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RESEARCH PAPER

Study of the behavior of iodine and rhenium during oxidative roasting of lead cake

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ABSTRACT

Oxidative roasting aims to convert rhenium into a water-soluble form, followed by leaching into solution and subsequent sorption–desorption steps to obtain ammonium perrenate. It was found that the presence of iodine significantly affects the technological parameters of rhenium extraction during sorption and desorption stages, reducing the ion-exchange capacity for rhenium due to the simultaneous transition of iodide and perrenate species into solution. The main objective of this study was to determine the technological parameters that ensure effective separation of iodine and rhenium during oxidative roasting. Experimental data showed that the maximum transfer of rhenium (up to 95.6%) into water-soluble compounds occurs at 300–400 °C, when iodine compounds have not yet volatilized. At temperatures above 400 °C, iodine sublimates mainly as PbI_2, accompanied by a decrease in rhenium extraction efficiency. It was experimentally established that, under optimal roasting conditions, rhenium is concentrated in the solid phase as perrenates and iodides, ensuring almost complete dissolution during subsequent leaching. The volatilisation of iodine at elevated temperatures leads to the decomposition of rhenium iodides and the formation of insoluble metallic phases, thereby negatively affecting extraction.

Keywords: rhenium, iodine, lead cake, oxidative roasting, leaching, sorption, perrenates, iodides.

INTRODUCTION

Rhenium is an indispensable element used in the production of heat-resistant, corrosion-resistant alloys for the aviation, space, and power industries [1–3]. Owing to the limited availability of natural rhenium resources and its high cost, increasing attention is paid to the processing of rhenium-bearing technogenic materials. Among such sources, lead cakes formed during wet gas cleaning in the converting of sulfide copper concentrates are of great interest.

These cakes are anthropogenic mineral formations containing rare and dispersed elements — rhenium, osmium, iodine, and selenium. They are typically filter cakes, whose main component is lead sulfate ($PbSO_4$), formed through the interaction of lead oxide with sulfur trioxide in the flue gas mixture according to reaction (1):

$$PbO + SO_3 = PbSO_4 \quad (1)$$

The high specific surface area of $PbSO_4$ promotes the adsorption of rare-element and halogen compounds. Along with physical adsorption, chemisorption occurs, forming stable compounds such as lead, zinc, and copper perrhenates [4–8].

In addition to inorganic phases, the cakes contain 3–15 % organic matter (carbon), which plays an important role in the fixation and sorption of iodine and rhenium. Average contents of target elements are: Re — 0.05–0.15 %, I — 0.02–0.07 %, Se — 0.10–0.30 %. An increase in organic content correlates with higher Re and I concentrations, indicating their co-migration and organophilic associations.

This distribution arises from their geochemical origin. Lead cakes inherit the composition of the original copper ores, genetically associated with the hydrocarbon-bearing sedimentary basins of Central Kazakhstan. According to geochemical studies [9], cupriferous sandstones and shales in this region contain hydrocarbons, humic substances, and mineral brines acting as natural concentrators of rhenium and iodine. These components migrate during oxidative–hydrothermal processes into ore-forming zones and ultimately into the gas-cleaning residues of copper smelting, creating secondary technogenic accumulations of valuable elements in the form of lead cakes.

Researchers at the National Center on Complex Processing of Mineral Raw Materials of Kazakhstan have developed several processing schemes for lead cakes aimed at extracting rhenium and osmium [10–14]. The most straightforward and well-proven method is oxidative leaching, in which rhenium passes into solution while osmium is concentrated in the gas phase. However, this method is effective only for cakes with ≤ 3–4 % organic matter. Higher organic content increases hydrophobicity, hindering oxidant access and reducing rhenium recovery to 15–20 %.

Therefore, alternative methods have been proposed, including:

- Reducing smelting of lead cakes at 1100–1200 °C, enabling element separation between crude lead, slag, and fumes [10–12];
- Oxidative roasting at 300–500 °C followed by aqueous leaching of rhenium [13, 14].

For rhenium-bearing molybdenum concentrates, oxidative roasting is traditionally used to transfer Re into the gas phase as Re_2O_7 [15–17]. In the case of lead cakes, the method is modified mainly to oxidize and remove organic matter and to convert Re into a water-soluble form, providing high extraction (up to 95 %) without external oxidants.

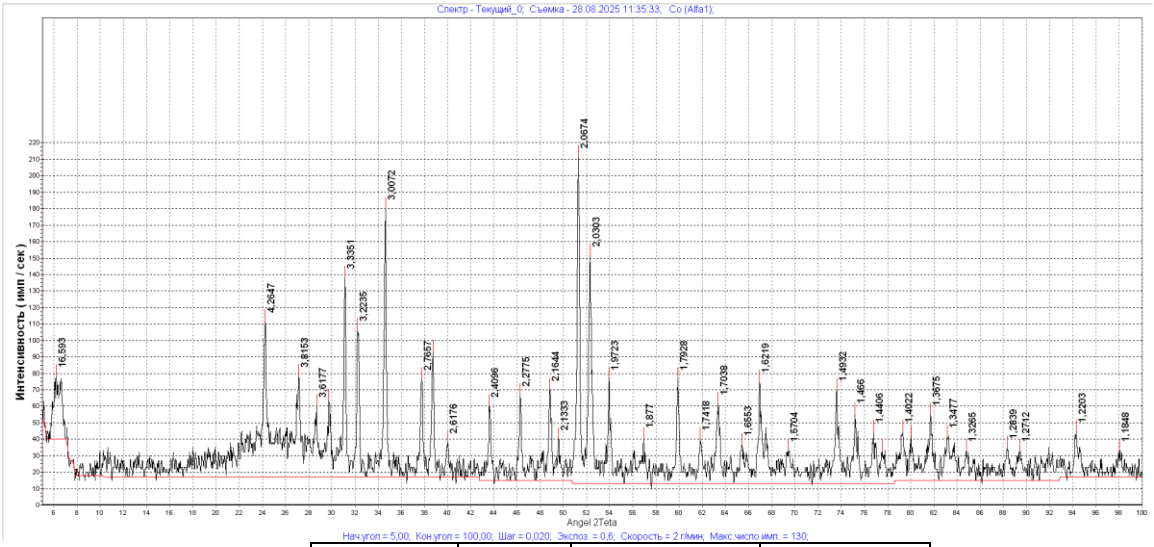
However, during roasting, iodine also dissolves along with rhenium. At the sorption–desorption stage, this co-migration reduces the ion-exchange capacity for rhenium due to competitive sorption of iodide species. Despite the high overall efficiency of oxidative roasting, this factor limits selectivity.

Thus, the present study aims to investigate the behavior of iodine during oxidative roasting of lead cakes, determine the temperature range of its volatilization, and optimize roasting conditions for effective separation of iodine and rhenium at early processing stages.

MATERIAL AND METHODS

The lead cakes investigated from copper production had the following chemical composition (wt.%): Pb 53.9; Cu 2.03; Zn 0.64; As 0.09; Se 0.81; total S 14.24; I 0.05; Re 0.098; Fe 1.1; total C 9.45.

The main phase is anglesite ($PbSO_4$), confirmed by XRD **(Fig. 1).**



Phase name	Formula	PDF card number	Content(%)
Anglesite	$PbSO_4$	00-089-7356	100

Fig. 1 X-ray diffraction pattern of lead cake

Roasting was conducted in a rotary tubular furnace at 300–600 °C.
Feed was dosed at up to 5 kg/min. Furnace parameters: drum inclination 1°, rotation 0.8 rpm.
Gaseous products were cooled in water-jacketed condensers and exhausted by a blower ensuring airflow and oxidation control.
After roasting, the calcine was weighed and analyzed for Re, I, and organic carbon. Leaching was performed at a solid/liquid ratio = 1:4, 70 °C, 30 min.
Fume products were analyzed to determine the distribution of iodine and rhenium between solid and gas phases.
Analytical methods:

- XRD – for phase identification before and after roasting;
- TGA/DSC – for mass-loss stages, endo/exothermic reactions, and oxidation onset/completion;
- EDS/XRF – for elemental analysis of calcines, fumes, and ion-exchange resins to assess Re, I, Pb, Cu, Zn, Se distribution

RESULTS AND DISCUSSION

Direct water leaching of the original lead cake yielded almost no rhenium dissolution due to hydrophobic organic films on particle surfaces.
During oxidative roasting at 300–400 °C, organic matter decomposes and rhenium oxidizes into stable water-soluble perrenates, readily leached without external oxidants. Under these conditions, rhenium recovery reached 95–96 % (**Table 1**).

Table 1 Effect of Roasting Temperature on Rhenium and Iodine Extraction

№	Temperature, °C	Re retained in calcine, %	I retained in calcine, %	Re extracted into solution, %
1	300	100	100	95.6
2	400	100	95.6	95.2
3	450	100	55.0	43.5
3	500	100	52.0	20.0
4	600	100	8,2	12,6

Iodine behavior strongly depends on temperature. Up to 400 °C, it remains in the solid phase; above 400 °C, volatilization occurs [18]. This reduces the iodine content in the calcine and decreases rhenium extraction, down to 43.5% at 450 °C and 20% at 500 °C.
During subsequent sorption from leachates (300 – 400 °C calcines), iodine was co-adsorbed with rhenium on the ion-exchange resin (**Fig. 2, Table 2**). The iodine content was roughly twice that of rhenium, suggesting that Re is sorbed as ReO_4^- and $[ReI_4]^-$ complexes, while iodine enters as I^- ions.

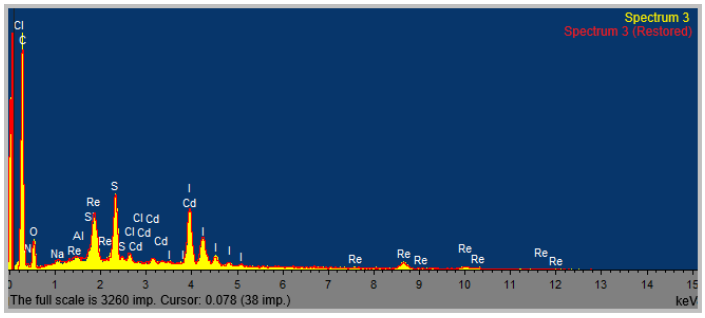


Fig. 2 EDS/XRF spectrum of rhenium-loaded ion-exchange resin

Table 2 Chemical Composition of Rhenium-Saturated Ion-Exchange Resin

Spectrum	**C**	**N**	**O**	**Na**	**Al**	**Si**	**S**	**Cl**	**Cd**	**I**	**Re**	**Total**
Spectrum 1	54,96	9,15	7,81	0,26	0,06	0,10	3,40	1,34	0,99	14,53	7,41	100,00
Spectrum 2	53,91	7,72	10,40	0,98	0,04	0,16	3,74	1,14	0,90	14,05	6,95	100,00
Spectrum 3	54,31	7,44	7,62	0,37	0,09	0,17	3,83	1,42	0,89	16,03	7,83	100,00
Average	**54,39**	**8,10**	**8,61**	**0,54**	**0,06**	**0,14**	**3,66**	**1,30**	**0,93**	**14,87**	**7,40**	**100,00**

After desorption with ammonia solution, Re and I contents decreased markedly (**Fig. 3, Table 3**), confirming that both elements pass into solution as ammonium complexes.

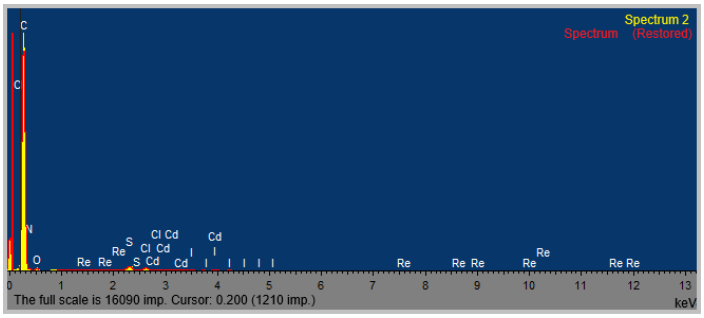


Fig. 3 EDS/XRF spectrum of ion-exchange resin after rhenium desorption

Table 2 Composition of Resin after Desorption with Ammonia

Spectrum	C	N	O	S	Cl	Cd	I	Re	Total
Spectrum 1	78.66	15.14	2.98	0.77	1.36	0.21	0.88	0.00	100.00
Spectrum 2	78.19	15.78	3.79	0.52	0.84	0.25	0.63	0.00	100.00
Spectrum 3	80.29	13.90	3.12	0.71	1.14	0.11	0.66	0.06	100.00
Average	**79.05**	**14.94**	**3.30**	**0.67**	**1.12**	**0.19**	**0.72**	**0.02**	**100.00**

TGA/DSC results revealed three major mass-loss stages (**Fig. 4**):

1. 100–200 °C – moisture removal and initial dehydration ($\Delta m_1+\Delta m_2 \approx$ 7,5 %).
2. 240–320 °C – oxidation of organics with O_2 uptake.
3. 380–430 °C – melting of low-melting PbI_2 and onset of iodine sublimation [19].

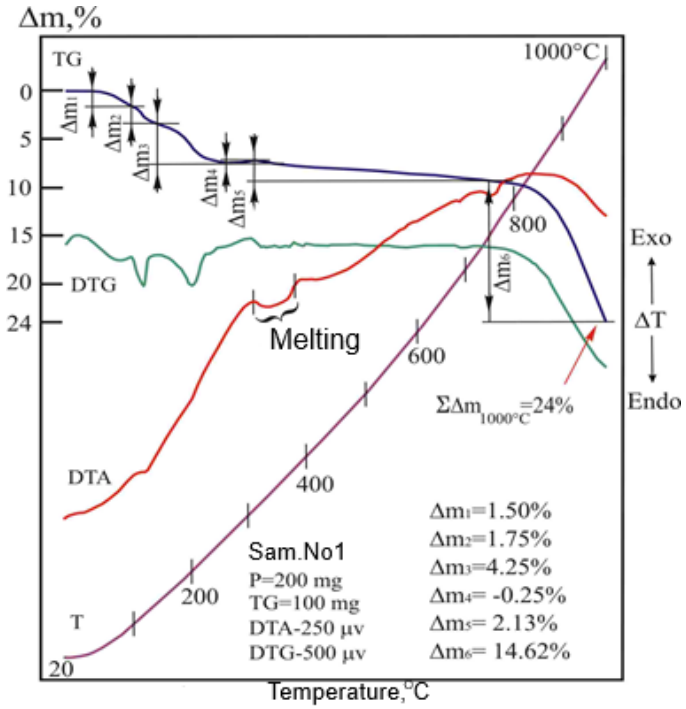


Fig. 4 Thermogravimetric curve of lead cake (20–1000 °C)

These correlate with the reduced rhenium solubility above 400 °C, confirming that Re remains in calcine as perrhenates and iodides that fully dissolve at ≤ 400 °C.

At higher temperatures, decomposition of rhenium iodides and PbI_2 formation occur, limiting O_2 diffusion into the solid phase.

XRD of the fume condensate (**Fig. 5, Table 4**) revealed PbI_2 (36 %) and $PbSO_4$ (64 %) as major phases, with Zn (6.3 %) and Se (7 %) impurities, indicating co-migration of volatile elements.

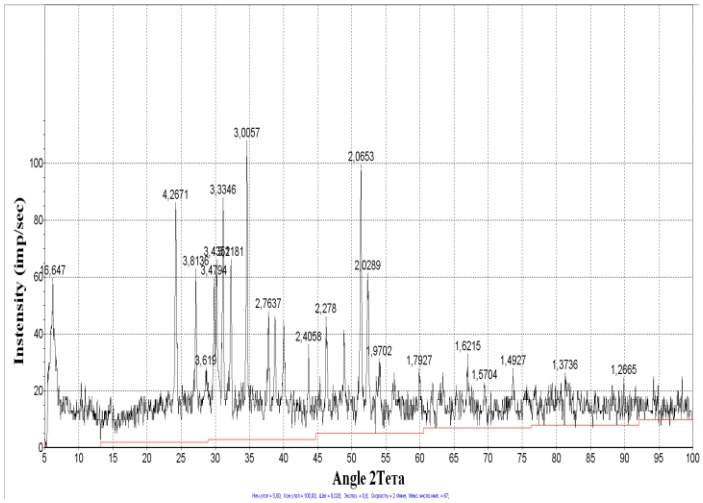


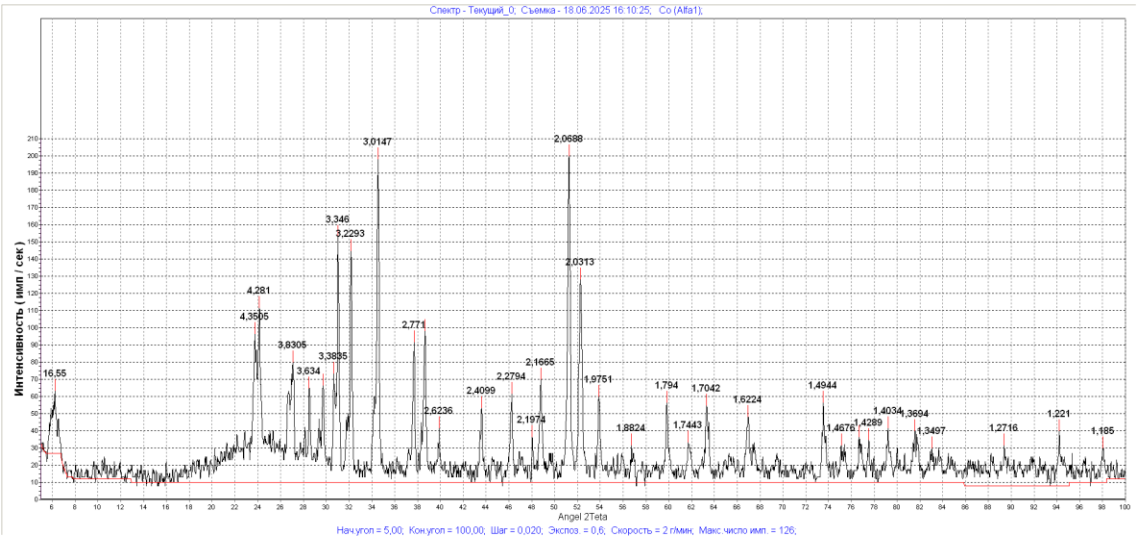
Fig. 5 XRD pattern of fume condensate

Table 4 Chemical composition of fume condensate, %

Spectrum	O	Si	S	Cl	Fe	Cu	Zn	Se	I	Pb	Total
Spectrum 1	19.61	0.80	6.99	1.53	1.73	0.77	6.81	7.68	11.47	41.61	100,00
Spectrum 2	19.22	0.71	7.48	1.70	1.36	0.75	6.85	6.93	10.66	44.34	100,00
Spectrum 3	18.38	0.58	7.26	1.52	1.95	0.97	5.28	6.39	12.86	44.81	100,00
Average	**19.07**	**0.69**	**7.24**	**1.58**	**1.68**	**0.83**	**6.32**	**7.00**	**11.66**	**43.92**	**100,00**

Thus, the reduced Re extraction from calcine is due to the transformation of rhenium iodides into insoluble forms via PbI_2 formation. Attempts to leach rhenium from iodine-free calcines using oxidants were unsuccessful, likely because thin surface films blocked oxygen diffusion. Increasing the roasting temperature increases the likelihood of oxidation but also promotes iodine loss.

To utilize the iodine-rich condensates, their leaching was tested. Literature reports dissolution of metallic Re from spent catalysts in ammonium iodide solutions at 160 °C [20, 21]. Lead iodide dissolves readily in water, leaving $PbSO_4$ and PbO residues (**Fig. 6**). Leaching of fume condensates was carried out at 30–50 °C (S/L = 1:3). The resulting solutions contained (ppm): Sb 144.7; W 161.5; Ni 1172.5; Fe 10597.6; Cr 1103.4; Si 1472.1; Cl 1044.8; S 3983.5; I 18786; Pb 156.9; Zn 563.3. These iodine-rich solutions (up to 18,786 ppm I) could replenish iodide ions during subsequent rhenium leaching.



Phase name	Formula	DB card number	Content(%)
Lead Sulfate	$Pb(SO_4)$	00-082-1855	92
Minium, syn	Pb_3O_4	00-071-0561	8

Fig. 6 XRD of residue after aqueous leaching of fume condensate

Solutions with various iodine concentrations (100–10,000 ppm) were prepared by dilution and used to leach calcines obtained at 450–600 °C. The rhenium extraction did not exceed 12–20 %, comparable to water leaching.

Therefore, the behavior of iodine and rhenium during lead-cake processing is governed by the thermochemical properties of their compounds and their mutual interactions during roasting and leaching.

CONCLUSIONS

Rhenium in lead cakes occurs as perrenates of base metals (Pb, Cu, Zn) and as rhenium iodides, enabling efficient extraction via aqueous leaching without external oxidants.

The optimal roasting range is 300–400 °C, providing up to 95 % Re conversion to water-soluble species.

Above 400 °C, iodine volatilizes as PbI_2, leading to the decomposition of rhenium iodides and the formation of insoluble oxides, thereby lowering extraction yield.

Complete selectivity can be achieved by separating Re and I at the desorption stage, optimizing ammonium-salt recrystallization to minimize iodine interference and improve ammonium perrenate purity.

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