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Development of a Roasting Process for Arsenic Gold-Bearing Concentrates to Recover Arsenic Into a Low-Toxic Product and Produce Calcine Suitable for Further Processing

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The processes of sulphiding roasting of arsenopyrite concentrate with arsenic sulfide transition into the gas phase have been studied under laboratory and large-scale laboratory conditions. The roasting shall be carried out in neutral atmosphere (nitrogen or complete fuel combustion products), pyrite concentrate is recommended to use as sulphidizer, mixture of arsenopyrite concentrate and sulphidizer previously undergoes briquetting. Sublimates produced from roasting have been investigated by biotest methods, their correspondence to Hazard Class IV has been determined. Based on the investigation results, the process of gold-containing arsenopyrites treatment to produce low-hazardous sublimates and calcine suitable for further gold recovery has been proposed.

Keywords: arsenic sulfide, arsenopyrite concentrate, sublimation, dearsenification, sulphiding roasting.

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Разработка технологии обжига мышьяковистых золотосодержащих концентратов с выделением мышьяка в низкотоксичный продукт и получением годного для дальнейшей переработки огарка

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В лабораторных и укрупнённо-лабораторных условиях исследованы процессы сульфидирующего обжига арсенопиритного концентрата с переводом сульфида мышьяка в газовую фазу. Обжиг проводится в нейтральной среде (азот или продукты полного сгорания топлива), в качестве сульфидизатора рекомендуется использовать пиритный концентрат; смесь арсенопиритного концентрата и сульфидизатора предварительно подвергается брикетированию. Полученные при обжиге возгоны исследованы методами биотестирования, установлено их соответствие IV классу опасности. По результатам исследований предлагается технология переработки золотосодержащих арсенопиритов с получением малоопасных возгонов и огарка, годного для дальнейшего извлечения золота.

Ключевые слова: сульфид мышьяка, арсенопиритный концентрат, возгонка, деарсенизация, сульфидирующий обжиг.

Introduction

In today’s conditions of ever increasing gold production, the mining industry is forced to involve refractory arsenic (arsenopyrite) ores in processing. Gold from these ores cannot be recovered via cyanide leaching without pre-treatment, in particular, the roasting.

The essential problem of the arsenopyrite concentrate roasting technology is arsenic removal and disposal, burial or use. Industrial consumption of arsenic and its compounds does not exceed 1.5% of the amount of the element reported with feed to non-ferrous operations, while deactivation or disposal of arsenic products due to their high toxicity incurs high costs.

According to the literature, one of the most promising options to prepare arsenopyrite gold concentrates for precious metals recovery is their roasting to recover arsenic into non-toxic sulfide sublimates. The development of such technology is a subject of many studies offering many variants of this process, though, to date none of them is widely employed on an industrial scale. Some of the offered options envisage oxidation-sulfidizing roasting [1], the use of water vapor [2], and the implementation of the process in a fluidized bed furnace [3], however, they increase the risk of production of toxic arsenic compounds (trioxide, arsenic hydride) and their transition to waste, making the latter difficult to dispose.

The purpose of this work was to develop a process of dearsenification of arsenic gold concentrate to produce a calcine containing the minimum amount of arsenic, suitable for further processing, with the transition of arsenic to the dust and gas phase in the form of low-toxic compounds. Based on the requirements of maximum environmental safety of the process, it was found appropriate to

Table 1. Chemical composition of concentrates

Material Type	W/W, %									
	As	Fe	S	Cu	Pb	Zn	Si	Al	Ca	Mg
Arsenopyrite concentrate	22.2	18.3	11	0.129	0.012	0.0055	14.28	4.03	0.87	0.44
Pyrite concentrate	0.226	32	39.8	0.55	0.7	1.64	7.51	1.2	0.47	0.41

try sulfidation roasting of concentrate in an inert atmosphere (nitrogen or complete fuel combustion products) in an easily sealed installation (shaft reactor or other sealed unit). Pyrite concentrate and elemental sulfur were tried as sulfidizer.

Initial materials

The dearsenification roasting technology was developed for the concentrates produced under the contract with Engineering Dobersek GmbH; their chemical composition is given in Table 1. The concentrates were analyzed by SEM, EPMA, and XRD methods.

Arsenopyrite in arsenopyrite concentrate makes up 45-50% of the total volume, primarily, in a free form. No less than 95% of arsenic is concentrated in arsenopyrite. Other minerals of the concentrate are pyrite and chalcopyrite; bismuthine, galena, telluronevskite are present in small quantities. All discovered gold-bearing particles are observed in arsenopyrite and associated with bismuth- or bismuth-tellurium-based minerals.

The pyrite content in the pyrite concentrate is 60-65% of the total volume of the sample. About 70% of pyrite grains are represented by a free form, the most common aggregates are intergrown with other sulfide minerals and silica; 95% of arsenic in pyrite concentrate is an impurity in pyrite. Other minerals of the concentrate are sphalerite and chalcopyrite, as well and minor amounts of galena, anglesite, barite. No precious metals in the pyrite concentrate are discovered.

Laboratory investigations

A complex of laboratory investigations to find the optimal modes of feed preparation for the processing and dearsenification roasting in particular, and to select necessary reagents and process parameters was performed.

As a method for the preparation of the charge (mixture of arsenopyrite concentrate and sulfidizer) for roasting, providing a low dust removal from the unit and high rate interaction of the components, briquetting was tested. Using a laboratory roller briquette press, the optimum moisture of the charge, the type and flow rate of the binder were selected.

Laboratory experiments on briquette roasting were carried out in a sealed horizontal quartz reactor placed in an electric resistance-type furnace.

First, the minimum required consumption of sulfidizer (pyrite) was determined to achieve the set residual arsenic content in calcine (less than 0.5%). It has been found that to obtain this arsenic content (with the value higher than required, to be on the safe side), it is sufficient to consume 66% of pyrite concentrate as a ratio of arsenopyrite concentrate (Fig. 1).

The residual arsenic content in calcine as a function of the roasting time was studied. Figure 2 shows that the most intense dearsenification occurs at the initial stage of the roasting, and the removal of the major part of arsenic (to a residual content of 2%) takes 7-11 minutes. Further dearsenification runs slower, at a 66.7% sulphidizer rate and a temperature of 700 °C (Fig. 3), the arsenic content in calcine reaches an acceptable level of 0.5% in 17-18 minutes, and 40 minutes later it becomes equal to 0.196%.

When instead of pyrite sulfur is used in an amount of 26.5% by weight of arsenopyrite concentrate, dearsenification runs slowly, in 30 minutes of the roasting arsenic content in calcine still exceeds 5%.

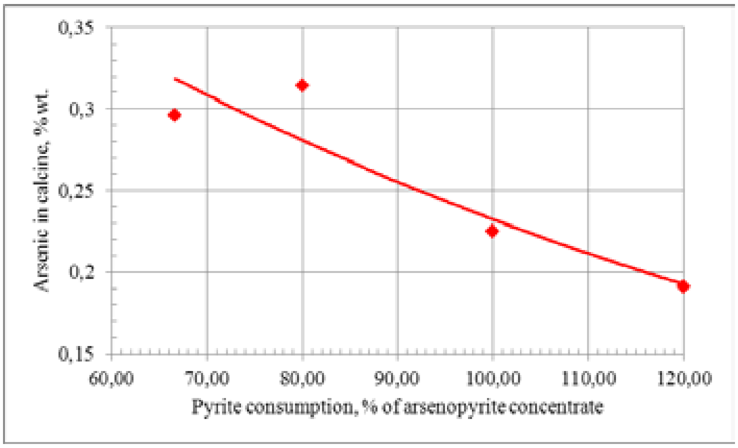

Fig. 1. Residual arsenic content in calcine as a function of pyrite consumption

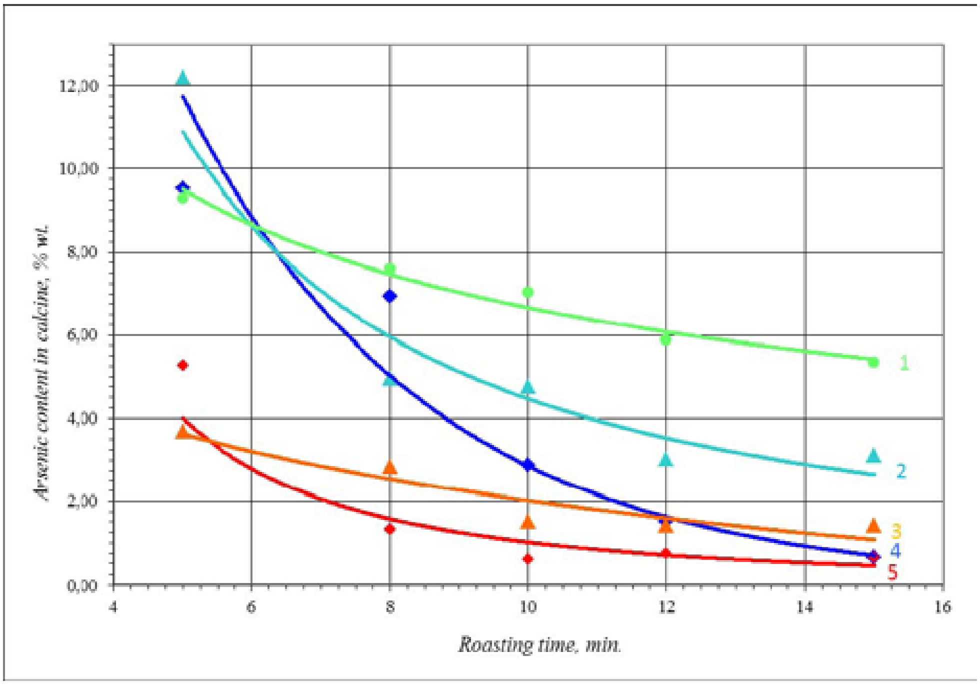

Fig. 2. Residual arsenic content in calcine as a function of roasting time: 1 – sulphur, 650 °C; 2 – 50%, 650 °C; 3 – 50%, 700 °C; 4 – 66,7%, 650 °C; 5 – 66,7%, 700 °C

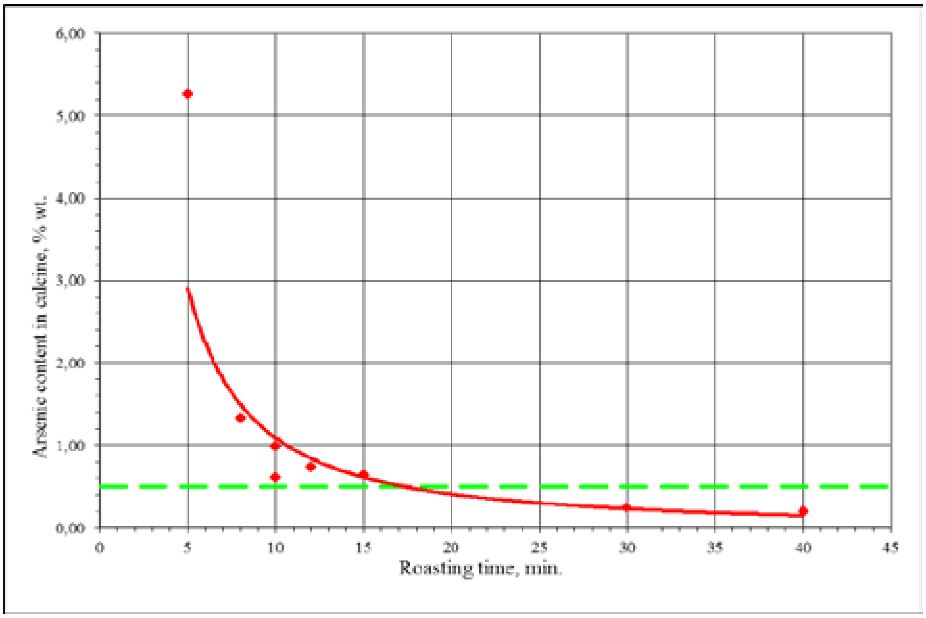

Fig. 3. Residual arsenic content in calcine as a function of roasting time (66.67% of pyrite, 700 °C)

Thus, to achieve the set residual arsenic content in calcine, the retention time within high temperatures is required as no less than 20-30 minutes. When designing a commercial reactor, a particular attention was given to the observation of the required roasting time for all briquettes inside the installation.

Based on the results of the laboratory studies it was found that to obtain the set residual arsenic content in calcine (less than 0.5%) and produce sublimates, containing virtually no metallic or oxide arsenic it is necessary to:

- feed pyrite (to the furnace feed) as sulphidizer, at least 50-66% wt. of arsenopyrite concentrate;
- maintain the roasting temperature in the range of 650-700 °C;
- provide the roasting time of at least 30 minutes.

To carry out large-scale experiments on the dearsenification roasting of briquettes, the sealed vertical shaft reactor was used (Fig. 4). The principle of operation of this unit implies thermal treatment of the concentrate briquettes passing by gravity from the top to the working area of the sealed reactor and being discharged by plate to a lower hopper. The operation rate of the plate and, respectively, the residence time of briquettes in the hot zone are adjusted so as to provide a maximally complete process of dissociation of the concentrate arsenopyrite component and to recover arsenic to sublimates, followed by their condensation and capture. Inert gas (nitrogen) is fed to the reactor to prevent the material from oxidation and convey sublimates to the condensation zone (cooler).

As a result of research works carried out in the large-scale unit, calcines containing <0.5% As and arsenic sulfide sublimates bearing neither oxides, nor metallic arsenic were produced. Roasted briquettes were strong enough for their transporting (Fig. 5).

Calcine and sublimate samples were investigated via SEM and EPMA.

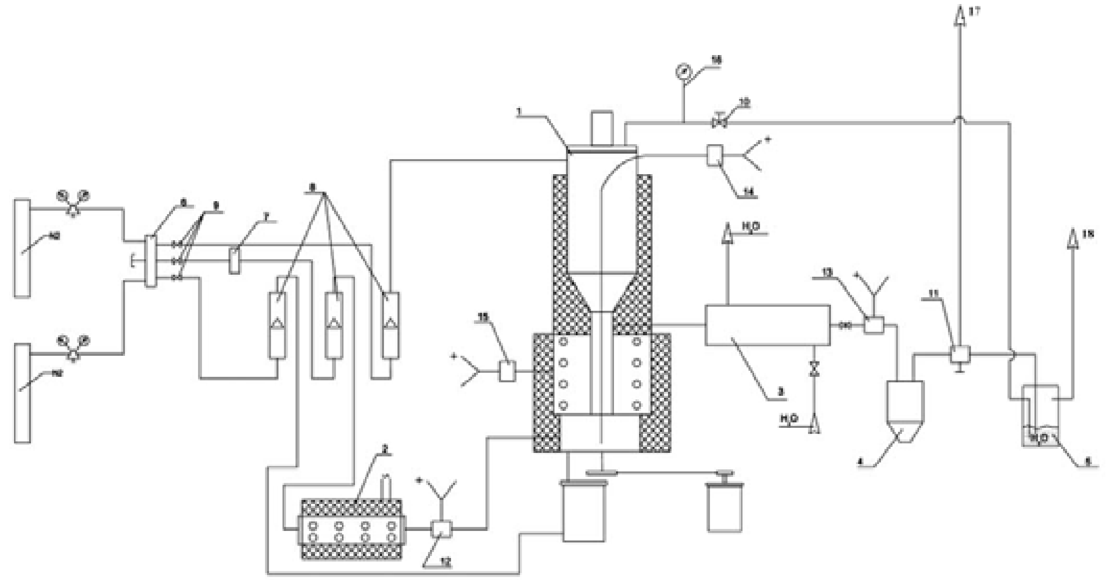

Fig. 4. Diagram of large-scale unit for dearsenification roasting: 1 – reactor, 2 – gas preheater, 3 – cooler, 4 – filter, 5 – water seal, 6 – gas distributor, 7 – inert gas flow meter and controller, 8 – flowmeters, 9 – fine leveling valves, 10 – emergency gas discharge ball valve, 11 – gas bleed ball valve, 12-15 – sealed inlets for thermocouples, 16 – gas overpressure gauge, 17 – to mass spectrometer, 18 – off-gas

Fig. 5. General view of briquettes before and after roasting

Calcine

It has been found that about 50-60% (by volume) of calcine particles are represented by nonmetallic minerals of the initial concentrates. Sulfur, arsenic, noble metals in these components are not diagnosed[1], they are predominantly (up to 90-95% relative to all arsenic contained in arsenic calcines and no less than 80-85% relative to sulfur) concentrated in the products of arsenopyrite decomposition. In terms of decomposition degree, arsenopyrite particles vary greatly: from solid particles with their composition similar to the original minerals (Fig. 6), to spongy formations having the composition close to troilite (iron monosulfide, FeS) with residual arsenic content from the first tenths %wt. to 0.8% wt. (Fig. 6 (a, b)).

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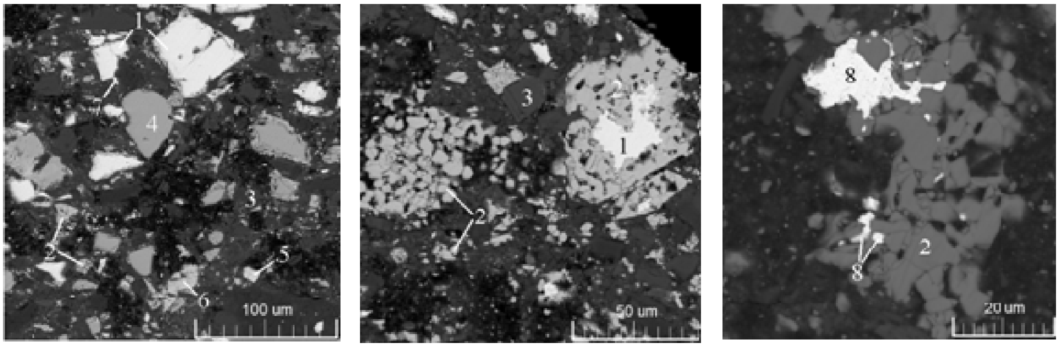
[1] Within the sensitivity of the EPMA method when using EDS detector



a b c

Fig. 6. The structure of calcine samples: 1 – arsenopyrite relic, 2 – iron sulfide, 3 – non-metallic minerals, 4 – pyrite relic, 5 – sphalerite relic, 6 – chalcopyrite relic, 7 – galena relict, 8 – gold-based phase

In addition to the above components, the samples contain relics of galena, chalcopyrite, sphalerite, barite and pyrite, the volume of about 3-5 vol.%, which include unstable arsenic impurity diagnosed at a level of 0.1-0.2% wt. Apart from that, gold-based components – micron and submicron inclusions in iron sulfide particles (Fig. 6, c), have been discovered in all samples.

When analyzing cross-sections of briquettes, it was found that the removal of sulfur and arsenic occurs uniformly in the material: the average compositions of central and peripheral areas coincided[2], undecomposed arsenopyrite was evenly distributed in briquettes, size of “residual” arsenopyrite was consistent as well.

Sublimates

At least 95% of the mass of material in the sample (Fig. 7) are represented by As-S particles of a volatile composition (13-25 wt.% As). These particles are a fine mixture of arsenic sulfides, As_4S_4, and As_4S_3 (dimorphite). In the volume of solitary particles, micron and submicron inclusions based on bismuth and lead, are distinguishable.

In addition to the sulfide particles, the following components are present in the sample:

- iron arsenosulfide particles corresponding by composition to arsenopyrite of the initial concentrate, and the iron particles of the troilite composition. The mentioned compounds by their composition and size coincide with the calcine components, and are the dust formed during the motion of briquettes (when loading and discharging) in process of roasting (partial briquettes destruction during chemical reactions).
- Fe-O-based particles with unstable sulfur, carbon, and arsenic impurities. These particles are a product of interaction of the scale from the walls of the reactor with sulphide sublimates.

No arsenic oxide forms have been discovered in sublimates. Phases containing noble metals have not been diagnosed in the samples either.

The research of the size of sublimates produced in the cooler was conducted with the help of Microtrac laser particle analyzer via the ‘wet’ method. Since sublimates, both dry ones and as slurry

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[2] Within the range of values determined by slightly uneven distribution of non-metallic minerals in briquette

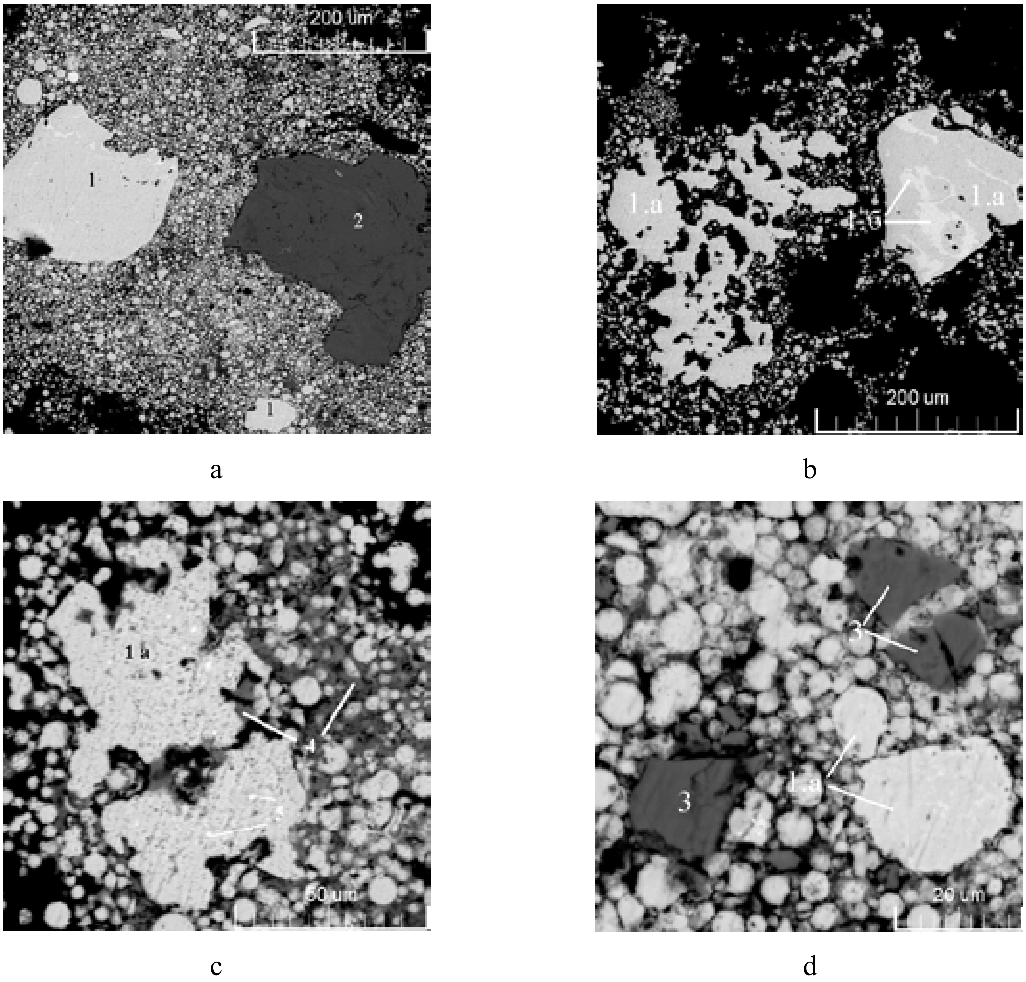

Fig. 7. Structure of sublimate samples from the large-scale unit cooler: 1 – particles of As-S composition (a –As_4S_3 composition, b – As_4S_4 composition), 2 – Al silicate particles, 3 – Fe-O-based components, 4 – fine multicomponent mass, 5 – Bi/Pb-based inclusions

in water, showed a clear tendency to sticking, size analysis was performed in ethyl alcohol (after two day retention in it) (Fig. 8).

It is seen that, according to the size analysis, the greatest proportion of the sample accounts for 20 µm particles. In the study conducted in water, a ratio of the particles of over 40 microns is significantly higher as compared to that carried out in alcohol, which is related to a high tendency of sublimates to form conglomerates.

Toxicity of resulting materials

The experimental hazard class definition of waste has been performed in the dedicated accredited Testing Laboratory Centre FBUZ "Hygiene and Epidemiology Centre in St. Petersburg". The study was conducted by bioassay methods, based on the response of living organisms to the negative impact of pollutants. In determining the toxicity index of sublimates, granular bull semen and water fleas (daphnia magna) were used as test objects. According to the research, sublimates can be attributed

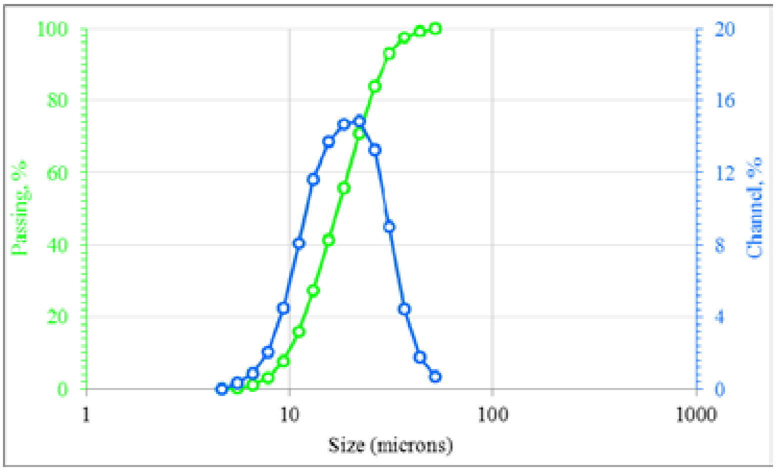

Fig. 8. Size distribution of sublimates from the cooler (ethyl alcohol)

to Hazard Class IV in compliance with Regulations 2.1.7.2570-10 'Amendment No1', Regulations 2.1.7.2850-11 'Amendments and Additions No2' in Regulations 2.1.7.1386-03 and Order of the Ministry of Natural Resources of June 15, 2001 No 511.

The calcine, based on the results of laboratory tests, corresponds to Hazard Class IV in accordance with the requirements of sanitary norms and regulations SanPiN 2.1.7.1322-03, and Regulations 2.1.7.1386-03 (in Revised Amendment No1, approved by Resolution of the Chief State Sanitary Doctor of the Russian Federation of 12.02.2010 No 2, Amendments and Additions No2, approved by Resolution of the Chief State Sanitary Doctor of the Russian Federation of 31.03.2011 No 28).

Basic diagram of arsenopyrite concentrate processing

On the basis of the results of the conducted research, the general scheme of arsenopyrite concentrate processing under industrial conditions has been developed, basic parameters of the process have been calculated, and the process procedure has been performed (Fig. 9).

According to the process diagram, arsenopyrite and pyrite concentrates are mixed together and undergo drying. Dried concentrates are then mixed with a binder and briquetted in the roller press. Briquettes pass through strengthening drying on the belt dryer and fed to the roasting.

For the roasting implementation, the design of the vertical sealed shaft reactor with horizontally placed (in the shaft) electric heaters in protective tubes has been proposed. The countercurrent of briquettes sinking by gravity and hot nitrogen carrying sublimates to the gas cleaning system is provided in the reactor. Dearsenificated briquettes at the bottom of the reactor pass to the water cooled cone hopper, grow cold and are discharged onto a screen. Suitable calcine is sent for further processing, fines are reverted to the mixer.

The gas cleaning system of the reactor provides separate trapping of dust and sublimates. The dust containing precious metals is reverted to the mixer, and sublimates are packaged and buried.

Thus, Gipronickel Institute LLC has developed a technology for processing gold-bearing arsenopyrite concentrate to recover arsenic into a slightly toxic sulfide product. Based on the same scheme with due corrections other arsenic-containing materials, e.g., gas cleaning cakes, could be

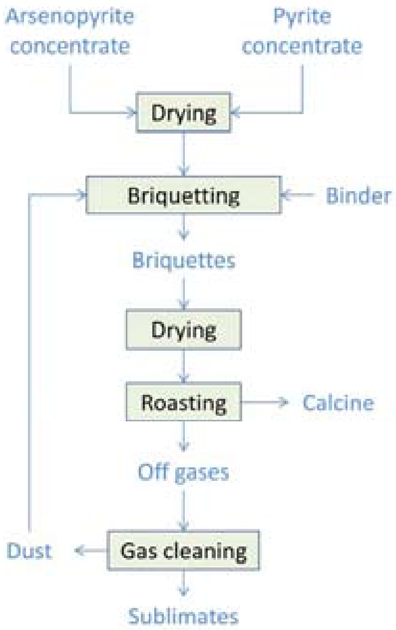

Fig. 9. Principal diagram of the processing of arsenopyrite concentrate

processed; furthermore, due to the removal of arsenic the hazard class would be lower. Gipronickel Institute LLC can perform the entire scope of works necessary to adapt the technology to the customer's materials, from thermodynamic modeling and laboratory studies to the reactor design.

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