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A. R. Mambetaliyeva¹, orcid.org/0000-0003-1536-5259, K. K. Mamyrbayeva¹, orcid.org/0000-0002-1094-5345, D. K. Turysbekov², orcid.org/0000-0003-0904-1565, T. S. Dauletbakov³, orcid.org/0000-0003-3786-0218, M. B. Barmenshinova¹, orcid.org/0000-0003-0534-2387 1 – Satbayev University, Almaty, the Republic of Kazakhstan, e-mail: Alima 78@mail.ru

2 – JSC Institute of Metallurgy and Enrichment, Almaty, the Republic of Kazakhstan

3 – Innovative Eurasian University, Pavlodar, the Republic of Kazakhstan

INVESTIGATION OF THE PROCESS OF SULFIDING OF GOLD-ARSENIC CONTAINING ORES AND CONCENTRATES

Purpose. Research of the removal of arsenic by sulfiding from gold-arsenic containing concentrates of the Bakyrchik deposit.

Methodology. To determine the composition of the samples, chemical and electron probe analysis were carried out; to determine the phase composition of materials, X-ray analysis was conducted. In order to predict the process of sulfidation of arsenic and its compounds in the range of 298–2000 K, a thermodynamic analysis was performed. To establish the optimal conditions for the process of sulfiding arsenic and its compounds, studies were carried out to determine the effect of temperature and the consumption of elemental sulfur on the degree of sublimation of arsenic from gold-arsenic concentrate. The sulfiding roasting of the concentrate was carried out with elemental sulfur vapor coming from a new design evaporator with a mixture of gaseous nitrogen.

Findings. The main minerals of the original concentrate are pyrite, marcasite, arsenopyrite, native gold and silver. Significant elements in the concentrate are, %: arsenic 2.9–3.1, iron - 70–7.3, gold - 40. It has been calculated by thermodynamic analysis that when the main minerals of gold-arsenic containing refractory ores and concentrates interact with sulfur in a neutral environment and in the range of 500-1000 °C, reactions of formation and removal of arsenic in the form of sulfides As_2S_3 and As_4S_4 occur. When a new design evaporator supplies elemental sulfur in a mixture with neutral gas and with an increase in firing temperature from 700 to 850 °C at S: As = 0.35: 1, the degree of sublimation of arsenic increases from 94.7 to 98.2 %, with FeS $_2$: As = 1.3: 1 - from 94.0 to 99.5 %. With an increase in the consumption of elemental sulfur vapor (with an increase in the S: As ratio from 0.35: 1 to 0.6: 1 and a temperature from 700 to 800 °C), the degree of sublimation of arsenic from the gold-arsenic product reaches up to 99 %. The condensed sublimes contained up to 98.5-99 % As_4S_4 and As_2S_3 , the dust caught in cyclones is close in its composition to the composition of cinder.

Originality. A new technology for the removal of arsenic from gold-arsenic containing concentrates in an oxygen-free atmosphere in the temperature range of 700-850 °C with the removal and capture of arsenic sulfides up to 100 % is proposed. The regularity of the degree of sulfidation of arsenic and its oxidized compounds by elemental sulfur vapors in a mixture with a neutral gas to As_4S_4 and As_2S_3 has been established.

Practical value. The use of the new technology makes it possible to completely convert arsenic into sulfide forms which are environmentally friendly, convenient for storage, burial, or for use as antiseptics. The development can be used for processing arsenic-containing polymetallic ore materials.

Keywords: arsenic, gold-arsenic containing sulfur concentrate, sulfide roasting, sublimation, arsenic sulfides, evaporator, sulfidation

Introduction. The problem of arsenic is still one of the unresolved problems in the production of heavy non-ferrous metals. The distribution of arsenic during the processing of arsenic-containing raw materials between all products sharply worsens working conditions, creates problems with the removal and disposal of harmful arsenic compounds, reduces the quality of commercial products, and pollutes the environment in the areas where enterprises are located. For this reason, at present, a number of refractory gold-arsenic containing ores with a significant number of valuable metals are not used for processing. Currently it is given increased attention and requirements to increasing the complexity of the use of mineral raw materials, as well as environmental safety in its processing.

At many metallurgical enterprises, arsenic entering the metallurgical production along with raw materials of non-ferrous and noble metals is removed from the technological cycle in the form of conditionally dumped calcium arsenate cakes. These products have significant solubility and during storage have a pronounced negative effect on the components of the environment.

Literature review. Among the effective and environmentally friendly technologies for processing copper arsenic-containing concentrates and middlings is the method of sulfide

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pyroselection. Conducting the processing process in a sulfide atmosphere, taking into account the high reactivity of sulfur, can drastically reduce the volume of reaction gases, reduce dust entrainment and improve working conditions and eliminate environmental pollution by eliminating the formation of toxic oxide compounds of arsenic.

Various options for pyro- and hydrometallurgical processing of refractory gold-bearing concentrates have been proposed: roasting at a relatively low temperature [1] and two-stage firing in a fluidized bed furnace [2, 3], direct reduction smelting [4], pretreatment of concentrates using microwave pyrolysis [5, 6], direct [7] and combined methods of leaching [8, 9]. Some of them allow complex processing of mineral raw materials, but require multi-stage processing, expensive equipment and reagents. Others are characterized by insufficiently complete breaking up of the raw material, and hence the incomplete extraction of gold and the removal of arsenic in the form of a neutral compound.

In this regard, in the world practice research is currently underway in the direction of obtaining less toxic arsenic compounds during the processing of gold-arsenic materials, for which various pyrometallurgical methods are used with the introduction of a sulfidizing agent (pyrite) directly into the processed material [10, 11]. However, it should be noted that only part of the sulfur from the decomposition of pyrite at temperatures of 700–750 °C is consumed for the sulfidization

of arsenic according to the reaction: $FeS_2 = FeS + 0.5S_2$, while the rest from the decomposition of pyrite pyrrhotite (FeS), concentrating together with gold in the residues, deplete the gold-bearing product, which in turn creates significant difficulties in the subsequent extraction of gold due to the iron of pyrrhotites.

Unsolved aspects of the problem. The vast majority of the methods described above are not universal, require passing through several stages, are often complex or do not allow obtaining the extraction of valuable components to the required degree. The main disadvantage of all the technologies described above is the unresolved problem of environmental pollution.

In this regard, it is necessary to develop or improve existing technologies for the complex processing of gold-arsenic-containing ores and concentrates with the removal and utilization of arsenic in the form of environmentally friendly neutral compounds (sulfides) and the production of a commercial arsenic-free gold-containing product in one metallurgical unit.

Purpose. The purpose of this work was to study the optimal conditions for sulfiding roasting of gold-arsenic containing concentrates with the extraction and utilization of arsenic in an environmentally friendly sulfide form using a new design sulfur evaporator.

The flotation gold-arsenic concentrate obtained from the processing of ore from the Bakyrchik deposit was used as a feedstock for research.

Methods. To determine the material composition of the initial substances and the resulting products, chemical and electron probe analyzes were carried out; to determine the phase composition of materials and phase transformations, X-ray analysis was used on an XPert MRDPRO (PANalytical) diffractometer, and to study the oxide film on sulfides — a JEOL ISM — 25S 3 scanning electron microscope was applied.

For thermodynamic calculations, allowing one to indirectly determine the nature and direction of reactions during the firing process, the expanded Gibbs-Helmholtz formula was used, which makes it possible to calculate the change in the Gibbs free energy and the equilibrium constants of chemical reactions depending on the temperature change.

For the calculation, a program generated by the Delphi compiler was used, using temperature data: initial temperature, polymorphic transformation temperatures, firing temperature and final temperature (in the range of 773–1273 K).

For the calculation, we used the thermodynamic characteristics of substances published in the reference literature, as well as refined data on thermochemical constants for arsenopyrite and arsenides [12].

Sulfiding roasting of samples of gold-arsenic containing concentrates was carried out in a laboratory fluidized bed installation (Fig. 1) under the following conditions: a concentrate sample of 25 g, the firing temperature in the reactor (2) and in the evaporator was maintained in the range of 873—1023 K.

Results. Experimental part.

A flotation gold-arsenic concentrate was used as a feedstock for research, the chemical composition of which is given in Table 2.

As the results of chemical analysis show (Table 2), the content of arsenic in the concentrate is high and amounts to $2.9-3.1\,\%$, iron $7.0-7.3\,\%$, and a relatively high gold content is noted $-40\,\%$. The X-ray phase analysis of the samples showed that the main minerals of the concentrates are pyrite, marca-

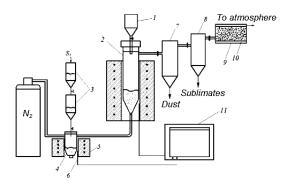


Fig. 1. Laboratory fluidized bed plant for sulfiding gold-arsenic containing concentrates:

1 — bunker for concentrate loading; 2 — reactor for roasting in the "fluidized bed" mode; 3 — hopper for supplying sulfur powder; 4 — sulfur evaporator; 5 — electric furnace; 6 — thermocouples; 7 — dust collector; 8 — heat exchanger-condenser; 9 — filter; 10 — filter packing; 11 — electropotentiometer

site, arsenopyrite, native gold and silver. Among the leading of the non-metallic minerals, there is quartz, micaceous minerals, feldspars, clay minerals, carbonates, and others. Native gold occurs in sizes from 0.0001 to 0.001 mm. Table 3 shows the content of the main components in gold-arsenic concentrates.

The main elements of the concentrates entering the sulfidizing roasting are iron, sulfur and arsenic (Table 3).

To predict the behavior of the main components of the arsenic-containing concentrate during firing in the fluidized bed mode, we performed a thermodynamic analysis using the main data shown in Table 4.

The reactions occurring as a result of the sulfiding process of gold — arsenic-containing material are shown in Table 5.

The calculated values of the isobaric-isothermal potentials of the proposed reactions are summarized in Table 6. In the calculation, it was assumed that sulfur in a given temperature range is in a vapor state in the form of S_2 molecules, and arsenic at a temperature of $600-650\,^{\circ}\text{C}$ passes into the gas phase in the form of As_4 molecules.

According to reactions (1-8), it can be assumed that the lower iron arsenide Fe₂As is sulfided by sulfur to form both FeAs monoarsenide and FeS pyrite.

Sulfidation of iron arsenides with sulfur is also possible with the formation of arsenopyrite, which reacts in the presence of an excess sulfidizing agent to obtain arsenic tetrasulfide, iron sulfide and pyrite. Arsenic in the gas phase exists in two molecular forms As_4 and As_2 [13, 14].

From a comparison of the results obtained, it follows that sulfur sulfiding can remove arsenic in the form of sulfides at relatively low temperatures. The reactions taking place can be written in the following form

$$2\text{FeAsS} + S_{2(\text{gas})} = 2\text{FeS}_{\text{T}} + 1/2\text{As}_{4}S_{4(\text{gas})}$$

$$2\text{FeAsS} \rightarrow \text{FeS}_{2} + \text{FeAs}_{2}$$

$$4\text{FeAsS} \rightarrow 4\text{Fe}_{1-x}S + 4x\text{FeAs}_{2} + (1-2x)\text{As}_{4}$$

$$\text{FeS}_{2} \leftrightarrow \text{FeS} + 1/2\text{S}_{2}$$

$$\text{Fe}_{1-x}S + 2x\text{FeAs}_{2} \rightarrow \text{FeS} + \text{As}_{4}$$

$$\text{FeAs}_{2} + 2S_{2(\text{gas})} = \text{FeS} + \text{As}_{2}S_{3}$$

Table 2

Chemical composition of the flotation concentrate, %

| Au | Ag, g/t | Fe | As | S _{tot} | SiO ₂ | Al ₂ O ₃ | MgO | Cu |
|-------|------------|---------|---------|------------------|------------------|--------------------------------|------|-----------|
| 39-40 | 1.5-2.5 | 7.0-7.3 | 2.9-3.1 | 2.7-3.9 | 42.5-58.2 | 13.4—14.5 | 0.66 | 0.04-0.05 |

Table 3
The content of the main components in the materials used for firing

| Material name | Component content, % | | | | | | |
|------------------------------------|----------------------|-------|----|------|------|------|--|
| Wiateriai name | Cu | Fe | Zn | С | S | As | |
| Low arsenic Bakyrchik concentrate | 0.04 | 17.62 | _ | 12.9 | 5.3 | 2.39 | |
| High arsenic Bakyrchik concentrate | 0.12 | 24.45 | _ | _ | 18.0 | 11.0 | |

According to the developed technology for the processing of gold-arsenic polymetallic raw materials in a fluidized bed, in order to remove arsenic in a non-toxic sulfide form, we have developed a new design of the sulfur evaporator, which (Fig. 2) provides a direct supply of elemental sulfur vapor mixed with a neutral gas to the layer of the processed material [15].

The use of a new design of the evaporator made it possible to control the consumption of elemental sulfur, the flow of gaseous sulfur into the reactor provided the mode of fluidization and sulfiding of the processed concentrate.

Table 4

Initial thermodynamic characteristics of substances

| Substance, | $\Delta H_{298}^{\circ},$ | $\Delta S_{298}^{\circ},$ | $C_p = a + bT + c'T^{-2}$, J/mol · K | | | nol · K | <i>T</i> , K |
|--------------------------------------|---------------------------|---------------------------|---------------------------------------|--------|-------------------|---------------------|--------------|
| aggregate state | kJ/mol | kJ/mol · K | J/mol · K | а | $b \cdot 10^{-3}$ | c · 10 ⁵ | 1, K |
| As ₄ (gas) | 143.68 | 329.70 | 77.40 | 83.07 | _ | -5.02 | 298-2000 |
| As ₂ (gas) | 193.80 | 242.37 | _ | 37.39 | _ | -2.18 | 298-2000 |
| As ₄ S ₄ (gas) | -5.44 | 451.45 | 164.01 | 177.44 | 7.95 | -13.81 | 298-1073 |
| As ₂ O ₃ (gas) | -656.89 | 107.11 | _ | 35.04 | 203.5 | _ | 273-548 |
| FeAsS (solid) | -137.03 | 67.95 | 68.49 | 62.88 | 40.55 | -1.42 | 298-975 |
| S ₂ (gas) | 127.52 | 228.04 | 35.73 | 36.48 | 0.67 | -3.77 | 298-3000 |
| FeAs ₂ (solid) | -85.73 | 80.21 | 70.88 | 76.15 | 3.92 | 3.97 | 298-1173 |
| Fe ₂ As (solid) | -4.60 | 144.64 | 72.93 | 76.74 | 0.48 | 3.92 | 298-1173 |
| FeAs (solid) | -43.47 | 60.00 | 50.58 | 35.32 | 44.06 | 7.14 | 298-1173 |

Table 5
Reactions of the sulfiding process of gold-arsenic containing material

| Reaction | (1) |
|---|------|
| $2\text{FeAsS}_{(\text{sol})} + S_{2(\text{gas})} = 2\text{FeS}_{(\text{sol})} + 1/2\text{As}_4S_{4(\text{gas})}$ | (2) |
| $FeAsS + FeS_{2(gas)} = 2FeS_2 + 1/4As_4S_{4(gas)}$ | (3) |
| $2/3 \text{FeAs}_{2(\text{gas})} + \text{S}_{2(\text{gas})} = 2/3 \text{FeS}_{(\text{sol})} + 1/3 \text{As}_4 \text{S}_{4(\text{gas})}$ | (4) |
| $FeAs_2 + 4S_{2(gas)} = 4FeS + As_4S_{4(gas)} + 4As$ | (5) |
| $2Fe_2As + 1/5S_{2(gas)} = 2FeS + 1/4As_4S_{4(gas)}$ | (6) |
| $FeAs_2 + 2S_{2(gas)} = FeS + As_2S_3$ | (7) |
| $2\text{FeAs}_s + \text{S}_{2(\text{gas})} = 2\text{FeS}_2 + 1/4\text{As}_4\text{S}_{4(\text{gas})}$ | (8) |
| $FeAsS + S_{2(gas)} = FeS_2 + 1/4As_4S_{4(gas)}$ | (9) |
| $2As_2O_3 + 3.5S_{2(gas)} = As_4S_4 + 3SO_{2(gas)}$ | (10) |
| $2As_2O_3 + 4.5S_{2(gas)} = 2As_2S_3 + 3SO_{2(gas)}$ | (11) |
| $As_4 + 2S_{2(gas)} = As_4S_{4(gas)}$ | (12) |
| $As_4 + 3S_{2(gas)} = 2As_2S_{3(gas)}$ | (13) |
| $1/4Cu_3As + FeS_2 = 3/4CuFeS_2 + 1/16As_4S_{4(gas)}$ | (14) |
| $2Cu_3As + 2.5S_2 = 3Cu_2S + 1/2As_4S_{4(gas)}$ | (15) |

 $\begin{aligned} 4FeAs_2 + 4S_2 &\rightarrow 4FeS + As_4S_4 + As_4 \\ 4FeAsS &\rightarrow 4FeS + As_4 \\ As_4 + 3S_{2(gas)} &= 2As_2S_{3(gas)} \\ As_4S_2 &\rightarrow As_4S_4 \end{aligned}$

Sulfur supply device. The complex processing of arseniccontaining polymetallic ores and concentrates is largely associated with the removal of arsenic from the technological process and its disposal.

Table 6

The value of the Gibbs energy (ΔG_0) of the main reactions

| Change in the Gibbs energy value (ΔG_0), kJ/mol | | | | | | | |
|---|----------|----------|----------|----------|----------|--|--|
| 773 K | 873 K | 973 K | 1073 K | 1173 K | 1273 K | | |
| -162.692 | -152.546 | -142.090 | -131.283 | -120.105 | -108.559 | | |
| -48.266 | -57.141 | -65.842 | -74.342 | -82.639 | -90.749 | | |
| -79.301 | -69.064 | -58.989 | -49.062 | -39.274 | -29.626 | | |
| -331.601 | -285.834 | -241.108 | -197.345 | -161.964 | -129.041 | | |
| -232.818 | -220.914 | -210.231 | -200.648 | -192.086 | -184.493 | | |
| -154.857 | -131.130 | -108.525 | -86.921 | -66.234 | -46.399 | | |
| -267.284 | -206.884 | -147.148 | -87.917 | -29.039 | 29.633 | | |
| -112.719 | -90.556 | -68.573 | -46.719 | -24.952 | -3.236 | | |
| -132.270 | -134.017 | -134.712 | -134.484 | -133.436 | -131.645 | | |
| -204.081 | -189.086 | -174.793 | -161.142 | -148.081 | -135.564 | | |
| -154.461 | -110.263 | -67.603 | -26.315 | 13.738 | 52.667 | | |
| -233.100 | -184.727 | -138.388 | -93.859 | -50.962 | -9.548 | | |
| -33.820 | -40.63 | -48.462 | -56.89 | -65.772 | -75.064 | | |
| -371.135 | -355.930 | -341.095 | -326.524 | -312.129 | -297.839 | | |

Results of sulfidation and sublimation of arsenic sulfides. The studies were carried out when the same amount of supplied vapors of elemental sulfur and sulfur vapors from the decomposition of pyrite were supplied to the layer of the processed gold-arsenic concentrate.

The process of sulfiding and sublimation of arsenic sulfides was analyzed. The results of the conducted studies are shown in Table 7.

As can be seen from the data obtained, when blowing the same amount of sulfur vapor for sulfiding, it is necessary to

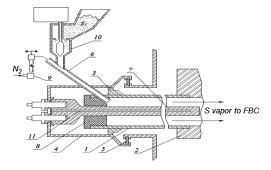


Fig. 2. Longitudinal section of the sulfur evaporator:

1 — sulfur evaporator; 2 — gas distribution block; 3 — sealing ring; 4 — cover; 5 — gasket; 6 — branch pipe; 7 — graphite heater; 8 — sealant; 9 — rotameter; 10 — nozzle; 11 — electric heaters

Table 7

The results of experiments on the sulfiding of arsenic with vapors of elemental sulfur and sulfur from the decomposition of pyrite

| Temperature, °C | Initial sample weight, g | Mass ratio S : As | Mass ratio FeS ₂ : As | Sublimation degree of arsenic, % |
|-----------------|-----------------------------|----------------------|-------------------------------------|--|
| 700 | 25 | 0.35:1 | _ | 94.7 |
| 750 | 25 | 0.35:1 | _ | 96.5 |
| 800 | 25 | 0.35:1 | - | 98.2 |
| 700 | 25 | _ | 1.3:1 | 94.0 |
| 750 | 25 | _ | 1.3:1 | 95.4 |
| 800 | 25 | _ | 1.3:1 | 98.7 |
| 850 | 25 | _ | 1.3:1 | 99.5 |

decompose pyrite in an amount 3 times greater than the volume of elemental sulfur.

With an increase in the firing temperature from 700 to 850 °C at S: As = 0.35: 1, the degree of sublimation of arsenic increases from 94.7 to 98.2 %, with pyrite: As = 1.3: 1 – from 94.0 to 99.5 %.

Studies to determine the degree of distillation of volatile compounds from copper-antimony-gold-containing raw materials were carried out depending on the temperature in the range of 700-800 °C, the weight of the sample was from 25 to 50 g, the S: As mass ratio was from 0.35:1 to 0.6:1. Sulfur injection was carried out with a neutral gas — nitrogen.

The results of the studies to determine the effect of temperature and elemental sulfur consumption on the degree of sublimation of arsenic from the gold-arsenic product at a processing time of 45 minutes are shown in Table 8.

It has been established that the optimal mode of arsenopyrite sulfiding is carried out when neutral gas is supplied to the material layer in a mixture with gaseous sulfur in a ratio of 1: (0.25–0.3) and sulfur consumption at the rate of 35–60 % of the mass of arsenic in arsenopyrite [14].

From the data of chemical, spectral, petrographic, X-ray diffraction methods of analysis, the sublimates obtained during sulfiding consisted of 97.5–98.5% of low-toxic arsenic sulfides, and 1–1.5% of mechanically removed particles of the processed material.

The sublimates condensed on the cold walls of the quartz retort, inside which the reaction vessel with the initial sample was placed, contained up to 98.5-99 % As₄S₄ and As₂S₃ [15].

In this case, the nature of the occurring reactions is presented in the following form

Effect of temperature and consumption of elemental sulfur on the degree of sublimation of arsenic

| Temperature, °C | Initial sample weight, g | Cinder weight, | Mass ratio S : As | Arsenic content in cinder, % | Sublimation degree of arsenic, % |
|-----------------|--------------------------------|----------------|----------------------|------------------------------|----------------------------------|
| 700 | 25 | 20.03 | 0.35:1 | 0.25 | 94.7 |
| 750 | 25 | 19.52 | 0.35:1 | 0.17 | 96.5 |
| 800 | 25 | 19.25 | 0.35:1 | 0.09 | 98.2 |
| 700 | 25 | 19.80 | 0.45 : 1 | 0.20 | 95.8 |
| 750 | 25 | 19.30 | 0.45 : 1 | 0.11 | 97.8 |
| 800 | 25 | 18.31 | 0.45 : 1 | 0.05 | 99.0 |
| 700 | 25 | 19.72 | 0.6:1 | 0.18 | 96.3 |
| 750 | 25 | 19.15 | 0.6:1 | 0.10 | 98.0 |
| 800 | 25 | 18.52 | 0.6:1 | 0.05 | 99.0 |
| 700 | 35 | 28.7 | 0.35:1 | 0.17 | 96.3 |
| 750 | 35 | 27.32 | 0.45 : 1 | 0.09 | 98.2 |
| 800 | 35 | 27.00 | 0.6:1 | 0.06 | 98.8 |
| 700 | 50 | 42.59 | 0.35:1 | 0.18 | 96.0 |
| 750 | 50 | 41.35 | 0.45 : 1 | 0.09 | 98.0 |
| 800 | 50 | 40.20 | 0.6:1 | 0.07 | 98.5 |

$$2FeAsS \rightarrow FeS_2 + FeAs_2$$

$$4FeAsS \rightarrow 4Fe_{1-x}S + 4xFeAs_2 + (1 - 2x)As_4$$

$$FeS_2 \leftrightarrow FeS + 1/2S_2$$

$$Fe_{1-x}S + 2xFeAs_2 \rightarrow FeS + As_4$$

$$4FeAs_2 + 4S_2 \rightarrow 4FeS + As_4S_4 + As_4$$

$$4FeAsS \rightarrow 4FeS + As_4, \quad As_4 + 2S_2 \rightarrow As_4S_4$$

Thus, during sulfiding roasting, iron arsenopyrite FeAsS dissociates to form lower iron sulfides and elemental arsenic and sulfur. At high temperatures, in the presence of arsenic and sulfur in the system, the formation of As_4S_4 is inevitable.

Sublimates of arsenic sulfides, obtained during the roasting of arsenic-containing polymetallic raw materials, are mostly finely dispersed material with a developed surface, which contributes to oxidation and leaching upon contact with the external environment. To clarify this conclusion, we studied the effect of the granulometric composition (pulverization) of arsenic and arsenic-containing sulfides on the degree of their oxidation.

The following materials were used as initial substances: elemental arsenic; sublimes of arsenic sulfide condensed and fused; arsenic sulfides, obtained by a hydrochemical method. All samples were kept in an air atmosphere at room temperature for 60 days.

As a result of the studies carried out, it was established (Table 9) that the oxidation of elemental arsenic in air is accompanied by a gradual increase in weight up to the expiration of 60 days, after which the increase practically stops. During the same time, the weight of samples with arsenic sulfides remains unchanged.

As follows from the data in Table 9, the oxidizability of arsenic and its sulfides is significantly affected by the size of the starting material. Arsenic sulfide compounds are arranged in descending order of oxidation degree: $As_{met} \rightarrow As_2S_{3amorph} \rightarrow As_2S_{3cryst} \rightarrow As_4S_4(As_4S_3)_{crystal.} \rightarrow sulphide fumes.$ After

The degree of oxidation of elemental arsenic and its sulfides in the air (at 60 days)

| No | Substance | Fineness, mm | Contents As, % | The amount of oxidized As, % |
|----|---|--|----------------------|------------------------------|
| 1. | Arsenic crystalline | $-0.5 + 0.1 \\ -0.1 + 0.08 \\ -0.08$ | 99.9 99.9 99.9 | 2.5 7.9 16.5 |
| 2. | As ₂ S ₃ , melted pounded | $-0.063 \\ 0.08 + 0.063 \\ -0.1 + 0108$ | 60.1 60.1 60.1 | 0.45 0.16 0.07 |
| 3. | As ₂ S ₃ , obtained by hydrochemical method | amorphous | 59.8 | 1.7 |
| 4. | As ₄ S ₄ , melted pounded | $-0.063 \\ -0.08 + 0.063 \\ -0.1 + 0.08$ | 69.2 | 0.24 0.09 0.025 |
| 5. | Condensed sulphide fumes | < 1 · 10 ⁻⁴ | 67.2 71.8 | 0.23 0.31 |
| 6. | Sulfide sublimates, fused in the form of a monolithic piece | 1-10 | 67.2 71.8 | _ |

60 days, in addition to a monolithic piece of melted sulfide sublime, an oxide film appeared in all samples. Its thickness calculated using an electron microscope on arsenic sulfides was $(2.3-3.0)\ 10^{-4}$ cm.

Thus, as the results show, it is most preferable to obtain sulphide sublimates in a monolithic molten form, which will allow them not only to be safely buried, but also simply stored under sheds. In addition, arsenic sulfides can be used in the woodworking industry as antiseptics for impregnating wood, as well as for impregnating railway sleepers. Arsenic-based antiseptics are highly toxic to wood pests and destroyers, have strong fixation and do not cause negative changes in the technological, physical and mechanical properties of wood products, and ensure their resistance to decay. Arsenic acid and sodium arsenate, which are part of most preparations, are also currently used [16].

Conclusions.

- 1. For the processing of high-arsenic concentrates, the processes of sulfiding roasting with the production of arsenic sulfides as a commercial product and arsenic-free cinders processed by traditional methods are promising.
- 2. Thermodynamic analysis revealed a stepwise nature of the sulfidation of arsenic and its oxidized compounds with elemental sulfur vapors. It has been established that already at a sulfur pressure of more than 0.1–1 Pa, arsenopyrite (FeAsS) decomposes into iron sulfides with the release of arsenic into the gas phase.
- 3. A sulfur evaporator has been developed and designed, which allows not only controlling the consumption of elemental sulfur, but also ensuring a uniform supply of sulfur vapor mixed with a neutral gas (nitrogen) to the initial sample layer for fluidization and sulfiding of the processed material.
- 3. With an increase in firing temperature from 700 to 850 °C at S: As = 0.35: 1, the degree of sublimation of arsenic increases from 94.7 to 98.2 %, at FeS₂: As =1.3: 1 from 94.0 to 99.5 %.
- 4. With an increase in the S: As ratio from 0.35:1 to 0.6:1 and a temperature of 700 to 800 °C, the degree of sublimation of arsenic from the gold-arsenic product reaches up to 99 %.
- 5. The optimal mode of arsenopyrite sulfiding is carried out when neutral gas is supplied to the material layer mixed with vaporous sulfur in a ratio of 1: (0.25–0.3) and sulfur con-

sumption at the rate of 35–40 % by weight of arsenic in arsenopyrite. Sulfidation of concentrates under such conditions makes it possible to obtain sublimates containing up to 98.5–99 % of low-toxic arsenic sulfides.

- 6. It has been established that it is most preferable to obtain sulfide sublimates in a monolithic molten form, which will allow not only safely burying them, but also simply storing them.
- 7. The proposed technology of sulfide sublimation roasting can be used for processing similar arsenic-containing polymetallic materials.

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Дослідження процесу сульфідування золото-миш'яковмісних руд і концентратів

А. Р. Мамбеталієва¹, К. К. Мамирбаєва¹, Д. К. Турисбеков², Т. С. Даулетбаков³, М. Б. Барменшинова¹

- 1 Satbayev University, м. Алмати, Республіка Казахстан, e-mail: Alima 78@mail.ru
- 2 AT «Інститут металургії та збагачення», м. Алмати, Республіка Казахстан
- 3 Інноваційний Євразійський університет, м. Павлодар, Республіка Казахстан

Мета. Дослідження виведення миш'яку сульфідуванням з золото-миш'яковмісних концентратів і руд Бакирчікського родовища.

Методика. Для визначення складу проб проведено хімічний та електронно-зондовий аналіз; для визначення фазового складу матеріалів — рентгенографічний аналіз. З метою прогнозування процесу сульфідування миш'яку та його сполук в інтервалі 298—2000 К виконано термодинамічний аналіз. Для встановлення оптимальних умов процесу сульфідування миш'яку і його сполук проводилися дослідження з визначення впливу температури й витрати елементної сірки на ступінь сублімації миш'яку із золото-миш'якового концентрату. Сульфідуючий випал концентрату проводився парами елементної сірки, що надходить із випарника нової конструкції із сумішшю з газоподібним азотом.

Результати. Основними мінералами вихідного концентрату є пірит, марказит, арсенопірит, самородне золото та срібло. Значущі елементи в концентраті, %: миш'як 2,9-3,1, залізо -7,0-7,3, золото -40. Термодинамічним аналізом розраховано при взаємодії основних мінералів золото-миш'яковмісних руд і концентратів із сіркою в нейтральному середовищі та інтервалі 500-1000 °C протікання реакцій утворення й видалення миш'яку у вигляді сульфідів As_2S_3 і As_4S_4 . При подачі випарником нової конструкції елементної сірки в суміші з нейтральним газом і зі збільшенням температури випалу з 700 до 850 °C при S: As = 0,35: 1 підвищується ступінь сублімації миш'яку від 94,7 до 98,2 %, при FeS_2 : As = = 1,3: 1 — від 94,0 до 99,5 %. Зі збільшенням витрати парів елементної сірки (при збільшенні співвідношення S: As від 0,35 : 1 до 0,6 : 1 і температури від 700 до 800 °C) ступінь сублімації миш'яку із золото-миш'якового продукту досягає до 99 %. Сконденсовані возгони містили до 98.5— 99 % As_4S_4 і As_2S_3 , уловлений у циклонах пил за своїм складом близький до складу недогарка.

Наукова новизна. Запропонована нова технологія виведення миш'яку із золото-миш'яковмісних концентратів у безкисневій атмосфері в діапазоні температур 700-850 °C з видаленням і уловлюванням сульфідів миш'яку до 100 %. Встановлена закономірність ступеня сульфідування миш'яку та його окислених сполук парами елементної сірки в суміші з нейтральним газом до As_4S_4 і As_2S_3 .

Практична значимість. Застосування нової технології дозволяє повністю перевести миш'як у сульфідні форми, що екологічно безпечні, зручні для зберігання, захоронення або для використання в якості антисептиків. Розробка може бути використана для переробки миш'яковміних поліметалічних рудних матеріалів.

Ключові слова: миш'як, золото-миш'яковмісний концентрат сірки, сульфідуючий випал, сублімація, сульфіди миш'яку, випарник, сульфідація

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