

TECHNOLOGIES FOR WASTEWATER TREATMENT FROM ARSENIC

(analytical review)

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The current recycling water supply of metallurgical enterprises does not completely eliminate the discharge of wastewater into environmental water bodies, where the maximum permissible concentration (MPC) of arsenic is 0.05 mg/dm^3 . Arsenic accumulates in large quantities in washing solutions for cleaning exhaust gases sent to produce sulfuric acid. In this case, a closed gas washing system is used, aimed at concentrating the washing water with arsenic to 10 g/dm^3 and sulfuric acid to 40 g/dm^3 in order to reduce the volume of wastewater discharge. Another source of arsenic contamination of the hydrosphere is the waters of tailings from enrichment plants, due to the possible oxidation of arsenopyrite and the formation of a soluble form of arsenic compounds.

A number of methods for arsenic precipitation have been developed: pyrolusite, lime in the form of calcium arsenate; ions of ferric iron and other metals; adsorption by iron (III) hydroxide, aluminum hydroxide, carbon, etc.; sludge flotation; metal sulfides, sorption and extraction. The main criterion for the operation of purifying a solution from arsenic is the possibility of recycling the resulting sediment or the formation of its compounds with minimal solubility in aqueous solutions, allowing its burial in burial grounds.

Keywords: wastewater, arsenic, treatment technologies, arsenates, arsenic sulfides, sorption, extraction.

МЫШЬЯКТАН АҒЫН СУЛАРЫН ТАЗАЛАУ ТЕХНОЛОГИЯЛАРЫ

(аналитикалық шолу)

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Металлургиялық кәсіпорындардың ағымдағы қайталама сумен қамтамасыз етілуі мышьяқтың шекті рұқсат етілген концентрациясы (ШРК) $0,05 \text{ мг/дм}^3$ құрайтын қоршаған орта су объектілеріне сарқынды сулардың ағуын толығымен жоймайды. Күкірт қышқылын өндіруге жіберілетін пайдаланылған газдарды тазалауға арналған жуу ерітінділерінде мышьяк көп мөлшерде жиналады. Бұл жағдайда ағынды суларды ағызу көлемін азайту мақсатында мышьякпен 10 г/дм^3 дейін және күкірт қышқылымен 40 г/дм^3 дейін жуу суын шоғырландыруға бағытталған жабық газды жуу жүйесі қолданылады. Гидросфераның мышьякпен ластануының тағы бір көзі арсенопириттің ықтимал тотығуына және мышьяк қосылыстарының еритін түрінің түзілуіне байланысты байыту зауыттарының қалдық сулары болып табылады.

Мышьяқты тұндырудың бірқатар әдістері әзірленді: пиролюзит, кальций арсенаты түріндегі әк; темір және басқа металдардың иондары; темір (III) гидроксидімен, алюминий гидроксидімен, көміртегімен және т.б.; адсорбция; шламды флотациялау; металл сульфидтері, сорбция және экстракция. Ерітіндіні мышьяктан тазарту операциясының негізгі критерийі - алынған шөгінділерді қайта өңдеу немесе оның су ерітінділерінде ерігіштігі аз қосылыстарын түзу мүмкіндігі, оны қорымдарға көмуге мүмкіндік береді.

Түйін сөздер: ағынды сулар, мышьяк, тазарту технологиялары, арсенаттар, мышьяк сульфидтері, сорбция, экстракция.

ТЕХНОЛОГИИ ОЧИСТКИ СТОЧНЫХ ВОД ОТ МЫШЬЯКА

(аналитический обзор)

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Действующее оборотное водоснабжение металлургических предприятий не устраняет полностью сброс сточных вод в водоемы окружающей среды, где предельно допустимая концентрация (ПДК) мышьяка составляет 0,05 мг/дм³. Мышьяк в больших количествах накапливается в промывных растворах очистки отходящих газов, направляемых на получение серной кислоты. При этом применяется замкнутая система промывки газов, направленная на концентрирование промывной воды мышьяком до 10 г/дм³ и серной кислотой до 40 г/дм³ с целью снижения объема сброса сточных вод. Другим источником загрязнения гидросферы мышьяком являются воды хвостохранилищ обогатительных фабрик, вследствие возможного окисления арсенопирита и образования растворимой формы соединений мышьяка.

Разработан целый ряд методов осаждения мышьяка: пиролюзитом, известью в виде арсената кальция; ионами трехвалентного железа и др. металлов; адсорбцией гидроксидом железа(III), гидроксидом алюминия, углеродом и др.; флотацией осадка; сульфидами металлов, сорбцией и экстракцией. Основным критерием операции очистки раствора от мышьяка является возможность утилизации образующегося осадка или образования его соединений с минимальной растворимостью в водных растворах, позволяющего его захоронение в могильниках.

Ключевые слова: сточные воды, мышьяк, технологии очистки, арсенаты, сульфиды мышьяка, сорбция, экстракция.

Introduction. Despite the huge amount of work devoted to the production of stable arsenic compounds, this concept itself remains quite vague. The work [1] provides a methodological approach to assessing the stability of arsenic compounds and its toxicity, used by the American Environmental Protection Agency. The methods involve long-term studies, over a number of years, using statistical or dynamic methods. The results obtained using this method can only approximately reflect the conditions of the real environment.

According to existing requirements, the technology for treating wastewater from arsenic must provide:

- eliminating the discharge into water bodies of solutions containing arsenic above the maximum permissible concentration;
- the possibility of maximum use of water circulation at the enterprise;
- obtaining low-toxic sediments for disposal;
- simplicity of technological operations and availability of used reagents and materials;
- safety for personnel;
- minimal energy costs;
- use of standard equipment.

Table - Chemical composition of wastewater before and after treatment

Component	Content of components in wastewater, мг/дм ³	
	Original	After cleaning
As	2000-20000	0,05-0,5
Cu	60-400	0,07
Zn	50-1650	0,03
Fe	390-8670	Not detected
H ₂ SO ₄	10000-50000	Not detected
SO ₂	1000-3000	Not detected
Sb	10-69	Not detected
Suspended solids	700	20-40

Precipitation of arsenic in the form of poorly soluble arsenates of iron, calcium and a number of other metals

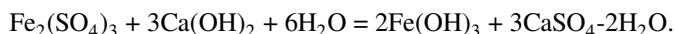
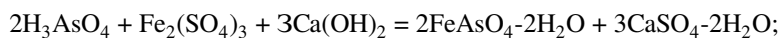
A number of technologies for treating wastewater from arsenic that are of industrial interest have been developed and are being used, including *pyrolusite technology*. The technological scheme for deep purification of acidic industrial wastewater from arsenic includes: partial degassing of the solution (80°C, 1 hour), oxidation of arsenic with pyrolusite (80°C, 3 hours, 4-6 g MnO₂ per 1 g As), neutralization of the solution and precipitation of arsenic (pH 8-9, 30-40 min), filtration of pulp, solution and burial of arsenic cakes in waterproof trenches [1].

During industrial tests, the concentration of arsenic in treated wastewater reached the MPC level (0,05 mg/dm³).

Using pyrolusite technology, it is possible to purify acidic wastewater not only from arsenic, but also from other toxic impurities, for example, copper, zinc, cadmium, etc. (table).

In practice, the most applicable methods are the neutralization and purification of wastewater and other industrial solutions using lime milk with the precipitation of arsenic in the form of arsenites and calcium arsenates. If there are heavy metal ions in the wastewater due to the coprecipitation of arsenic with their hydroxides, the purification process is much more complete. Arsenates are less soluble than arsenites, which necessitates pre-treatment and oxidation of As(III) ions to As(V) by one of the methods, for example [2-7]:

- oxidation by atmospheric oxygen in the presence of iron salts (oxidation degree 45%);



The removal of arsenic from acidic solutions containing copper and other non-ferrous metals in the form of sulfates or chlorides is carried out in several stages [8]. By bubbling air, oxygen, or a mixture of both, metals are oxidized to the highest oxidation state and excess iron sulfate is added to bind arsenic into the poorly soluble compound FeAsO₄. Add CaO until the pH rises to 3,0. Along with FeAsO₄, excess Fe(III) is precipitated in the form of Fe(OH)₃, and excess calcium in the form of gypsum. Copper sulfate and chloride remain in solution.

The data from [9] are interesting, where it was shown

- evaporation of wash water to a syrupy state, dissolution of the resulting precipitate in a 45% sodium hydroxide solution when heated, filtration and oxidation of arsenic with atmospheric oxygen at a temperature of 80-90°C in the presence of copper sulfate (with the maximum degree of oxidation ~80%);

- oxidation at ordinary temperature with potassium bichromate (oxidation degree 94% at a consumption of 0,7 t of potassium bichromate per 1 t of arsenic).

A typical calcium arsenate process flowsheet includes:

- precipitation of arsenic using lime in the form of calcium arsenites (pulp temperature 60-80°C, time 1 hour, pH 8,5-9,5, lime consumption five times relative to stoichiometric) to a residual arsenic content (III) in solution 0,1-0,2 g/dm³;

- filtration and use of part of the filtrate to prepare a lime milk solution;

- additional purification of the filtrate by treating it with mother liquors formed during the production of xanthates (residual arsenic concentration 20-30 mg/dm³);

- electrolytic treatment of solutions with soluble iron anode;

- drying and calcination of the precipitate to obtain calcium arsenate, its cooling and burial.

The effectiveness of use for neutralizing lime increases with the simultaneous supply of excess iron (III) salts to the solution [1]. Interactions with the formation of both arsenate and iron hydroxide proceed through the following reactions:

that carbonates reduce the stability of calcium arsenate sediments in contact with an aqueous environment. Precipitates of Ca₃(AsO₄)₂ become more soluble in aqueous solutions after they are treated with lime. From this it was concluded that more stable precipitates in aqueous solutions are arsenates of heavy metals - Fe, Cu, Pb, Ni, Zn, Ti etc. A positive stabilizing effect on arsenic sediments from the presence of phosphates in solutions was also noted.

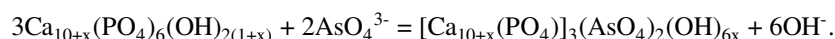
Work to find optimal solutions in this direction does not stop. Thus, at the Chemical-Metallurgical Institute named after Zh. Abishev, together with

the Karaganda University named after E.A. Buketov (Kazakhstan, Karaganda), research was carried out on the development of physico-chemical principles and methods for removing arsenic from technological solutions of copper production [10-14].

Phosphate method. It has been established that the solubility of calcium arsenate decreases in the presence of phosphate ions in the aqueous solution. When the ratio of calcium and phosphorus is about 1,7, almost all arsenic passes into sediment. The use of phosphate ions in the liming of arsenic-containing wastewater ensures deep purification of solutions from arsenic and other

toxic substances [15]. Due to the isostructural nature of the PO_4^{3-} and AsO_4^{3-} anions, as well as their tendency to isomorphism, deep purification of solutions from arsenic occurs through the formation of solid solutions in the PO_4^{3-} - AsO_4^{3-} -Ca system, in which arsenate and phosphate ions replace each other [16]. To form such compounds, it is enough to have a molar ratio of $\text{PO}_4^{3-}/\text{AsO}_4^{3-} > 1,5:1$ in solution.

In general, the process of coprecipitation of arsenic with calcium phosphate can be described by the following equation:



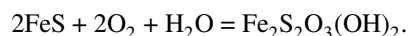
Studies on the solubility of arsenic-containing sediments based on hydroxyapatite have shown that with increasing contact time, the solubility of the sediments decreases and amounts to 1,5-2,0 mg/dm³, which is 20-25 times lower than the solubility of calcium arsenate, equal to 32 mg/dm³ and more.

Based on these ideas, a phosphate method for deep purification of arsenic from solutions was developed. The technology provides for the purification of industrial wastewater containing 0,3-0,4 g/dm³ As to sanitary standards and below. At the same time, other impurities (copper, lead, iron, etc.) are precipitated to concentrations close to the maximum permissible concentration.

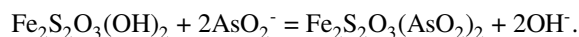
Precipitation of arsenic sulfides and sorption by sulfide minerals. This method, along with others, is used in metallurgical practice. For example, the

Kennecott plant in the USA uses a two-stage process for the precipitation of copper and arsenic from acidic wastewater in the form of sulfides, which makes it possible to convert arsenic into a low-hazard solid product and return the main amount of copper from dust to copper smelting production. The process is carried out in a continuous mode at normal temperature and pressure and completely solves the problem of arsenic supplied with raw materials [1, 17].

The work [18] was devoted to the study of As (III) sorption from aqueous solutions on iron sulfide. The maximum sorbent capacities, equilibrium constants and thermodynamic functions of ion exchange were calculated depending on the process temperature. It has been established that sulfide in contact with a solution is oxidized to thiosulfate, forming an active surface thiosulfate complex:



The process of sorption of trivalent arsenic by pyrrhotite is described by the reaction



It has been established [19] that during flotation there is a decrease in the arsenic content in the pulp - arsenic is sorbed by sulfide minerals, mainly pyrite. Sorption of arsenic by sulfide minerals occurs most effectively at pH 6,2-7,0. The maximum capacity of pyrrhotite for As (V) is 0,82, and for As (III) - 0,74 mmol/g.

The use of pyrite concentrates in sorption treatment was tested for the treatment of wastewater from the lead workshop of the Leninogorsk polymetallic plant (Russia) and the Krasnouralsk copper smelter (Russia). After loading the pyrite concentrate into the solution, air was blown through the pulp. The arsenic concentration decreased from 30-300 to 0,05-

0,1 mg/dm³.

That is, pyrrhotite and sulfides of other non-ferrous metals are effective arsenic sorbents. This method is effective, especially when using natural sorbents - industrial waste (tailings from processing plants, etc.).

Sorption and extraction. To purify solutions from arsenic, a wide range of different sorbents of both inorganic and polymer types are used [1, 20]. The use of ion exchange methods in hydrometallurgical metal extraction processes allows for simultaneous desalination of water, which can be important for ensuring complete water circulation at the enterprise.

For example, a technological scheme for treating wastewater from a copper-electrolyte plant (low-concentrated weakly acidic salt solutions) containing, mg/dm³: 42,5 Cu; 5,7 Ni; 5,7 Fe; 1,20 As; 0,71 Sb; 100 SO₄²⁻; up to 30 CaO, includes operations to clean them from copper, nickel, iron and calcium using KU-2x8 cation exchanger in H⁺ form; for the purification of industrial wastewater from arsenic, antimony and SO₄²⁻ anions using AN-2FN anion exchanger; for purification of alkaline eluate from arsenic and antimony using the pyrolusite method and subsequent mutual neutralization of unused acidic and alkaline wash waters before discharging them into the sludge storage tank. After purification of wastewater from arsenic anions, antimony and SO₄²⁻ ion using AN-2FN anion exchanger in hydroxyl form, the sum of residual concentrations does not exceed the maximum permissible concentration. The saturated ion exchanger is regenerated with a 7% sodium hydroxide solution. The eluate is sent for the precipitation of arsenic and antimony using pyrolusite technology. At the same time, deep purification of wash water from toxic elements is achieved, the return of valuable metals to the main production cycle, which ensures the reuse of purified wash water and complete water circulation.

The use of organic, inorganic and carbon sorbents for the purification of process solutions from arsenic is often associated with large volumes of poor eluates obtained, complicating the precipitation of arsenic and the water balance of the circuit. The most common extractants for the selective extraction of arsenic from spent copper electrolyte are reagents of the class of neutral organophosphorus compounds, in particular, tributyl phosphate (TBP) [21].

Extraction of arsenic from acidic TBP solutions

consists of the following main stages:

- extraction of arsenic from acidic solutions into the organic phase:
- re-extraction of arsenic from the organic phase with water or sodium sulfate solution:
- precipitation of arsenic from the re-extract in the form of calcium arsenate or arsenic sulfide.

The degree of extraction of As(V) ions using TBP depends on its basicity, temperature, number of stages, ratio of arsenic to extractant, and concentration of sulfuric acid. Under optimal process conditions, the loss of sulfuric acid does not exceed 5-10%.

Conclusions. Thus, by the beginning of the new millennium, in the areas of mining and operation of metallurgical enterprises processing these raw materials, a huge amount of waste containing high concentrations of arsenic compounds had accumulated in dumps and tailings. In them, arsenic is in the form of compounds such as high-calcium arsenates, arsenapatites, scorodite - chemical complexes that are poorly soluble in water and stable under normal conditions in closed systems of natural equilibrium. Under conditions of free contact of the dump mass with the external environment, chemical interactions occur in it with the formation of new mobile arsenic compounds that are easily soluble in aqueous media, posing a danger to the flora and fauna of the environment in the regions where they are stored.

Therefore, all technical solutions on the issue of arsenic neutralization must fit into the dynamic equilibrium of the arsenic cycle in nature. The optimal solution to this problem, apparently, can only be achieved if conditions are provided that correspond to the processes of formation of natural systems.

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