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Sulphatization roasting of dump industrial product of «Tuvacobalt» combine

Data on research of removal possibility of arsenic from dump cakes of «Tuvacobalt» combine are presented. Possibility of deep removal of arsenic from these dumps by means of their preliminary calcination and the subsequent sulphidation at 900–950 ºC at a sulphatizator ratio to a candle-end is shown, equal 1:2 to 0.28–0.30; at a ratio 1:4, 1:5 and 1:6 respectively to 0, 5 and to 0.8 %.

Key words: arsenic, dump sludge, calcination, sulphatization firing, environment, steam solutions, aqueous extract, sulfide-arsenide sublimates.

In this XXI century, as well as in the previous times, at mining and processing the arsenic containing ores and concentrates of non-ferrous metals and gold remains steadily an arsenic conclusion tendency from technological process in waste with the subsequent their burial (warehousing) in the form of pulps and sediment in tailings dams (technogenic lakes) or as a solid in specially equipped dumps or burial grounds. It leads to violation of dynamic balance of a circulation of arsenic in the nature and to infection with compounds of arsenic of placement regions of these warehousings and burials.

The wide-ranging field researches of hyper genesis of dump massifs of sulfide and the arsenic containing industrial products of a number of mining and processing productions conducted at the beginning of this century showed a real picture of threat to environment [1, 2]. Thus the attention that with storage period of dumps (including also ferric arsenate complexes) extent of environmental pollution progresses sharply was paid.

At a turn of the XX–XXI centuries to a problem about danger of the arsenic containing dumps was devoted a large number of works. After the analysis of materials of these works authors of the monograph [3] came to a conclusion that any warehousing or burial of arsenical waste is temporary and constitutes potential ecological danger, and the problem of the arsenic containing dumps bearing threat for environment can be solved at the organization of large-tonnage use of arsenical production in economic activity. However such approach to this problem doesn't find a proper understanding yet and the problem of the arsenic containing dumps remains with existence of dumps of previous years and their intensive growth on account of new receipts of waste of the working productions.

Special danger of environment pollution is constituted by old dumps of the enterprises which are once functioning, but closed and stopped the production. As a rule, in such cases control of them is weakened, and often is stopped completely, necessary preventive measures aren't undertaken. It leads to serious environmental problems and subsequently forces to acceptance of urgent measures for environment protection.

One of the most ecologically dangerous objects in the Republic of Tuva are dumps of the arsenic containing waste received at the hydrometallurgical enrichment of polymetallic ore of a Khovu-Aksy field at «Tuvacobalt» combine during its work (1970–1991). The solution of this ecological problem is possible obviously within complex processing of these dumps with development of ecologically safe and without the dump technology of receiving products and simultaneous elimination of a source of environmental pollution.

The Khovu-Aksy field of the arsenide nickel-cobalt ores is unique on mineral structure [4]. In its ores existence ~ 60 minerals is established. Arsenic in them is presented in mineral forms of primary arsenide: shmaltin-hloantit — (Co, Ni)As_{3-x}, skutterudite — $CoAs_3$, nickeline — NiAs, loellingite — $FeAs_2$, safflorite — (Co, Fe)As_2, and the secondary arsenates relating to group of vivianites: erythrite — $(Co, Ni)_3[AsO_4]_2 \cdot 8H_2O$ and annabergite — $Ni_3[AsO_4]_2 \cdot 8H_2O$. The main part of the arsenide minerals is presented by massive or continuous stringer ore. The oxidized minerals are only in a type of thin inclusions.

Unlike the arsenous cobalt ores of other fields in Khovu-Aksy ores the content of sulfur and iron is rather low (~ 1 % of sulfur and 4–5 % of iron), and arsenic and calcium oxide — raised (~10 % of arsenic and ~20 % of calcium oxide). Sulfides are in ore in the form tennantite — $Cu_{12}As_4S_{13}$, chalcopyrite — $CuFeS_2$, pyrites — FeS_2, galena — PbS, chalcocite — Cu_2S. Gross ore contains, %: cobalt — 0.2–1.2; nickel — 0.4–2.0; copper — 0.2–1.0. Waste has the quartz and carbonate structure including calcium carbonates, magnesium, oxide of silicon, clay, minerals of skarn (the grenade, a pyroxene and etc.).

On the developed autoclave ammoniac and carbonate technology cobalt, nickel and copper are transferred to solution. Also arsenic is passed into solution. All other components of ore form dump sludge. According to the chemical analysis slag products generally have carbonate and silicate structure at the content in them of oxides, %: SiO_2 ~35–40; CaO ~18; Al_2O_3 ~8; MgO ~8; Fe_2O_3 ~10 [5].

Arsenic from autoclave solution was besieged a magnesium oxide pulp on reaction [6]:

$$(NH_4)_2HAsO_4 + MgO = MgHAsO_4 + 2NH_3 + H_2O$$

For this purpose a technical magnesia from 75 % of active oxide, previously crushed in a spherical mill for 80–85 % to fineness — 0.1 mm which entered into a pulp in the form of magnesia milk, with the ratio S:L = 1:4 is used. The consumption of magnesium oxide made ~13 kg/kg of cobalt. The residual content of arsenic in solution shouldn't have exceeded 0.05 g/l. After sedimentation its concentration in a carbonate pulp in terms of dry weight reaches 2.4 %. However, the real final industrial products transferred to cobalt production, so-called concentrates often contained to 4 % of As.

The received solution was pumped over in a thickener, and the washed slime (tails from a condensation of a pulp of autoclave leaching) averaging 93–97 % of the mass of ore was directed to the tailings dam. In leached tails, as a rule, there was a quantity of metals in an arsenide form — from 10 to 25 % of the general content of cobalt in tails (at the level of 0.1 %) [7]. Arsenate-magnesia sediment after purification of solution from arsenic was buried with tails of autoclave enrichment.

In 20 years of work of «Tuvacobalt» combine more than 2 million $м^3$ of waste of ammoniac and autoclave concentrating repartition with the contents not less 75 thousand tons are received and stored in dumps. T of materials [8; 5–13] and concentration of arsenic in them within 3.5–6.4 %, and also valuable metals on average, %: Co — 0.18; Ni — 0.22; Cu — 0.11; Ag — 45 g/t and Au — 60 mg/t [5]. Complex field approbation of tailings dams of combine [5] showed that the steam waters formed as a result of long storage of tails (slime) are characterized as magnesia-calcium with the raised content of NH_4^+, nitrate and hydro carbonate type with the varying contents of chlorides. The laboratory researches conducted in work [5] showed that high concentration of arsenic in sample of steam moisture (2.2 mg/l), and also its high concentration in an aqueous extract (5.5 mg/l). The raised content of arsenic in the aqueous extract indicates existence of water-soluble forms of arsenic in combine dumps. Earlier it was noted [8; 21] that in gradually drying out water part of the tailings dam (map 5) concentration of arsenic reached 29.5 mg/l that answers 50 maximum concentration limits for this type of the stored waste.

On the basis of researches authors of work [8; 84–87] concluded that now the high speed of leaching of arsenic of various types is noted by solutions. At impact of rainfall and seasonal floods on dumps dissolution of arsenic in them can reach 10–12 mg/l in 144 days. In case of increase in acidity of solutions solubility of arsenic can increase at increase of the maximum concentration to 16 mg/l. Dissolution increases in the alkaline environment to concentration of 43 mg/l at rather slow speed of leaching.

From the review given above follows that the arsenical waste which is saved up in dumps of «Tuvacobalt» combine in the conditions of continuous contact and chemical interaction with environment constitutes serious ecological danger to the region. In this regard removal of arsenic from cobalt industrial products and dumps of a field is represented actual to Khovu-Aksa. Besides, difficult geographical conditions of the region, its remoteness from industrial centers, existence of problems of transport connection sets a task of the maximum use of local sources of raw materials, including also technogenic waste, for ensuring development of industrial and social spheres of the Republic.

In this regard, for complex use of dumps of «Tuvacobalt» combine as technogenic raw materials, with additional recovery from them valuable components and receiving industrial products (building materials, ceramics, etc.) it is necessary to clean arsenic from dump materials.

Large volume of works on an arsenic conclusion from technological processes of processing of the arsenic containing persistent raw materials of heavy non-ferrous metals and gold to dump low-toxic products with use of sulphatization roasting was carried out in the second half of the XX century within the MG-16/20 MFM USSR program (ChMI AS KazSSR, Karaganda [9–11]; «Gidrotsvetmet» Institute of MFM USSR, Novosibirsk [12–15]). In particular, sulphatization roasting was used (ChMI) during developing technology of receiving cobalt, gold and other accompanying metals from the gold and arsenical ores of the Sayak-4 field (Kazakhstan). The technology passed trial tests with receiving high rates [16, 17].

Making use of this positive experience, we conducted researches whenever possible of use of sulphidation roasting for an arsenic conclusion from dumps of «Tuvacobalt» combine.

Iron sulfides (pyrrhotite or pyrites) and their mixes with element sulfur are used as a sulphatizator. As a reducer a coke breeze is added to fusion mixture. The dump slimes sample used in this research on the data obtained by means of a nuclear and absorbing method contained 4.25–4.40 % of As.

According to the X-analysis data, the basis of material has a carbonate component like calcite. Besides, in sample are available: silicates and hydrosilicates, and also arsenical compounds like arsenates and arsenide.

Data of an X-ray fluorescence method give the following quantitative picture of contents of oxide forms of elements. The obtained data show the greatest content of silica (30.27 %), further on decrease there are calcium oxides (15.86 %), and magnesium (9.11 %), iron oxides (8.12 %) and aluminum (7.74 %).

The X-ray analysis (XRA) of this sample gives the following mineralogical composition of slime. In a sample two main mineral phases are fixed accurately: it is a phase of a parasymplesite — $Fe_3(AsO_4)_2 \cdot 8H_2O$ and calcite — $CaCO_3$.

Compound with structure of $Fe_3(AsO_4)_2 \cdot 8H_2O$ differs from a natural scorodite of $FeAsO_4 \cdot 2H_2O$ in that in it iron is bivalent and contains not two, but eight molecules of crystal water, as well as other arsenates of group of a vivianite [18; 624]. Data on this compound for the first time were published in 1954 (Japan). Later it was revealed in ores of the Belorechenskoe field (Russia). Having the same a chemical composition and a formula, as simplezite [18; 624], it is polymorphic analog of the last, however has distinction in a crystal lattice and a crystal system (monoclinic, unlike triclinic at a symplesite).

Further, the sample contains the following mineral phases: dolomite — (Mg, Ca)CO_3, kaolinite — $Al_4[Si_4O_{10}] \cdot 8(OH)$, smectite — $K_{<1}Al_2[(Si, Al)_4O_{10}] \cdot nH_2O$. Traces of chlorite, mica, and also potassium feldspar are found. Proceeding from data of the X-ray fluorescence analysis, it is possible to draw a conclusion that the total contents the aluminosilicate phases in material of slime can exceed the total content of the parasimplezit and calcite.

Determination of nature of behavior of sludge at its heat treatment was carried out by using of a derivatograph of system of MOM-1000 (Paulik, Paulik-Erdey, Hungary) in the atmosphere of own gas environment. The temperature limit of heating was limited 1000 ºC.

According to XFA in a product of a thermoengraving there are following mineral phases: quartz — α-SiO_2, amortized aluminosilicate, hematite (Fe_2O_3), dzhonbaumite — $Ca_5(AsO_4)_3OH$. Also a plagioclase — $[(100–n)\ NaAlSi_3O_8 + nCaAl_2Si_2O_8]$, portlandite — $Ca(OH)_2$, goethite — FeOOH, and also traces of Ca–Fe–Mg-grenade (the general formula (Ca, Fe, Mg)[SiO_4]) are found.

According to the data of chemical analysis the content of arsenic in material after heat treatment, practically, remained completely. Thus instead of the parasymplesite in a sample the new chemical compound — dzhonbaumit $Ca_5(AsO_4)_3OH$ was revealed. Data on him were published for the first time in 1980 (USA). In the subsequent it was revealed in ores of a field of Solongo (Buryatia, Russia). The chemical formula of this compound can be presented in the form $3Ca_3(AsO_4)_2 \cdot Ca(OH)_2$. From this it follows that this compound is the main calcic salt of arsenical acid where three acid parts have one base — a hydrate of calcium oxide.

On the basis of the obtained data it is possible to present as follows the thermochemical process proceeding by heating this sample of slime. In the field of temperatures to ~200 ºC there is a removal from material of the main part of crystalline hydrate water of the parasymplesite and other crystalline hydrates. At the subsequent temperature increase there is a further decomposition of mineral structures, aluminosilicates (a smectite, chlorite, mica, kaolinite, etc.) with removal of hydrate, crystallization and molecular moisture. Thus, as data of XFA of tests of a sample showed after their heating to temperatures of 300 and 600 ºC, in them, as well as in the sample plunged to high-temperature roasting (to 900 ºC), parasymplesite $Fe_3(AsO_4)_2 \cdot 8H_2O$ wasn't found. In both samples the phase of a $3Ca_3(AsO_4)_2 \cdot Ca(OH)_2$ is found accurately. From this it follows that parasymplesite already at a temperature up to 300 ºC reacts with a calcium component of the sample (likely with calcite). In the field of temperatures with ~600 and to 900–950 ºC there is a decomposition of dolomite, calcite and the hydrated aluminosilicates with formation of amorphous oxide structures.

The chemical analysis showed preservation and even some increase in a candle-end of concentration of arsenic (with 4.0–4.5 to 5.3–5.4 %) that is caused by a decrease of the total sample mass and preservation in it steady arsenic compounds. It indicates total absence in initial slime of magnesium arsenates which are formed at magnesia cleaning of arsenic of autoclave solutions as according to literary data magnesium arsenate should decompose with distillation of arsenic trioxide at a temperature of 450–600 ºC by the reactions:

$$2MgNH_4AsO_4 \cdot 6H_2O = 2NH_3 + 7H_2O + 2MgO + As_2O_3 + O_2$$

and

$$Mg_3(AsO_4)_2 \cdot 4H_2O = 3MgO + As_2O_3 + 4H_2O + O_2$$

This implies that the long-term storage in dumps magnesium arsenate react with the components of tails of autoclave leaching, forming secondary arsenide and arsenate compounds of arsenic. Last ones as a result of hyper genesis can further pass into soluble forms. Also it is possible that the insignificant part of arsenic in this material can be in an initial mineral form of arsenides and arsenates of cobalt and nickel.

Experiments on sulphidation roasting were made in a closed system in neutral and recovery environments: in a horizontal tubular furnace with a suction of gaseous products of reactions of decomposition and sulphidation. Results of primary experiences of sulphidation of initial sludge didn't yield positive results. Only some decrease in concentration of arsenic is noted (to 3.5 %) at a ratio slime/sulphatizator = 2. Apparently, stripping of arsenic in this case in the form of sulfide is obstructed by the complex composition of the sludge, and the reaction occurring during the firing with formation of a stable arsenic sulfide of cobalt blocking formation of arsenic sulfides [17]. Experiments on sulphidation of a candle end after burning of initial sludge at 900–950 ºC yielded positive results. At a ratio in candle-end batch:Sulfur:Pyrrhotite = 2:1:1.3 in a sulphidation candle-end the content of arsenic decreased to 0.28 %. Satisfactory results were received and on batches with ratios a candle-end:Sulfur = 4:1 and Candle-end:Sulfur:Pyrrhotite = 4:1:1, respectively, equal 0.46 and 0.42 % of As. At a blending only of one pyrites or pyrrhotite (in the ratio 2: 1) the residual content of arsenic in a candle-end decreases only respectively to 1.60 and 0.88 %.

Experiments on influence of temperature on sulphatization roasting of a candle-end of an initial cake showed that the lower temperature limit is defined 900 ºC. Sulphidation of a candle-end at temperatures below 900 ºC reduces rather sharply indicators on removal of arsenic from a candle-end. So, at temperatures of process of sulphidation equal 700 and 800 ºC, the content of arsenic in a candle-end decreases only to 2.30 and 2.10 % respectively. At the same time sulphatization roasting at 900 and 950 ºC reduces concentration of arsenic in a candle end to 0.53 and 0.30 % respectively.

The best results of a control series of experiments on removal of arsenic from products of preliminary roasting of initial sludge were received at the sulphatizator expense in the relation to a candle-end equal 1:2–1:1. Thus the content of arsenic in a candle-end of sulphidation decreases to 0.28–0.30 %. Also expenses of sulphidation reagents in ratios 1:4 and 1:5 at which the content of arsenic decreases to ~0, 5 %, or in the ratio 1:6 (~15 % to a candle-end) when the residual content of arsenic in a candle-end reaches 0.7–0.8 % can be technologically accepted.

Thus, the conducted researches showed the possibility of deep removal of arsenic from dump products of «Tuvacobalt» combine by means of conducting the technological process including preliminary calcination of initial sludge at a temperature ~900 ºC and the subsequent sulphatization roasting.

Element sulfur, sulfur mix with iron sulfides (pyrites and pyrrhotite) can be used as the sulphatizator.

Residual content of arsenic in material decreases to 0.28–0.30 % at the sulphatizator expense in the ratio to the candle-end 1:1–1:2; at a ratio 1:4.1:5 — to ~0,5 % and at a ratio 1:6 — to 0,8 %.

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«Тувакобальт» комбинатының аралық өнімдерінің сульфодизирлеп күйдірілуі

Мақалада «Тувакобальт» комбинаты аралық кектерді күшәладан жою мүмкіндіктері зерттеліп ұсынды. 0,5-тен 0,8 % аралыққа сай 900–950 ºC сульфидірлеу кезінде осы 1:2 0,28–0,30; 1:4, 1:5 және 1:6 қатынасына сәйкес, тереңнен күшәланы жою мүмкіндіктері көрсетілді.

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Сульфидизирующий обжиг отвальных промпродуктов комбината «Тувакобальт»

В статье представлены данные по исследованию возможности удаления мышьяка из отвальных кеков комбината «Тувакобальт». Показана возможность глубокого удаления мышьяка из данных отвалов посредством их предварительной прокалки и последующего сульфидирования при 900–950 ºC при соотношении сульфидизатора к огарку, равном 1:2 до 0,28–0,30; при соотношении 1:4, 1:5 и 1:6 соответственно до 0,5 и до 0,8 %.

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