

Conference Paper

Arsenic in Chemical and Metallurgical Conversions of Copper-zinc Concentrates

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Abstract

Due to the deterioration of the quality of obtained sulfide-copper concentrates, arsenic circulates and accumulates in the intermediate products, which reduces the quality of the metal and associated product – sulfuric acid. A method of estimation the distribution of impurity elements can be created using the recycling of sulfide concentrates by various technologies (including autogenous smelting, matte conversion and flotation of slags). This technique is based on solving balance equations for iron, copper and arsenic with known compositions of the resulting products. The obtained data were used to assess of the extraction of arsenic into produce outputs (slag, matte, dust, etc.). In this study, the concentration of arsenic in the dust of metallurgical processes and sludge for cleaning acid solutions is confirmed. The increased temperature in the electrostatic precipitator of gas purification of autogenous processes lead to a partial transition of arsenic into the gas stream directed to the sulfuric acid production. It is possible to regulate the fraction of transition of arsenic to dust and sulfuric acid while changing the operating temperature in the electrostatic precipitator. To a lesser extent arsenic is concentrated in the tails of flotation of slag (11.7%) and metallic copper (2.9%). These data are useful for substantiating measures for the wastes recycling and improvement of the ecological environment in the enterprise operating districts.

Keywords: arsenic, autogenous melting, matte conversion, slag flotation, purified gas treatment, distribution, dust, sludge.

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The importance of the arsenic utilization's problem in non-ferrous metallurgy is connected with the necessity of liquidation of accumulated arsenic-containing wastes, streamlining its removal from technological processes and reducing internal and inter-plant circulation. In conditions of depletion of natural resources, metallurgical enterprises are forced to work on substandard raw materials, that have a high content of impurities, including arsenic. This determines the importance of carrying out fundamental and applied researches connected with the study of the forms of arsenic's


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configurations and redistribution among the products of chemical and metallurgical industries [1]. Taking into account the low demand of industrial enterprises in arsenic and products based on it, actions for its storage and disposal in the form of sparingly soluble non-toxic compounds are becoming more important.

One of the main sources of arsenic are sulfide copper-zinc concentrates processed at Ural cooper-melting plants. The decrease of the quality of the extracted raw was led to the increase of arsenic's content from 0.5 to 2.0%. Recycling of sulfide concentrates was processed at SUMZ using autogenous smelting methods (PV furnace) for matte with 45-55% Cu with the following conversion to 97.0-99.5% Cu as a crude metal. From the resulting slag copper is recovered by flotation methods. Arsenic is distributed unequal among the processed products; the main quality passes into gas during the pyrometallurgical processing of raw. The gases are subjected to cooling (recovery boiler - KU, cooling tower) and purification (electrostatic precipitator - EF) with the release of dust containing up to 10% As. Purified gases are directed to the production of sulfuric acid, which involves purification from arsenic with the release of sludge, consisting mainly of As_2S_3 . The cooling systems and dust removal equipment of metallurgical machines create the conditions for condensation and partial capture of As_2O_3 in electrostatic precipitators. The cooling of dust in a gaseous environment ($N_2-SO_2-O_2-H_2O-CO_2$) of an electrostatic precipitator was led to a change of the new forms of arsenic and to the formation of oxyarsenates. The proximity of temperatures in the electrostatic precipitator to the boiling point of As_2O_3 ($\sim 460^\circ C$) should be explained by low efficiency in capturing arsenic compounds, over 40% of which remains in gases and then getting into sulfuric acid production [2]. Changes of the raw's compound, growth of the ratio of impurities, shift to melting modes providing the release of matte with a high copper content and also changing the oxygen / air ratio in the blast modify the allocation of arsenic among the melting products.

A lot of methods of removing arsenic from technological processes allow to remove it efficiently, however, products suitable for direct storage are obtained only in some methods. [3]. In general arsenic is aimed to convert to dump products, the composition of which depends on the feedstock, methods of its processing and waste disposal [4]. Long-term storage of arsenic-containing products is possible when arsenic is converted into stable, insoluble compounds [5], for example, arsenopyrite ($FeAsS$), realgar (As_4S_4), and auripigment (As_2S_3). An analysis of long-term practice of copper melting plants and data of the distribution of arsenic by pyrometallurgical processing products [6] allows us to conclude that the processes of arsenic removal in the form of sulfides, arsenides and sulfoarsenates is effective, which are compact, slightly soluble in groundwater, easy to transport, for storage and burial.

For the quantitative estimation of arsenic's distribution were used data of the composition of raw materials and resulting products. (Table). By solving the systems of balance equations for Fe, Cu, and As for each of the stages, the masses of the products formed were estimated that allowed to calculate the distribution of arsenic according to the technological scheme of copper smelting (Figure). The using of intermediate products (concentrates of flotation of slag, dust) as working materials influence on the distribution of arsenic - its content in all materials is increased.

TABLE 1: Composition of raw materials and processed products of copper-zinc concentrates, %

Materials	Cu	Fe	SiO ₂	CaO	As	Zn	Sb	Pb
Concentrate	18.9	32.2	0.9	0.2	0.3	2.8	0.1	0.4
Dust of electrostatic precipitators PV	12.4	15.0	0.5	0.4	7.2	10.3	0.58	11.3
Matte PV	51.1	20.4	0.6	0.1	0.1	2.0	0.1	0.6
Slag PV	0.93	38	31.1	3.8	0.06	3.1	0.07	0.12
Dust of converters	1.22	0.34	1.1	<0.01	1.95	23.9	0.3	24.6
Converters slag	5.5	43.5	19.2	0.2	0.06	3.2	0.06	0.32
Blister copper	99.4	0.0	0.1	0.08	0.05	0.02	0.04	0.07

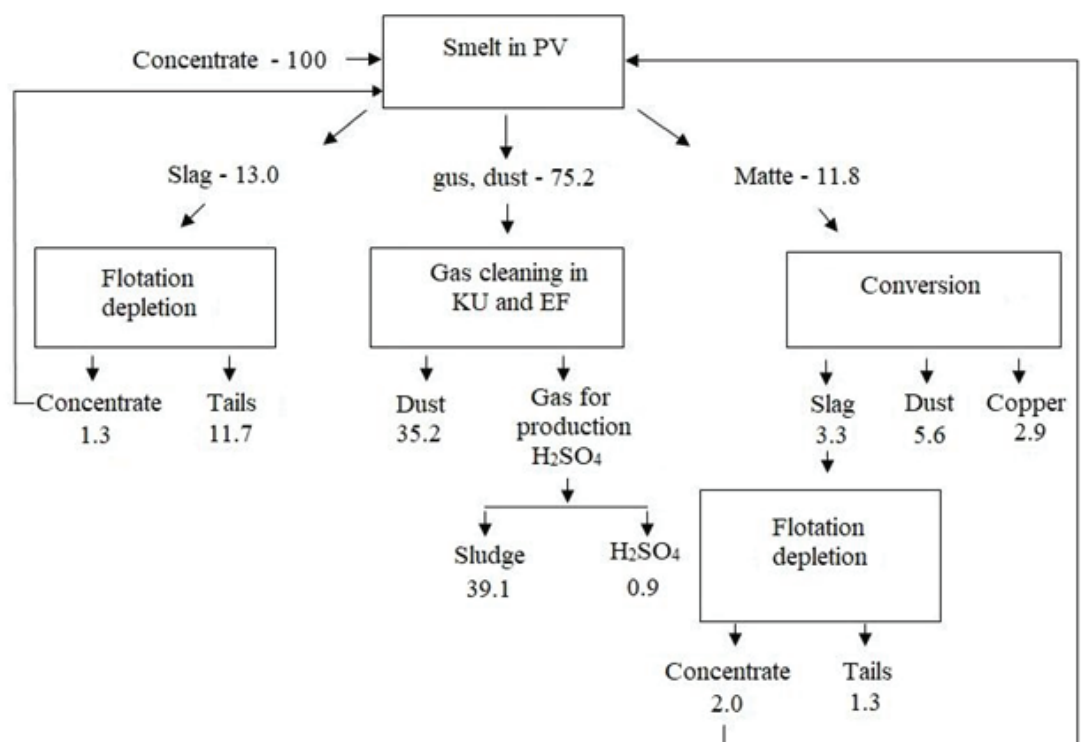


Figure 1: Arsenic distribution among the processing products of copper-zinc concentrate

The data obtained allow us to objectively assess the leaching of arsenic during long-term storage of waste and also offer measures to prevent soil and air pollution. So the storage of slag in the form of pieces limits the leaching of arsenic because of the

slagging of its oxides and sulfides and the deceleration of diffusion processes in solids. To eliminate the harmful effects of dispersed materials (dust), it is necessary to treat them with the release of non-ferrous metals (Cu, Zn, etc.) and the precipitation of arsenic in a low toxic form. Dispersed materials (sludge, cake) with a high arsenic content in the form of arsenates and sulfides are advisable to agglomerate with materials that create a solid shell or convert into a mineral-like form.

It has been proposed that arsenic sulfide should be melted with reagents (sulfur, metallic iron, iron sulfide), what launched to the formation of mineral-like phases [6, 7] — non-stoichiometric arsenic and iron sulfides with minimal solubility in aqueous solutions closed to the compositions of groundwaters. In addition, the conversion of materials into a water-insoluble form is achieved by the method of its compaction (fusion, briquetting). In this case, the volume of the obtained product corresponds to one fourth from the dried dispersed starting material.

Thus, evaluation methodology of the arsenic's distribution among the products of metallurgical production was developed. The directions of reducing the potential threats of arsenic-containing wastes were founded.

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