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Pyrometallurgical Scheme Intended to Process Arsenic-Containing Concentrates with Recovery of Precious Metals

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Abstract: The practicability of a pyrometallurgical scheme for raw material processing is established as a result of the analysis of methods intended to dearsenate and process gold-arsenic concentrates as well as equipment for the process execution. The conceptual design of vacuum equipment without forced movement of the dispersed material in the sublimator and of the reaction zone materials is proposed. In-process tests for the sublimation of arsenic sulfides from gravity and flotation concentrates received from the Bakyrchik deposit were executed at the pilot facility. As a result, it was found that more than 97–99% of arsenic passes into the gas phase and condenses in a sulfide form suitable for compaction by smelting. More than 99.5% of precious metals are concentrated in the sublimation residue. As a result of smelting residue from the sublimation of arsenic sulfides in a cyclone furnace, together with copper concentrates to copper matte, the gold recovery was 93.7–93.9% of the total amount loaded. Silver was 65.7–68% concentrated in copper matte, with a considerable amount in the dust. If the cyclone smelting dust is involved, the recovery rate of gold and silver can be increased to 97–99% and 94–95%, respectively. As a result of crucible smelting, the degree of recovery of gold in matte was 95.4%, with its content in slag being 3.6 g/t. The received matte according to the proposed scheme can be directed to the conversion process by obtaining blister copper, which is subjected to electrolytic refining with the recovery of gold from slimes.

Keywords: gold; silver; copper; arsenic; concentrate; sublimator; cyclone; matte; slag; dust; recovery

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1. Introduction

A high quantity of deposits with concentrations of 20–1600 g/t gold, up to 6% copper, up to 23% carbon, and significant amounts of arsenic (0.6–42%) in their composition are found in the territory of Kazakhstan, Central Asia, Russia, Australia, China, and other regions [1,2]. Table 1 shows the content of the main components from some gold–arsenic-containing concentrates. Due to the fact that arsenic prevents gold recovery, a significant amount of work is devoted to the development of highly efficient technologies intended for dearsenation of this kind of raw materials. However, the problem of how to achieve a high degree of precious metal recovery is still unresolved.

Thus, a considerable number of studies are devoted to hydrometallurgical methods of arsenic removal from concentrates using different solvents and combinations of process flows [3–6], including autoclave oxidation [7,8] and microwave leaching [9]. The main disadvantage of processing raw materials under these schemes is the insufficient recovery of gold inclusions into the main concentrate minerals.

Table 1. Composition of gold- and arsenic-containing concentrates.

Concentrate	Contents						References
	Au, g/t	Ag, g/t	As, wt. %	Cu, wt. %	Fe, wt. %	S, wt. %	
Concentrate of gold mine in Liangshan District (Sichuan Province, China)	63.76	69.30	8.90	0.09	21.03	18.48	[10]
Serrenti-Furtei gold-bearing deposit in Southern Sardinia (Italy)	90.25	no data	12.55	33.15	9.16	no data	[7]
Arsenic-containing gold-bearing concentrate from Hunan Province (China)	60.16	50.27	13.84	0.097	32.33	23.62	[3]
Gold concentrate from Golden Sun Co. Ltd. (Jeollanam-do, Korea)	130.20	986.6	0.25	0.19	8.68	0.25	[4]
Concentrate from Uderey deposit (Krasnoyarsk Region, Russia)	30.00	no data	12.20	no data	21.60	20.00	[11]
Arsenopyrite concentrate from New England Antimony Mine (New South Wales, Australia)	no data	no data	31.60	no data	36.80	28.0	[12]
Gravioconcentrate from the Vasilkovskoye deposit (Kazakhstan)	5–50	16–20	1.60–5.10	0.29–4.00	4.00–9.00	2.05	[13]
Concentrate from a deposit of Yenisei ridge (Yakutia, Russia)	15–80	no data	3.00–13.20	no data	7.26–22.44	8.22–22.44	[14]
Concentrate from pyrite-arsenopyrite mineralization in northern Finland	no data	no data	6.00	no data	21.60	19.50	[15]
Concentrate from Olympias deposit (Chalkidiki, Greece)	21.00	no data	7.50	no data	43.70	no data	[16]
Concentrate from GENMIN'sFairview Mine (Barberton, South Africa)	131.50	no data	6.71	no data	no data	no data	[17]
Concentrate from Hunan (China)	30.00	66.90	8.87	no data	19.94	30.71	[18]

The process of flotation of Au-Cu-containing concentrate dearsenation [7] using autoclave alkaline leaching with a mixture of Na_2S and NaOH solutions was studied. The concentrate was preliminarily crushed to a coarseness of 0.02 mm. The results showed that this method can recover 98% of arsenic. However, a part of the gold in the form of thiosulfates and polysulfides is leached together with arsenic.

With the purpose of increasing the degree of gold recovery from arsenopyrite concentrate during cyanidation, it was proposed to use preliminary dearsenation of raw materials by two-stage bio-oxidation [3]. As a result of this method, the degree of gold recovery after cyanidation increased from 34.86 to 95.66%. The arsenic content in the residue after bio-oxidation was 1.81%. In [5], preliminary dearsenation is performed by alkaline leaching with the use of sodium hydroxide and hydrogen peroxide as an oxidizer. The concentrate is preliminarily subjected to an oxidative–sulfidizing and oxidative–roasting process. This approach provides a high recovery rate of arsenic into the solution (89.58–95.12%) and reduces its content in the cakes from 1.2–1.4 to 0.06–0.15%. The gold recovery degree according to the described scheme is 97.3–97.9%.

In [4], the authors propose recovering arsenic by water leaching of roasted concentrate in the presence of sulfuric acid. The preliminary roasting stage contributes to the transfer of arsenic and impurity elements (Fe, Zn, Cu, Pb) into water-soluble compounds. Gold and silver are concentrated in the oxide form in the leaching residue. The maximum degree of arsenic recovery during the leaching process was 78.2%.

Several types of reagents were used by the authors [6] to develop a dearsenation process in order to minimize arsenic recovery in the subsequent stage of gold recovery with thiosulfate solution. The process consists of two stages: alkaline leaching in NaOH solution and arsenic leaching. It was noted that the use of oxalic acid at the second stage helps to reduce the release of arsenic in thiosulfate leaching of gold by 97.7%.

The authors [8] suggest using a high-temperature autoclave water leaching process for subsequent cyanidation in order to uncover the refractory gold-arsenic concentrate. As a result of this method, the arsenopyrite present is transformed into claudetite (As_2O_3) and skorodite ($FeAsO_4 \cdot 2H_2O$). Pyrite is completely destroyed. This method made it possible to

achieve a gold recovery rate of 97.13% in cyanidation. Arsenic is removed from the process in the form of iron arsenate.

The authors [18] tested a microwave leaching process for refractory gold-containing concentrate in nitric acid solution. Technological experiments showed that the following maximum recovery rates: arsenic—84.0%, copper—85.8%, iron—98.7%, and zinc—14.9%. The gold content in the residue was about 132.55 g/t.

The main method used for arsenic removal from raw materials continues to be improved. The oxidative roasting process [19] is used to prepare raw materials for subsequent gold recovery by leaching, including additional chloride roasting [20], as well as the transfer of arsenic to slag in the process of flash smelting of copper [21].

Attempts were made to process gold- and arsenic-containing concentrates by the bloomery process method. It consists of the reduction of iron compounds with the help of coke or calcium carbide to metallic ones with gold concentration and the subsequent separation of blooms by magnetic separation. In this case, arsenic is taken out in the gas phase, mainly in the form of sulfide [22]. The technology did not find its application due to the gold distribution in the processing products—more than 20% of the precious metal was transferred into the non-magnetic fraction, meaning it could not be considered a waste product.

Recently, considerable attention was paid to the study of the roasting process for arsenic-containing raw materials in an atmosphere of superheated water steam at 700–1000 °C when arsenic is released into low-toxic sulfide forms—arsenic disulfide and sesquisulfide—as a result of secondary reactions [23–25].

The attempts to suppress high-temperature sublimation of arsenic sulfides by loading calcium oxide, carbonate, sulfate, and sulfite on the melt surface to prevent the sublimation of arsenic compounds and its subsequent oxidation to trioxide were unsuccessful [26].

Soda smelting of gold concentrate with a low arsenic content (0.25%) on a lead collector [27] with the use of an oxide-sulfate fraction from the cutting of battery scraps is accompanied by the formation of arsenic oxide in the gas phase and is not applicable for high-arsenic concentrates, despite a fairly high recovery rate of precious metals.

Reduction smelting of gold-containing carbon-bearing ore of the Sayak-4 deposit (Kazakhstan) with 3.5 g/t Au; 1.76 Ag; 3.3% As for collector iron-copper alloys [28] and coal-arsenic gold ore from the Bakyrchik Deposit (Kazakhstan) [29] with 5.5–12 g/t Au, 0.8–1.2 g/t Ag and 1–2.05% arsenic per matte was accompanied by a very high yield (50–55%) of slag in the first case and even higher yield (61.0–70.6%) in the second case. The gold content in the slag during iron-copper alloy smelting ranged from 0.38 to 0.50 g/t, while matte smelting was 0.29–0.57 g/t, resulting in huge losses of precious metals, and was not rational from an economic or environmental point of view, taking into account the transfer of almost all arsenic into the gas phase.

In this regard, dearsenation of concentrates by sublimation of arsenic compounds in a vacuum at moderate temperatures with their condensation in sulfide form and compacting of dispersed sublimations by the smelting process at 260–300 °C in ingots with a density of about 3000 kg/m^3 [30] is a preferable method. However, gold recovery did not exceed 65–67% during direct cyanidation [31] and thiocarbamide leaching [32] of residues after vacuum sublimation of arsenic compounds.

Additional hydrometallurgical processing studies for residues from vacuum processing of gold-arsenic concentrates that consisted of preliminary leaching of iron by hydrochloric acid solution, additional grinding of the residue to a coarseness of less than 0.074 mm, and repeated cyanidation process improved the technological performance, but the maximum gold recovery degree did not exceed 87.5% [33].

Significantly higher gold recovery rates from the residues of vacuum-thermal processing of concentrates were achieved during the crucible smelting process for ferrous matte in a high-frequency furnace with pyrite addition and copper matte smelting in a cyclone furnace together with copper concentrate. Gold recovery into the ferrous matte was 95.4% in the first case and 96–99% in the copper matte and circulating dust in the second

case [34]. The latter testifies in favor of pyrometallurgical scheme of arsenic-gold-containing concentrate processing.

Studies, design development, and factory tests were conducted at the Institute of Metallurgy and Ore Beneficiation (Almaty, Republic of Kazakhstan) for many years. They were intended for vacuum thermal processing of various arsenic-bearing ores and concentrates [35–40] in a stationary and vibratory fluidized bed. The laboratory facility for vibratory fluidized bed tests consisted of a vertically mounted quartz beaker connected to an electrodynamic vibrator. The beaker was hermetically closed by a quartz retort connected to a vacuum pump. A preheated electric furnace was put on the retort. Large-scale technological tests of the developed technology were executed with a vacuum electric furnace where a vibrating conveyor in the form of a screw with sides coiled on a carrying tube with a heater inside was used as a working body. The movement was performed at the expense of the directed vibrations reported to the tube.

Thus, laboratory tests for vacuum thermal technology of arsenic recovery in the vibratory fluidized bed were performed with a sample of concentrates obtained from Central Asia [36] containing wt. %: 9.6 As; 16.3 S; 20.9 Fe; 31.2 SiO_2; 0.44 CaO; 0.13 Cu; and 0.16 Zn, shown as follows. Dearsenation should be executed at 600–650 °C at a pressure of 2.67–13.3 kPa for 15 min at vibration acceleration 1–2 (frequency of 24 Hz, the range 1 mm or frequency of 50 Hz, the range 0.2–0.3 mm) for the most complete removal of arsenic (97.71–98.6%).

It was found that the arsenic sublimation degree was 96.19–98.04% at a process temperature of 650–750 °C, pressure of 6.65 kPa, and process duration of 5–15 min when the technology was tested in relation to the PRC concentrates [37]. The concentrate sample contained wt. %: 1.4–1.44 As; 3.9 Sb; 35.10–35.32 Fe; 35.24 S; 14.1 SiO_2. The gold and silver contents were 59.0 and 38.6 g/t, respectively. Given the presence of antimony in the concentrate, the optimal parameters were 750 °C, 6.65 kPa, and a 10 min process duration. The recovery degrees of arsenic and antimony were 98.04 and 94.80%, respectively. When a vibratory fluidized bed was created, the vibration amplitude was 1 mm, and the vibration frequency was 24 Hz.

High arsenic recovery rates (98–99%) were also achieved by testing the technology for PRC concentrate samples of another batch [38] at 700–750 °C, pressure 0.13 kPa, for 5–15 min. The chemical composition of the samples was as follows: wt. %: 16.2 As; 0.037 Sb; 19.38 S, 0.078 Cu; 24.3 SiO_2; 11.9 Fe. The gold and silver contents were g/t: 88.45 g/t and 282 g/t, respectively. The obtained char contained 0.2–0.3% arsenic in large-scale experiments performed at 700–750 °C with a pressure of 1.33–2.66 kPa.

Vacuum-thermal technology was also tested for gold-containing concentrates from Yakutia [39], containing up to, wt. %: 15.9 As; 35.66 Fe; 32.44 S. The contents of gold and silver were up to 104 and 153 g/t, respectively. The degree of arsenic sublimation was 95–99% at 700–800 °C, at a pressure of 0.13–6.67 kPa within 1–15 min for this kind of raw material in the laboratory conditions. During large-scale technological tests, 1109 kg of concentrate was processed at 700 °C in the reactor, with a residual pressure of 13.3 kPa and average productivity of the vibro-vacuum unit of 3 t/day. The yield of the cinder was 69.25%, its arsenic content was 0.67%, and the degree of distillation was 97.1%. Condensate was a yellow powder containing 70.2% arsenic and 28.7% sulfur.

The enlarged tests were also carried out for the Kazakh gravity gold-arsenic concentrate [40]. Vacuum thermal processing was carried out on the enlarged laboratory vibro-vacuum unit with productivity of 200 kg/day at 720–750 °C and pressure of 2.66–5.32 kPa. The content of arsenic, iron, and sulfur in the concentrate was, wt. %: 20.85; 38.2; 36.6 S, respectively; gold and silver, g/t: 250 and 10.8, respectively. It was found that the degree of arsenic distillation was 99.17%, with a residue containing 0.26 wt. % arsenic, 270.9 g/t gold, and 15.1 g/t silver.

As can be seen, vacuum thermal technology and the vibro-vacuum unit proved themselves in the dearsenation of various concentrates. However, due to the need to transfer a high power heat flow from the heater inside the carrier tube to the processed

concentrate on the vibroconveyor, and due to the aggressiveness of sulfur-containing steam, there is an insurmountable obstacle in the form of residual deformations and corrosion of structural materials of the working body [41]. This fact affects the service life of reactors and makes it practically impossible to create vacuum apparatuses with a high capacity for a highly efficient technological processes proceeding at 600–800 °C in the reaction space.

This paper presents the results of design works to improve the vacuum sublimator and the results of technological testing of the proposed design solution and pyrometallurgical processing scheme (Figure 1). Technological tests were executed with gold-arsenic concentrate from the Bakyrchik deposit (Eastern Kazakhstan) [42,43].

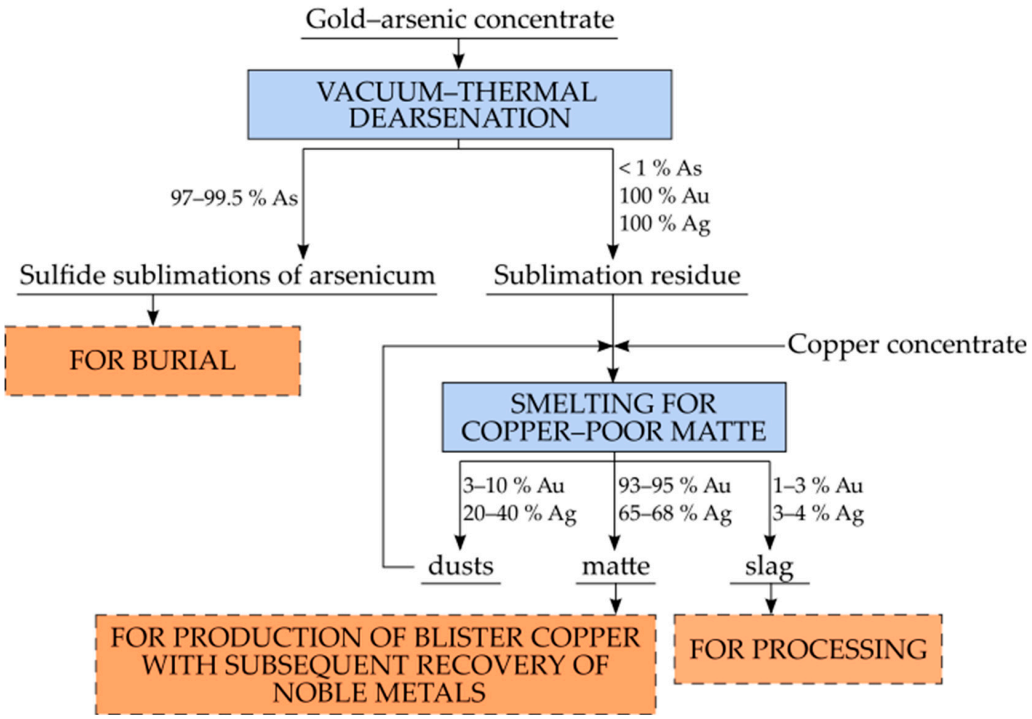


Figure 1. Proposed processing scheme for gold-arsenic concentrates with indication of arsenic and noble metal distribution in the processing products.

2. Materials and Methods

2.1. Equipment

The scheme of a pilot unit for the sublimation of arsenic sulfides and the simplest-to-manufacture assembly of inclined surfaces, i.e., plates assembled in the form of a vertical shaft, are shown in Figure 2. The unit is a sublimator (1) heated with an electric furnace (2) with a shaft inside formed from a pair of plates with inclined slots. These slots have an angle (to the horizon) greater than the angle of the natural slope of the bulk material. The plates in pairs form a gap between themselves and the lower pair of plates so that the bulk material pouring out at an angle of natural slope does not "flow" from the upper edge of the lower plates. The sublimator is connected to a water-cooled condenser (5) with the help of a heated steam line (4). A water-cooled tube (6) with a fabric filter (7) intended to collect fine condensate is coaxially mounted inside the condenser. The unit is equipped with a hopper (8) for raw materials and a vibrating loader (9) for feeding the latter to an intermediate vessel (10). The intermediate vessel is separated from the sublimator space by a movable hollow rod with a cone gate (11) with a thermocouple inside. There is a vibrating unloader (12) mounted below the sublimator. It forms a gate together with the bulk material in the mouth (13) that separates the receiving hopper residue from the processing (14) from the sublimator. Arsenic sulfides crumbling from the condenser walls accumulate in the hopper (15). The gases are evacuated from the apparatus through a vacuum conduit (16).

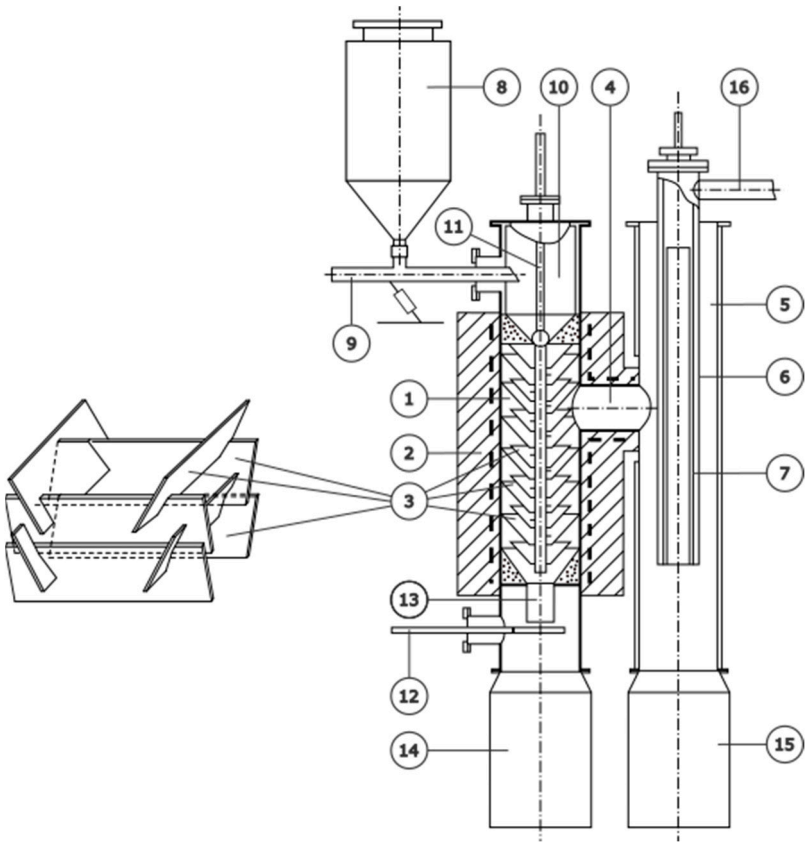


Figure 2. Scheme of vacuum sublimation unit with rheological movement of disperse materials: (1) sublimator, (2) electric furnace, (3) inclined surfaces, (4) steam pipeline, (5) condenser, (6) pipe, (7) fabric filter, (8) hopper for raw materials, (9) vibrating loader, (10) intermediate vessel, (11) rod with a cone gate, (12) vibrating unloader, (13) mouth, (14) receiving hopper for residue, (15) receiving hopper for condensate, (16) vacuum conduit.

Dispersed material from the hopper for raw materials is fed by means of a vibrating loader into the intermediate vessel above the sublimator in the process of sublimation of arsenic sulfides, where the inner cavity of the shaft formed by the plates is filled. The treated material is heated by radiation on the exposed surface areas formed by the dispersed material due to natural overflow and facing the external heater. The surface area for steam escape (open surface areas) was about 5×10^{-2} m^2.

The processing time for the bulk material (staying in the reaction space) is regulated by the performance of the vibrating unloader located with a gap relative to the mouth. Dispersed material in the mouth and on the unloader with sides form a gate that separates the sublimation volume from the bunker space, which prevents the penetration and condensation of the sulfide vapor phase in the latter. The vapor phase from the sublimator through a steam pipeline is sent to a cyclone-type condenser for solid-phase condensation of arsenic sulfides.

2.2. Materials

Technological tests of the sublimation process intended to remove arsenic sulfide with the help of the developed sublimator were executed with samples of gravity and flotation concentrates taken from the Bakyrchik deposit. Two batches of gravity concentrate and one batch of flotation concentrate were processed; their compositions are specified in Table 2.

Table 2. Composition of Bakyrchik concentrates.

Concentrates	Composition										
	Au, g/t	Ag, g/t	wt. %								
			As	Fe	S	C	Cu	Pb	Zn	SiO_2	Al_2O_3	CaO
Gravitational I	230	20	21.4	35.8	32.0	0.6	0.05	0.24	0.06	4.80	2.38	1.12
Gravitational II	230	21	26.3	37.0	28.2	0,7	0,04	0.20	0.06	1.35	0.77	0.82
Flotation	81	59	14.1	22.3	20.1	9.2	0.19	1.0	0.80	16.8	4.89	1.65

The bulk density of gravity concentrates was 2700 kg·m^{-3}, the flotation concentrate was 1480 kg·m^{-3}, and the densities determined by the pycnometric method were 5200 and 3900 kg·m^{-3}, respectively.

When the particle size distribution was determined, it was established that more than 76% in the gravitational concentrate was presented by fractions from 0.063 to 1.6 mm, and in the flotation concentrate, more than 90% by a fraction with a size of less than 0.043 mm.

2.3. Technological Experiment Procedure

The order of technological tests with the sublimator of the proposed design was as follows. Preliminarily, the shaft formed by the plates inclined in pairs was filled with inert dispersed material—quartz sand—then the charging hopper was filled with the initial concentrate. The temperature in the reaction space and in the steam pipeline was raised with the help of electric heaters to the technologically established temperature. The temperature was measured using chromel-alumel thermocouples with potentiometer output. The air was evacuated from the sublimator through the condenser to the maximum achievable rarefaction by means of the evacuation system. The pressure was measured before the vacuum pump inlet with an M110-type vacuum gauge.

When the voltage was supplied to the electromagnetic vibrating loader and unloader, the material flow from the receiving hopper to the residue hopper was organized by sliding the material along inclined surfaces in the reaction space from top to bottom. The time when the vibrating unloader with the intermediate feedstock container filled with concentrate started to operate was considered as the beginning of the dearsenation process for concentrates. The speed of unloading and, thereby, movement of the concentrate along the inclined surfaces in the sublimator was changed by the amplitude of oscillations of the vibrating unloader.

The amount of inert material at the startup stage that moved into the residue hopper was taken into account when the composition and distribution of arsenic in the processed products were determined. Subsequently, the unloading system was equipped with a device for sluicing from two hoppers and gates. In this case, the inert material of the initial stage and the residue from the vacuum sublimation of arsenic sulfides were sent to different containers.

2.4. Characterizations

The material composition was studied by X-ray fluorescence analysis using the wave dispersive combined spectrometer Axios "PANalyical". The content of gold and silver in the products of processing was determined by assay analysis.

An X-ray diffractometer D8 Advance "Bruker" and Cu-Kα radiation and the ICDDPDF-2 reference database (2020) were used to identify the phase composition.

Mineralogical analysis was performed with a LEICA DM2500P optical polarization microscope (Leica Microsystems).

3. Results and Discussion

As a result of many years of searching for a solution to the problem of the technical design of the sublimation process for arsenic sulfides from gold-containing concentrates, the authors of this work proposed abandoning the forced movement of the material in the sublimator. Movement is proposed to arrange due to the physical properties of the

processed raw materials—pouring from top to bottom along the surfaces with the angle of slope more than the angle of the natural slope of the disperse material. In this case, the inclined surfaces are placed so that when the material moves from one inclined surface to another, there are formed slopes of dispersed material with an open surface facing the heater. It makes it possible to arrange the heating of the dispersed material by direct radiation from the heater, which is the most common method of heat transfer in a vacuum.

The developed sublimator design (Figure 2) enables the creation of units of high productivity by placing several vertical shafts and their variants of inclined surfaces as well as heater(s) of resistance inside the reaction space. One of the main advantages of this design is the possibility to manufacture plates for inclined surfaces from ceramic materials inert to the treated disperse material and aggressive vapor sulfur-containing medium. The absence of any moving material handling devices greatly simplifies the process of sealing the unit when moving and stationary assemblies are connected. The sintering temperature of most arsenic-containing concentrates significantly exceeds 800 °C; the sintering temperature is about 1000 °C for Bakyrchik flotation concentrate. Therefore, there will be no interference with the free movement of raw materials in the sublimator volume and in the unloading of residues from vacuum degassing during the processing of gold arsenic-containing concentrates.

3.1. Vacuum-Thermal Dearsenation of Gold-Arsenic Concentrate

Preliminary experiments showed that the granulometric composition of gravity concentrate under the vacuum sublimation process did not create significant difficulties for the escape of sulfide vapor into the free space above the dispersed material.

The layer thicknesses up to 25 mm for flotation concentrate had no effect on the transfer degree of arsenic into the vapor phase, but diffusion resistance became noticeable at a layer thickness greater than this value. Noticeable dust formation due to the entrainment of concentrate particles by the steam flow of arsenic sulfides and disruption of the descent of the processed material along inclined surfaces inside the sublimation shaft was also noted when flotation concentrate was used. In this regard, the flotation concentrate was subjected to granulation with the addition (about 2%) of sulfite-cellulose liquor, under the following conditions: bowl rotation frequency—0.5 s^{-1}, inclination angle—0.7 radian. After granulation, the concentrate was dried at 100 °C up to a residual moisture content of 1–3% and sieved. The fraction of a size ranging from 0.1 to 3.0 mm was sent for processing; the fine fraction of less than 0.1 mm was returned to granulation. The specified preliminary stage also promoted a reduction in the resistance of the steam stream exit from a disperse material layer in a free space that, in turn, reduced a natural slope angle and, in addition, promoted the process of unobstructed movement of processed raw materials.

The dearsenation process of concentrates was performed at 750 °C and a pressure of less than 130 Pa. The test results containing information on the distribution of some element byproducts and their content are shown in Table 3.

Most of the gold in the Bakyrchik deposit (95–97%) is associated with pyrite (FeS_2) and arsenopyrite (FeAsS) [44]. The main mineral forms of arsenic in ores, in addition to arsenopyrite, are lellingite ($FeAs_2$), realgar (AsS), and auripigment (As_2S_3). Therefore, the behavior of arsenic, sulfur, and iron was studied based on a priori information on the distribution of gold, metals, and minerals in the vacuum-thermal processing products in the technological tests on the developed equipment.

As can be seen from the results presented in Table 3, arsenic was transferred into condensate almost completely (97.39–99.36%) during vacuum-thermal processing of gold-arsenic concentrates, and less than 1% remained in the sublimation residue. Chemical analysis did not find the content of precious metals in the condensate; assay analysis found less than 1 g/t gold. That is, precious metals almost completely remain in the sublimation residue with a minimum possible content of arsenic. This residue is further sent to the recovery of precious metals by known methods, including pyrometallurgical ones.

Table 3. Content and distribution of elements in products of vacuum-thermal processing of Bakyrchik concentrates.

Products	Quantity		As		S		Fe	
	kg	%	Content, %	Distribution, %	Content, %	Distribution, %	Content, %	Distribution, %
Gravity concentrate I								
				Loaded:				
Gravitational concentrate I	26.13	100	21.40	100	32.00	100	35.80	100
Residue	15.46	59.17	0.26	0.72	32.81	60.66	57.68	95.33
Condensate	9.55	36.55	57.90	98.88	29.78	34.01	0.04	0.04
Loss + discrepancy	−1.12	−4.28	–	−0.40	–	−5.33	–	−4.63
Gravity concentrate II								
				Loaded:				
Gravitational concentrate II	24.65	100	26.30	100	28.20	100	37.00	100
Residue	14.85	60.24	0.21	0.48	33.17	70.86	57.79	94.10
Condensate	8.41	34.12	76.59	99.36	19.96	24.15	0.03	0.03
Loss + discrepancy	−1.39	−5.64	–	−0.16	–	−4.99	–	−5.87
Flotation concentrate								
				Loaded:				
Flotation concentrate	22.41	100	14.10	100	20.10	100	22.30	100
				Received:				
Residue	16.23	72.42	0.12	0.62	14.66	52.82	29.32	95.22
Condensate	5.02	22.40	61.30	97.39	37.71	42.03	0.02	0.02
Loss + discrepancy	−1.16	−5.18	–	−1.99	–	−5.15	–	−4.76

X-ray phase (Figure 3) and petrographic (Figure 4) analyses found arsenic sulfide compounds that were different from natural minerals in the condensates: As_2S_3 (PDF 01-071-2435) and AsS (PDF 00-053-0529). Quantitative phase analysis showed that the auripigment phase (As_2S_3) was predominant. Under the microscope, auripigment was light gray with medium reflectivity, with clear anisotropy masked by strong straw-yellow internal reflexes. In turn, realgar (AsS) was a gray mineral with a bluish hue, low reflectivity, and strong anisotropy. Auripigment and realgar were very similar. Their main difference was that realgar had orange-red inner reflexes while auripigment had straw-yellow reflexes.

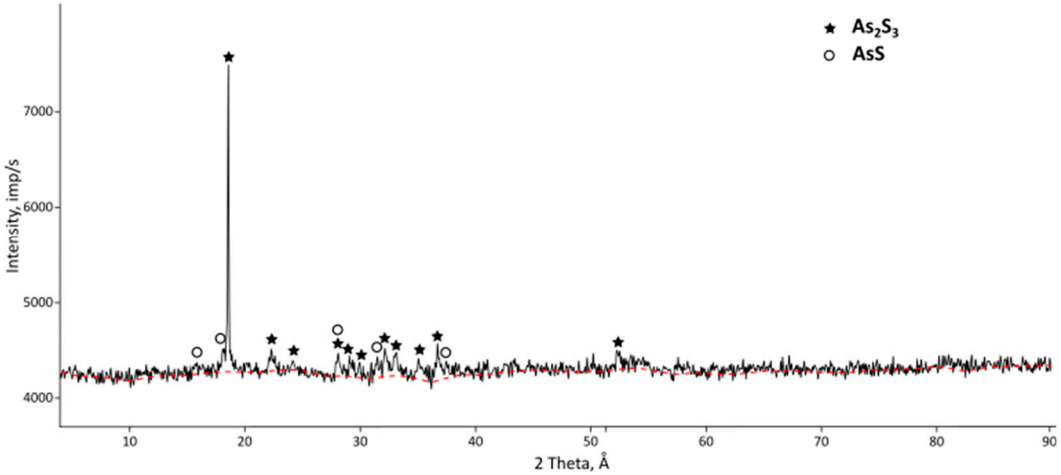


Figure 3. X-ray patterns of arsenic condensate.

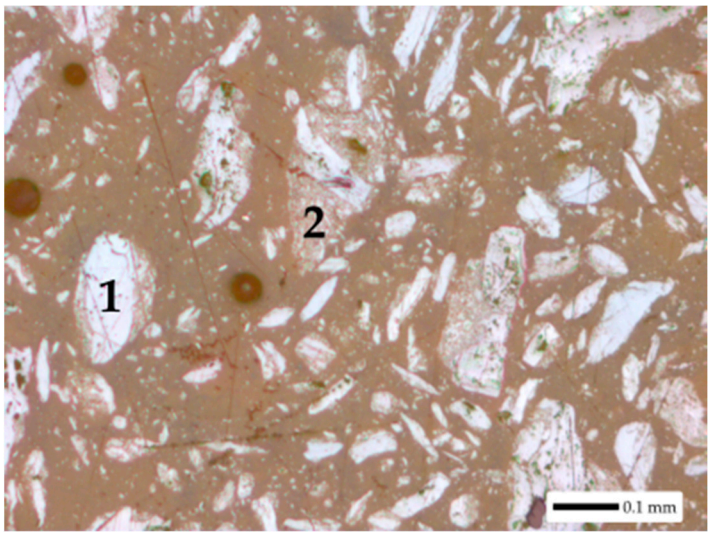


Figure 4. X Microphotograph of the condensate: (1) auripigment; (2) realgar.

3.2. Pyrometallurgical Processing of Arsenic Sublimation Residues from Gold-Containing Concentrates

Copper is known to be a material that is good for collecting gold. Therefore, smelting of copper-poor matte was tested in order to increase the recovery of gold from the sublimation residue.

Smelting of sublimation residues of gold-arsenic gravity and flotation concentrates was performed in a cyclone unit with a capacity of up to 1 ton per day at an air excess of 1.1–1.27 with the addition of copper concentrates of different compositions. Limestone was added as a slag-forming agent. The charge capacity of the unit was 41–47 kg/h. The dust collection system included a dust chamber, cyclones, and bag filters.

Examples of the distribution of copper and precious metals by residue processing products from dearsenation of gravitational concentrate are specified in Table 4, and from the flotation concentrate in Table 5.

Table 4. Metal distribution during cyclonic smelting of arsenic sublimation residue from Bakyrchik gravity concentrate.

Products	Quantity		Cu		Au		Ag	
	kg	%	Content, %	Distribution, %	Content, %	Distribution, %	Content, %	Distribution, %
Loaded:								
Residue	51.40	71.38	0.07	1.48	3.90×10^{-2}	99.85	3.40×10^{-3}	45.90
Copper concentrate	10.30	14.31	23.30	98.52	3.00×10^{-4}	0.15	2.00×10^{-2}	54.10
Limestone	10.30	14.31	–	–	–	–	–	–
Total	72.00	100.00	–	100.00	–	100.00	–	100.00
Received:								
Matte	16.8	23.33	13.01	89.73	1.12×10^{-1}	93.72	1.49×10^{-2}	65.74
Slag	34.9	48.47	0.17	2.44	7.36×10^{-4}	1.28	3.20×10^{-4}	2.93
Chamber dust	4.30	5.97	1.82	3.21	1.97×10^{-2}	4.22	1.46×10^{-2}	16.49
Cyclone dust	1.00	1.40	2.66	1.09	1.54×10^{-2}	0.77	1.34×10^{-2}	3.52
Bag filter dust	8.10	11.25	1.13	3.76	1.13×10^{-2}	4.56	1.17×10^{-2}	24.89
Total	65.10	90.42	–	100.23	–	104.55	–	113.57
Loss + discrepancy	−6.90	−9.58	–	+0.23	–	+4.55	–	+13.57

Table 5. Metal distribution during cyclonic smelting of arsenic sublimation residue from Bakyrchik flotation concentrate.

Products	Quantity		Cu		Au		Ag	
	kg	%	Content, %	Distribution, %	Content, %	Distribution, %	Content, %	Distribution, %
Loaded:								
Residue	62.70	66.57	0.26	3.58	1.12×10^{-2}	100.00	8.14×10^{-3}	50.51
Copper concentrate	12.50	13.33	35.10	96.42	–	–	4.00×10^{-2}	49.49
Limestone	18.80	20.00	–	–	–	–	–	–
Total	94.00	100.00	–	100.00	–	100.00	–	100.00
Received:								
Matte	14.40	15.32	29.64	93.79	4.58×10^{-2}	93.92	4.77×10^{-2}	67.98
Slag	56.10	59.68	0.24	2.96	3.00×10^{-4}	2.40	6.14×10^{-4}	3.41
Chamber dust	1.00	1.06	2.10	0.46	2.38×10^{-3}	0.34	1.47×10^{-2}	1.45
Cyclone dust	1.10	1.17	4.10	0.99	4.08×10^{-3}	0.64	1.85×10^{-2}	2.01
Bag filter dust	7.30	7.77	2.37	3.80	2.32×10^{-3}	2.41	2.38×10^{-2}	17.20
Total	79.90	85.00	–	102.00	–	99.71	–	92.05
Loss + discrepancy	−14.10	−15.00	–	+2.00	–	−0.29	–	−7.95

Smelting of sublimation residues from gravity and flotation concentrates resulted in matte containing 13.01 and 29.64% copper, respectively. The recovery rates of copper in the matte were 89.73 and 93.79% of its total amount loaded with the sublimation residue and copper concentrate. Most of the gold (93.72 and 93.92%) and most of the silver (65.74 and 67.98%) are concentrated in the matte. Their matte contents were 1.120 and 458 g/t gold and 149 and 477 g/t silver.

The gold losses with slags were 1.28 and 2.40% at contents of 7.36 and 3.0 g/t. The slag also includes 2.93 and 3.41% of silver at its content of 3.20 and 6.14 g/t in it. The slag yield was 59.68% with 0.24% of copper, 3 g/t gold, and 6.14 g/t silver. Significant amounts of gold (9.95% and 3.39%) and silver (44.9% and 20.66%) were contained in the pooled dust. Their average gold and silver contents were 25 and 222 g/t, respectively, which suggests that they were returned to the turnover. The arsenic concentration in them did not exceed 1%. The return of dust to a turnover during joint processing with residuals from dearsenation of concentrates with the addition of copper concentrates can increase the recovery of copper in matte up to 97%, gold up to 98–99%, and silver up to 95%.

Crucible smelting has also been tested for dearsenated Bakyrchik flotation concentrate. During smelting, copper concentrate was added to the concentrate in the amount necessary for the formation of slag of a given composition, wt. %: 45.3 SiO_2; 24.1 FeO; 11.9 CaO; 16.5 Al_2O_3. The composition of the copper concentrate is shown in Table 6. The process temperature was 1300–1350 °C. The yield of matte was 50.7% at its content, wt. %: 10.0 Cu; 55.9 Fe; 25.8 S. Recovery of gold in matte was 95.4%; its content in slag was 3.6 g/t.

Table 6. Composition of copper concentrate.

Elements and Compounds	Cu	Pb	Zn	Fe	S	SiO_2	CaO	Al_2O_3	Others
Content, wt. %	33.12	2.41	1.75	6.75	15.6	23.0	1.76	4.71	10.49

The received matte can then be put through a converting process to obtain blister copper exposed to electrolytic refinement with the recovery of gold from sludge according to the offered scheme (Figure 1).

4. Conclusions

It is possible to state a high degree of recovery of precious metals under this scheme, reaching 97–99% of gold and up to 94–95% of silver if the conducted technological tests on dearsenation of gold-arsenic concentrates on the developed sublimation equipment in combination with smelting of residues after arsenic sublimation together with copper concentrates for matte are analyzed.

Thus, the proposed technical solution for the design of the sublimation process for arsenic sulfides from gold-arsenic concentrates enables the scaling of equipment and simplifies the choice of materials for the structural design of the process, and the results of sublimation residue processing by smelting together with copper concentrates make it possible to implement a pyrometallurgical scheme with the use of the obtained matte accumulating precious metals in the copper production process.

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