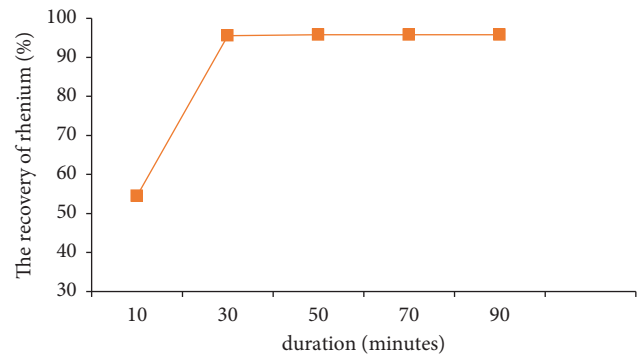


FIGURE 4: Influence of the duration of the leaching process on the degree of extraction of rhenium ($S:L = 1:3$, temperature: 70°C, and stirring speed: 200 rpm).

degree of rhenium extraction in solution. Duration of leaching more than 30 minutes is not reasonable, as a significant increase of rhenium into the solution is not observed in Figure 4.

Stirring speed of the reaction mixture for maximum extraction of rhenium should be at least 200 revolutions per minute in Figure 5, since the specific gravity of lead sludge is 2.1 g/dm³ that is two times higher compared with the specific gravity of the leaching solution at a stirring speed of 50–100 revolutions interaction efficiency of the reactants is reduced.

For the industrial realization of the process, we consider the optimum temperature of the process 70°C, as a leaching agent 20% aqueous solution of sodium peroxocarbonate Na₂CO₃ · 1.5H₂O₂ leaching time 30 minutes, $S:L = 1:3$, stirring speed 200 revolutions per minute.

Cake yield to optimal conditions 89–91.5%. X-ray phase analysis of the cake after leaching shows the presence of phase changes in the slurry. In the beginning, the content of lead sulfate content was 82.7% and lead carbonate 17.3%, in the cake after leaching 48.8% and 51.2% accordingly (Figure 6).

Also, chemical analyses did not reveal any organic compounds in the solution and in the leach cake. These results show the efficiency of lead slurry leaching with sodium peroxocarbonate Na₂CO₃ · 1.5H₂O₂, which is an oxidizer simultaneously for organic compounds with their subsequent decomposition. And rhenium passes into solution in the form of perrhenate ion ReO₄⁻.

To obtain rhenium from solution by sorption-desorption method on ion-exchange resin MTA-170 in chloride form according to previously established conditions, we worked out solutions of rhenium in volume of 5 liters. Feeding solutions into the sorption columns was carried out at a rate of 4 vol./rpm. Slippage of rhenium on the second column was not observed. Results of sorption of rhenium are shown in Table 3.

The distribution of elements in the sorption process is shown in Table 4. Non-ferrous metal ions such as lead, copper, and zinc go into the ion-exchange resin phase along with rhenium. Alkali metal ions practically remain in the sorption matrix. It can be assumed that the resulting rough ammonium perrhenate will contain non-ferrous metal ions,

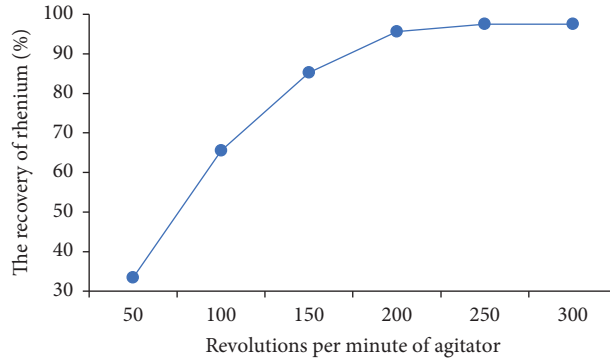


FIGURE 5: Influence of stirring speed on the degree of rhenium extraction ($S : L = 1 : 3$, process duration: 30 minutes, and temperature: 70°C).

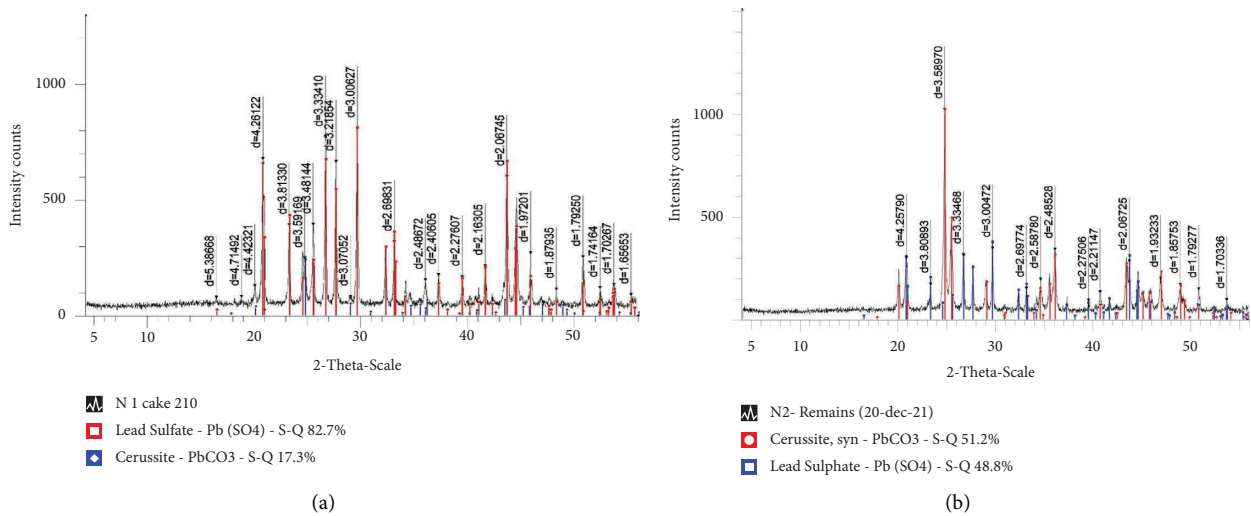


FIGURE 6: Cake before (a) and after (b) leaching.

TABLE 3: Results of rhenium sorption.

Volume of rhenium solution (mL)	Rhenium content in the sorption matrix after the first column (mg/L)	Degree of rhenium extraction into the resin in the first column (%)	Rhenium content in the sorption matrix after the second column (mg/L)	Extent of rhenium extraction into the resin in the second column (%)
500	<0.01	100	<0.01	0
500	<0.01	100	<0.01	0
500	<0.01	100	<0.01	0
500	2.3	98.95	<0.01	1.05
500	6.1	97.2	<0.01	2.80

from which the rhenium salt can be purified by recrystallization.

The results of elemental analysis and infrared spectroscopy of rhenium-saturated resin show the presence of iodide ion along with rhenium (Table 5, Figures 7 and 8), and the ratio Re/I in the original slurry is 5.3; then, this ratio in the ion-exchange resin phase is 1.2–1.59 that shows a strong competing ability to sorption of iodide ion on the

ion-exchange resin that leads to a decrease in the degree of saturation of resin with rhenium.

Desorption of rhenium from the resin was performed at a rate of 1 vol.r/vol.p. of resin per hour in two stages: the first stage with a 10% ammonia solution with 1 volume per volume of resin and the next stage with 2 volumes of 8% ammonia solution. Temperature of ammonia solution is at least 40°C . Desorption of rhenium with a stronger ammonia

TABLE 4: Distribution of elements in the sorption process.

Elements	Initial solution (mg/L)	Sorption matrix (mg/L)	Degree of extraction of elements in the ionite phase (%)
Cu	17.53	16.67	4.90
Pb	342.20	159.65	53.34
Zn	42.0	37.65	10.35
As	0.54	0.63	—
Fe	<0.01	0.01	—
Na	235.0	240.0	—
K	90.0	90.0	—
I	96.5	<0.01	100
Re	521	<0.01	100

TABLE 5: Results of analysis of rhenium-saturated ion-exchange resin.

Sample no. 4: resin with rhenium ions and other impurities
 Processing parameters: performed analysis of all elements (normalized)
 All results in weight (%)

Area	Elements									Total
	C	O	S	Cl	Fe	Zn	Cd	I	Re	
1	68.44	14.47	1.03	0.28	0.18	0.16	0.28	5.85	9.31	100.00
2	66.66	12.44	1.23	0.31	0.25	0.28	0.33	7.65	10.85	100.00
3	63.59	9.80	1.44	0.42	0.30	0.31	0.45	10.65	13.05	100.00
Average	66.23	12.24	1.23	0.34	0.24	0.25	0.35	8.05	11.07	100.00

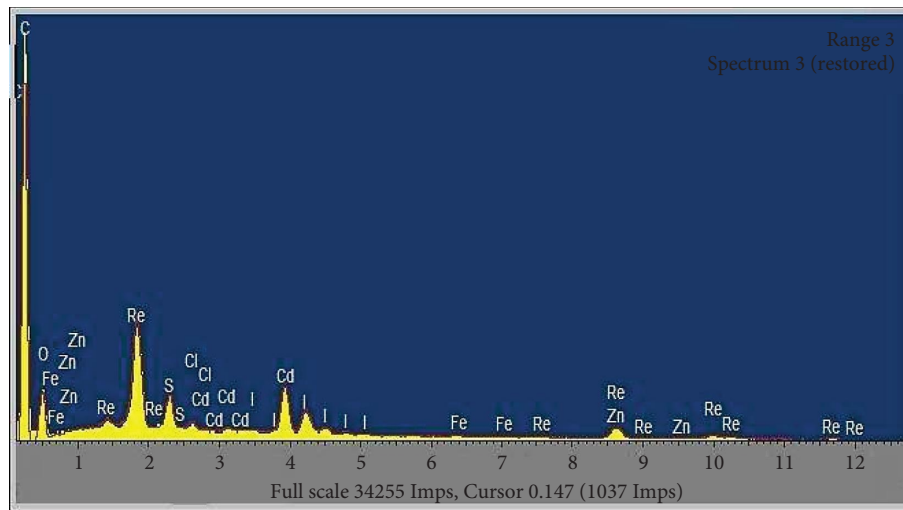


FIGURE 7: Spectrum of saturated resin.

solution in the first stage is necessary to eliminate solid-phase desorption and to obtain rhenium-rich eluates in the first stage. This method is a cost-effective option because the first stage desorbs 70–72% of resin-sorbed rhenium. Results of rhenium desorption are shown in Table 6.

After the desorption process, ammonium perrhenate crystals were obtained from the eluates. The content of

rhenium in obtained ammonium perrhenate is 67.93%. Composition of impurities in the rough salt of rhenium, %: <0.0002 Fe, 0.050 Ca, 0.0001 Mg, 0.0001 Mn, 0.0016 Cu, <0.0002 Ni, 0.0008 K, 0.0060 Na, <0.005 Mo, 0.0082 P. Iodide ion in rough ammonium perrhenate was not detected due to the good solubility of ammonium iodide (NH₄I solubility: 172.3 g/100 g H₂O).

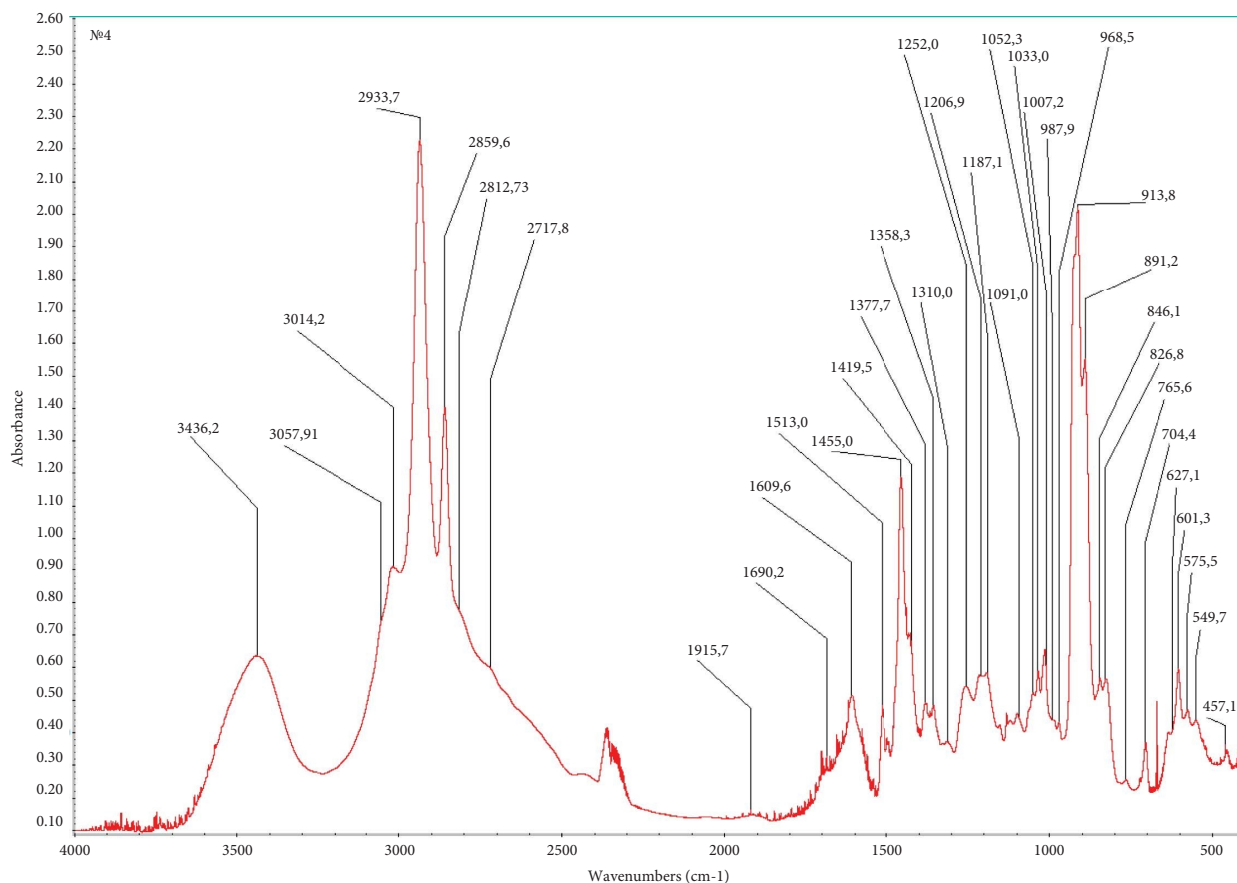


FIGURE 8: Sample no. 4: resin with rhenium ions and other impurities.

TABLE 6: Results of rhenium desorption.

Desorption stage	Rhenium content in the eluate (g/L)	Extent of rhenium extraction into the eluate (%)
1	6.21	71.8
2*	10.08	15.3
3	0.58	6.8
4*	0.75	2.0

* In the second and fourth stages, the eluate of the 1st and 3rd stages was used as desorbing solution, respectively.

After two-stage recrystallization, we received ammonium perrhenate of grade AP-0 containing 69.21% rhenium, the degree of extraction of rhenium in the final product is 73%, and 12–15% of rhenium is in the mother liquors of crystallization.

4. Conclusions

The method of rhenium extraction from lead slurry containing complex organic compounds interfering with oxidation of rhenium compounds in order to transfer it into solution has been developed. The method includes leaching of raw materials with sodium peroxocarbonate solution that serves as an oxidizer simultaneously for organic compounds and for rhenium compounds. The optimum leaching regimes have been

established. The concentration of sodium peroxocarbonate $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ in leaching aqueous solution is 20%, process temperature 70°C, leaching duration 30 minutes, $S:L = 1:3$, stirring speed 200 rpm. The recovery of rhenium in solution as ReO_4^- is 95–96%, they contain up to 520 mg/L of rhenium.

Data Availability

The data used to support the findings of this study may be released upon application to the RSE “National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan,” who can be contacted at pheruza_b@mail.ru; Tel.: (8 727 259 00 70 +(175)).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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