

One-stage leaching of osmium-rhenium containing lead cake using various oxidizing agents

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ABSTRACT

The subject of this study is osmium–rhenium-containing lead cake, which, along with dust, sulfuric acid wash, and sludge, is a byproduct of the pyrometallurgical processing of copper concentrate. The study examined the leaching of osmium–rhenium-containing lead cake using aqueous solutions of hydrogen peroxide, sulfuric and nitric acids, sodium hypochlorite-containing "Belizna," and potassium dichromate. The objective was to select an effective oxidizer for cake leaching. Rhenium is concentrated in an acidic solution as rhenium acid, and rhenium extraction from the solution has been well studied. Osmium is sublimated into the gas phase, then dissolved in an alkali solution containing sodium sulfide, forming commercial osmium sulfide. Novelty and Results: A leaching plant with continuous cake and solution feed and continuous leaching slurry discharge was created. The plant enables the production of rhenium acid solution for ammonium perrenate and commercial osmium sulfide in a single stage. The sum of the plant's parameters (operation continuity, specific productivity, and osmium and rhenium extraction degrees) exceeds those of existing methods. The dependence of osmium and rhenium extraction on the consumption of water, hydrogen peroxide, sulfuric and nitric acids, bleach preparation, potassium dichromate, and the leaching temperature and duration was studied. Close to optimal conditions for leaching 100 grams of cake are as follows: distilled water consumption of 60 milliliters; concentrated sulfuric acid consumption of 70 milliliters; bleach preparation consumption of 400 milliliters; liquid-to-solid ratio (L/S) of 5.3; a temperature of 60 °C; and a specific productivity rate of 100 grams of cake per hour. In this case, the rhenium extraction percentage is 99.1%, and the osmium extraction percentage is 96.8%.

Keywords: osmium, rhenium, cake, leaching, oxidizer, solution.

1. INTRODUCTION

According to the data published by Alshanov R.A. in 2004 [1], the Republic of Kazakhstan is practically the only producer of the radioactive isotope "Osmium-187" in the world and, like Chile, is one of the main suppliers of the rare metal rhenium. The producer of osmium and rhenium in Kazakhstan is the JSC "Kazakhmys Corporation". The price of osmium per gram in 2025 is 10,000 dollars, and on the speculative market it is 100,000 dollars per gram [2]. According to [3], the cost of rhenium in 2024 was 1370 dollars per kilogram, and according to [4], the cost of rhenium increased to 3000 - 4200 dollars per kilogram in 2025. Therefore, significant research on osmium and rhenium has been conducted by Kazakhstani researchers.

Rhenium is a strategically important metal used to produce heat-resistant alloys and platinum–rhenium catalysts. Rhenium is essential in the aerospace and petrochemical industries. Due to the limited reserves of rhenium in ores, extracting rhenium from secondary sources, such as spent catalysts, spent heat-resistant alloys, and pyrometallurgical dust, has become increasingly relevant and reliable. Osmium is essential for the development of anti-cancer and anti-inflammatory drugs, in the production of heat-resistant alloys, and in orientation and guidance systems for aerospace technology.

The extraction of osmium and rhenium from byproducts of copper production in the Republic of Kazakhstan (dust, sulfuric acid wash, sludge, and cakes) has been well documented in the literature [5-14]. Methods for extracting osmium and rhenium from sulfuric acid wash (SAW) [5-8], used in the smelting of copper-containing materials, have been studied, tested on an industrial scale, and implemented in production. However, significant quantities of osmium and rhenium are found in solid middlings formed during the purification of gases from the pyrometallurgical processing of copper concentrates: dust, sludge, and cakes [9].

A pyrometallurgical method for extracting osmium and rhenium from solid middlings of copper production is described in [15, 16]. Osmium–rhenium-containing lead material is smelted with sodium salt and coke to produce slag and a metallic phase consisting primarily of lead matte. Rhenium is concentrated in the slag, from which it is extracted by aqueous leaching. Osmium remains in the difficult-to-process metallic phase. Pyrometallurgical methods are characterized by multi-stage processes, high process temperatures reaching 1000–1300°C, and

the loss of osmium and rhenium with gases containing toxic carbon monoxide and sulfur dioxide. The issue of isolating osmium from the resulting lead alloy remains largely unresolved.

Hydrometallurgical methods are free from the aforementioned drawbacks and can be highly effective in extracting osmium and rhenium from solid middlings of pyrometallurgical processes. The earliest hydrometallurgical methods for processing solid middlings of copper production were characterized by insufficient recovery of rhenium into solution and osmium into the gas phase; we review these methods in our article [8]. Later studies using hydrogen peroxide and certain acids [17–23] achieved high results in extracting rhenium into solution; however, recovery of osmium into the gas phase is not always satisfactory. Under the influence of hydrogen peroxide and acids, osmium is released into the gas phase under near-optimal conditions and captured in absorbent traps with a sodium hydroxide solution, while rhenium is released into the acidic solution as perrenates. Reference [17] provides an excellent overview of the achievements of rhenium leaching from secondary resources between 1998 and 2025, taking into account the influence of temperature, leaching duration, reagent concentration, and the liquid-to-solid ratio on process efficiency. It is shown that rhenium recovery of over 98% is possible through a combination of pyrometallurgical and hydrometallurgical processes. The authors of [18] investigated methods for separating rhenium, osmium, and molybdenum by distillation and anion-exchange chromatography. The authors found that distillation of osmium tetroxide from a mixture of sulfuric acid and hydrogen peroxide is preferable to anion-exchange chromatography. It is recommended to load rhenium from the distillation residue onto an ion-exchange column and then elute with nitric acid.

In [19], lead sludge from copper production, a wet middling (30% moisture content) containing sulfuric acid, was leached. High recovery of rhenium into solution and osmium into the gas phase was demonstrated. However, this method is not suitable for leaching lead cake from copper production. Lead sludge from copper production is neutralized with soda and dried to form a cake before being transported in steel buckets. Therefore, lead cake is a different product, with a different metal compound content and virtually no moisture or sulfuric acid.

In [20], leaching of the lead middling was carried out with a solution containing sulfuric acid and hydrogen peroxide. To reduce foaming, the process was carried out in two stages: the first stage involved heating at a temperature of 50–78°C for one to two hours, and the second stage involved heating at 97–100°C for two to

four hours. This method allowed for the extraction of 88.76–99.25% of rhenium into solution and 83.5–88.1% of osmium in the solid phase of lead sulfate (in the leach cake). A disadvantage of this method is that osmium remains in the solid phase, requiring additional processing to extract it.

Publication [21] presents information on the leaching of osmium from lead cake roasting cinders using several oxidizing agents. A drawing of a leaching apparatus using a three-necked flask as the primary leaching apparatus is provided. One approach achieved good results in converting osmium into the gas phase. A distinctive feature of the method described in [21] is that the cake is roasted to a cinder state for leaching, requiring an additional step. Furthermore, the behavior of rhenium during leaching is not described.

In [22], the leaching of several cakes with solutions containing sulfuric acid and hydrogen peroxide was studied in some detail, using a setup we later described in [21]. The influence of distilled water consumption concentrated sulfuric acid, 33% hydrogen peroxide, temperature, and leaching duration on the conversion of rhenium to an acidic solution and osmium to both acidic and alkaline solutions was determined. Near-optimal leaching conditions for 100 grams of cake are as follows: a consumption rate of 100 milliliters of distilled water, 10 milliliters of sulfuric acid, 100 milliliters of hydrogen peroxide, a leaching time of 4 hours, and a leaching temperature of 80–90°C. These conditions allow conversion of more than 90% of rhenium and 12% of osmium into acidic solutions, and up to 80–85% of osmium into an alkaline solution. The specific throughput of the equipment is 100 grams of cake in 4 hours.

In [23], lead cake was leached in a flask with a 1:1 mixture of nitric and sulfuric acids at a temperature of 65–69 °C with the addition of hydrogen peroxide at a concentration of 33% and a cake ratio of 0.5:1 in portions of 0.1–0.3 milliliters at intervals of 2–3 seconds. An amount of 50 grams of lead cake was loaded into the flask and then filled with 50 milliliters of a solution consisting of a mixture of nitric and sulfuric acids. Leaching was carried out for 90 minutes, and then hydrogen peroxide was added in portions over 2.8–12.5 minutes. The total leaching time ranged from 92.8 to 102.5 minutes (1.55–1.7 hours). The specific productivity rate was 29–32 grams of cake per hour. This method is not suitable for column leaching because it maintains a 1:1 liquid-to-solid ratio, resulting in a pasty mass and reduced flowability. Furthermore, the specific cake productivity is low.

Hydrometallurgical methods for extracting osmium and rhenium from copper production byproducts have advantages over pyrometallurgical methods, including lower process temperatures and simpler instrumentation. The disadvantages of the methods described here include the experiments' periodicity and laboratory scale. The objective of this study is to develop and experimentally validate an effective hydrometallurgical process for leaching osmium- and rhenium-containing lead cakes using a continuous column apparatus. The study aims to increase the recovery of valuable metals (Re and Os) from solid industrial byproducts of pyrometallurgical processing of copper raw materials by optimizing the composition of oxidizing solutions and the leaching regime. The novelty and results of the study are as follows: A cake leaching unit with continuous loading for leaching, a continuous supply of leaching solutions, and continuous discharge of leaching pulp was used. The unit enables the production of a rhenium acid solution for the production of crude ammonium perhenate, commercial osmium sulfide, and lead-containing leaching cake in a single stage. The dependence of osmium and rhenium recovery on the consumption of water, hydrogen peroxide, sulfuric and nitric acids, bleach, potassium dichromate, and the temperature and duration of leaching was studied. Near-optimal conditions for leaching 100 grams of cake are as follows: consumption of 60 milliliters of distilled water; 70 milliliters of concentrated sulfuric acid; 400 milliliters of "whiteness" preparation consumption; a liquid-to-solid ratio (L/S) of 5.3; a temperature of 60 °C; and a specific productivity rate of 100 grams of cake per hour. In this case, the percentage of rhenium extraction is 99.1%, and that of osmium extraction is 96.8%.

2. MATERIALS AND METHODS

Characteristics of raw material: The object of the study was lead-containing cake. According to mass spectrometry data, the elemental composition of the starting material includes (w, %) Pb—59.51; S—11.98; carbon compounds—3.95; Na and Mn—0.39 each; Si—0.9; and Fe and Cu—0.68 each. The content of accompanying components, namely Se, Al, and Ca, does not exceed 0.25, group elements K, Zn, As, Bi, and Mg comprise up to 0.18, P comprises up to 0.025, and Ni comprises up to 0.004. The concentrations of noble and rare metals were 34 g/t for Os and up to 1450 g/t for Re. The main forms of lead were determined using X-ray phase (XRD) and chemical analysis as follows: lead sulfate PbSO_4 —77.64; carbonate PbCO_3 —5.80; oxide PbO —2.71; metallic lead Pb—up to 0.84; and sulfide PbS —

trace amounts (other phases—13.01). Based on chemical phase analysis, rhenium distribution was established as follows: 38%—disulfide ReS_2 ; 30%—lower oxides; and 25%—water-soluble forms. Osmium is represented by sulfite complexes and oxide compounds in a 1:1 ratio. Experimental setup and analytical equipment: The laboratory leaching complex (Fig. 1) was operated in continuous mode for the solid and liquid phases, with discrete unloading of the reaction products.

The reaction unit design included a jacketed glass distillation column, thermally stabilized with an LOIP LT-300 circulating thermostat. Vacuum filtration was performed using a Bunsen flask, a Buchner funnel, and a ROAIRVAC R321.5 pump (or a water-jet equivalent). Of the known liquid oxidizers, the simplest and least expensive were hydrogen peroxide, sulfuric and nitric acids, and the "Belizna" (whiteness) preparation used in bleaching and disinfection, along with sodium hypochlorite, potassium dichromate, and osmium analysis [15]. Rare metal concentrations in the liquid phase were monitored photometrically using standardized methods [15, 16] on a KFK-3-ZOMZ spectrophotometer. The detection limits of the target components were $1 \cdot 10^{-5}$ –2% for Os and $1 \cdot 10^{-4}$ –20% for Re. The elemental compositions of the initial and extracted cakes were analyzed using atomic absorption (PerkinElmer 240 FSSA) and emission spectrometry (DFS-8) [17, 18].

Unit operation: The unit is placed in a fume hood. A slurry of cake and liquid is fed into heated water column 1 from above. To prevent the slurry from entering the oxidation line, column 1 is equipped with a fine mesh (2), through which an oxidizer solution enters from below, via tube 3. The oxidizer flows from tank 4, located above the level of column 1; the oxidizer flow rate is regulated by valve 5. In tank 6, a slurry comprising cake, sulfuric acid, and water, sometimes with hydrogen peroxide, is prepared. To prevent separation of the slurry into cake and solution, the unit is equipped with a stirrer (7). The slurry then flows through the central tube to the bottom of column 1, where it mixes with the oxidizer solution entering from below, and the leaching process begins, producing a pulp containing rhenium acid HReO_4 and osmium tetroxide OsO_4 , which rises to the top of the column. At the top of column 1, the leaching pulp cools and flows through tube 8 into a funnel (9), which is hermetically sealed with a lid. The filtrate is collected in a flask (10) and heated by a hotplate (11). Volatile osmium tetroxide, OsO_4 , evaporates and is captured in adsorbers (12) filled with a solution of $\text{NaOH} + \text{Na}_2\text{S}$ to yield OsS_2 . The efficiency of osmium tetroxide capture is 100%. Rhenium, in the form of rhenium acid (HReO_4), remains in the acidic solution in a flask (10). Leach cake, containing lead compounds and suitable for use in lead metallurgy, is collected in a funnel (9). The thermostat (13) ensures the required leaching temperature is maintained in column 1. The leach cake and solutions were discharged as they accumulated. The feed cake, leach cake, and acidic and alkaline solutions were analyzed for osmium, rhenium, acidity and oxidizer concentrations.

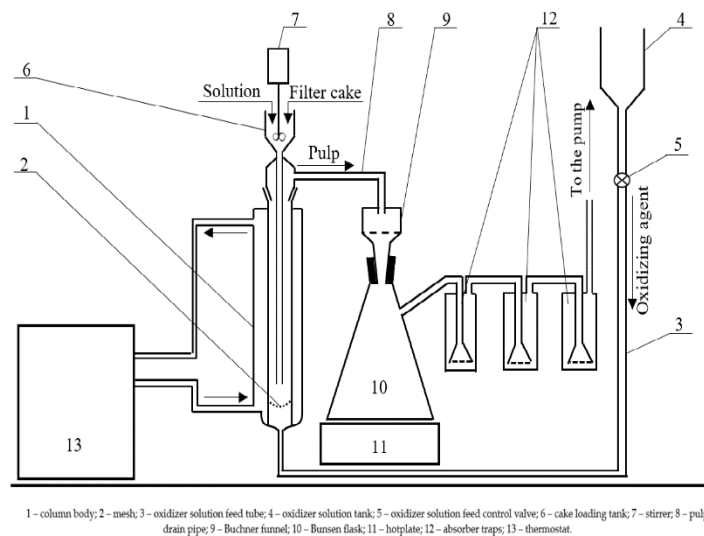


Fig. 1. Schematic diagram of the cake leaching plant.

The surface morphology and phase heterogeneity of the samples were studied using a JXA-8230 electron probe microanalyzer (JEOL). Surveying and local analysis were performed at an accelerating voltage of 20 kV and an electron beam current of up to 15 nA; the detector dead time did not exceed 21%. The selected scanning parameters provided a spatial resolution from the submicron level to hundreds of micrometers in the magnification range of 40x to 4000x. Microstructure visualization of target areas was performed primarily in backscattered electron imaging (BSE/COMPO) to provide Z-contrast between phases with different average atomic numbers. Secondary electron imaging (SEI) was additionally used to compare the morphological features of individual zones. A total of 33 high-resolution micrographs were obtained and systematized during the experiment. The elemental composition of microregions was determined using X-ray spectral analysis. The local quantitative composition of phases was studied by performing 33 energy-dispersive spectroscopy (EDS) microanalyses. Qualitative and semi-quantitative identification of elements at critical points was verified using wave-dispersive spectroscopy (WDS, 9 determinations). To confirm the reproducibility of the structural-analytical matrices and exclude anomalous compositional fluctuations, a series of rapid analyses was performed without spectral storage. Element concentrations were calculated, and matrix corrections were performed using the standard EPMA software based on the standard ZAF method.

3. RESULTS AND DISCUSSION

3.1 Results and Discussion of the Oxidative Leaching of Rhenium and Osmium from Lead Cake

The experiments used distilled water, a 30% H₂O₂ solution, 17.9 mol/L of H₂SO₄, 15.18 mol/L of HNO₃, a "Belizna" solution with a 15% sodium hypochlorite NaOCl concentration, and an aqueous K₂Cr₂O₇ solution with a concentration of 33 to 200 grams/liter. The leaching temperature was maintained between 60 and 70°C. Some of the sulfuric acid is consumed by the reaction with lead and its compounds to form lead sulfate, water, and gases, which promote pulp mixing and the movement of OsO₄ toward the adsorbers. As noted above, the cake contains lead in the form of lead sulfate (PbSO₄—77.64%), impurities of lead oxide and carbonate (2.71% PbO and 5.80% PbCO₃), and metallic lead at a content of up to 0.84%. Data from chemical phase analysis showed that 25% of rhenium is contained in the form of water-soluble compounds, 38% is contained in the form of ReS₂, and 30% in the form of lower oxides. Half of the osmium is in the form of sulfite complexes, while the rest is in the form of the most volatile oxide, OsO₄. During cake leaching using sulfuric acid, it reacts with lead carbonate, its oxide, and lead. Below are thermodynamic calculations of these reactions at temperatures of 60 and 800 °C, showing the formation of the PbSO₄ phase with the release of H₂O, CO₂, and H₂:

	ΔG_{60}^0 kJ/mol	ΔG_{80}^0 kJ/mol	
$\text{PbCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O} + \text{CO}_2$	-79,96	-82,36	(1)
$\text{PbO} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2\text{O}$	-73,35	-72,35	(2)
$\text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2$	-23,33	-25,53	(3)

Next, the liquid components of the pulp react with osmium and rhenium compounds to form osmium tetroxide (OsO₄) and rhenium acid (HReO₄).

When leaching 100 grams of cake, the mass of the solid residue decreases by ~135 milligrams as a result of the extraction of Os and Re and increases by 2.78 grams as a result of reaction (1), for a total of ~2.645 grams.

The column had an internal diameter of 50 millimeters and a working length of 920 millimeters; the working volume of the column was ~1.8 liters. A suspension of the following composition was loaded into the column from the top: 100 grams of cake + H₂O + concentrated H₂SO₄. The L/S ratio was ~1.3. An oxidizer solution entered the column from the bottom, and the L/S ratio increased to 5.5 in some experiments. The specific column productivity under near-optimal conditions is 100 grams of cake per hour. The main experimental results are presented in Tables 1 and 2, where the total Os recovery, solution recovery, and gas recovery are listed. Each experiment in Tables 1 and 2 was repeated three times. The variation in Os and Re recovery across replicate experiments was 1.8%. **Table 1** shows the experimental conditions with H₂O₂ + H₂SO₄ oxidants, while **Table 2** shows the experimental conditions with the addition of HNO₃, Belizna with 15% NaOCl, and K₂Cr₂O₇ at 60°C. The solution concentrations and recovery of Os and Re in the tables are rounded to the nearest tenth.

Commercial compounds of rhenium (ammonium perrhenate) and osmium (osmium sulfide) were obtained as follows. A rhenium-containing solution with a Re concentration of ~700 mg/liter was sorbed on the Pirolite anion exchange resin; desorption was performed with an 8% ammonia solution. The desorption rate was 98%. The anion exchange resin was then regenerated with a 4% hydrochloric acid solution and used to sorb the next batch of rhenium solution. An amount of 500 grams of the anion exchange resin sorbs ~4 grams of rhenium in one cycle. The ammonium perrhenate solution after desorption contained a small amount of copper and iron impurities; it was refined to obtain crude ammonium perrhenate using known methods [6]. The resulting crude ammonium perrhenate was recrystallized, resulting in pure commercial ammonium perrhenate NH₄ReO₄ containing 69.3% rhenium. In adsorbers, osmium is precipitated with sodium sulfide Na₂S or ammonium sulfide (NH₄)₂S to obtain commercial osmium sulfide OsS₂ using the method described in [23].

Table 1. Dependence of Re and Os extraction on parameters during leaching of 100 grams of cake with sulfuric acid and hydrogen peroxide.

Experiment No.	Consumption, mL			F/T	t, °C	τ, min	v of solution, mL/min	Concentration in solution		Extraction, % (mean±SD)	
	H ₂ O	H ₂ O ₂	H ₂ SO ₄					H ₂ O ₂ , %	H ₂ SO ₄ , g/l	Re	Os
1	300	50	1.0	3.5	53	66	5.3	4.3	1.4	76.7±1.4	17.2±0.3
2	300	40	1.5	3.4	48	64	5.3	3.5	4.0	80.2±1.4	32.3±0.6
3	246	54	2.0	3.0	70	61	4.9	5.4	7.5	88.2±1.6	35.4±1.8
4	250	50	2.0	3.0	51	60	5.0	5.0	7.5	88.3±1.9	37.9±0.7
5	262	47	2.8	3.1	61	61	5.2	4.5	11.7	88.5±1.6	38.1±0.9
6	180	67	3.0	2.5	68	58	4.3	8.0	16.0	94.9±1.7	48.1±1.7
7	165	46	1.0	2.1	54	52	4.1	6.5	2.3	84.1±1.5	56.0±1.0
8	130	65	4.8	2.0	71	51	3.9	9.8	35.8	91.2±1.6	68.7±1.2
9	125	71	4.7	2.0	72	50	4.0	10.6	35.0	95.2±1.7	71.5±1.3

Table 2. Leaching of 100 grams of cake with various oxidizing agents.

Experiment No.	Consumption, mL				F/T	τ , min	Extraction, % (mean $\pm$ SD)	
	H ₂ O	H ₂ O ₂	H ₂ SO ₄	Oxidant			Re	Os
1	50	30	50	HNO ₃ -50 mL	1.8	90	20.8 $\pm$ 0.4	71.6 $\pm$ 1.3
2	60	40	30	HNO ₃ -30 mL	1.6	90	38.8 $\pm$ 0.9	79.2 $\pm$ 1.4
3	70	50	20	HNO ₃ -20 mL	1.6	90	48.9 $\pm$ 0.7	85.6 $\pm$ 1.5
4	80	-	50	"Belizna" -100 mL	2.3	64	66.5 $\pm$ 1.5	46.4 $\pm$ 0.8
5	70	-	60	"Belizna" -300 mL	4.3	70	85.0 $\pm$ 1.2	75.9 $\pm$ 1.4
6	60	-	70	"Belizna" -400 mL	5.3	60	99.1 $\pm$ 1.8	96.8 $\pm$ 1.7
7	300	30	100	K ₂ Cr ₂ O ₇ -25g.	4.3	120	77.9 $\pm$ 1.4	98.6 $\pm$ 1.8
8	300	-	150	K ₂ Cr ₂ O ₇ -50g.	4.5	60	90.6 $\pm$ 1.3	99.8 $\pm$ 1.6
9	350	-	200	K ₂ Cr ₂ O ₇ -90g.	5.5	60	91.2 $\pm$ 1.6	98.8 $\pm$ 1.9

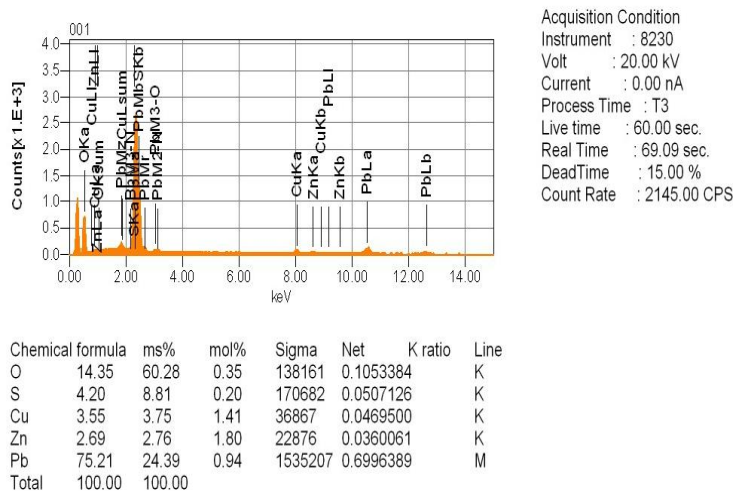
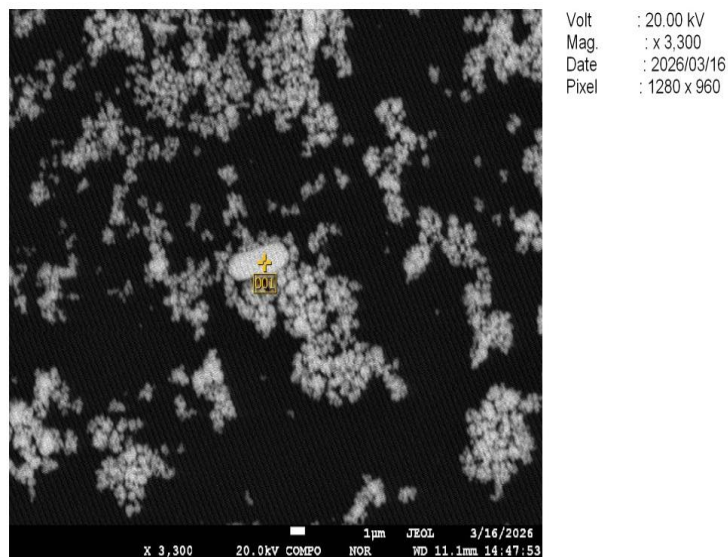
The following conclusions can be drawn from the data in the first table: 1—Distilled water consumption correlates with the L/S ratio and has virtually no effect on Os and Re recovery. 2—Increasing the consumption of 30% H₂O₂ and concentrated H₂SO₄ increases Os and Re recovery. 3—Leaching temperatures in the range of 48–72°C have virtually no effect on Os and Re recovery. 4—Leaching duration in the unit was 50–66 minutes. 5—The specific productivity rates of the unit in the tenth and eleventh runs in Table 1 were 117.6 and 120 grams of cake per hour, respectively.

According to the data in the second table: 1—The sum of the oxidizing agents H₂O₂, H₂SO₄, and HNO₃ is insufficiently active. 2—The "Belina" oxidizing agent with NaOCl leaches satisfactorily at higher flow rates. 4—K₂Cr₂O₇ performs well, with rhenium recovery of 91.16% and osmium recovery of 98.81%. However, due to the high toxicity of potassium dichromate, its use on an industrial scale is not recommended.

Near-optimal conditions for cake leaching were achieved using Belina with H₂O and H₂SO₄, as well as potassium dichromate with H₂O and H₂SO₄. Disadvantages of potassium dichromate are as follows: 1) complex technology is needed to obtain ammonium perhenate from a solution containing K₂Cr₂O₇; 2) the K₂Cr₂O₇ reagent has high toxicity; and 3) the process of decontaminating the solution after using potassium dichromate is expensive. When using Belina, the solution contains an increased amount of sodium, which does not interfere with the sorption-desorption process of ammonium perhenate. Based on the above, the authors believe the optimal whitening agent usage is as follows per 100 grams of cake: 60 milliliters of distilled water; 70 milliliters of concentrated sulfuric acid; 400 milliliters of whitening agent; a liquid-to-solid ratio of 5.3; a temperature of 60°C; and a specific productivity of 100 grams of cake per hour. In this case, rhenium recovery is 99.1%, and osmium recovery is 96.8%.

Based on the sixth run in Table 2, a material balance for Os and Re was compiled. An amount of 3.4 milligrams of Os was loaded with 100 grams of cake. Os was recovered in the adsorbers as OsS₂, amounting to 3.29 milligrams. Os loss with the gas phase due to the vacuum system operation was 0.11 milligrams, which is 3.235% of the initial amount. An amount of 145 milligrams of Re was loaded with 100 grams of cake, and 143.7 milligrams of rhenium were recovered in the flask as HReO₄. Rhenium losses with the leaching cake amounted to 1.3 milligrams, which is $0.897 \approx 0.9\%$ of the original amount.

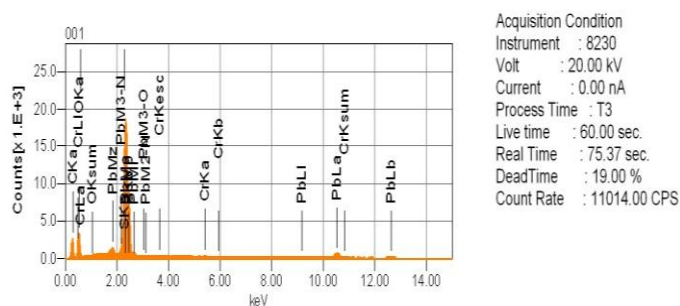
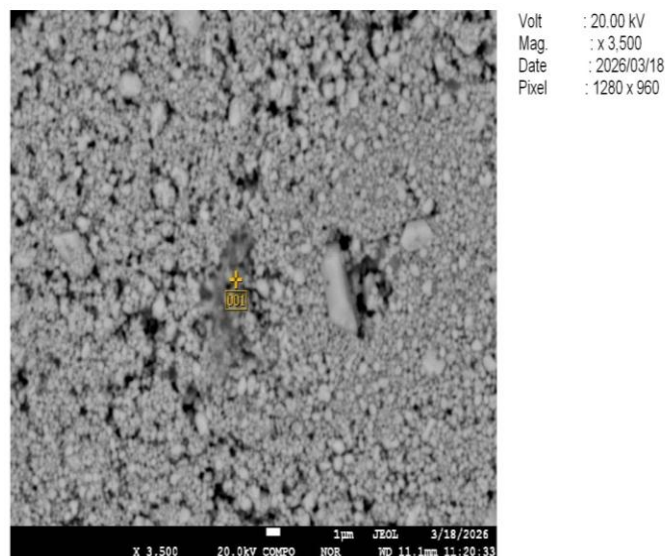
Considering the capacity of Kazakhmys Corporation JSC, the authors recommend two insulated plastic columns with a diameter of 200 mm and a height of 2000 mm, heated by a nichrome coil and powered by an adjustable power source, to process the resulting osmium-rhenium-containing cake. The remaining components of the plant, magnified to the appropriate scale, are shown in Fig. 1. Scanning electron microscopy (SEM) studies of the cakes after leaching were conducted. Fig. 2 shows an SEM image of the cakes after leaching, where nitric acid was used as the oxidizer. The sample contained fine particles much smaller than 1 μ m, along with agglomerates of these particles, and solid particles up to 10 μ m in size. EDS and WDS microanalyses (both in areas of continuous, uniform contrast and at points with different contrast) indicate that the substance is a mixture of lead salts (PbSO₄ and PbCO₃) with impurities (Na, Mg, Si, Al, K, Ca, Fe, Cu, and Zn).

**Fig. 2.** SEM image of the cakes after leaching, where nitric acid was used as the oxidizing agent.

The sulfate-oxide phase of lead dominates with minor Zn and Cu impurities, indicating that the material has compositional heterogeneity and a complex microstructure.

Thus, the use of nitric acid as an oxidizing agent during the leaching of osmium and rhenium-containing lead cake does not effectively destroy the mineral matrix and is impractical for industrial use in a column process.

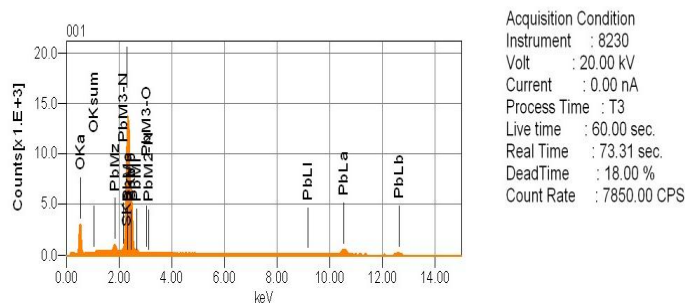
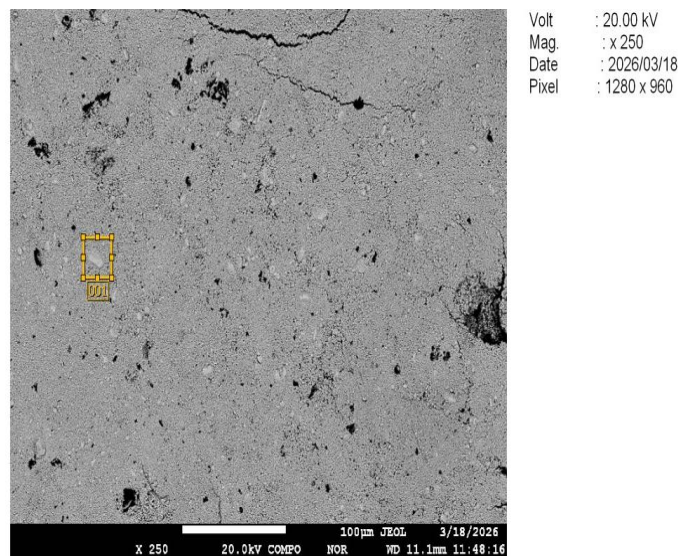
Fig. 3 shows an SEM image of the cakes after leaching, where bleach was used as the oxidizing agent.



Chemical formula	ms%	mol%	Sigma	Net	K ratio	Line
C	16.65	52.27	0.13	375503	0.0090812	K
O	12.27	28.91	0.21	660064	0.0695374	K
S	5.61	6.60	0.09	1735175	0.0712366	K
Cr	0.58	0.42	0.27	86836	0.0069637	K
Pb	64.89	11.81	0.40	100772960.6345735		M
Total	100.00	100.00				

Fig. 3. SEM image of the cakes after leaching, where bleach was used as an oxidizing agent.

This sample also contained fine particles much smaller than 1 μm in size, along with agglomerates of these particles, and solid particles up to 10 μm in size. EDS and WDS microanalyses (both in areas of continuous, uniform contrast and at points with different contrast) indicate that the substance is a mixture of lead salts (PbSO_4 and PbCO_3) with impurities (Si, K, and Cr). The use of Belizna as an oxidizer in the leaching of osmium–rhenium-containing lead cakes is satisfactory. **Fig. 4** shows an SEM image of the cakes after leaching, where potassium dichromate was used as the oxidizer.



Chemical formula	ms%	mol%	Sigma	Net	K ratio	Line
O	13.93	60.44	0.16	610958	0.0919757	K
S	5.86	12.69	0.09	1128516	0.0662060	K
Pb	80.21	26.87	0.40	7757503	0.6980545	M
Total	100.00	100.00				

Fig. 4. SEM image of the cakes after leaching, where potassium dichromate was used as the oxidizer.

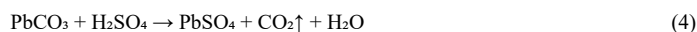
This sample similarly contained fine particles much smaller than 1 μm , along with agglomerates of these particles, and solid particles up to 10 μm in size. EDS and WDS microanalyses indicate that the substance is pure lead sulfate, PbSO_4 . No impurities were detected.

This composition and morphology indicate the high efficiency of the oxidizer $\text{K}_2\text{Cr}_2\text{O}_7$: the original compounds were almost completely decomposed, and impurity elements and valuable components (Re and Os) were extracted into solution. Potassium dichromate ensures very complete leaching of osmium and rhenium from leach cakes; however, due to its high toxicity and carcinogenic properties, the authors do not recommend its use on an industrial scale.

3.2 Oxidation Mechanism of Re and Os Compounds during Leaching

The efficiency of Re and Os extraction is determined not only by the nature of the oxidizing agent used, but also by the oxidation–reduction potential of the environment, the rate of destruction of the lead cake's mineral matrix, the stability of the oxidizing agent in acidic solutions, and the continuous removal of oxidation products from the reaction zone. According to phase analysis data, Re in the cake under study is present predominantly as disulfide ReS_2 (38%), lower oxides (30%), and water-soluble compounds (25%), while osmium exists as sulfide (or sulfite) compounds and oxide forms. Therefore, achieving high extraction rates for both metals requires complete oxidation of their compounds to their most stable forms in an acidic environment.

In the first stage of the process, sulfuric acid reacts with the main Pb compounds:





The formation of poorly soluble PbSO_4 promotes the destruction of the original cake structure and the release of Re and Os compounds. The simultaneously released CO_2 and H_2 cause intense mixing of the pulp, reduce the thickness of the diffusion layer, and accelerate the transfer of volatile OsO_4 to the absorption system.

Re oxidation mechanism

The most stable rhenium phase is the disulfide ReS_2 . Its dissolution requires the destruction of the Re–S covalent bond, followed by oxidation of rhenium to the oxidation state of +7. In an acidic oxidizing medium, the end product is rhenium acid [17]:



The released electrons are consumed by the oxidizing agent (H_2O_2 , HOCl , or $\text{Cr}_2\text{O}_7^{2-}$). As a result, rhenium completely dissolves in the form of rhenium acid:



or



The resulting rhenium acid is stable in a sulfuric acid environment and forms virtually no poorly soluble compounds, which explains the high recovery of Re.

Mechanism of OsO_4 Formation

Osmium is extracted by a different mechanism. Osmium compounds are initially in lower oxidation states (+2, +3, or +4). Under the influence of strong oxidizing agents, the oxidation state sequentially increases to Os(VIII) , forming volatile OsO_4 [27]:



or, for oxide compounds, in total,



Osmium tetroxide exhibits high volatility even at temperatures of 40–60 °C. Therefore, after formation, it is continuously removed from the reaction zone, which, according to Le Chatelier's principle, shifts the equilibrium toward further oxidation of osmium compounds. In absorbers, OsO_4 is absorbed by a solution of sodium hydroxide and sodium sulfide, forming commercial osmium sulfide:



The virtually complete removal of OsO_4 from the reaction medium prevents its reduction and ensures a high degree of Os recovery.

The Role of Various Oxidizing Agents: Hydrogen Peroxide

In an acidic environment, hydrogen peroxide is a strong oxidizing agent; however, in the presence of Fe^{2+} , Cu^{2+} ions, and mineral surfaces, its catalytic decomposition occurs:



As a result, the concentration of the active oxidizing agent gradually decreases, limiting the complete oxidation of the most stable osmium compounds. This explains the gradual increase in Os and Re extraction with increasing H_2O_2 consumption (Table 1).

Nitric Acid

In concentrated acid, nitrate ion is reduced:



Despite the high standard potential of the NO_3^-/NO pair, nitric acid preferentially oxidizes the surface of mineral particles. The resulting dense PbSO_4 shell limits

further diffusion of the reagent into the grains, resulting in some Re and Os compounds remaining unoxidized. Sodium Hypochlorite

In an acidic environment, hypochlorite quickly converts to hypochlorous acid:



HOCl becomes the main active oxidizing agent:



The high oxidation potential of hypochlorous acid ensures the rapid destruction of the ReS_2 sulfide matrix and the almost complete conversion of osmium compounds to OsO_4 . Unlike H_2O_2 , hypochlorite retains its high oxidizing capacity for significantly longer, allowing the solution's Eh to be maintained throughout the process. This explains the achievement of maximum rhenium recovery (99.1%) while maintaining high osmium recovery (96.8%). Potassium dichromate In an acidic environment, dichromate is reduced by the reaction



This system has the highest oxidation potential among the reagents studied, ensuring the almost complete destruction of stable sulfide compounds and the maximum formation of OsO_4 . This is confirmed by the results of SEM analysis, according to which the residual cake after dichromate treatment consists almost entirely of PbSO_4 without noticeable impurity phases. However, residual Cr(VI) compounds significantly complicate subsequent processing of the solutions and require an additional decontamination step, which reduces the industrial appeal of this oxidizing agent.

Relationship of the Mechanism with SEM Results

The obtained scanning electron microscopy data are in good agreement with the proposed mechanism. After treatment with HNO_3 , heterogeneous particles of PbSO_4 , PbCO_3 , and impurity minerals remain in the residue, indicating incomplete destruction of the original mineral matrix. The use of sodium hypochlorite leads to a significant reduction in the amount of impurity phases, whereas after treatment with potassium dichromate, the residue is almost entirely composed of PbSO_4 crystals. This consistent simplification of the phase composition fully correlates with the increase in the recovery of rhenium and osmium, as shown in Table 2, and confirms that the process efficiency is determined not only by the thermodynamic strength of the oxidizing agent but also by the rate of destruction of minerals containing valuable metals.

Thus, the developed process represents a set of interconnected chemical and mass-transfer stages: destruction of the lead matrix with sulfuric acid, oxidation of rhenium compounds to HReO_4 , the sequential formation of volatile OsO_4 , its continuous removal from the reaction zone, and subsequent capture in alkaline absorbers. It is the combination of high oxidation rates and continuous removal of reaction products that ensures high rhenium and osmium recovery using the H_2SO_4 – NaOCl system.

The proposed oxidation mechanism for Re and Os demonstrates that high recovery efficiency is determined by the combined action of several factors: destruction of the lead matrix with sulfuric acid, the sequential oxidation of Re compounds to HReO_4 and Os to volatile OsO_4 , and the continuous removal of oxidation products from the reaction zone. A comparison of chemical mechanisms with SEM results and recovery data confirms that the superiority of the H_2SO_4 – NaOCl system is due to a combination of high redox potential, oxidizer stability in acidic environments, and efficient oxidation kinetics of sulfide phases. These results provide a scientific basis for selecting the optimal oxidizer for industrial processing of osmium–rhenium lead cakes and enable targeted optimization of hydrometallurgical processes for valuable metal extraction.

3.3 Comparison of the Developed Technology with Previously Published Studies

The efficiency of hydrometallurgical extraction of rhenium and osmium is determined by the nature of the oxidizing agent, the acidity of the medium, and the process conditions. In published studies, H_2O_2 , HNO_3 , NaOCl , and $\text{K}_2\text{Cr}_2\text{O}_7$ are most commonly used for oxidative leaching. However, most known processes are characterized by either increased reagent consumption, long leaching times, or environmental limitations associated with the use of Cr(VI) compounds or concentrated nitric acid.

Unlike previously published technologies, the developed process combines continuous column leaching with the H_2SO_4 – NaOCl system, which provides a

stable, high redox potential. The resulting hypochlorous acid effectively oxidizes Re compounds to HReO_4 and Os to volatile OsO_4 , while continuous removal of OsO_4 from the reaction zone facilitates further process progression.

The developed technology ensures the recovery of 99.1% Re and 96.8% Os at 60°C, a leaching time of 60 minutes, and atmospheric pressure. Compared to most published hydrometallurgical processes, the proposed method combines high recovery rates with mild process conditions and eliminates the need for Cr(VI) compounds or autoclave equipment. These results confirm the scientific and practical potential of the developed technology for processing osmium–rhenium lead cakes.

CONCLUSIONS

1. A literature review suggests that cake leaching, which involves converting rhenium and osmium into solutions and then extracting these elements into marketable products, offers a promising approach for processing osmium- and rhenium-containing lead cakes from copper production.
 2. A setup was used in which the main leaching apparatus is a heated column with a suspension of leached cake and liquid fed from the top and an oxidizing solution fed from the bottom. The setup operates in continuous mode.
 3. The most popular oxidizing agents used for leaching were hydrogen peroxide, concentrated sulfuric and nitric acids, a sodium hypochlorite-containing product called "Belizna," and potassium dichromate.
 4. Near-optimal conditions for leaching 100 grams of cake were determined as follows: distilled water consumption of 60 milliliters; concentrated sulfuric acid consumption of 70 milliliters; a whiteness consumption rate of 400 milliliters; a liquid-to-solid ratio (L/S) of 5.3; a temperature of 60°C; and a specific throughput of 100 grams of cake per hour. The rhenium recovery is 99.1%, and the osmium recovery is 96.8%.
 5. Commercial ammonium perrhenate is obtained from a rhenium acid solution using known methods such as sorption–desorption on a Pirolite anion exchange resin. Commercial osmium sulfide is precipitated in adsorbers and separated by filtration.
- The proposed mechanism for the oxidation of Os and Re demonstrates that the high extraction efficiency is determined by the combined action of several factors: the destruction of the lead matrix by sulfuric acid, the sequential oxidation of Re compounds to HReO_4 and Os to volatile OsO_4 , and the continuous removal of oxidation products from the reaction zone. A comparison of chemical mechanisms with SEM results and recovery data confirms that the superiority of the H_2SO_4 – NaOCl system is due to a combination of high redox potential, oxidizer stability in acidic environments, and efficient oxidation kinetics of sulfide phases. These results provide a scientific basis for selecting the optimal oxidizer for industrial processing of osmium–rhenium lead cakes and enable targeted optimization of hydrometallurgical processes for valuable metal extraction.

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