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Output of arsenic from dumps of plant «Tuvakobalt» by combined method

The presented materials of research show the possibility of the output of arsenic from dump sludge cake of plant «Tuvakobalt» through their burning at 800–850 ºC in a mixture of with soda and subsequent aqueous leaching into the solution forming of sodium arsenate. Arsenic from the solution can be transferred to the arsenic sulphide by known techniques (by means of sodium sulphide, hydrogen sulphide, etc.). Thus the obtained products can be used in practice for as antiseptics in agriculture, in the processing timber; as a biocide in anti-fouling coatings for the navy, hydraulic structures and other constructions operated in the bioaggressive environments.

Key words: waste dump, slurry, soda, burning, aqueous leaching, arsenic, arsenic compounds, sodium sulphide, hydrochloric acid, sulphidation.

Plant «Tuvakobalt» on the ores Khovu-Aqsa was operated 20 years and was closed in 1991 due to the a planned unprofitability of production. Huge amounts of gangue containing oxidized sulphides and arsenides were accumulated, and more than 2 million m^3 of tailings mixture of ammonium autoclave redistribution and sludge cakes of magnesia cleaning of the solution were stored on site of five pool maps and trench burial for years of work on drainage dumps [1].

According to the results of audit examinations conducted by UIGGM SB of RAS (Novosibirsk) and TuvaIENR SB of RAS (Kyzyl) [2] dumping products have predominantly carbonate-silicate composition with a mass content (in terms of oxides), %: SiO_2 ~ 35–40; CaO ~ 18; Al_2O_3 ~ 8; MgO ~ 8; Fe_2O_3 ~ 10. Arsenic concentration is in the range of 3.5–6.4 %, partial (10–20 %) in the form of metal arsenides not decomposed during pressure leaching. Concentrations of metals were increased: Co — 0.14–0.21 %; Ni — 0.15–0.29 %; Cu — average 0.11 % and Ag — average 45 ppmw, Au — average 6 ppmw.

Waste from the processing of ore, accumulated in the five-maps storage and in the trench, located in the 0.8–1.2 km from the industrial area of the plant and 3 km from the village Khovu-Aqsa. The plan of maps represents rectangle of 250×50 m by diked dykes. Initially the waste entered to dumps by special transport, then subsequently (and in generally) as a pulp through tubing in the pool-settlings. After clarification of the liquid fraction of the pulp and compaction of solid sediment in the maps of disposal of waste (sludge) periodic pumping of clarified water are carried out into the hydrometallurgical plant. After that the remained solution dried under the influence of external factors. Maps of Khovu-Aqsa can be attributed to the drained and partially recultivated tailing dumps on the morphological type.

The formation of underground waters, which belong to the calcium-magnesian nitrate hydrocarbonate type with high concentration of NH_4^+, occurs in the dumps upon prolonged storage of waste. They contain a high concentration of arsenic (2.2 mg/l). High content of arsenic (5.5 mg/l) were also found in the aqueous extract. Increased content of arsenic in the aqueous extract indicates the presence of aqueous-soluble forms of arsenic in dumps of plant as compared to the underground waters. It was noted in the work [1] that the concentration of arsenic reached 29.5 mg/l in dried out aqueous part of one of the maps of the dump, which corresponds to 50 TLV for this type of stored waste dumps.

As a result of detailed comprehensive studies carried out by UIGGM SB of RAS [2], geochemical mobility of arsenic and the unsuitability of magnesia-arsenate salts for a long storage were established under conditions of waste storage in the dumps of Khovu-Aqsa. High concentrations of arsenic and magnesium (up to 150 mg/l) in solution confirmed this fact. The underground water and the aqueous extracts are found to not be saturated in regards to all arsenic compounds that cause the complete solubility of the last ones in these aqueous systems [3]. Interaction with water containing atmospheric CO_2 and bicarbonate-ion, which is formed by dissolution of calcite, inevitably initiates reactions of dissolution of technogenic arsenates with the transition of $HAsO_4^{2-}$ and Mg^{2+} into the solution. Compounds of $Mg(OH)_{2(s)}$ and $Ca_3(AsO_4)\cdot 4H_2O$ also decompose under the influence of carbon dioxide at high pH value and arsenic also goes into the solution.

After stopping of plant, ponds of tailing pits were completely drained and exposed by wind erosion at a given time. According to [4, 5] formed «dry» dumps contain arsenic compounds of between 57 to

75 thousand tonnes of except to their the presence of commercially concentrations of cobalt, nickel, copper and some other metals. Due to the natural rain flushing of toxic compounds occurs in the lower layers of dump. Perhaps they also got into the groundwater during the aging and the restructuring of the material of the protective membrane of the bottom deck was occurred. The main centre of contamination is found to cover an area of 2 km^2, where the content of arsenic in the soil lies between 23 to 40 TLV. The arsenic content reduced from 12 to 2.7 TLV in the soils of areas far from the plant to 5–30 km [6].

Except on environmental problems of disposal of arsenic-containing dumps of Khovu-Aqsa, practical interest for the Republic of Tuva, in view of its specific mining and geographical position, represents the using of dump materials as technogenic raw materials for the production of national economic destinations. For using these dumps as a secondary technogenic raw materials with additional recovery of valuable components (metals) and obtaining industrial commodity products (building materials, ceramics) the output of arsenic need to carry out from dump material. A study on the possibility of deep cleaning of arsenic from dump materials with transfer it into nontoxic (commodity) products was carried out.

At the first stage the study of the release of arsenic from the dump waste Khovu-Aqsa were held by technology sulphide burning.

Experiments on sulphidation burning with preliminary calcination showed the possibility of deep removal of arsenic from dump waste of Tuvakovalt plant (a decrease of the content in a cinder to 0.28–0,80 % with a ratio of sulfidizator to a calcination product from 1:2 to 1:6).

This method of outputting arsenic from industrial products of metallurgical production allows to deduce the arsenic stored in a compact form of sulphide and promising to use it as a biocide in anti-fouling coatings for ships.

In terms of technology the process based on solid-phase reactions of decomposition and interaction, must be carried out at closely interacting of components and ensuring of good diffusion of gaseous reaction products produced in the conditions of countercurrent gas – solid, for which the most preferred one may be special oven of shaft type. Appropriate special equipment is required for condensation and trapping of arsenic sulphide fumes and capturing and utilization of the sulfur dioxide formed. All this requires certain financial investment to start implementation of this technology that under the conditions of modern market relations creates certain difficulties of introducing new technologies [5, 7].

However in the literature analysis of the results of several studies on processing of products of arsenic of copper-cobalt-nickel metal production, in particular, speiss leads to the conclusion about the small prospects of existing search directions [8]. However in the practice of lead production the number of methods for processing speiss of lead production was successfully tested [9]. The method of combined processing of speiss of lead production which includes burning-sintering of speiss mixture with soda at red heat and subsequent aqueous leaching of obtained cinder should be regarded as the most appropriate one. This method was used in industrial practice abroad [10]. This technology was tested by domestic researchers too [11, 12], positive results being obtained.

So the technology including its burning in the mixture with soda and the subsequent aqueous leaching of the formed cinder-cake was developed for processing of speiss of Leninogorsk lead plant (East Kazakhstan) [11]. Arsenic is recovered as the sodium arsenate into the solution. Experiments were performed on samples of speiss obtained by melting of copper drosses in a shaft furnace of slurries. The following elements are included in the composition,%: 9.6 of lead; 26.1 of copper; 24.8 of iron; 25.6 of arsenic; 1.0 of antimony; 3.0 of sulfur; 0.97 of nickel; 0.2; of cobalt; 1.45 of zinc; 0.4 of tin and 120 ppmw gold and 119 ppmw of silver. According to the mineralogical analysis of average sample consisted mainly of copper arsenide (Cu_3As), iron arsenide (Fe_2As), metallic lead and small quantities of copper and iron sulphides. The obtained cinder-cakes were leached by aqueous at 60–70 ºC, at L:S = 5:1 within an hour. Optimal conditions of burning is the temperature of 650 ºC and time 4 hours. Consumption of soda was equal to the mass of speiss. At aqueous leaching of cinder-cake extracting of arsenic in the solution was 97–98 %. Arsenic was precipitated with calcium oxide to conditioned calcium arsenate from solution. Solution from leaching contained 27.6 % copper, 8.0 % lead, 0.7 % of arsenic, 26.3 % iron; 10.5 % nickel. It was exposed to further sulfuric processing for the purpose of extraction of lead into the sludge cake and its transfer to lead production, and solution to extraction of copper and nickel. Thus the proposed technology provides a complex removal of the main components of speiss into marketable product at the soda recovery in the form of sodium hydroxide with the following consumption of reagents per 1 ton of speiss: 1 ton of soda; 0.45 tons of calcium oxide; 0.06 tons of concentrated sulfuric acid (specific weight 1.84).

In order to study the influence on indicators of the process of technological modes, consumption of reagents and determination of their optimal parameters, the study on processing speiss of lead production were repeated in the work [12]. Thus the optimum schedule of burning provided by the following parameters: temperature 650 °C, duration of 4 hours, the consumption of soda 1 weight part per 1 weight part of the speiss, which enables the extraction of arsenic arsenate to 97–98 % of its content in the cinder. Lead remains the whole, 93 % of copper remains in oxide form in the cinder. During of arsenic leaching the solution with 23–26 g/l of arsenic and traces of iron and copper was obtained that provides high-quality obtaining of calcium arsenate. Consumption of 1.9 g of calcium oxide per 1 g of arsenic was determined optimal for precipitation of arsenic from the solution.

Our laboratory experiments by using this combined method (burning-sintering + aqueous leaching) on samples of technical cobalt concentrate containing 2,4–4,0 % of As, prepared by the ammonia-alkali autoclave technology at the plant of «Tuvakobalt» showed the possibility of deep removal of arsenic from the product at temperatures 600–650 °C of burning. After the leaching and washing, sludge cake contained <0.5 % of As and increased metal concentrations, %: Co ~ 9,0; Ni ~ 39,0; Cu ~ 16,5 [13].

In the development of this direction rather large research program on the possibility of using this method for the development of output technologies of arsenic from dump waste of the plant «Tuvakobalt» was carried out including a large numbers of laboratory experiments, big testing for the combined method and experiments on the transfer of arsenic from the resulting solution in a compact sulphide product.

Laboratory experiments was carried out on an average sample of waste dump of Khovu-Aqsa containing 4,33 % As by the combined scheme.

According to IR analysis the sample contains mostly carbonate component, such as calcite. Also the presence of sulphates, such as $MeO \cdot SiO_2 \cdot H_2O$ and arsenates is noticed.

According to X-ray diffraction (XRD), the original waste dump has the following mineral composition. Two main phases are recorded clearly in the sample. This is phase of parasymplesite $Fe_3(AsO_4)_2 \cdot 8H_2O$ and phase of calcite $CaCO_3$ (with the advantage of the last one). The phase of composition of pasymplesite differs from natural scorodite $FeAsO_4 \cdot 2H_2O$ in that iron is divalent and contains not two, but eight molecules of crystallohydrated water as well as other arsenates of group of a vivianit in it [14]. Having the same chemical composition and the formula as symplesite this arsenate of iron is polymorphic analogue of the latter, but unlike it has others a crystal lattice and a singoniya (monocline, but not triclinic, as at a simplezit). Further, in the sample the following phases there were found: dolomite — $(Mg, Ca)CO_3$, kaolinite — $Al_4[Si_4O_{10}] \cdot 8(OH)$, smectite — $K_{<1}Al_2[(Si, Al)_4O_{10}] \cdot nH_2O$. There are traces of chlorite, mica, potassium feldspar. The total content in the sample of aluminosilicate phases prevails over the amount of arsenate and carbonate phases.

The results of the carried out thermal analysis (Differential Thermal Analysis) of the sample in the temperature range up to 1000 °C are in agreement with previous studies and confirm occurring decomposition of carbonates during heating and stability of arsenic compounds. Thus according to the chemical analysis of iron content in the cinder is 4.5 % that exceeds slightly the initial ones.

Experiments on alkali sintering were carried out in the range of temperature of 600–900 °C, holding time from 1,5 to 4,0 hours at the temperature given and a ratio variation in charge of initial slurry of dump to soda ranging from 4/1 to 1/1. In a number of experiences of an additives of coal dust or a coke breeze at a rate of 0,1–0,2 introduced into the common weight portion of charge.

The leaching of cinder was carried out by water at 60–80 °C, the leaching time is from 0.5 to 2 hours, the ratio of S:L is maintained between 1:5–1:7.

The obtained data of laboratory experiments showed that the main factors determining the transition of arsenic slimes into a soluble form of sodium arsenate are the temperature and the ratio in the mixture of sludge and soda. As the results of experiments the holding time during the burning is not determinative. So, under a temperature of burning of blend of 600–650 °C and changing of the ratio of the sludge/soda is equal to 4/1, 2/1 and 1/1, the arsenic content in the sludge cake of aqueous leaching of cinder was equal to 3.75; 2.10; 1.35 %, respectively. When the temperature rises to 800 and 900 °C arsenic content in the sludge cake of leaching decreases to 0.95–0.80 %. At introduction of coal additive (~10 % of the mass of the slurry) in the initial coal charge and with ratio of mixture components of 1/1–1.5/1, at temperature of burning 850 °C the content of arsenic in the sludge cake of aqueous leaching is reduced to 0.50–0.71 %.

According to X-ray diffraction (XRD) in the obtained sample of sludge cake dominant phases are silicate, which chemical formula is $Na_4Mg_2Si_3O_{10}$ (or $2Na_2O \cdot 2MgO \cdot 3SiO_2$), magnesian calcite — $(Mg, Ca)CO_3$, magnetite — Fe_3O_4 with a mixture of hematite — α-Fe_2O_3.

After leaching the following oxides were identified as part of an average sample by quantitative X-ray fluorescent analysis, %: SiO_2 — 27.88; Al_2O_3 — 7.04; Fe_2O_3 — 7.68; MgO — 7.99; CaO — 14.75; Na_2O — 18.91; K_2O — 0.41; NiO — 0.163; CuO — 0.160; amorphous phase — 12.91.

Based on the successful results of laboratory experiments on scientific and industrial base of TuvaIENR SB of RAS, experimental tests in the bigger scale of technological scheme of the extraction of arsenic from waste dumps of plant «Tuvakobalt» were carried out to produce of arsenic sulphide.

Burning-sintering was performed under the following conditions such as the ratio in the mixture: waste:soda:coal = 1:1:0.1; temperature 850 ºC; burning time of 3 h. At burning of arsenic compounds interact with soda, while arsenic in aqueous-soluble form — arsenate persists in alkali slurry. A cinder obtained by burning-sintering contained an average of ~ 3 % As. In addition it was determined by X-ray flurorescence that the mineralogical composition of the resulting product also contains orthoclase (23.27 %), silicon carbide (26.32 %), magnesite (3.38 %), goethite (3.32 %), dolomite (3.26 %).

The process of aqueous leaching of burning product was carried out on a pilot plant for the hydrochemical processing of mineral and technogenic raw materials. 80 l of water was poured into a stirred reactor and heated up to 80 ºC, then 20 kg of burning product was loaded (ratio S:L = 1:4). The leaching was carried out under constant stirring during 0.5 h. After completion of leaching pulp is filtered on a nutsch filter under vacuum. The filtered arsenate-carbonate solution is directed from the receiver to the storage tank.

The precipitate on the filter is subjected to 2-times washing out by hot water. The washings from the receiver is pumped into the reactor for leaching of next portion of product. According to Analytical Department of UIGGM SB of the RAS (atomic adsorption methods) as a result of 13 kg of dried product was obtained from the aqueous leaching containing arsenic of 0.47 %. Extraction of the arsenic in the solution was 90 %.

In subsequent carried out experiments, arsenic obtained from the arsenate-carbonate solution was precipitated by sodium sulphide under acidic conditions in the form of sulphide on the hydrochemical apparatus for processing of minerals. 30 % of solution of HCl was used as an acid reagent. The precipitation of arsenic sulphide was carried out at pH = 3 by using a solution of 12 % Na_2S. The optimal conditions of precipitation of sulphide were identified such as the solution temperature 50 ºC, an excess of sodium sulphide 70 % from the stoichiometrically required amount, precipitation time of 0.5 hour. As a result the degree of precipitation of arsenic sulphide was 99.6 %. The arsenic content in the filtrate was 0.02g/l. The obtained precipitate of arsenic sulphide was washed out by hot water, was subjected to drying and was stored.

Thus investigations showed that this combined technology allows to deduce arsenic of dump waste of plant «Tuvakobalt» in a stable stored form of sulphide. Moreover the obtained products can be used in the following directions:

– as sodium arsenate solution obtained in the leaching as a main component in the manufacture of an antiseptic for wood processing and agriculture;

– the sulphide of an arsenic obtained by sulphidation of leaching solution of alkali caking coal is nontoxical (Group IV toxicity), stored middlings. In the future it can be used as a biocide of anti-fouling and anti-corrosion coatings for ships, hydraulic structures as well as pipelines and other construction operated in the bioaggressive environments.

References

1 *Забелин В.И., Заика В.В., Лебедев В.И.* Экология и здоровье. — Кызыл: Тув. кн. изд-во, 1995. — 45 с.

2 *Гаськова О.Л., Бортникова Е.П., Бортникова С.Б., Андросова Н.В.* // Химия в интересах устойчивого развития. — 2000. — Т. 8, Вып. 3. — С. 373–380.

3 *Бортникова С.Б., Гаськова О.Л., Бессонова Е.П.* Геохимия техногенных систем. — Новосибирск: Гео, 2006. — 169 с.

4 *Ондар С.О., Путинцев Н.И., Крыцин А.Н.* О состоянии окружающей среды Республики Тува. — Кызыл: ЦКЛ ТувИКОПР СО РАН, 2000. — 101 с.

5 *Копылов Н.И.* Проблемы мышьяксодержащих отвалов / Под ред. акад. Г.А.Толстикова. — Новосибирск: Гео, 2012. — 182 с.

6 *Ондар У.В.* Разработка методического описания на базе рентгено-флюоресцентного анализа для контроля загрязнения мышьяком объектов окружающей среды: Автореф. дис. … канд. хим. наук. — Иркутск: ИркГУ, 2001. — 20 с.

7 *Исабаев С.М., Ковальчук В.А., Мильке Э.Г., Клименко В.А.* Об извлечении золота из упорных мышьяковистых концентратов // Цветные металлы. — 1983. — № 2. — С. 30, 31.

8 *Резник И.Д., Соболь С.И., Худяков В.М.* Кобальт. — Т. 2. — М.: Машиностроение, 1995. — 470 с.

9 *Пономарёва Е.И., Соловьёва В.Д., Боброва В.В. и др.* Мышьяк в свинцово-цинковой промышленности / Отв. ред. чл.-корр. АН КазССР Е.И.Пономарёва. — Алма-Ата: Наука, 1975. — 101 с.

10 *Гофман Г.О.* Металлургия свинца / Пер. с нем. и доп.; под общ. ред. акад. Г.Г.Уразова. — М.-Л.: Цветметиздат, 1932. — 687 с.

11 *Андреев В.М., Донченко П.А., Салин А.С.* Переработка свинцовой шпейзы // Цветная металлургия: Бюлл. ЦНИИЭИ-Цветмет. — 1956. — № 1. — С. 12–15.

12 *Садилова Л.Г., Лоскутов Ф.М.* Переработка шпейзы свинцового производства // Изв. высших учебных заведений. Цветная металлургия. — 1958. — № 5. — С. 38–49.

13 *Каминский Ю.Д., Копылов Н.И., Тимошенко Е.Н.* Низкотемпературный обжиг кобальтового концентрата // Химическая технология. — 2009. — Т. 10, № 12. — С. 735–741.

14 *Бетехтин А.Г.* Минералогия. — М.: Госгеоиздат, 1950. — С. 624.

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Құрамды әдіс арқылы «Тувакобальт» комбинатының аралық өнімнен күшәланы шығару

800–850 ºС температурада натрий арсенаты алынатын ерітіндіні сулы сілтісіздендіру және сода қоспаларын күйдіру арқылы аралық кектардан күшәнді жою үшін «Тувакобальт» комбинаты зерттеулер жүргізді.Белгілі технологиялар арқылы күшән ерітіндісі күшән сульфидіне ауыстырылады (күкіртті натрий, кукіртті сутек және т.б). Сонымен бірге алынған өнім антисептик ретінде ауыл шаруашылығында,ағашты қайта өндеу,теңіз флоты үшін қарсы өсетін жабындарда биоцид ретінде қолданылады.

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Вывод мышьяка из отвалов комбината «Тувакобальт» комбинированным способом

Представленные материалы исследования показывают возможность вывода мышьяка из отвальных кеков комбината «Тувакобальт» посредством их обжига при 800–850 ºС в смеси с содой и последующего водного выщелачивания в раствор образующегося арсената натрия. Мышьяк из раствора может быть переведён в сульфид мышьяка по известным технологиям (сернистым натрием, сероводородом и др.). При этом получаемые продукты могут быть использованы в практической деятельности: в качестве антисептиков в сельском хозяйстве, при обработке древесины; в качестве биоцида в противообрастающих покрытиях для морского флота, гидротехнических конструкций и других сооружений, эксплуатируемых в биоагрессивных средах.

References

1 Zabelin V.I., Zaika V.V., Lebedev V.I. *Ecology and health*, Kyzyl: Publ. House of Tuva, 1995, p. 45.

2 Gas'kova O.L., Bortnikova Ye.P., Bortnikova S.B., Androsova N.V. *Chemistry for Sustainable Development*, 2000, 8, 3, p. 373–380.

3 Bortnikova S.B., Gas'kova O.L., Bessonova Ye.P. *Geochemistry of Technogenic Systems*, Novosibirsk: Geo, 2006, p. 169.

4 Ondar S.O., Putintsev N.I., Krytsin A.N. *About the State of Environment of the Republic of Tyva*, Kyzyl: CCL TuvaIENR SB of RAS, 2000, p. 101.

5 Kopylov N.I. *Problems of arsenic containing dumps*, Ed. by acad. G.A.Tolstikova, Novosibirsk: Geo, 2012, p. 182.

6 Ondar U.V. *Development of methodical description based on X-ray fluorescence analysis to control arsenic contamination of environmental objects*: Abstract. dis. ... cand. chem. sciences, Irkutsk: IrkSU publ., 2001, p. 20.

7 Isabaev S.M., Kovalchuk V.A., Mil'ke E.G., Klimenko V.A. *Non-Ferrous Metallurgy*, 1983, 2, p. 30, 31.

8 Reznik I.D., Sobol' S.I., Khudyakov V.M. *Cobalt*, Vol. 2, Moscow: Mashinostroyeniye, 1995, p. 470.

9 Ponomareva E.I., Solovyova V.D., Bobrova V.V. et al. *Arsenic in Lead-zinc Industry*, Alma-Ata: Nauka, 1975, p. 101.

10 Hoffman G.O. *Metallurgy of lead*, Moscow; Leningrad: Tsvetmetizdat, 1932, p. 687.

11 Andreev V.M., Donchenko P.A., Salin A.S. *Non-ferrous metallurgy: Bull. CREITsvetmet*, 1956, 1, p. 12–15.

12 Sadilova L.G., Loskutov F.M. *Bull. of higher educational institutions. Non-Ferrous Metals*, 1958, 5, p. 38–49.

13 Kaminsky Yu.D., Kopylov N.I., Tymoshenko Ye.N. *Chemical Engineering*, 2009, 10, 12, p. 735–741.

14 Betekhtin A.G. *Mineralogy*, Moscow: Gosgeoizdat, 1950, p. 624.