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The Presence Form Iridium In Waste Gases Of Copper Production

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Abstract: The modern development of metallurgy requires comprehensive processing of raw materials with the extraction of valuable components from technogenic waste. Despite the presence of significant quantities of valuable components in technogenic waste, a significant aspect is the form of occurrence and properties of the extracted component, as their physicochemical properties during interaction with process reagents lead to unpredictable interactions. To select an effective technology and assess the quality of the resulting product, it is necessary to investigate and analyze the chemical and mineralogical formations of compounds in the raw materials. Consequently, iridium is present in the exhaust gases of the copper smelting section. Iridium belongs to the rarest and most refractory elements of the platinum group. Despite its extremely low content in nature, it can be present in the waste flows of non-ferrous metallurgy, especially during the processing of copper-nickel and copper-molybdenum sulfide ores containing platinum metal impurities. The capture and extraction of iridium from exhaust gases is becoming both ecologically relevant and resource-saving. This article is dedicated to the analysis of the forms of iridium's presence in gases, the thermodynamic aspects of its behavior in various types of furnaces, and the technical possibilities of its capture and extraction.

Keywords: Technogenic waste, dust-like waste, exhaust gases, inert metals, oxidizing medium, thermodynamics of sulfide formation, iridium occurrence form.

INTRODUCTION:

Non-ferrous metal ores are among the most complex natural raw materials, as they contain a wide range of valuable components in addition to the main industrial metals. The principal elements of interest include copper, lead, zinc, nickel, cobalt, molybdenum, tungsten, and bismuth, which constitute the primary basis for metallurgical extraction. Along with them, such ores also serve as important sources of precious and rare elements, including gold, silver, cadmium, indium, selenium, tellurium, rhenium, thallium, gallium, and rare earth elements. Furthermore, they often contain sulfur, barite, fluorite, quartz, and other gangue minerals, which can influence both the beneficiation processes and the efficiency of subsequent metallurgical treatment. The polymetallic nature of these ores makes their processing highly challenging, requiring the development of advanced technologies for comprehensive utilization.

During the pyrometallurgical processing of sulfide copper ores, particularly those rich in noble and rare metals, the behavior of these elements becomes extremely important for both economic and technological considerations. In such processes, iridium, along with other platinum group metals, can be redistributed into different technological flows. The largest share of iridium typically remains concentrated in the matte and slag phases. However, under the high-temperature conditions of smelting and in the presence of an oxidizing atmosphere, a certain fraction of iridium can volatilize and be carried into the off-gases. This occurs either as fine dispersed particles or in the form of gaseous oxides, which subsequently settle in dust or are released into the environment. Such losses are especially significant in enterprises engaged in the processing of sulfide copper-porphyry ores, where the volumes of raw materials are enormous and the noble metal content, though relatively low, represents considerable economic value when accumulated over large tonnages.

The continuous development of non-ferrous metallurgy is closely linked to a deeper understanding of the mechanisms responsible for the losses of both base and noble metals during pyrometallurgical treatment. One of the key unresolved issues in this field, and thus the relevance of the present work, is the lack of consensus in scientific literature on the exact forms in which rare and noble metals are lost to pyrometallurgical by-products. Researchers disagree as to whether these elements volatilize predominantly as oxides, sulfides, or complex mixed compounds. Clarifying this question is crucial, since it directly affects the design of recovery technologies and determines the efficiency of utilizing non-ferrous ores to their fullest potential.

To address this challenge, it is necessary to study in detail the thermodynamics of the formation and stability of oxide and sulfide compounds of noble and rare metals under pyrometallurgical conditions. The data available in published sources show significant discrepancies, which may arise from differences in experimental methods, temperature ranges, or the chemical composition of the ores under investigation. Therefore, a systematic thermodynamic analysis of the behavior of these metals, including the conditions of oxidation, sulfidation, and volatilization, is essential.

The development of new and efficient methods for extracting rare and noble metals from copper smelting off-gases can be achieved through such studies. In particular, the investigation of the thermodynamic properties of oxide and sulfide compounds of elements such as scandium, iridium, and other noble metals offers valuable insights into the mechanisms of their transfer between different phases of the metallurgical process. This knowledge not only contributes to the scientific understanding of high-temperature metallurgy but also provides a foundation for the creation of advanced technologies aimed at minimizing metal losses, improving resource efficiency, and ensuring the comprehensive utilization of complex non-ferrous raw materials.

MATERIALS

The present study examines the thermodynamic aspects of iridium behavior during copper smelting processes carried out in different pyrometallurgical aggregates of “Almalyk MMC” JSC. In particular, three furnace types were considered: the oxygen-fuel furnace (OFF), the Vanyukov furnace, and the reverberatory furnace (RF). Each of these units operates under distinct temperature ranges, oxygen potentials, and gas compositions, which strongly affect the distribution of iridium between the matte, slag, and waste gas phases.\

To assess the potential pathways of iridium migration, a detailed chemical analysis of the exhaust gases and process dusts from the AMMC copper smelting plant was conducted. The results are summarized in Table 1, which provides the comparative composition of the furnace charge and mixed dust collected from the gas-cleaning systems.

Table 1. Chemical analysis of the charge and waste gases of the AMMC copper smelting plant

Material name	Fe	Pb	Cu	Zn	Ir	Au	Ag	S	Al
Mixed dust	20.0	29.2	15.6	6.73	0.82	0.08	0.04	16.5	1.46
Vanyukov furnace charge	35.0	1.21	19.8	1.93	0.07	ND	0.031	27.0	2.74

From Table 1, it can be seen that the iridium content in mixed dust is significantly higher (0.82%) compared to its amount in the initial Vanyukov furnace charge (0.07%). This observation strongly suggests that iridium tends to migrate into the dust phase during the smelting process. The mechanism of such transition may involve either fine metallic particles mechanically entrained from the melting zone or sulfide inclusions that volatilize and subsequently condense in the off-gases. At the charging stage, iridium is introduced together with the raw material and is primarily concentrated in solid phases, later undergoing partial transfer to the dust phase during high-temperature treatment.

METHODOLOGY

To clarify the chemical forms in which iridium is present during smelting, its possible states were analyzed on the basis of thermodynamic stability, phase equilibria, and literature data. The following principal forms were considered:

a) Metallic Iridium (Ir^0).

Iridium may occur as mechanically included metallic particles, ranging from the nano- to the microscale. This is particularly characteristic for the charge, where the relatively low iridium concentration (0.07%) may originate as a trace impurity from platinum-bearing ores, anode slimes, or associated concentrates. Due to its extraordinary chemical inertness, metallic iridium can remain in the solid state without reacting even under intense smelting conditions. Consequently, Ir^0 particles may be physically carried away by gas flows and concentrated in dust collectors.

b) Iridium Sulfides.

Compounds such as Ir_2S_3 can form and coexist with other sulfide phases, including those of copper, iron, and lead. These sulfides remain thermodynamically stable in sulfur-rich, reducing environments and may be transported into dust as solid inclusions. In the high-temperature sulfide melt, iridium may enter complex mixed sulfides and later escape into the gas phase in finely dispersed form.

c) Iridium Oxides.

Oxide compounds of iridium, such as IrO_2 and Ir_2O_3, are less likely to form under reducing smelting conditions due to the high stability of iridium in the presence of reductants such as CO, SO_2, and H_2. Nevertheless, in localized oxidizing zones, particularly near the gas outlet where oxygen partial pressure is higher, finely dispersed oxide particles may appear and enter the dust. Among these, IrO_2 is considered the most stable oxide in the gas phase at high temperatures:

$Ir + O_2 \rightarrow IrO_2$, $\Delta G° < 0$ at $T > 1000$ °C

In contrast, in reducing atmospheres rich in sulfur, the formation of iridium sulfides becomes more probable, with compounds remaining in solid form and mechanically transferred with gas flows. Thus, iridium demonstrates strong resistance to oxidation but partial volatility under complex furnace conditions.

d) Characterization of Known Iridium Oxides.

Of the oxide phases, the most well-studied are Ir_2O_3 and IrO_2.

- Iridium (IV) oxide (IrO_2): a blue-black powder with a metallic sheen, soluble in mineral acids, obtained by heating $Ir(OH)_4$ to ~350 °C.
- Iridium (III) oxide (Ir_2O_3): a black powder insoluble in aqua regia, produced by mild calcination of iridium sulfide (Ir_2S_3) or by heating potassium hexachloroiridate ($K_3[IrCl_6]$) with sodium carbonate.

The reactions for Ir_2O_3 formation can be written as:

$$Ir_2S_3 + 9/2\ O_2 \rightarrow Ir_2O_3 + 3SO_2$$

$$2K_3[IrCl_6] + 3Na_2CO_3 \rightarrow Ir_2O_3 + 6KCl + 6NaCl + 3CO_2$$

RESULTS AND DISCUSSION

Iridium oxides may form in the low-temperature zone with residual oxygen:

Ir (gas or dust) + $O_2 \rightarrow IrO_2$ (solid) or Ir_2O_3 (solid)

The formation of finely dispersed iridium oxides is likely. They condense and are captured in dust. The results are presented in Table 2.

Table 2. Scheme of iridium distribution by phases (conditionally):

Phase	Form Ir	Share, % (approx.)
Metallic	Ir^0 (inclusions)	30–50
Sulfide	Ir_2S_3, IrS_2	30–50
Dust/volatile	IrO_2, Ir_2O_3 (oxides)	10–20

In mixed dust, iridium demonstrates a clear tendency to accumulate because it is not effectively retained by the molten slag phase. Instead of dissolving or being chemically bound within the silicate matrix of the slag, iridium is released from the smelting zone in the form of extremely fine metallic particles or sulfide inclusions. These finely dispersed solid phases are highly mobile and are easily transported by the upward gas flow, eventually condensing and becoming enriched in the dust fraction. Such a mechanism explains the relatively high concentration of Ir observed in mixed dust samples compared to the initial furnace charge.

One of the most critical parameters influencing the chemical form of iridium in the metallurgical environment is the partial pressure of sulfur-containing gases such as S_2 and H_2S. Elevated sulfur activity favors the transformation of metallic iridium into sulfide compounds (Ir_2S_3, IrS_2, etc.), while insufficient sulfur pressure prevents the stabilization of these phases. The reaction can be represented as:

Ir (solid) + 3/2 S_2 (gas) $\rightleftharpoons Ir_2S_3$ (solid)

This equilibrium process strictly follows the law of mass action. When the activity of sulfur in the system is low, the equilibrium shifts toward the left-hand side of the reaction, meaning that the formation of Ir_2S_3 does not occur, and iridium remains in its metallic state. Conversely, at sufficiently high sulfur pressure, the equilibrium moves toward the right, resulting in the stabilization of iridium sulfides.

From the standpoint of thermodynamics, the compound Ir_2S_3 is known to be stable only under conditions of relatively high sulfur partial pressure, particularly at elevated temperatures exceeding 1000 °C. At these temperatures, the Gibbs free energy of formation becomes negative, making the sulfide phase energetically favorable. For such stability to be maintained, the logarithm of the sulfur partial pressure, $\log_{10}(P_{(S_2)})$, must surpass a critical threshold value. This threshold can be quantitatively determined through thermodynamic stability diagrams, which illustrate the regions of predominance for different iridium phases (metallic, sulfide, or oxide). As shown in Figure 1, these diagrams are indispensable tools for predicting the behavior of iridium under variable furnace atmospheres and temperature regimes, thereby enabling a more accurate understanding of its distribution across different process phases.

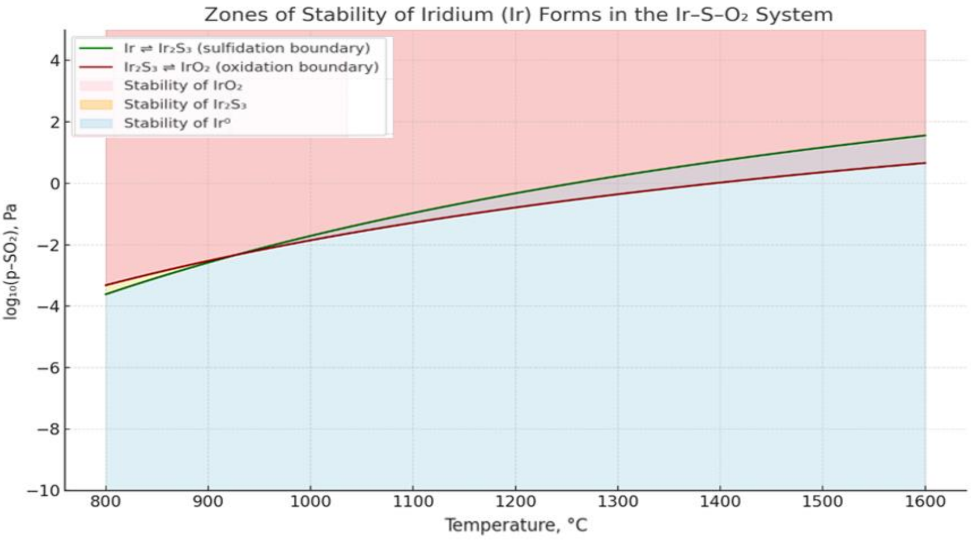

Fig.1. Dependence of iridium form formation in the Ir-S-O₂ system on the partial pressure of SO₂

◍ Low SO_2 → stable metallic form of Ir^0, □ Average SO_2 → possible presence of sulfide Ir_2S_3, ● High SO_2 and high temperature → IrO_2 is formed (oxidation).

The higher the partial pressure S2 or the presence of H2S - the higher the probability of Ir sulfide formation.

As is known, sulfur dioxide is released in metallurgical furnaces. Sulfur dioxide is not a direct sulfidizing reagent. It cannot react directly with iridium as it does, for example, with S2 or H2S.

$Ir + SO_2 \rightarrow Ir_2S_3$ or IrS_2

does not occur because SO2 is already an oxidized product, not an active form of sulfur for sulfidation.

SO2 regulates the oxidation-reduction potential of the medium (fO2) The partial pressure of SO2 affects the equilibrium of such reactions:

$S_2 + O_2 \rightleftharpoons 2SO_2$

The higher the partial pressure of SO2, the lower the activity of free sulfur S2, especially in the presence of oxygen. This makes it difficult to form iridium sulfides, as the concentration of sulfur in the required form (S2, H2S) decreases. SO2 can participate in the indirect desulfurization of Ir2S3.

If iridium sulfide has already formed and SO2 is abundant in the medium, the reverse process - sulfide oxidation - is possible:

Ir_2S_3 (solid) + $3SO_2$ (gas) $\rightleftharpoons$ 2Ir (solid) + $3S_2$ (gas) + $3O_2$ (gas)

Or in a more realistic form:

$Ir_2S_3 + O_2 \rightarrow 2Ir + 3SO_2$

This is thermodynamically possible at high temperatures and excess oxygen, especially in zones where gases are cooled. The oxidizing medium is detected at a high concentration of SO2. Under such conditions, iridium can remain a metal or transition to its oxide form (IrO2).

Based on the results of studying the shape of iridium, it was concluded that when the partial pressure of SO2 increases, the stability zone of sulfides narrows and shifts towards lower temperatures. This confirms that a high P_(〖SO〗 _2)is unfavorable for retaining Ir in the form of sulfides.

CONCLUSION

The conducted research demonstrates that iridium, due to its high chemical stability, exhibits a selective distribution across different phases in copper smelting systems. A significant portion of Ir is not retained by the slag but rather transitions into the dust fraction in the form of finely dispersed metallic particles and inclusions. The thermodynamic analysis confirms that the stability of iridium sulfides (Ir_2S_3, IrS_2) is strongly dependent on the partial pressure of sulfur-containing gases (S_2, H_2S). At low sulfur activity, iridium remains in its metallic state, while elevated sulfur pressure and temperatures above 1000 °C promote the formation of stable sulfide phases. Additionally, iridium oxides (IrO_2, Ir_2O_3) can form in oxygen-rich low-temperature zones and are also carried away with the dust.

Thus, the behavior of iridium in metallurgical aggregates is largely governed by the interplay of oxygen and sulfur activities in the gas phase. This explains its significant enrichment in mixed dust, which serves as a secondary raw material source for noble metal recovery. The results provide valuable insights for optimizing metallurgical processes aimed at minimizing noble metal losses and improving the efficiency of dust recycling technologies.

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