ХИМИЯЛЫҚ ТЕХНОЛОГИЯ ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ CHEMICAL TECHNOLOGY

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Study of the influence of initial contents of arsenic of the Khovu-Aksy dumps on effectiveness of the developed regimes of their dearsenization

Dumps of arsenic-containing wastes from the former Tuvakobalt combine are one of the most dangerous objects of Tuva. The combine's wastes were accumulated in ponds (dumps) for 20 years of operation of the combine. After its closure, the ponds were drained and are now exposed to the external environment, namely, groundwater, precipitation and wind erosion. The accumulated dumps contain industrial contents of nonferrous metals and about 50 thousand tons of arsenic. Due to natural precipitation, toxic compounds are flushed to the lower layers of dump maps with subsequent ingress into groundwater and the environment. Long-term studies carried out at the Institute of Solid State Chemistry and Mechanochemistry and the Tuvinian Institute for Exploration of Natural Resources of the Siberian Branch of the Russian Academy of Science were devoted to the issue of dearsenization of arsenic dumps of Khovu-Aksy of the «Tuvakobalt» combine with the aim of processing them and obtaining the secondary raw materials for the production of materials on their basis that can be used as recyclables in the national economy such as cake — as a flux in the production of ceramic and arsenic sulphide in the production of antiseptics in the processing of wood or biocide for antifouling coatings of hulls of ships and hydrotechnical structures. Studies carried out using initial samples of dumps sludge taken from different burial sites and differing in the content of arsenic (1.88 and 4.21%) showed the possibility of effective dearsenization of slurry materials on the tested technological regimes of the process, regardless of the concentration of arsenic in them, with the formation of cake (with a content of As ≤ 0.3 %) and arsenic sulfide (IV degree of toxicity).

Keywords: sludge, cake, arsenic sulfide, soda, roasting, leaching, solution pH.

Introduction

According to the technology designed for the Khovu-Aksy deposit (the Republic of Tuva, Russia), the arsenic was withdrawn from autoclave leaching solutions by magnesian «milk» precipitation at S:L=1:4 and manganese oxide consumption ~ 13 kg/kg of arsenic [1]. The residual arsenic content in the carbonate pulp in terms of the dry mass should be no more than 2.4 % (herein and after, % wt.).

The washed sludge (tails of thickening pulp of autoclave leaching), comprising up to 93–97 % of the mass of the ore, was sent to the dump. In the tails, as a rule, 10 to 25 % of cobalt was remained from the content in the ore (~ 0.1 % of the sludge mass) in the initial arsenide form [2]. The arsenic-magnesian precipitate of the solution dearsenization was sent to the dump along with the autoclave leaching sludges.

Over 20 years of operation of the combine, more than 2 million m³ of wastes were stored in the Khovu-Aksy dumps [3] with a content of As in the range of 3.5–6.4 % and metals on average, %: Co — 0.18; Ni — 0.22; Cu — 0.11 as well as Ag — 45 g/t and Au is 60 mg/t. As field investigations of the dumps have shown [4] pore waters that area complex magnesia-calcium ammonia-hydrocarbonate type of solutions are formed

as a result of waste storage. A high content of arsenic was found there (2.2 mg/L). Also, high levels of arsenic are found in water extracts (5.5 mg/L). This indicates the presence of soluble forms of arsenic in the dumps. There was also an increase in arsenic content in the drying slag of dumps (Map No. 5) to 29.5 mg/L, which corresponds to 50 MPC for this type of storage [3].

Thus, there is an intensive leaching of arsenic of various types by solutions formed or coming from outside, and its subsequent migration with drainage waters into the environment. Consequently, the arsenic-containing waste of the combine in conditions of constant contact with the environment represents a serious environmental hazard for the region. In addition, the dump wastes of Khovu-Aksy contains high iron contents (up to ~ 10 %) and alkaline earth oxides (CaO, MgO, total 25–30 %) and moderate concentrations of refractory oxides (SiO₂ and Al₂O₃), which determines their low refractory temperature ~ 1180 °C) and fusibility. Therefore, the removal of arsenic, its neutralization and the possible integrated use of dumps as technogenic raw materials with extraction of metals from them, obtaining marketable products (building materials, ceramics, etc.) is an actual problem.

Fundamental work on the removal of arsenic from technological processes was carried out in the second half of the 20th century within the framework of the All-Union Program MP-16/20 (CMC USSR) [5], in particular, on the removal of arsenic from concentrates of heavy non-ferrous metals in the head of the process by sulphidizing firing and transfer it into a slightly soluble (4 hazard category) sulphide form [6, 7 etc.].

Using this positive experience, later studies were carried out on the application of this technology to neutralize the Khovu-Aksy dumps. The possibility of deep removal of arsenic from the materials of the dumps was shown. The content of arsenic in the initial material (on average ~ 5 %) was decreased to 0.80–0.28 %, respectively, at a ratio of the sulphidizer to the product from 1:6 to 1:2 at a roasting temperature of 900–950 °C [8]. At the same time, the simultaneous burning of the sludge without a sulphidizer showed the absence of magnesium arsenates (initially the main dump form of arsenic according to the technology of dearsenization of autoclave solutions [1]), which should decompose with distillation of arsenic trioxide at 450–600 °C according to the reactions [9]:

$$2MgNH_4AsO_46H_2O = 2NH_3 + 7H_2O + 2MgO + As_2O_3$$

 $Mg_3(AsO_4)_24H_2O = 3MgO + As_2O_3 + 4H_2O + O_2$

Since this is not observed in our case, this is explained by the fact that in the dumps during storage magnesian arsenates decompose as a result of hypergenes with the formation of secondary arsenic compounds such as vivianite forms of arsenates.

In the technological aspect, the sulphitizing roasting process must be carried out in the kinetic conditions of the countercurrent solid-gas. For this purpose, a shaft type furnace can serve as an optimal unit, and appropriate equipment is required for condensation and trapping of arsenic sulphide fumes and utilization of sulfurous anhydride [6]. All this requires certain initial financial investments. Therefore, despite the high performance, its practical use is currently quite problematic.

In the metallurgy of lead, as early as the beginning of the 20th century, a method was developed for the processing of spikes, including burning-sintering at a temperature of red heat of a mixture of spice with soda and subsequent aqueous leaching of the formed sinder [10, 11]. In the experiments carried out on this method, the Khovu-Aksy dumps of the Tuvakobalt combine obtained leaching cakes of a soda-slime cake with a content of 0.47 to 0.71 % of arsenic in them. More than 90 % of the arsenic contained in the sludge of the heap is concentrated in the leach solution [12].

As the practice of research has shown, the phase and chemical compositions of the dumping products of metallurgical industries, in particular the Khovu-Aksy dumps are determined by the initial composition of the raw materials, the processing technology, and also depend on the time and storage conditions. While storing wastes in dumps, their chemical and mineral compositions can be sharply different both in the area of the dump and its vertical section, as well as from the trench to the trench, from the map to the map. So, for example, (according to the data of 2006 [13]), in the volume of the last map No. 5 of the Khovu-Aksy dumps, iron and arsenic are distributed in the following order. In terms of the surface layer, the iron content is fixed by a 2-fold concentration spread (the average content is 4.4 %, the maximum is 6.2 %, the minimum is 3.1 %), and the arsenic content is 16-fold (with an average content of 2.1 %, the maximum is 4.8 % and the minimum is 0.3 %).

The average borehole test at a depth of ≥ 1 m contains 5.1 % of iron — and 2.5 % of arsenic. Despite the short shelf life, leaching and washing out of elements in the lower layers of the map, their vertical migration and possible interaction, in particular arsenic with natural and technological solutions, have already been

noted. According to the results of the study, it is concluded in [4] that the bulk of the elements (metals) of the upper horizons is assimilated by pore solutions and, as they are deposited in the maps, are gradually washed out into the lower layers by natural precipitation, where they concentrate on the active surfaces of the formed mineral rocks as a result of sorption. In this regard, it seems interesting to consider the influence of the formed composition of the sludge material on the process of its processing, with the transfer of arsenic to the sulphide according to the technology being developed.

At the same time, all work on the development of arsenic removal technology from the Khovu-Aksy dumps and optimization of optimal process regimes was carried out on samples with high arsenic concentrations (within $\sim 3-4.5$ %) [14, 15]. No experiments were performed on the material with low concentrations of arsenic (within $\sim 1-2$ % of As). In this connection, it is of interest to check the effectiveness of previously worked out technology regimes on the material of the dump with a low initial arsenic content.

Experimental

The study was carried out on samples of sludge from the dump of map No. 5, selected (06.2012) from different horizons and differing in their arsenic content: 1.88 % is an average sample taken from a depth of ~0.1–0.15 m from the upper horizon, and 4.21 % is the average sample from the lower horizons of the dump (>1.0 m). Firing sludge mixtures with soda and adding coal was carried out at the ratio sludge: soda: coal = 1:1:0.1. Further, aqueous leaching, cake separation, arsenic precipitation from the solution with sodium sulphide was carried out. Experiments to check the effect of the initial slurry composition on the arsenic content on the final indicators of the technology were carried out on the following regimes obtained earlier as a result of joint research by the Institute of Solid State Chemistry and Mechanochemistry and the Tuvinian Institute for Exploration of Natural Resources of the Siberian Branch of the Russian Academy of Science [14, 15]:

- roasting procedure with the ratio of components in the initial charge, sludge:soda:coal = 1:1:0.1, in the temperature range 650–850 °C and holding time 1.0 h;
- the operation of aqueous leaching at S:L = (1:6)–(1:10); temperature 70–80 °C and time 1–1.5 hours, followed by separation by filtration of cake and arsenic-containing aqueous solution and aqueous washing of cake at a temperature of 40–50 °C;
- sulphidation operation by introducing into an aqueous arsenic-containing sodium sulphide solution heated to \sim 50 °C, calculated from 1.7 to 2.0, stoichiometrically necessary to bind arsenic to As₂S₃ sulphide;
- removal of the silicic acid formed in the process by introducing an acid (HCl) into the solution until the pH of the solution decreases from 11–12 to 8–9;
- precipitation of arsenic sulphide from the solution by further lowering the pH to a value of 2–3, its removal by filtration from the solution into a separate solid, environmentally less hazardous product.

There are a series of experiments using an average sample of sludge from the lower horizons of the dump. The initial sample of the sludge contained 4.21 % As. The cinder (soda flake) obtained after heat treatment of the charge in the prescribed regimes practically completely retains arsenic in the range of 2.27–2.38 % (on average 2.31 %) according to the chemical analysis.

The resulting firing products were leached with distilled water at stirring. After the operation, the pulp was filtered; the cake was washed with hot water and dried. The minimum arsenic content in the cake was obtained at a firing temperature of 720 °C. The chemical analysis gives the following average content of elements in the cake: 0.34% — As; 6.04% — Fe; 16.20% — Ca; 0.075% — Co; 0.069% — Ni; 3.73% — Al. The resulting arsenate solution is alkaline with a pH of \sim 12 and a content of As \sim 4 g/L.

Since it was found that during the operation of sulphidation of the resulting arsenate solution together with arsenic sulphide precipitation of a silicon dioxide impurity takes place, therefore, prior to sulphiding, it was necessary to remove the siliceous constituents from the solution. To this end, the solution, heated to ~ 60 °C, was acidified (with a concentrated solution of hydrochloric acid) to pH 8–9. Upon subsequent cooling to room temperature, formation and subsequent structuring of the silicic acid precipitate occurred. The precipitate was separated and calcined at ~ 800 °C. The sample of the obtained silica precipitate contained: $O_2 - 55.2$ %; Si - 35.12 %. A certain amount of impurity of sodium and chlorine was also found in the resulting solid product. The silicon dioxide content in it is about 85 %.

From the filtrate, after the removal of silicon dioxide, arsenic is precipitated by introducing into the solution at 100 % excess of sodium sulfite and acidifying the solution to pH = 2–3, by adding the necessary amount of hydrochloric acid. The degree of separation of arsenic in the form of sulphide precipitate from the

solution was 99.5 %, with the content of arsenic being up to 40 % arsenic and up to 60 % sulphur. According to elemental chemical analysis, the sulphide precipitate, in addition to arsenic sulphide, contains about 10 % of elemental sulphur.

There are experiments using an average sample of the upper horizon sludge. The initial sample of the sludge contained 1.88 % — As; 0.057 % — Co and Ni; 0.048 % — Cu; 5.0 % — Fe; 3.98 % — Al; 4.78 % — Mg; 14.0 % — Ca; 18.0 % — Si. Analysis shows the presence of quartz, calcite, a number of silicate, aluminosilicate mineral constituents in the material, as well as the vivian form of arsenates.

After calcination-sintering of the prepared charge (sludge:soda:coal = 1:1:0.1), products were obtained whose average elemental composition is as follows 1.13 % — As; 5.0 % — Ca; 2.01 % — Mg; 6.88 % — Si; 2.13 % — Fe; 1.41 % — Al; 21.09 % — Na; 14.31 % — C. According to the X-ray analysis phases of quartz, silicates and aluminosilicates, vivianite forms of arsenate have been preserved in the material. There is no calcite.

The cake of the aqueous leaching of the soda ash contains: 0.27 % — As; 16.20 % — Ca; 6.04 % — Fe; 3.73 % — Al; 0.075 % — Co; 0.069 % — Ni; 0.074 % — Cu; 16.22 % — Si; 7.24 % — Na; 5.48 % — Mg; 0.08 % — C. According to the analysis, the material is mainly represented by quartz, silicate and aluminosilicate mineral constituents. The phases of arsenides and arsenates in the cake material are absent.

After the extraction of the cake from the arsenate solution, then, at a temperature of ~ 60 °C, the removal of silicon by a solution of hydrochloric acid (an aqueous solution in a ratio of 1:1) was carried out with a decrease in the pH of the solution to 9–8. The silica residue obtained after cooling and daily settling was calcined at 800 °C. The resulting sample of the silica precipitate contains up to 37 % of Si. The sample also contains impurities of sodium and chlorine. The content of silicon dioxide is of the order of ~ 83 %.

For deposition of arsenic sulphide from the solution, its pH was further reduced to 3–2 at a solution temperature of 60 °C, followed by exposure (during the day at room temperature). The product obtained contained 45.7 % of As, which approximates As to the composition of arsenic pentasulphide.

Results and discussion

Thus, in order to determine the effect of arsenic content in the initial sample of the sludge on extracting it into a separate, slightly toxic product, experiments on sludge dearsenization were carried out on a number of initial samples of sludge (map 5), taken from the surface and lower horizons of the dump, which differed sharply in content of arsenic in them (1.88 and 4.21 %, respectively).

In work previously elaborated the following optimal modes of technology were used:

- composition of the charge and the ratio of components in it: sludge:soda:coal = 1:1:0.1;
- aqueous leaching at S:L = (1:6)–(1:10), temperature 70–80 °C, time 1.5 h and the subsequent filtration with allocation of a cake from a solution;
- precipitation of silica from the solution by lowering the pH of the solution to 9–8 and subsequent removal of the silica precipitate by filtration;
- sulphidization of the solution with sodium sulphide with 100 % excess of reagent;
- precipitation of arsenic sulphide with a decrease in the pH of the solution to 3–2 and its subsequent isolation from the solution by filtration.

As a result, it was shown that this technology provides the maximum withdrawal of arsenic into a separate low-toxic product, with its any content in the original sludge. When calcining the charge (in the composition of sludge:soda:coal = 1:1:0.1) and subsequent aqueous leaching of the resulting cinder, the residual arsenic concentration in the formed cake is in the range from 0.23 to 0.34 %. The extraction of arsenic from the slurry into the solution is of the order of 90–95 %. With further acidification of the leach solution to pH = 8–9, precipitation of a white precipitate occurs. After its calcination at 800 °C, it contains up to 85 % of SiO₂ according to the chemical analysis. Subsequent decrease in the pH of the solution to 2–3 leads to a complete (by 98–99 %) precipitation of arsenic in the form of sulfide from a solution. According to the chemical analysis a certain amount of sulphuris present in the sediment, which is close to its content in the product corresponding to the composition of pentlandite (As₂S₅).

Conclusions

The studies carried out using initial samples of slurry of the Khovu-Aksy dumps of the Tuvakobalt combine selected from different burial sites and differing in their arsenic content (1.88 and 4.21%) have shown the possibility of effective dearsenization of the slurry materials of the given dumpson the tested process regimes, regardless of the concentration of arsenic in them, with the formation of practically low-toxic

cake (with a content of $As \le 0.3$ %) and arsenic sulphide (hazard of IV category). The obtained materials can be used as recyclables in the national economy: cake as a smelter in the production of ceramic products, and arsenic sulphide in the production of antiseptics for woodworking or biocide of anti-fouling coatings for hulls of ships and hydraulic structures.

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Хову-Аксы үйінділеріндегі күшәләнің бастапқы құрамдарын оларды деарсенизациялаудың өңделген тәртібінің тиімділігіне әсерін зерттеу

Туваның ең қауіпті нысандарының бірі болып бұрынғы «Тувакобальт» комбинатының күшөләқұрамды қалдықтарының үйінділері табылды. Комбинат қалдықтары комбинаттың 20 жыл жұмысы барысында қалдықтарды көму тоғанды үйінділерінде жинақталды. Комбинат жабылған соң тоғаншалар кептіріліп, осы уақытқа дейін сыртқы ортаның әсері: ағын сулар, атмосфералық жауыншашын, жел эрозиясы жатады. Жинақталған үйінділерде түсті металдардың өнеркәсіптік құрамдары және күшәләнің 50 мың тоннаға жуық мөлшері бар. Табиғи жауын-шашындардың салдарынан улы қосылыстар төменгі қабаттарға шайылады, соңынан ағын суларға және қоршаған ортаға түседі. РҒА СБ ХТТМИ және ТувКОПРИ жүргізілген көпжылдық зерттеулер «Тувакобальт» комбинатының Хову-Аксы күшөләқұрамды үйінділерін деарсенизациялау, олардың өңделу және солардың негізінде халық шаруашылығында екіншілік шикізат ретінде қолданылуы мүмкін, материалдарды өңдеуге қажет екіншілік заттарды: кекті-керамикалық өнімдерді алуда немесе жол салу саласында қолданылатын плавеньдер ретінде, ал күшәлә сульфиді-теңіз жайықтарының өсетін жабындарын немесе гидротехникалық құрылғылар үшін, ағаштарды немесе биоцидті өңдеуге қажет антисептиктер өндірісінде қолданылатын заттарды алу мәселесіне арналған. Үйінділер шламдарының, көмүдің әртүрлі деңгейлерінен алынған және олардың құрамындағы күшәләнің құрамы бойынша ажыратылатын (1,88 және 4,21 %), сынамаларын қолданып жүргізілген зерттеулер әртүрлі технологиялық режимдерде зерттеліп, нәтижесінде құрамындағы күшеләнің мөлшеріне қарамастан, шлам

материалдарын тиімді деарсенизациялау мүмкіндігі бар екенін және құрамында (As≤ 0,3 % және улылығы IV күшәлә сульфиді бар) кек түзілетінін көрсетті.

Кілт сөздер: шламдар, кек, күшәлә сульфиді, сода, күйдіру, сілтісіздендіру, ерітіндінің рН, өнер-кәсіптік құрамы.

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Изучение влияния исходных содержаний мышьяка отвалов Хову-Аксы на эффективность разработанных режимов их деарсенизации

Одним из наиболее опасных объектов Тувы являются отвалы мышьяксодержащих отходов бывшего комбината «Тувакобальт». Отходы комбината накапливались в прудковых захоронениях (отвалах) в течение 20 лет работы комбината. После его закрытия прудки были осущены и в настоящее время подвергаются воздействию внешней среды: грунтовых вод, атмосферных осадков и ветровой эрозии. В накопленных отвалах содержатся промышленные содержания цветных металлов и порядка 50 тыс. т мышьяка. За счёт естественных осадков происходит смывание токсичных соединений в нижние слои карт отвала с последующим попаданием в грунтовые воды и окружающую среду. Многолетние исследования, проводимые в ИХТТМ и ТувИКОПР СО РАН, были посвящены вопросу деарсенизации мышьяксодержащих отвалов Хову-Аксы комбината «Тувакобальт» с целью их переработки и получения на их основе вторичного сырья для производства материалов, которые могут быть использованы в качестве вторсырья в народном хозяйстве: кека — в качестве плавня при производстве керамической продукции или дорожного строительства, а сульфида мышьяка — в производстве антисептиков при обработке древесины или биоцида для противообрастающих покрытий корпусов морских судов и гидротехнических сооружений. Проведенные исследования с использованием исходных проб шлама отвала, отобранных из различных уровней захоронения и отличающихся по содержанию в них мышьяка (1,88 и 4,21%), на отработанных технологических режимах процесса показали возможность эффективной деарсенизации шламовых материалов, вне зависимости от величины концентрации в них мышьяка, с образованием кека (с содержанием ≤ 0,3 % As) и сульфида мышьяка (IV степени токсич-

Ключевые слова: шламы, кек, сульфид мышьяка, сода, обжиг, выщелачивание, рН раствора, промышленное содержание.

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