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The disposal of sulfide-arsenic cake

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Abstract: When processing sulfide copper-zinc concentrates at copper smelters, sulfide-arsenic cakes are formed, which are subject to disposal. To solve the global environmental problem of arsenic in the metallurgical and mining industries, it must be reliably concentrated and fixed in technological flows with subsequent waste disposal. The fusion of arsenic cake with elemental sulfur leads to the formation of vitreous sulfides, which are less toxic in comparison with dispersed powdered cake, homogeneous and compact in shape. The fusion product is represented by non-stoichiometric arsenic sulfide, similar in composition to As_2S_5. The high chemical stability of glassy arsenic sulfides is confirmed by the results of leaching by TCLP method. The fusion products have 100 times lower solubility compared to the initial cake. Achieving the solubility of arsenic in the alloy below the threshold concentration (5 mg/dm^3) makes it possible to recommend the disposal of arsenic cake by fusing it with elemental sulfur. The fusion products belong to non-hazardous waste and are suitable for long-term storage. The composition and structure of cake fusions with iron powder have been studied. New compounds of variable composition were identified in the fused samples: arsenides and sulfides of iron, arsenic sulfides and arsenopyrites. Studies have shown that the products of fusion with iron have a solubility 10–15 times lower than the arsenic compounds in the initial cake but above the threshold concentration as per TCLP method. Therefore, fusion with iron cannot be recommended for practical use for the disposal of arsenic cakes.

Key words: arsenic, sulfur, iron, arsenides, sulfides, oxides, structure, composition, sintering, leaching, cake, chemical analysis, concentration

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Утилизация сульфидно-мышьяковистого кека

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Аннотация: При переработке сульфидных медно-цинковых концентратов на медеплавильных заводах образуются сульфидно-мышьяковистые кеки, подлежащие утилизации. Для решения глобальной экологической проблемы мышьяка в металлургической и горнодобывающей отраслях промышленности он должен быть надежно сконцентрирован и иммобилизован в технологических потоках с последующим удалением отходов. Сплавление мышьяковистого кека с элементной серой приводит к образованию стекловидных сульфидов, которые менее токсичны в сравнении с дисперсным порошкообразным кеком, однородны и обладают компактной формой. Продукт сплавления представлен нестехиометрическим сульфидом мышьяка, близким по составу к As_2S_5. Высокая химическая устойчивость стеклообразных сульфидов мышьяка подтверждается результатами выщелачивания по методике TCLP. Продукты сплавления имеют в 100 раз меньшую растворимость по сравнению с исходным кеком. Достижение растворимости мышьяка в сплаве ниже пороговой концентрации (5 мг/дм^3) позволяет рекомендовать утилизацию мышьяковистого кека способом сплавления его с элементной серой. Продукты сплавления относятся к неопасным отходам и пригодны для длительного хранения. Изучены состав и структура сплавов кека с железным порошком. В сплавленных образцах выявлены новые соединения переменного состава: арсениды и сульфиды железа, сульфиды мышьяка и арсенопириты. Исследования показали, что продукты сплавления с железом обладают растворимостью в 10—15 раз меньшей, чем соединения мышьяка в исходном кеке, но выше пороговой концентрации по методике TCLP. Поэтому сплавление с железом не может быть рекомендовано к практическому использованию для утилизации мышьяковистых кеков.

Ключевые слова: мышьяк, сера, железо, арсениды, сульфиды, оксиды, структура, состав, спекание, выщелачивание, кек, химический анализ, концентрация

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Introduction

When processing sulfide copper-zinc concentrates at copper smelters, sulfide-arsenic cakes, being subject to disposal, are formed. To solve the global environmental problem of arsenic in the metallurgical and mining industries, it must be reliably concentrated and fixed in technological flows with subsequent waste disposal. A combination of cost-effective and selective physicochemical treatment methods such as ion exchange, leaching, precipitation, filtration and adsorption, along with biological methods, can constitute a safe alternative for the removal of arsenic from liquid and solid products to be purified. [1]. Arsenic immobilization stage can be performed by hydrometallurgical and pyrometallurgical methods. The initial stage of arsenic fixation is the oxidation of As(III) both to remove arsenic and to stabilize its final residues. Commonly, As(V) is precipitated using hydrometallurgical processes consisting of neutralization with lime, precipitation of sulfides, coprecipitation of arsenic with iron ions, including scorodite $FeAsO_4 \cdot 2H_2O$. In pyrometallurgical methods, arsenic and sulfur are captured using a fixing agent such as calcium and iron salts to obtain a stable residue. [2].

The separation of arsenic from solid-phase is possible through pressure oxidation leaching process (2.5 mol/dm^3 NaOH, $p(O_2)$ = 0.5 MPa, t = 120 °C, L : S = 4, τ = 3 h) and AsO_4^{3-} arsenate reduction to AsO_2^- arsenite with sulfur dioxide by ~93 % (pH = 4, t = 30 °C, $Q(SO_2)$ = 60 cm^3/min, τ = 2.5 h) [3]. The leaching of As_2O_3 by 89 % with 100 g/dm^3 Na_2S solution is possible at L : S = 6, t = 80 °C along with its precipitation from $Fe_2(SO_4)_3$, when 99.93 % of arsenic is removed in the form of amorphous ferric arsenate at pH = 4.8, Fe^{3+}/As molar ratio = 5 and H_2O_2/As = 4 [4]. Studies performed at the interface of precipitate and water suggest that the removal of As from the surface and deep layers is associated with the adsorption of As(V) by Fe oxides and the formation of a precipitate, and/or adsorption by Fe sulfides, respectively [5]. Arsenic adsorbed on hydrated ferric oxide (HFO) can redissolve as a result of the bioreactivated reductive dissolution of HFO at almost neutral pH with the corresponding oxidation of organic matter [6]. Calcium arsenates are also unstable and subject to transformation. When neutralizing CaO with different Ca/As ratios at pH = 7÷12 in the presence of atmospheric CO_2, the various types of crystalline calcium arsenate, which determine the stability of $Ca_3(AsO_4)_2$, are formed. When pH values increase from 8 to 10—12, the solubility of arsenic increases [7].

When sulfating hematite-rich calcines (56—62 % Fe_2O_3) with sulfuric acid, ferric sulfate solution (13.4 g/dm^3 Fe and 2.3 g/dm^3 As) was obtained and used for the precipitation of arsenic by ~99.8 % from waste waters (from 1,583.4 to 5.3 mg/dm^3 of As). Arsenic carriers were ferric (aluminum) or calcium arsenate/arsenites (up to 72.8 % of As), as well as ferric oxyhydroxides [8]. Amorphous rather than crystalline arsenic trisulfide (As_2S_3) was unstable under alkaline and oxidizing conditions. The release of arsenic in the form of arsenite, which is subsequently oxidized to arsenate, and sulfur in the form of thiosulfate with a transition to sulfate by oxidation and disproportionation, increases upon the increase of pH, dissolved oxygen concentration and temperature [9].

Arsenic leaching from Zn—Pb mine tailings increased to a greater extent under acidic rather than alkaline ones, growing with an increase in the L : S ratio and duration of contact of the tailings with water, reaching a maximum for the samples with particle sizes of 500—600 and 150—250 μm [10]. Acid leaching combined with pressure oxidation was used to release 98.2 % of arsenic from lead plant fumes (100 g/dm^3 H_2SO_4, $p(O_2) = 2.5$ MPa, $t = 170$ °C, L : S= 10, $\tau = 2.5$ h, $\omega = 500$ r/min) [11]. Injection of calcium-based adsorbent into flue gases can ensure high arsenic removal efficiency. Further development of advanced adsorbents that are inexpensive, separable and suitable for recycling as well as resistant to high-temperature sintering and deactivation caused by the competitive adsorption of acid gases, having a large specific surface area, is to be the main focus of the future research [12].

Arsenate (2 mg/dm^3) is sorbed by ~85 % from aqueous solutions on 0.3 g/dm^3 $CuFe_2O_4$ within 90 min at pH = 7 [13]. Hydroxyl-Eggshell (ES-OH), being inexpensive chemical compound, removes arsenic from aqueous solutions in less than 15 min with a description of the process by a pseudo-second order model and a maximum As adsorption in 529 mg/dm^3 according to the Langmuir isotherm. The mechanism of As removal by means of ES-OH is caused by the precipitation of vladimirite $Ca_5(HAsO_4)_2(AsO_4)_2 \cdot 5H_2O$, which is followed by weak electrostatic interactions between precipitate and arsenate ions [14].

The pyrometallurgical roasting method is used for the treatment of dust with the addition of sulfuric acid and bitumen, for the reduction of As(V) and the oxidation of arsenic sulfides (consumption $H_2SO_4 = 0.2 \div 0.3$ g/g, 5 % of carbon, $t = 300 \div 400$ °C, $\tau = 2 \div 3$ h). About 98 % As was fumed, As content in the residue decreased to 0.57 %. The arsenic was eventually extracted as As_2O_3 with high purity of ~99.1 % [15].

The physical and chemical weathering of arsenic-rich industrial wastes can mobilize and disperse contaminated sediments in residential areas surrounding the industrial areas, putting humans at risk of chronic arsenic exposure. Arsenic content in mercury mine deposits (fraction ≤ 250 μm) is 114—678 mg/kg [16]. The highest bioavailability of As (19—32 %) was established for the fraction of fine particles (< 53 μm), represented mainly by crystalline (30—73 %) and amorphous (9—59 %) Fe/Al oxyhydroxides [17]. The metabolic activity of microorganisms was the main reason for the transformation and mobilization of arsenic in the composition of wastes in landfills. Arsenate is reduced to arsenite and additionally methylated to mono- (MMA) and dimethylarsine (DMA) that decreases the total content of arsenic during the waste disposal process, but facilitates its release into the liquid phase in the form of arsenite, MMA and DMA [18]. The deposits in the pond for the discharge of metallurgical production wastes were studied. The content of water-soluble arsenic compounds, HCl and NaOH, was determined. It was established that the oxidation of As(III) and the processes of sorption and precipitation of As(V) proceed upon dissolution. The content of water-soluble As does not exceed 7.4 % of the total As in precipitates, As(III) is below 7.4 % of the extracted As content. The bulk of arsenic compounds (~78 % As) is dissolved in 2 M HCl, As(V) is ~94 % of the extracted arsenic [19].

Two different additives, namely a combination of calcite and ferric sulfate (CC + Fe(III)) and a by-product obtained from the processing of aluminum salt slags (BP—AlO_x), were used to stabilize As. Upon leaching, a decrease in the concentration of dissolved As by 95—98 and 52—79 % respectively was noted, which is acceptable for mine waste storage in controlled landfills. [20]. In order to stabilize arsenic-calcium residue (ACR) formed during the treatment of wastewater containing As during a year, it is treated with $FeSO_4$—H_2SO_4. Leaching results in the decrease of As concentration from 162 to 1.2 mg/dm^3. The dissolution of As is stabilized by the formation of stable complexes Fe—O—As ($FeAsO_4 \cdot xFe(OH)_3$) [21]. The surface of nanosilica (~18 nm) was modified with a silane coupling agent containing a mercapto group and iron (II) salt to obtain an organic-inorganic hybrid containing —S—Fe—S (RNS-SFE) functional group. At a dosage of 3.0 wt.% RNS-SFE, it can immobilize bioavailable Pb, Cd and As by 97.1 %, 85.0 % and 80.1 %, respectively. Elements form insoluble compounds of mercaptometals (–S—Pb—S— and –S—Cd—S—) and less soluble ferric arsenate ($Fe_3(AsO_4)_2$, $FeAsO_4$), precipitating on the surface of nanosilica particles. Immobilized products Pb, Cd and As exhibit good resistance to acid leaching [22].

Notwithstanding previously performed studies, there remains a need for the development of new, relatively inexpensive and efficient ways to immobilize arsenic contained in intermediate products and industrial waste. The purpose of this paper is to justify a method for the thermal treatment of sulfide-arsenic cakes with elemental sulphur and iron so as to reduce the solubility of arsenic in long-term storage and disposal conditions.

Methods and materials

The chemical composition of initial materials and reaction products was determined by atomic emission spectroscopy by means of Spectroflame Modula S spectrometer (Spectro Analytical Instruments GmbH, Germany). *X*-ray spectral microanalysis (XSMA) of the samples was performed on EVO 40 XVP scanning electron microscope (Carl Zeiss, Germany) and INCA Energy 350 X-max 80 energy-dispersive *X*-ray spectrometer (Oxford Instruments, UK). *X*-ray phase analysis (XPA) of the formed products was performed on Dron 2.0 diffractometer (“Burevestnik” Research and Production Enterprise, St. Petersburg) with UVD-2000 high-temperature attachment (CuK_α radiation, graphite monochromator, Bragg–Brentano focusing), angle interval of $2\theta = 15.0\div80.0°$, film step of 0.02°, exposure time of 2 s). ICDD PDF-4 database was used to interpret radiographs [23].

Waste toxicity was characterized using Toxicity Characteristic Leaching Procedure (TCLP) [24, 25] developed by the US Environmental Protection Agency (EPA). The aforementioned method is based on the leaching of a solid sample under conditions simulating its presence in dumps. Leaching was performed on an agitator platform in sodium acetate buffer solution (pH = 4.93) with the ratio of S : L = 1 : 20, the agitation speed of 30 r/min and temperature of 25 °C for 18 h. After filtration in the solution, the concentration of arsenic was determined and compared with the table presented by EPA, containing maximum concentrations of the toxic substance. The current TCLP threshold concentration of arsenic is 5 mg/dm^3.

The object of the study was sulfide-arsenic cake of sulfuric acid production of the following composition, %: 55.3 As; 33.6 S; 2.58 Pb; 0.58 Zn; 0.18 Sb; 0.18 Se; 0.16 Cd; 0.097 Cu; 0.064 Fe; 0.034 Si; 0.21 Na available from “SUMZ”, OJSC (Revda city, the Sverdlovsk Region) [26]. The experiments were performed by fusing a mixture of sulfide-arsenic cake with the addition of elemental sulfur and iron. Pyrrhotite mineral (a piece), fused iron (a piece) and reduced iron powder were used as an iron-containing material. Charge fusion equipment: resistance furnace with graphite carbon heater (Tamman furnace), SNOL tube furnace and muffle furnace. Fuse mode: temperature 370—500 °C, time 0.25—2.0 h. To maintain inert atmosphere in the furnace, argon or nitrogen was supplied onto the charge surface at a flow rate of ~2 dm^3/h. The consumption of elemental sulfur was 5—50 %, and the consumption of iron (powder) was 50—200 % of the cake weight. The mixture was thoroughly mixed and placed in a porcelain crucible with a lid, which was placed into the preheated furnace. After heating the charge to a predetermined temperature and keeping it for a controlled period of time, the furnace was turned off, cooled, and the crucible was taken out. The products were weighed, ground to a particle size of less than 1 mm, analyzed by *X*-ray phase analysis, electron microscopy and *X*-ray spectral microanalysis, and the solubility of As in water and buffer solution was determined using TCLP method.

Results and discussion

The results of our studies of the microstructure and phase composition of the sulfide-arsenic cake were previously described in detail [26]. According to XRF results, the cake is represented by *X*-ray amorphous dispersed arsenic sulfide (As_2S_3), lead sulfate ($PbSO_4$) and arsenic oxide (As_2O_3) reflections were detected. The microanalysis of cake particles showed their heterogeneity both in structure and composition. According to XSMA data, individual sulfates and sulfides of lead and zinc were found in the cake. The phases characterizing aggregates of complex composition containing iron and lead sulfides, arsenic, zinc, copper, silicon oxide, etc. were detected at the points of local probing. A significant part of the aggregates contains non-stoichiometric arsenic sulfides of As_2S_x type, where $x = 3.1\div3.8$, with small inclusions of arsenic and copper oxides.

Testing the cake for solubility exhibits that the content of acid-soluble arsenic forms is 19166 mg/kg, and the content of water-soluble arsenic forms is 132 mg/kg. The cake leaching in water/buffer solution (under TCLP method) indicated that the liquid phase contains (mg/dm^3) 170/334 As; 1200/1240 S; 150/180 Zn; 3.1/0.4 Pb. The data obtained are many times higher than threshold concentrations of arsenic.

For the purpose of preselecting the cake processing mode, the thermodynamic modeling (TDM) of phase transformations upon cake heating was performed. The calculations were made per 100 kg of the weight of the working medium containing (%) 90 As_2S_3, 8.7 $PbSO_4$ and 1.3 CuS, with a composition approximating that of the arsenic cake base. The TDM results indicate a significant effect of temperature on the phase composition. The transformation of the initial compounds occurs, the metal occurrence form changes. In particular, most As_2S_3 is transformed into other sulfides and arsenic oxide. When the temperature of 370—380 °C is reached, the most significant of the formed phases are as follows: AsS, PbS, CuS, As_2S_3, As_2S_2. Sulfur is distributed among metal compounds, copper and arsenic are found in the lower sulfides of the same denomination. In the temperature range of 25–500 °C, a sequential transformation of As_2S_3 into AsS, As_2S_2, As_2O_3, As, As_4S_4 occurs. The increase in the amount of As_2O_3 can be explained by the following interaction:

$$As_2S_3 + 2{,}25PbSO_4 = As_2O_3 + 2.25PbS + 3SO_2.$$

The phase formation when heating the working medium in a mixture with elemental sulfur was evaluated with the addition of sulfur in the amounts of 5, 50 and 200 %. Upon the heat treatment of the charge, some part of sulfur transforms into the gas phase, and the other part reacts with arsenic sulfide at a temperature of 120—150 °C:

$$As_2S_3 + 2S = As_2S_5.$$

A decrease in the amount of As_2S_3, the appearance and growth of the proportion of other sulfides, AsS, As_2S_2 are observed during the charge heating. An increase in the amount of added elemental sulfur from 5 to 50 % almost does not change the pattern, and when it is added in the amount of up to 200 %, the transition of sulfur into the gas phase increases and the amount of newly formed arsenic sulfides decreases. The results of thermodynamic prediction revealed that the optimal addition of elemental sulfur is 5—10 % minimum , which allows to quantitatively bind arsenic into a poorly soluble non-toxic compound.

Heat treatment of the system consisting of a charge with iron revealed that iron reacts with arsenic sulfide resulting in the formation of secondary sulfides. Some of the possible interactions are as follows:

$$As_2S_3 + 2Fe = Fe_2S_3 + As_2,$$

$$As_2S_3 + 3Fe = 3FeS + As_2,$$

$$As_2S_3 + 2Fe = 2FeS + AsS + As,$$

$$As_2S_3 + Fe = FeAs_2 + 1.5S_2,$$

$$As_2S_3 + 3Fe = 2FeAsS + FeS.$$

The number of Fe_2S_3, FeS_2, FeAs compounds decreases at the predicted cake processing temperatures of 400—450 °C. $FeAs_2$, FeS, and AsS compounds quantitatively increase by the indicated temperatures, non-stoichiometric sulfide $Fe_{0.877}S$ and arsenopyrite FeAsS are formed as well. According to TDM results, the optimal addition of iron (~14 wt.%) results in the transition of arsenic-containing cake phases into such mineral forms as arsenides and arsenopyrites that correspond to the criteria of chemical inertness. Technological experiments on the heat treatment of a mixture of cake with additives revealed that the cake transforms into a compact glassy state after being fused with sulfur at a temperature of 420 °C (Fig. 1).

According to the performed calculations, it can be assumed that with an increase in the amount of added sulfur upon fusion, the form of arsenic changes from initial As_2S_3 to As_2S_5 and As_2S_7, which is consistent with the results of thermodynamic analysis and XSMA. At the points of local probing (Fig. 2, Table 1), the phases of non-stoichiometric arsenic sulfide $As_2S_{4,6}$ and lead sulfate, including its non-stoichiometric composition, were detected.

Testing of fusions for toxicity by TCLP method (Table 2) revealed that a small addition of sulfur (5 %) reduces the solubility of arsenic by an order of magnitude, and an increase in sulfur to 20 % reduces the solubility of arsenic below the threshold concentration (3.7—3.3 mg/dm^3), which allows to perform the disposal of fusions without special measures.

Preliminary experiments ensured the establishment of a temperature of 400—440 °C for the fusion of sulfide-arsenic cake with iron allowing to prevent losses with fumes. The heat treatment with iron presented in different variants was performed at a temperature of 400 °C for 2 h. The iron/cake ratio was 0.6/1.0, but a layer of iron was added to the surface of the reaction mix-

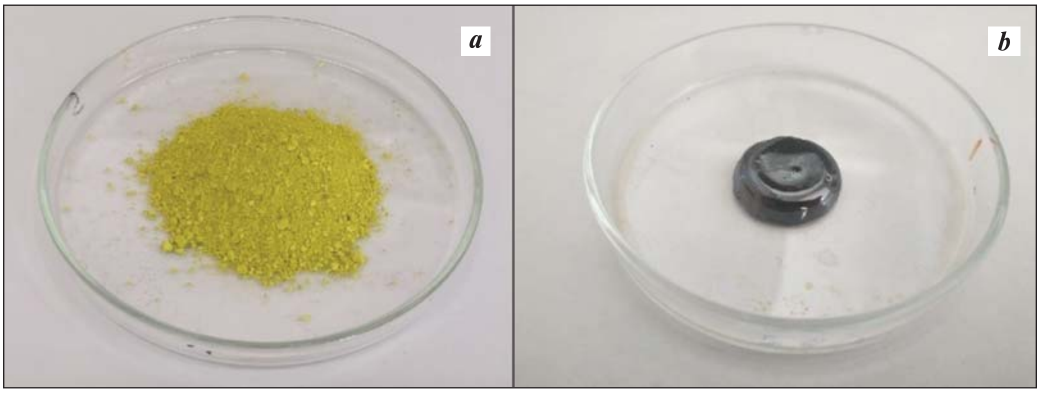

Fig. 1. The view of the cake before (***a***) and after (***b***) the fusion with sulfur

Рис. 1. Вид кека до (***a***) и после (***b***) сплавления с серой

Table 1. **The composition of the phases of the sample after fusion of the cake with 20 % S (as per Fig. 2)**

Таблица 1. Состав фаз образца после сплавления кека с 20 % S (по рис. 2)

Point No.	Composition, wt.%					Phase composition
	As	S	O	Pb	Zn	
1	50.87	49.13	–	–	–	$As_2S_{4.6}$
2	48.98	50.52	–	–	0.5	$As_2S_{4.6}$
3	–	11.98	20.79	67.23	–	$PbSO_4$
4	–	12.84	14.97	71.55	0.64	$PbS_{1.2}O_{2.7}$
5	50.55	49.45	–	–	–	$As_2S_{4.6}$
6	22.19	28.48	–	49.33	–	$PbAs_{1.2}S_{3.8}$

ture (300 % of the mixture) in the experiment with iron powder.

Upon the heat treatment of cake mixed with iron sulfide Fe_7S_8 (pyrrhotite), the phases of non-stoichiometric sulfide Fe_7S_x, where $x = 8.7$; 9.0; 9.5, were identified at the interface with the latter (Table 3). The saturation of initial Fe_7S_8 with sulfur can be observed. The following interaction might occur:

$$As_2S_3 + Fe_7S_8 = As_2S_2 + Fe_7S_9.$$

The chemical composition of the phases at the points of probing was determined by XSMA of the cake surface after heat treatment with molten iron (Table 4)

Such compounds of variable composition as sulfides of lead, iron and arsenic, oxysulfides of iron and sulfur, arsenopyrites FeAsSz, etc. were found in the fusion products.

Experiments for the fusion of cake with iron powder were performed with its consumption from 50 to 200 % of the cake mass (Tables 5, 6). The obtained fusions were subjected to a toxicity test. With iron consumption of ~60÷80 %, the solubility of arsenic in the buffer solution decreases by an order of magnitude compared to the initial cake, but its concentration in the solution remains high and significantly exceeds the threshold.

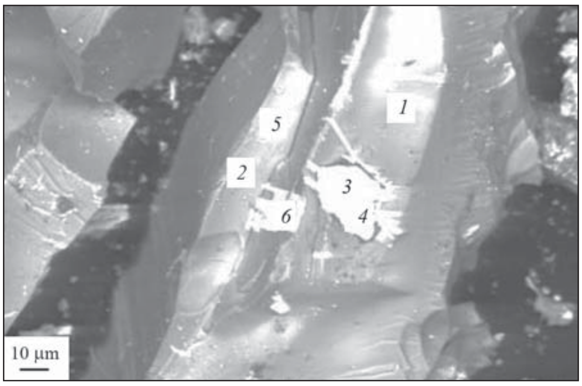

Fig. 2. The microstructure of cake fusion

Рис. 2. Микроструктура сплава кека

Table 2. **The results of leaching of samples after fusion with sulfur**

Таблица 2. Результаты выщелачивания образцов после сплавления с серой

Sulfur addition, %	Concentration in solution, mg/dm^3	
	As	S
0	70.0	117.0
5	7.2	51.2
20	3.7	52.9
40	3.6	54.7
50	3.3	52.1

Table 3. **The composition of fusion phases at the interface with iron sulfide**

Таблица 3. Состав фаз сплава на границе с сульфидом железа

Phase	S, %	Fe, %	Phase composition
1	41.6	58.4	$Fe_7S_{8.7}$
2	42.19	57.81	Fe_7S_9
3	43.53	56.47	$Fe_7S_{9.5}$

Table 4. **The chemical composition (%) of the phases of cake fusion with iron**
Таблица 4. Химический состав (%) фаз сплава кека с железом

Phase	S	Cu	Fe	As	Pb	O	Phase composition
1	22.63	–	–	19.45	43.3	8.51	$PbAsS_3O_3$
2	23.47	–	7.37	9.86	53.85	–	FeAsS PbS
3	29.77	–	70.23	–	–	–	FeS
4	22.88	1.58	9.81	14.42	23.79	16	$As_2S_4O_3$ $PbFeO_3$
5	24.96	4.2	4.78	14.31	–	27.9	AsS_4O_6

Table 5. **The results of cake fusion with iron powder**
Таблица 5. Результаты по сплавлению кека с порошковым железом

Iron consumption, %	Loss of weight, %	As concentration in solution, mg/dm^3	Fraction after leaching, wt.%	
			As	S
0	4.9	110	–	–
80	8.2	38	47.35	40.5
120	6.6	76	49.66	39.1
170	3.9	90	47.30	38.5
200	9.6	81	51.00	37.1

Such compounds of variable composition as sulfides of lead and iron of Fe_xS_y type, where $x = 1{\div}2$. $y = 1{\div}3$; arsenic sulfides As_mS_n, where m and n vary from 1 to 4, oxysulfides of iron and sulfur of FeS_2O_4 and FeS_3O_5 type, as well as the ones of arsenic and sulfur $As_2S_2O_5$; arsenates Fe_pAs_q, where p and q vary withih 1—2; arsenopyrites $FeAsS_z$, where $z = 1{\div}4$, were identified in the products of cake fusion with iron powder. An oxygen compound $FeAsO_4$, being one of the most stable arsenic compounds, was identified as well. It was established that the composition of the fusion products varies over a wide range. The possibility of binding arsenic into poorly soluble compounds (arsenopyrites, $FeAsO_3$. $FeAsO_4$, etc.) in autoclaving processes is known. The formation of poorly soluble compounds in the process of cake fusion with iron can facilitate reducing its solubility and transfer the cake from the category of hazardous wastes to the category of non-hazardous ones.

Table 6. **Chemical composition (%) at the points of probing of cake fusion with iron powder (according to XSMA data)**
Таблица 6. Химический состав (%) в точках зондирования сплава кека с порошком железа (по данным РСМА)

Point No.	O	S	Fe	Pb	As
1	6.46	21.35	48.58	12.39	5.86
2	28.56	13.10	5.19	7.61	33.48
3	10.16	20.48	53.95	2.41	11.54
4	11.93	26.06	52.65	–	8.46

Conclusion

The fusion of arsenic cake with elemental sulfur results in the formation of vitreous sulfides, which are less toxic compared to dispersed powder cake, homogeneous and compact in shape. The fusion product is in the form of a non-stoichiometric arsenic sulfide, being close in composition to As_2S_5. The high chemical stability of vitreous arsenic sulfides is confirmed by the results of leaching by TCLP method. The fusion products are 100 times less soluble than the initial cake. Obtaining the solubility of arsenic in the fusion below the threshold concentration (5 mg/dm^3) makes it possible to recommend the disposal of arsenic cake by transforming arsenic into poorly soluble compounds through its fusion with elemental sulfur. The fusion products are classified as non-hazardous wastes and are suitable for long-term storage.

The composition and structure of cake fusions with iron were studied. Such new compounds of variable composition as arsenides and iron sulfides, arsenic sulfides and arsenopyrites, etc. are found in the fused products. Experiments on cake fusion with iron revealed the possibility of transforming arsenic into poorly soluble compounds (arsenides and arsenopyrites), which results in a decrease in the fusion solubility and toxicity. Under the experimental conditions, a decrease in the solubility of the fusion products by 10—15 times with respect to the initial cake with the test concentration of arsenic in the solution above the threshold, was obtained. At the completed stage, iron-containing reagents cannot be recommended for the technology of disposal of arsenic cake by transforming arsenic into poorly soluble compounds.

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