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Chlorination Treatment for Gold Extraction from Refractory Gold-Copper-Arsenic-Bearing Concentrates

Nurlan Dosmukhamedov ¹, Valery Kaplan ², Erzhan Zholdasbay ¹, Aidar Argyn ^{1,*}, Erzhan Kuldeyev ¹, Gulzada Koishina ¹ and Yeleussiz Tazhiev ¹

¹ Department of Metallurgy and Mineral Processing, Satbayev University, Almaty 050000, Kazakhstan

² Weizmann Institute of Science, Rehovot 76000-76878, Israel

* Correspondence: aidarargyn@gmail.com

Abstract: New experimental results have been obtained on the behavior of arsenic and other associated metals (Re and others) under conditions of oxidative and reductive sintering. It has been established that the extraction of arsenic strongly depends on the process temperature during oxidative sintering. The extraction of arsenic into dust media at 873 K is 50% and rhenium is 88–90%. The effect of excess air on the extraction of arsenic and rhenium into dust was studied: the higher the excess air coefficient, the more complete the extraction of arsenic and rhenium into the dust. The obtained data indicate that achieving a high level of arsenic extraction from the initial product is not possible during oxidative sintering. The best arsenic removal results were reached under the conditions of reductive sintering of initial material by natural gas. The extraction of arsenic into dust at 823 K was 88%, and at 1373 K arsenic is almost completely converted into dust. Obtained new experimental results have a fundamental importance for the selection and organization of a comprehensive technology for the processing complex in composition refractory gold-copper-arsenic-bearing products.

Keywords: arsenic; gold; chlorine treatment; preliminary sintering; refractory gold-copper-arsenic-bearing products



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1. Introduction

In refractory gold-bearing concentrates, the gold metal is generally contaminated and encapsulated either in a sulfide matrix or in quartz, while the efficiency of the extraction of gold is low due to the structural/chemical characteristics of the concentrates itself [1]. Refractory concentrates, which have gold in the form of fine inclusions in sulfides, contain 30% of the global reserves of pristine gold metal [2]. For obvious reasons, the development of effective technologies for leaching gold from refractory concentrates has a great practical and economical importance. During the processing of gold-containing concentrates, attention should be focused on the particular form (or forms) of gold contained in—free metal or metal bound in a sulfide matrix (e.g., pyrite, arsenopyrite, chalcopyrite, galena, antimonite), in quartz, or in carbonaceous materials [2,3].

The main problems of the mineral resource base of gold in Kazakhstan are the lack of large reserve gold deposits that could be considered as basic facilities for the sustainable development of the industry in the long term.

Currently, more than half of the active gold reserves in Kazakhstan are “refractory” ores that are difficult to enrich and contain a significant content of arsenic. The process of removing arsenic not only complicates the technology of mineral processing but also requires additional costs for their storage in compliance with the conditions for preserving the ecology of the environment [4].

The gold mining industry in Kazakhstan faces the challenging problem of treating refractory gold-copper-arsenic-bearing concentrates [5].

The amount of gold in different phases of refractory gold-copper-arsenic-bearing concentrates has been described in ref. [1] (% from total gold quantity): metallic gold—23.32; gold as carbonate—0.14; gold as oxide—4.11; gold as sulfides (arsenopyrite and pyrite)—67.42; gold in gangue—5.01. Therefore, it is difficult to extract gold from such minerals directly by traditional processes without pretreatment; the extraction yield of gold from concentrates with a high content of arsenic and sulfur is much lower than from materials in which arsenic and/or sulfur are absent [6]. In the mining sector of Kazakhstan, rhenium (Re) is also present in copper concentrates. Kazakhstan is currently one of the largest producers of rhenium in the world [7,8]; Cu-Au-As concentrates contains 20–50 ppm of rhenium [9]. Since rhenium is used in the construction of jet engines and as a catalyst, the extraction of rhenium from gold-copper-containing concentrates is economically very important. Rhenium can be extracted to dust by oxidation sintering of the Cu-Au-As concentrates [10,11].

In this century, it is planned to ensure the main increase in gold production in the world through a wider involvement in the operation of refractory and complex gold-bearing ores. With the development of the planned general trend, one of the most important problems facing the modern gold mining industry should be questions of increasing the completeness of gold extraction from refractory (difficult-to-enrich) raw materials, as well as other gold-bearing sources (polymetallic concentrates, industrial waste), which requires comprehensive research in order to develop reasonable solutions.

Nowadays, in world practice, there is a depletion of the raw material base of non-ferrous metal ores with a low content of arsenic, containing gold. More and more materials of complex composition are supplied to metallurgical plants, and one of the poisoning harmful impurities there is arsenic.

Involvement in the processing of polymetallic concentrates accumulated in the East Kazakhstan Region, containing non-ferrous metals, gold, and other valuable metals, could become a significant reserve for increasing the volume of raw materials. For example, Berezhovskiy polymetallic concentrate can be a potential source of raw materials for Kazinc LLP for the complex extraction of non-ferrous metals and gold from them. Today, their high arsenic content restricts their processing.

The ores of the Berezhovskiy deposit are the gold-bearing sulfide-polymetallic type. The ores are characterized by a wide range of elements presented in the sulfide form: lead, zinc, copper, cobalt, nickel, molybdenum, etc. The high content of arsenic (from 1 to 1.5%) is noteworthy. Acicular arsenopyrite and lautite are gold-bearing. Gold is present in microscopic and submicroscopic forms. The distribution of gold in ores is uneven, the coefficients of variation for these ore bodies range from 56.5 to 86%. Most of the gold (95–97%) is associated with sulfides—arsenopyrite, lautite—the amount of which varies from 1 to 8%, i.e., in composition the ores are low-sulfide [12,13].

For Kazakhstan, as well as for Russia and Ukraine, gold-containing wastes, which are part of the structure of accumulated industrial wastes, have a particular concern in terms of the degree of impact on the environment and human life. Because of the activities of the industrial enterprises of the East Kazakhstan Region in 2007, about 1,401,130 thousand tons of industrial waste were accumulated.

Wastes of metallurgical production are placed in dumps, waste heaps, sludge collectors, and occupy an area of more than 430 hectares. Such disposal of waste leads to environmental pollution due to dust dispersion and erosion by rain and melt water and also pollutes surface and ground water.

With the accumulated waste generated in the production chain “mining–mineral processing–metallurgy”, more than a third of the non-ferrous and precious metals mined with ores are lost, huge reserves of various construction raw materials are frozen. The loss of lead is 33%, zinc—28%, copper—21%, gold—41%, silver—35%. The total losses during mining amount to 15–20% of non-ferrous and 8–12% of precious metals, during mineral processing—43–48% and 74–75%, respectively, in metallurgy 35–42% of non-ferrous and 14–17% of precious metals. The excess of losses of valuable components during mineral

processing by 2–3 times, compared with losses in mining and metallurgical processing, led to the emergence of numerous man-made deposits [14].

The processing of gold-bearing ore and technogenic raw materials, due to their complex composition and the presence of a high content of arsenic, on the one hand, and the lack of an alternative effective technology for their processing, on the other hand, restricts an increase in their processing volumes with a complex high extraction of valuable components into targeted products.

Nowadays, the existing technologies for processing gold-bearing raw materials by known methods do not provide a high complex extraction of valuable metals, including gold. There are many ways to remove arsenic from raw materials and intermediate products of lead and copper production. However, active work on improving the flowsheet for obtaining non-ferrous metals leads to a change in the movement of impurity components and the need to develop a new flowsheet for the utilization of arsenic.

One of the promising areas used for the processing of arsenic-, gold-containing poly-metallic raw materials is the use of modern bubbling processes for melting to matte [15,16]. The use of autogenous processes (Outokumpu, Isasmelt) [17] makes possible to minimize the loss of non-ferrous metals with slags and ensure a high extraction of As, Sb into dust. However, the obtained arsenic dusts are characterized by a complex composition and require special treatment for the subsequent extraction of non-ferrous metals from them.

According to the flowsheet that existed at Kazzinc LLP until 2012, the output of arsenic from the lead plant as part of arsenate cakes was 43.65%.

Copper-lead mattes contained, %: Cu—10–20, Pb—12–25, Zn—8–12, As—up to 1.5, Sb—up to 1.0; copper slips, %: Cu—15–20, Pb—18–30, Zn—2–4, As—4.0, Sb—up to 2.5; converter slag contained, % (wt.): Cu—3–5, Pb—up to 34, Zn—up to 4.5, As—2–2.5, Sb—up to 2.0, which accounted for the main part (up to 30%) of the structure of the initial feed [18,19].

During smelting, significant volumes of non-ferrous, precious, rare, and rare-earth, as well as accompanying impurity metals (As, Sb) circulate in the “melting-converting” process chain. Valuable metals are smeared over the smelting products, and the accompanying impurity metals (As, Sb) accumulate in the process chain. Their negative impact on the environment and life safety of workers increase; the quality of the products obtained decreases.

Recovery of copper to matte is low ~83% and lead to rough lead reaches 60%. The increased content of lead in slags (up to 2%) led to a high content of precious metals in them. According to practice, up to 4 g/t of gold and ~800 g/t of silver are concentrated in the resulting copper-lead mattes sent for further processing.

The process was accompanied by a high consumption of expensive coke and slag output (up to 60% of the weight of the loaded charge), high energy, and material costs. The dust yield was ~15% of the weight of the loaded mixture and is characterized by a high content of non-ferrous metals and gold, %: Pb—20; Cu—6–7; Zn—up to 10. The extraction of As, Sb into dust is low and amounts to 70% and 57%, respectively [18,19].

Modernization of the technological scheme for the production of lead and the launch of a copper plant at Kazzinc LLP in 2011–2012 solved the problem of removing arsenic from the technological scheme with arsenate cake, however, led to the need to solve a number of new tasks. Against the background of the modernization of the technological flowsheet, there was an increase in the distribution of arsenic in copper scraps of lead production. If earlier, according to the classical scheme “agglomerating roasting—blast smelting—refining”, 27.65% of arsenic from the total load to the lead plant was transferred to copper removals, then according to the new scheme—83.72%.

With an increased content of arsenic in the feedstock, the circulating load of arsenic between the lead and copper plants increased due to the processing of copper scrap. This led to the risk of obtaining low-quality commercial products, wear of the lining of pyrometallurgical units when interacting with aggressive copper arsenide, and environmental pollution with volatile arsenic compounds.

Today, at Kazzinc LLP the copper scraps are sent to the stage of electric smelting, where they are separated into lead- and copper-containing phases. Arsenic is then distributed between the smelting products: copper-lead matte, rough lead, and slag.

With the rough dehydrogenation of rough lead from mine smelting, copper strips are formed, containing up to 84% of arsenic from loading to the lead plant. This is three times higher than the distribution of arsenic in copper strips (27.65%) obtained by classical technology.

The general technological scheme, including the integration of copper and lead plants, is very complex, overloaded with the need to process copper, lead, arsenic, and gold intermediate products and is characterized by a high content of arsenic in the targeted products: copper-lead mattes (up to 3%) and draft lead (up to 6%). At the same time, the redistribution of gold and silver between the smelting products leads to their significant losses, which affects their total extraction from polymetallic raw materials into a commercial product [20].

Due to the lack of a rational technology for processing copper, lead, arsenic, gold-bearing concentrates, and intermediate products, the existing flowsheet is a forced measure with all the ensuing shortcomings, both technologically and from an environmental point of view.

The use of our own polymetallic raw materials containing copper, lead, gold, and high arsenic content is a significant reserve for increasing the volume of raw materials for the extraction of valuable metals. It is obvious that their processing by known-melting technologies to matte is currently not possible due to the high content of arsenic. This requires finding alternative solutions.

While processing the concentrates containing gold, copper, and arsenic, which are undoubtedly complex, chlorination is considered as a very effective method for fractionating the raw materials in order to obtain high purity metal. The advantageous features of the chlorination process are fast chemical reactions and the high level of chlorination of all components. For example, refractory gold-containing concentrates may be successfully processed to produce the sublimation of gold chlorides. Either solid sodium, calcium chloride, or gaseous chlorine can be used as chlorinating agents [3,21–24]. The chlorination process is very versatile and can extract gold from concentrates of almost any composition. An important advantage of this process is the possibility of the complex processing of concentrates, which result in the extraction not only of gold and silver, but also other valuable metals, such as rhenium [2]. However, when arsenic is present in refractory gold-containing concentrates, pretreatment (oxidation or reduction sintering) is required.

Therefore, in order to develop a method for extracting gold from gold-bearing concentrates, this work was carried out to select a method for removing arsenic. Two technology variants were tested: preliminary oxidation or preliminary reduction sintering of the initial material prior to chlorination.

2. Materials and Method

2.1. Materials

Cu-Au-As concentrate was obtained from mine fields located in East Kazakhstan (Table 1). The forms of presence of copper, arsenic, and gold are studied in detail in [25]. The main copper minerals in the concentrate are present in the form of sulfide and the arsenic is in the form of arsenopyrite. Gold is embedded in copper sulfide minerals.

The initial materials were crushed and milled to produce powders with particle size of <200 mesh (74 microns). Natural gas received from the Bukhara gas field (Uzbekistan) had the following composition (volume%): 92.6 CH₄; 4.1 C₂H₆; 1.0 C₃H₈.

2.2. Sample Preparation

Sample preparation for all analytical measurements included milling and averaging. Material composition, prior to and following gold extraction, was characterized by solution inductively coupled plasma mass spectroscopy (ICP-MS, Agilent Technologies, Santa Clara,

CA, USA). The ICP-MS measurements required preliminary aqua regia leaching of the sample at boiling temperature. For ICP-MS samples containing compounds, which are insoluble in aqua regia, the following protocol was used: a 250 mg sample was mixed with 1.5 g lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) and fused at 1373 K in a platinum crucible. After cooling to room temperature, the melt was dissolved in 10 vol.% hydrochloric acid and then analyzed.

Table 1. Chemical analysis of the initial material.

Cu-Au-As Concentrate (Berezovsky Field, East Kazakhstan Region)		
Elements	Unit of Measurements	Value
Cu	%	20.9
Fe	%	20.4
Pb	%	2.5
Zn	%	2.6
S	%	10.8
Au	ppm	11
Ag	ppm	85
As	%	6.3
Re	ppm	35
Sb	%	0.30
Al	%	0.3
Ba	%	0.004
Ca	%	0.1
Si	%	2.0
K	%	0.1
Mg	%	0.02
Mn	%	0.01
Na	%	0.2
P	%	0.02
Sn	%	0.28

2.3. Thermodynamic Calculations

Calculations of Gibbs free energy were carried out using a computer program developed by some of the authors and based on standard values for the pure substances [26].

2.4. Oxidation Sintering

The mixture of gases consisting of water vapor, carbon dioxide, nitrogen, and oxygen, corresponding to the products of natural gas combustion, was used as an initial gas phase. The composition of the initial gas mixture was calculated and depended on the excess air coefficient (Table 2). The excess air ratio varied from 100% to 170%.

Table 2. Composition of the initial gas mixture for preliminary oxidation sintering.

Excess Air Coefficient (% from Stoichiometric Air)	Composition of the Initial Gas Mixture (Volume %)			
	CO ₂	H ₂ O	N ₂	O ₂
100	9.7	18.8	71.7	0
150	6.4	12.5	71.6	9.5
170	5.6	10.9	70.4	13.1

The flow rate of the initial gas mixture was varied in the range from 150–300 cc/min. Once the desired sintering temperature was reached, it was held for 30 min. Experiments were performed at 623–873 K. Material quantity in each test was 50 g. The tests were carried out in a standard horizontal muffle furnace with Kanthal (FeCrAl) heating element. A diagram of the furnace is shown in Figure 1.

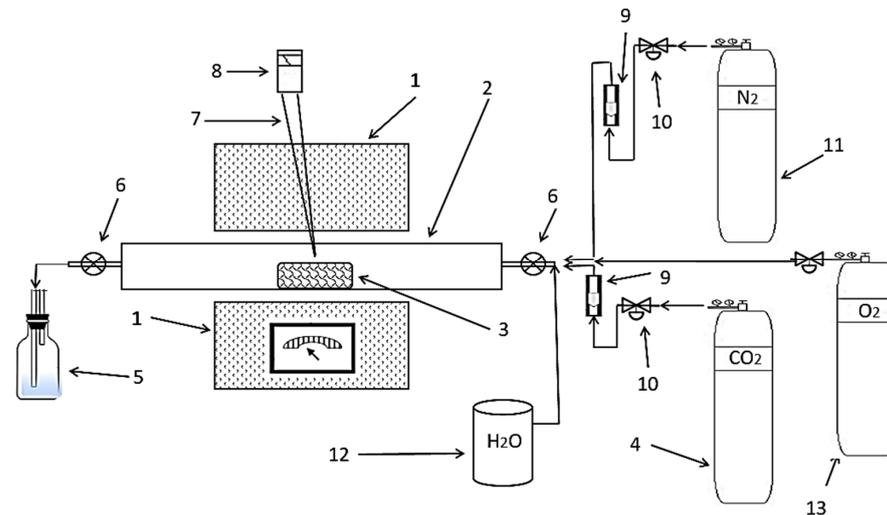


Figure 1. Laboratory setup for oxidation sintering: 1—furnace with temperature controller; 2—reactor; 3—sample; 4—CO₂ cylinder; 5—gas cleaning bottle; 6—gas sampler for GC analysis; 7—nitrogen cylinder; 8—additional temperature monitor; 9—flow meter; 10—valve; 11—air cylinder; 12—water vapor generator; 13—oxygen cylinder.

2.5. Reduction Sintering

Experiments were performed at 723–1373 K and all experiments repeated three times. Once the desired sintering temperature was reached, it was held for 60 min. Natural gas consumption was 10 cc/min, and air consumption was 2.5 cc/min. The gas atmosphere in the reactor was reducing significantly; the incomplete combustion coefficient, with respect to stoichiometric, was around 75%. A diagram of the reactor is shown in Figure 2.

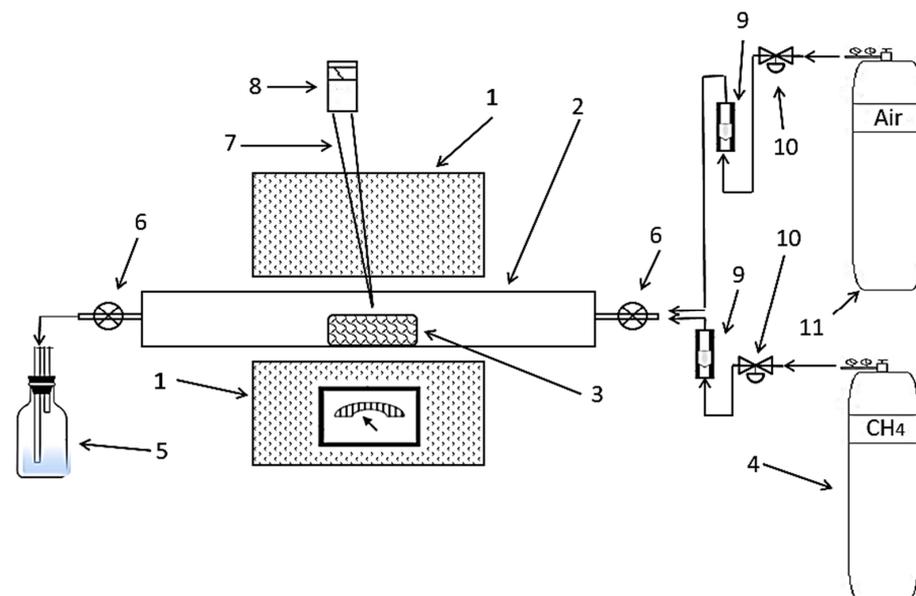


Figure 2. Laboratory setup for preliminary reduction sintering: 1—furnace with temperature controller; 2—reactor; 3—sample; 4—CH₄ cylinder; 5—gas cleaning bottle; 6—gas sampler for GC analysis; 7—thermocouple type K; 8—additional temperature monitor; 9—flow meter; 10—valve; 11—air cylinder.

2.6. Chlorination

Three alternative chloride sublimation-based gold extraction techniques were used: two with elemental chlorine and one with calcium chloride. The tests were carried out in a standard vertical muffle furnace with Kanthal (FeCrAl) heating element (length 250 mm, width 250 mm, height 300 mm). The temperature range was 473–1373 K. The furnace atmosphere was chlorine gas, when chlorine was used for extraction, or air, when calcium chloride was used. A diagram of the furnace, including placement of the crucible with the powdered sample, is shown in Figure 3. Two protocols were tested: (i) a powdered sample (Cu-Au-As ore) was treated in a stream of chlorine gas; or (ii) a dry mixture of the powdered sample (Cu-Au-As ore/calcium chloride/SiO₂ at various weight ratios), was sintered in an air stream. Alumina crucibles were used for sintering 30–60 g powder. Chlorine flow was 400 cc/min for tests with chlorine gas; air flow was 400 cc/min for tests with calcium chloride. The presence of a fine powder of SiO₂ in addition to the calcium chloride [22] improved process efficiency. Silica binds to calcium oxide to form calcium-silicate, which is then removed from the reaction zone. In both protocols (i) and (ii), once the desired temperature was reached, it was held for two hours. During this time, sublimation products were removed with the gas flow. Nitrogen was fed into the reactor during the heating and cooling stages (600 cc/min). Each experiment was performed at least twice in order to verify reproducibility of results. After cooling, the clinker was analyzed for elemental composition by ICP-MS spectroscopy.

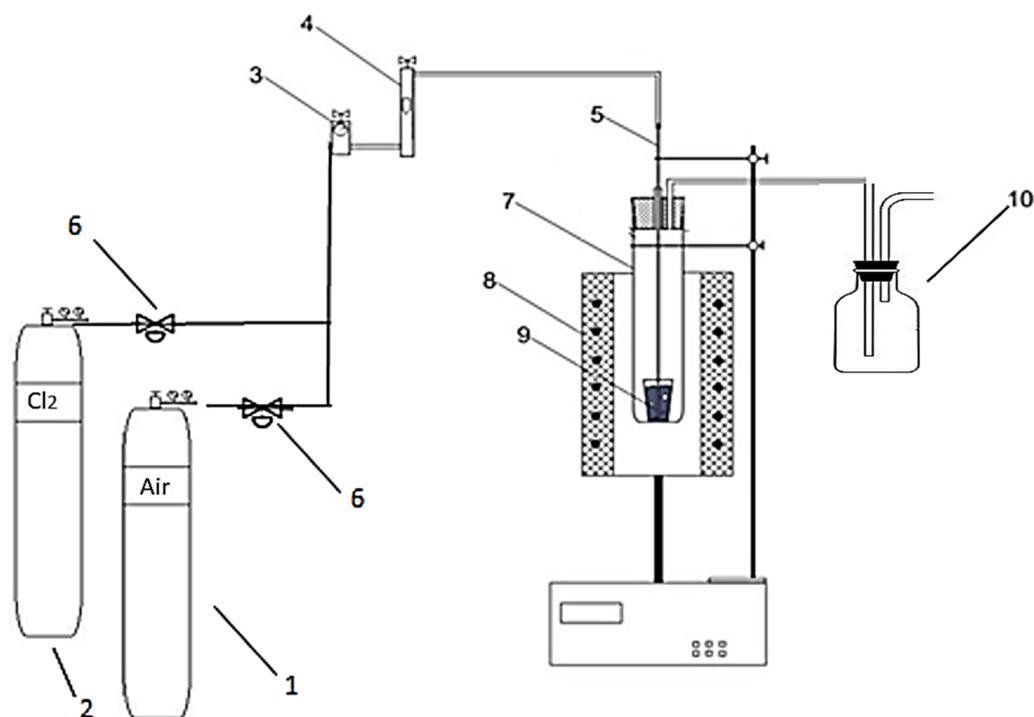


Figure 3. Laboratory setup for chlorination: 1—air cylinder; 2—chlorine cylinder; 3—valve; 4—flow meter; 5—chlorine or air inlet tube; 6—gas stop; 7—reactor; 8—furnace with temperature controller; 9—crucible; 10—gas absorption bottle.

3. Results and Discussion

3.1. Thermodynamic Calculations

The calculated values of the Gibbs energy for reactions of the pure substances within the temperature range 473–1473 K are shown in Table 3.

Table 3. Calculated values of the Gibbs energy (ΔG).

No.	Reactions	Gibbs Energy (ΔG), kJ/mol					
		Temperature, K					
		473	673	873	1073	1273	1473
Group 1							
1	$\text{FeAsS(s)} + 2.5 \text{O}_2(\text{g}) = 0.5 \text{Fe}_2\text{O}_3(\text{s}) + 0.5 \text{As}_2\text{O}_3(\text{g}) + \text{SO}_2(\text{g})$	−753	−721	−688	−654	−620	−585
2	$\text{As}_2\text{S}_3 + 4.5\text{O}_2(\text{g}) = \text{As}_2\text{O}_3(\text{g}) + 3\text{SO}_2(\text{g})$	−1133	−1128	−1113	−1095	−1072	−1056
3	$\text{As}_2\text{S}_3 + 5.5\text{O}_2(\text{g}) = \text{As}_2\text{O}_5(\text{g}) + 3\text{SO}_2(\text{g})$	−1428	−1335	−1240	−1147	−1056	−968
4	$\text{ReS}_2(\text{s}) + 3.75 \text{O}_2(\text{g}) = 0.5 \text{Re}_2\text{O}_7(\text{g}) + 2\text{SO}_2(\text{g})$	−926	−898	−871	−843	−816	−788
5	$\text{Cu}_2\text{S(s)} + 1.5\text{O}_2(\text{g}) = \text{Cu}_2\text{O(s)} + \text{SO}_2(\text{g})$	−343	−321	−298	−276	−254	−231
Group 2							
6	$\text{FeAsS(s)} + 0.5 \text{CH}_4(\text{g}) + 3.25 \text{O}_2(\text{g}) = \text{FeO}(\text{s}) + 0.5 \text{As}_2\text{O}_3(\text{g}) + \text{SO}_2(\text{g}) + 0.5 \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$	−1040	−1020	−1000	−978	−956	−932
7	$\text{FeAsS}(\text{s}) + 0.5 \text{CH}_4(\text{g}) + 3\text{O}_2(\text{g}) = \text{FeO} + 0.5 \text{As}_2\text{O}_3(\text{g}) + \text{SO}_2(\text{g}) + 0.5 \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$	−219	−217	−214	−211	−207	−204
8	$\text{As}_2\text{S}_3 + 1.5\text{CH}_4(\text{g}) + 3\text{O}_2(\text{g}) = \text{As}_2\text{O}_3(\text{g}) + 1.5\text{CO}_2(\text{g}) + 3\text{H}_2\text{S}(\text{g})$	−888	−931	−963	−991	−1016	−1032
9	$\text{As}_2\text{S}_3 + 1.5\text{CH}_4(\text{g}) + 2.25\text{O}_2(\text{g}) = \text{As}_2\text{O}_3(\text{g}) + 1.5\text{CO}(\text{g}) + 3\text{H}_2\text{S}(\text{g})$	−125	−142	−156	−169	−181	−192
10	$\text{ReS}_2(\text{s}) + 0.5\text{CH}_4(\text{g}) + 4.75\text{O}_2(\text{g}) = 0.5\text{Re}_2\text{O}_7(\text{g}) + 0.5\text{CO}_2(\text{g}) + 2\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$	−1326	−1299	−1271	−1244	−1216	−1187
11	$\text{ReS}_2 + 0.5 \text{CH}_4(\text{g}) + 4.5\text{O}_2(\text{g}) = 0.5 \text{Re}_2\text{O}_7(\text{g}) + 0.5 \text{CO}(\text{g}) + 2\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$	−287	−283	−279	−274	−270	−265
12	$\text{Cu}_2\text{S(s)} + 0.5 \text{CH}_4(\text{g}) + 0.5 \text{O}_2(\text{g}) = 2\text{Cu(s)} + \text{H}_2\text{S}(\text{g}) + 0.5 \text{CO}_2(\text{g})$	−128	−136	−143	−149	−155	−162
Group 3							
13	$\text{FeAsS(s)} + 3\text{Cl}_2(\text{g}) + \text{O}_2(\text{g}) = \text{FeCl}_3(\text{s}) + \text{AsCl}_3(\text{g}) + \text{SO}_2(\text{g})$	−784	−738	−701	−665	−629	−594
14	$\text{As}_2\text{S}_3 + 3\text{Cl}_2(\text{g}) + 3\text{O}_2(\text{g}) = 2\text{AsCl}_3(\text{g}) + 3\text{SO}_2(\text{g})$	−1296	−1278	−1250	−1220	−1186	−1150
15	$\text{ReS}_2(\text{s}) + 1.5\text{Cl}_2(\text{g}) + 2\text{O}_2(\text{g}) = \text{ReCl}_3(\text{s}) + 2\text{SO}_2(\text{g})$	−591	−556	−521	−488	−456	−425
16	$\text{Au}(\text{s}) + 1.5\text{Cl}_2(\text{g}) = \text{AuCl}_3(\text{g})$	−16	23	61	97	130	163
17	$\text{Au}(\text{s}) + 3 \text{Cl}(\text{g}) = \text{AuCl}_3(\text{g})$	−304	−230	−157	−86	−17	52
18	$\text{Cu}_2\text{S(s)} + 2\text{Cl}_2(\text{g}) = 2\text{CuCl}_2(\text{s}) + 0.5 \text{S}_2(\text{g})$	−179	−131	−84	−45	−9	26
Group 4							
19	$\text{FeAsS(s)} + 3\text{CaCl}_2(\text{s}) + 2.5\text{O}_2(\text{g}) + 3\text{SiO}_2(\text{s}) = \text{FeCl}_3(\text{s}) + \text{AsCl}_3(\text{g}) + 3\text{CaSiO}_3(\text{s}) + \text{SO}_2(\text{g})$	−643	−625	−614	−600	−568	−535
20	$\text{As}_2\text{S}_3(\text{s}) + 3\text{CaCl}_2(\text{s}) + 4.5\text{O}_2(\text{g}) + 3\text{SiO}_2(\text{s}) = 2\text{AsCl}_3(\text{g}) + 3\text{CaSiO}_3(\text{s}) + 3\text{SO}_2(\text{g})$	−1156	−1165	−1164	−1154	−1125	−1091
21	$\text{ReS}_2(\text{s}) + 1.5\text{CaCl}_2(\text{s}) + 2.75\text{O}_2(\text{g}) = \text{ReCl}_3(\text{s}) + 1.5\text{CaO}(\text{s}) + 2\text{SO}_2(\text{g})$	−386	−363	−341	−319	−289	−260
22	$\text{Au}(\text{s}) + 1.5 \text{CaCl}_2(\text{s}) + 0.75 \text{O}_2(\text{g}) = \text{AuCl}_3(\text{g}) + 1.5\text{CaO}$	189	216	241	266	297	329
23	$\text{Au}(\text{s}) + 1.5\text{CaCl}_2(\text{s}) + 1.5\text{SiO}_2(\text{s}) + 0.75\text{O}_2(\text{g}) = \text{AuCl}_3(\text{g}) + 1.5\text{CaSiO}_3(\text{s})$	54	80	104	129	161	192
24	$\text{Cu}_2\text{S(s)} + 2\text{CaCl}_2(\text{s}) + 2\text{SiO}_2(\text{s}) + 2\text{O}_2(\text{g}) = 2\text{CuCl}_2(\text{g}) + 2\text{CaSiO}_3(\text{g}) + \text{SO}_2(\text{g})$	−413	−369	−324	−286	−237	−189

(s)—solid, (g)—gas.

In the temperature range of interest, 473–1473 K, the Gibbs energy (ΔG) for four groups of reactions is shown in Table 3: group 1—oxidation reactions with oxygen; group 2—reduction reactions with natural gas; group 3—chlorination reactions with chlorine gas; group 4—chlorination reactions with calcium chloride. Under sintering conditions, the Gibbs energy of the reactions in group 1 is strongly negative (600–1400 kJ/mol). The thermodynamic calculations predict that the oxidation reactions of arsenopyrite, arsenic, copper, and rhenium sulfides can result in the formation of sublimated As_2O_3 , As_2O_5 , Cu_2O , and Re_2O_7 within a wide temperature range. Reactions in the group 2 with the sublimated As_2O_3 and Re_2O_7 have strongly negative Gibbs energies (900–1300 kJ/mol). Thermodynamic calculations predict that reduction reactions of arsenopyrite and rhenium sulfide can result in the formation of sublimated As_2O_3 and Re_2O_7 within a wide temperature range, including the range of interest 473–1473 K. In this case, the reactions of interaction of components with natural gas in the presence of oxygen can proceed both with the formation of CO_2 and with the formation of CO . A comparative analysis of the loss of the Gibbs free energy of these reactions shows that reactions with the formation of CO_2 are much more thermodynamically probable. This is due to the presence of oxygen in the gas phase, which oxidizes CO to CO_2 . The obtained results show the fundamental possibility of the decomposition of arsenic compounds (arsenopyrite, lautite, etc.) and their removal during reduction sintering of the material with natural gas. Groups 3 and 4 present chlorination reactions between remaining arsenopyrite, Cu_2S , As_2S_3 , ReS_2 , and gold with chlorine gas, pure CaCl_2 , and CaCl_2 in the presence of SiO_2 . The values of the Gibbs energy of the chlorination reactions for arsenopyrite (13, 19) are strongly negative (500–800 kJ/mol). The Gibbs energy of the chlorination reactions for As_2S_3 and ReS_2 (14, 15, 20, 21) is strongly negative (300–1200 kJ/mol) as well. Reactions (18, 24) with Cu_2S is negative (10–400 kJ/mol) as well. Reactions (13–15 and 20–21) with AsCl_3 and ReCl_3 production are thermodynamically more probable than chlorination reactions for gold. Obviously, for a more complete chlorination of gold, it is necessary to first remove arsenic and rhenium from the mineral ore to the possible extent. Results of experiments that were previously reported [3,15–19], as well as those reported below, demonstrate that the sublimation of gold metal following chlorination goes practically to completion. This was not anticipated based on thermodynamic calculations (Table 3, Groups 3, 4): only weak gold chlorination is predicted at high temperature. This discrepancy should disappear if atomic chlorine participates in the gold chlorination reaction (reaction (17)). The authors of the works [3,24] came to the same conclusion. Atomic chlorine can be formed during thermal decomposition of CaCl_2 [3,24]. Therefore, the chlorination of gold may take place in the temperature range of interest.

3.2. Oxidation Sintering

Preliminary oxidation sintering of Au- and Re-containing concentrate with high arsenic content was performed. Experimental results are shown in Figure 4.

We found that the extraction yield of arsenic depends strongly on sintering temperature. At 873 K, the extraction yield reached 50%. In this case, the extraction yield of rhenium sublimation was 88–90% and desulfurization during sintering was 35%. An effect of the excess air on the recovery yield of arsenic and rhenium, as well as the desulfurization of the ore, was also observed. The higher the excess air ratio the more complete the extraction of arsenic and rhenium and the desulfurization process.

3.3. Reduction Sintering

Preliminary reduction sintering of concentrate with a high arsenic content was also performed. Experimental results are shown in Figure 5.

Figure 5 shows the effect of temperature and test duration of the reduction sintering process on arsenic recovery. At 823 K, the arsenic extraction yield is 88%, and at 1373 K it reaches 100%. Extraction of rhenium is not successful: this failure is apparently due to the fact that volatile rhenium oxide (Re_2O_7) in a reducing atmosphere at temperatures >700 K

transforms into nonvolatile rhenium oxides, ReO_2 and ReO_3 [27]. Desulfurization also does not occur in this case.

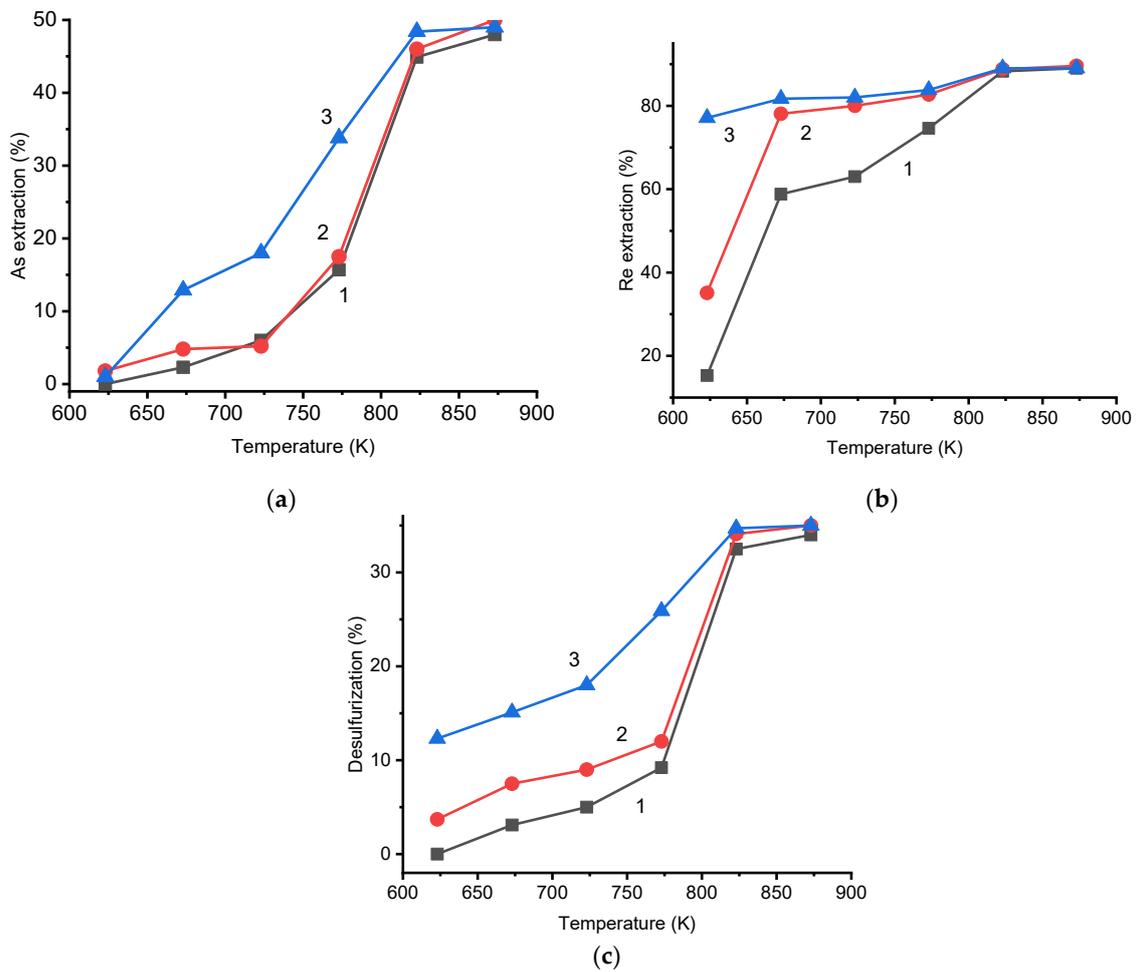


Figure 4. Effect of temperature on: (a) arsenic extraction yield; (b) rhenium extraction yield; (c) desulfurization. Curves are labeled: 1—excess air coefficient 100%, 2—excess air coefficient 150%, 3—excess air coefficient 170%.

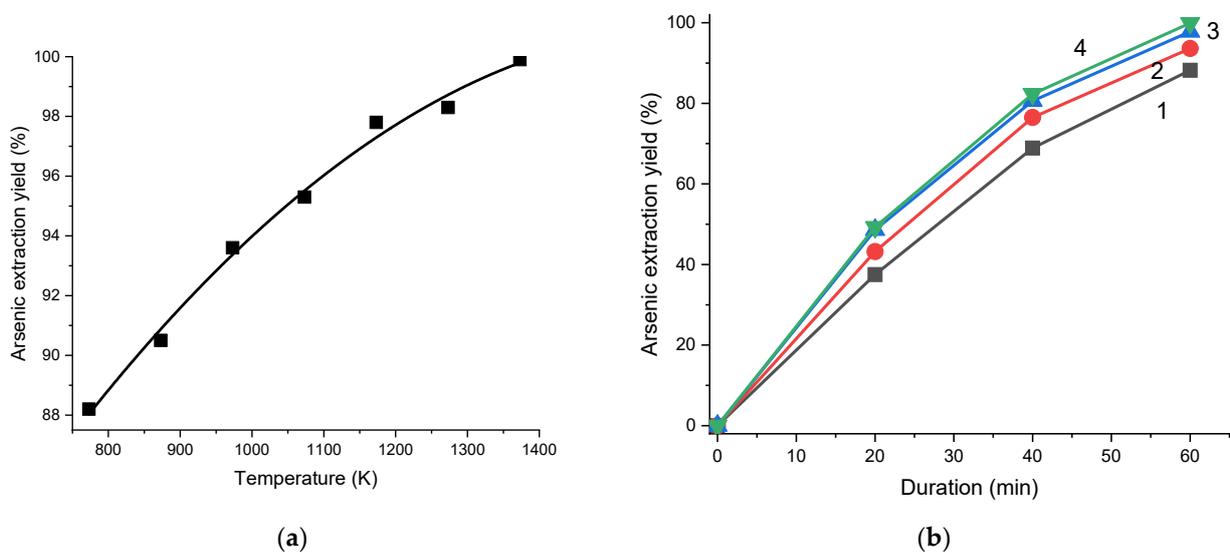


Figure 5. Dependence of arsenic extraction on (a)—temperature and (b)—time: 1—773 K, 2—973 K, 3—1173 K, 4—1373 K.

3.4. Chlorination Processing of the Cu-Au-As Concentrate

Experiments with the Cu-Au-As concentrate without preliminary oxidation or reduction treatment demonstrated that the proposed chlorination process does not allow efficient gold extraction from this material.

Gold sublimation was 30–50 wt.% for low-temperature chlorination of the concentrate with elemental chlorine. In all experiments, including low-temperature chlorination, considerable sublimation of other metals was observed. Chlorination at these low temperatures (523 K) does not cause noticeable sublimation of other metals (Fe, Cu, Zn, and Ag). However, 60–70% of the present tin does undergo sublimation, an effect which may be suppressed by sintering in air at 973 K, presumably due to the heavy oxidation of tin.

Gold extraction yield of 99% was reached only for high-temperature chlorination of the material with elemental chlorine. However, poor selectivity was the price paid. At higher temperatures, the sublimation of other metals also increased dramatically: extraction yield of Ag, Zn, Fe, As, and Sb was within the range of 50–70%, Cu ~10%, Sn ~75–85%.

Calcium chloride as an alternative chlorinating agent was mixed with the nanocrystalline SiO₂ under dry conditions. For high-temperature chlorination of the concentrate with calcium chloride gold extraction, yield reached 50–65% after 2 h at 1223 K. The sublimation of Fe and Cu was not observed; sublimation of Ag reached 30–40%. Sublimation of Zn, As, Sb, Sn was nearly complete: 80–90%. Gold extraction yield following sintering at 1273 K is lower than at 1223 K, presumably because at 1273 K the clinker begins to melt and agglomerate; therefore, successful chlorination and sublimation into the gas phase of gold-containing materials is not achieved.

Following preliminary oxidation, sintering at 873 K with 170% excess of air of Cu-Au-As concentrate, arsenic was removed from the concentrate to the extent of 50%; desulfurization was 35% complete. Rhenium sublimation yield was equal to 80%. The resulting clinker was sintered with chlorine gas at 523 K or with a mixture of CaCl₂ + SiO₂ at 1223 K. Gold recovery in both cases was only 75–80%. The recovery of the remaining non-ferrous metals was not higher than as without preliminary oxidation sintering. Tin sublimation is significantly reduced.

With preliminary reduction sintering of Cu-Au-As ore at 1123 K arsenic was completely removed. The resulting arsenic-free clinker was sintered with chlorine at a temperature of 523 K and with a mixture of CaCl₂ + SiO₂ at a temperature of 1223 K. Gold recovery was 87–93%. The recovery of the remaining non-ferrous metals was not higher than that obtained without preliminary reduction sintering.

Experiments with the dry mixture from Cu-Au-As concentrate + calcium chloride + nanocrystalline SiO₂ were carried out with slow heating: the crucible was heated in the furnace from room temperature to 1223 K at a heating rate of 8 K/min; or they were carried out with rapid heating: the crucible was inserted directly into the hot furnace at 1223 K, heating rate—100 K/min. Slow heating simulated the sintering process in a standard rotary kiln, while fast heating was similar to that obtaining in a fluidized bed furnace. Our previous experience with other products (coal fly ash, Cu-Zn-Pb polymetallic concentrates) has shown that the sublimation of some metals under fast heating with CaCl₂ increasing in comparison with slow heating (our unpublished data). We believe that this is due to the fact that, upon fast heating, thermal decomposition of calcium chloride occurs immediately in the chlorination reaction zone. Slow heating causes calcium chloride thermal decomposition to occur before the material reaches the temperature required for chlorination reactions. As can be seen in Table 4, our attempts at efficient gold sublimation from Cu-Au-As ore did not confirm the results of our previous investigations for other products.

It is known that chloride fumes are hygroscopic dust. The significant disadvantages of dry capture in the chlorination of gold-bearing materials are mechanical losses of the gold and difficulties with their storage and transportation [21]. It is known that gold chlorides are metastable and external factors also affect the stability of gold chlorides. So, in the case of contact of chloride fumes with the surface of dry capture devices, gold chlorides decompose with the formation of metallic gold, which settles on the surface of the device,

and it is practically impossible to remove them, especially when metal steel devices are used. As a result, there are significant losses and unbalances in gold in the process. When capturing sublimates in steel apparatus, the unbalance of gold is 30–60%. The recovery of gold from hydrochloric acid solution by these methods is 98–99% [21].

Table 4. Results of laboratory scale chlorination of the Cu-Au-As concentrate.

Procedure	T, K	Heating	Reagent	CaCl ₂ , % from Cu-Au-As Concentrate Quantity	SiO ₂ , % from Cu-Au-As Concentrate Quantity	Gold Extraction Yield, %
Cu-Au-As concentrate	523	Slow	Chlorine	-	-	51.3
Cu-Au-As concentrate	1223	Slow	CaCl ₂ + SiO ₂	37.5	6.4	58.7
Cu-Au-As concentrate	1223	Slow	Chlorine	-	-	99.4
Cu-Au-As concentrate	1223	Fast	CaCl ₂ + SiO ₂	43.2	10.1	56.5
Cu/Au/As concentrate following oxidation sintering at 873 K	523	Slow	Chlorine	-	-	74.3
Cu/Au/As concentrate following oxidation sintering at 873 K	1223	Slow	CaCl ₂ + SiO ₂	40.0	10.5	79.1
Cu/Au/As concentrate following oxidation sintering at 873 K	1223	Fast	CaCl ₂ + SiO ₂	40.0	10.5	78.3
Cu-Au-As concentrate following reduction sintering at 873 K	523	Slow	Chlorine	-	-	85.7
Cu-Au-As concentrate following reduction sintering at 873 K	1223	Slow	CaCl ₂ + SiO ₂	40.0	10.5	88.3
Cu-Au-As concentrate following reduction sintering at 873 K	1223	Fast	CaCl ₂ + SiO ₂	40.0	10.5	88.4

4. Conclusions

The problem of processing gold-bearing copper materials in Kazakhstan is becoming relevant due to their large, accumulated volumes. This is due to the lack of a rational processing technology, due to the significant content of arsenic in them. This paper presents the results of a new process for extracting gold from refractory gold-copper-arsenic-bearing products by chlorinating sintering.

The results of thermodynamic calculations showed the possibility of extracting gold in the form of its chloride from complex refractory gold-copper-arsenic-bearing products under the conditions of chlorinating sintering using chlorine gas and calcium chloride as chlorinating reagents. However, as shown by the experimental results, it is not possible to achieve a high extraction of gold during chlorinating sintering in the temperature range of 800–1000 K, where the recovery of gold is 35–60%. The high extraction of gold during sintering is restrained by the presence of arsenic and other impurities which stop the mechanism of gold reduction by chlorine-containing reagents. This requires preliminary operations to remove arsenic. According to this, the new experimental results on the behavior of arsenic and other associated metals (Re and others) under the conditions of oxidative and reductive sintering were obtained in the work.

We found that during oxidative sintering, the extraction of arsenic strongly depends on the process temperature: at 873 K, the extraction of arsenic into dust was 50%, rhenium—88–90%. The effect of excess air on the extraction of arsenic and rhenium into dust has been established. It is shown that the higher the excess air coefficient, the more complete the extraction of arsenic and rhenium into dust. The obtained data indicate that it is not possible to achieve a high removal of arsenic from the initial product during oxidative sintering.

The best results in arsenic removal are achieved under conditions of reductive sintering of the source material with natural gas: at 823 K, the extraction of arsenic into dust is 88%, and at 1373 K, arsenic is almost completely removed into dust from the initial product.

The obtained new experimental results have fundamental importance for the choice and organization of technology for the comprehensive processing of complex refractory gold-copper-arsenic-bearing products. For processing these products, we consider starting with reductive sintering with natural gas in order to completely remove arsenic from them, and then chlorinating sintering of the resulting cinder with chlorine or calcium chloride with a maximum extraction of gold. The residual condensed product after sintering is quite suitable and without much effort can be processed by existing methods of the extraction of copper.

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