

Conference Paper

Development of Technology of Arsenic Removal from Acidic Waste Solutions in the Form of Arsenic Trisulfide

Anna A. Grebneva¹, Irina L. Subbotina¹, Konstantin L. Timofeev², and Gennady I. Maltsev¹

¹ JSC «Uralelektromed», Verkhnyaya Pyshma, Sverdlovsk Region, Russia

²Non-state Higher Educational Establishment «UMMC Technical University», Verkhnyaya Pyshma, Sverdlovsk Region, Russia

Abstract

During the laboratory tests the conditions of arsenic removal from acidic waste solutions of metallurgical enterprise in the form of arsenic trisulfide were determined. The technology based on the reduction of pentavalent arsenic to trivalent state with sodium pyrosulfite solution and following arsenic trisulfide precipitation from acidic solution after treatment with sodium sulfide solution was proposed. The arsenic removal proceeds with mechanical stirring, dosing the calculated amounts of reagents and collecting emissions of hydrogen sulfide. With such treatment, about 95% of arsenic, which was in the initial solution, passes into the precipitate. An enlarged laboratory experiment was carried out and the precipitate with 42.6% of arsenic and 46.9% of sulfur was obtained. The precipitate yield was ~25.7 kg (dry weight) out of 1 m³ of the initial arsenic containing solution.

Corresponding Author:

Anna A. Grebneva

A.Grebneva@elem.ru

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Raw materials processed at metallurgical enterprises often contain arsenic as an impurity and highly toxic arsenic compounds are found at almost all stages of metallurgical processing, including industrial wastes (waste solutions, wastewater, solid products), which can pose a serious environmental hazard. Requirements of environmental supervision, international conventions and standards oblige metallurgical enterprises to work according to certain technologies that meet environmental requirements. In this regard, the problem of finding new rational methods of arsenic removal from technological processes, arsenic disposal, environmentally safe and cost-effective management of arsenic-containing waste is particularly actual for metallurgical enterprises.

The present study is a part of the current research program aimed for organizing the removal of arsenic from the technological processes of metallurgical enterprises of JSC "UMMC-Holding". The purpose of this study is to develop a technology for separate

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processing of arsenic-containing industrial waste solutions with the removal of arsenic in the form of a sulfide precipitate (arsenic trisulfide, As_2S_3).

In fact, there are several types of industrial waste solutions containing arsenic. During the research sulfuric acid waste solution was the object of the study. It is planned that further work will be carried out with arsenic-containing alkaline and sulfide-alkaline waste solutions.

It is known that arsenic can be removed from solutions by chemical deposition in the form of arsenic trioxide, arsenic trisulfide or in the form of its compounds with calcium (calcium arsenites and arsenates), manganese (manganese arsenate) or iron (iron arsenate).

A review of national and foreign literary sources on the processing of acidic arsenic-containing solutions leads to conclusion that the most promising way is the removal of arsenic from technological processes in the form of sulfides [1–6]. Neutralization of technological and waste solutions with sulfide reagents (sodium sulfide, etc.) favorably differs from other methods by low solubility and toxicity of arsenic sulfide precipitate, which does not require expensive waste burial sites. At a high concentration of arsenic in it, the volume of waste is reduced by more than 10 times compared to products derived from other technologies [2].

A small yield of precipitate allows its processing by compaction and encapsulation with obtaining of low-hazardous waste. In addition, arsenic trisulfide can be used for production of arsenic trioxide [3] that opens up prospects of arsenic removal in the form of a commercial product.

In the performed laboratory experiments, arsenic-containing sulfuric acid waste solution (its composition is given in Table 1) was treated with a solution of sodium sulfide (100 g/dm³ Na_2S) for binding arsenic into sulfide. The laboratory unit (see Figure 1) included dosing equipment, three-bladed stirrer (300 rpm), isolation of reaction beaker limiting the emission of hydrogen sulfide (H_2S) into the atmosphere, Drexel bottle filled with Na_2CO_3 solution (10 wt. %) for collecting gas from the beaker by a peristaltic pump.

The resulting yellow precipitate of arsenic sulfide was separated by filtration through a «blue ribbon» filter paper on a vacuum filter. With the consumption of sodium sulfide solution equal to 189 cm³ per 1 dm³ of the initial acidic solution, the residual arsenic content in the filtrate was 6.02 g/dm³ (see Table 1), which showed the expediency of increasing the consumption of injected reagent.

Taking into account that in the initial acidic solution arsenic was mainly presented in the form of As(V), in order to obtain arsenic trisulfide, preliminary reduction of As(V) to As(III) was carried out using sodium pyrosulfite solution (325 g/dm³ $\text{Na}_2\text{S}_2\text{O}_5$) with consumptions of 110.4 and 220.8 cm³/dm³. Solutions after the arsenic reduction

TABLE 1: The composition of the treated solution before and after the experiment (analysis was performed by atomic adsorption spectrometry). Author's own work.

Component	Initial content, g/dm ³	Final content, g/dm ³
As	12.80	6.02
As(III)	2.09	0.00
As(V)	11.31	0.00
Se	1.3	0.1
Te	0.130	0.014
H ₂ SO ₄	85.65	40.84
Na	88.9	84.9
Na ₂ S	0.0	< 0.5
Cu	0.016	< 0.004
Fe	0.018	0.008
Ca	0.13	0.16
Mg	0.11	0.08
K	0.38	0.35
Sb	0.028	0.017
Sn	< 0.01	< 0.01

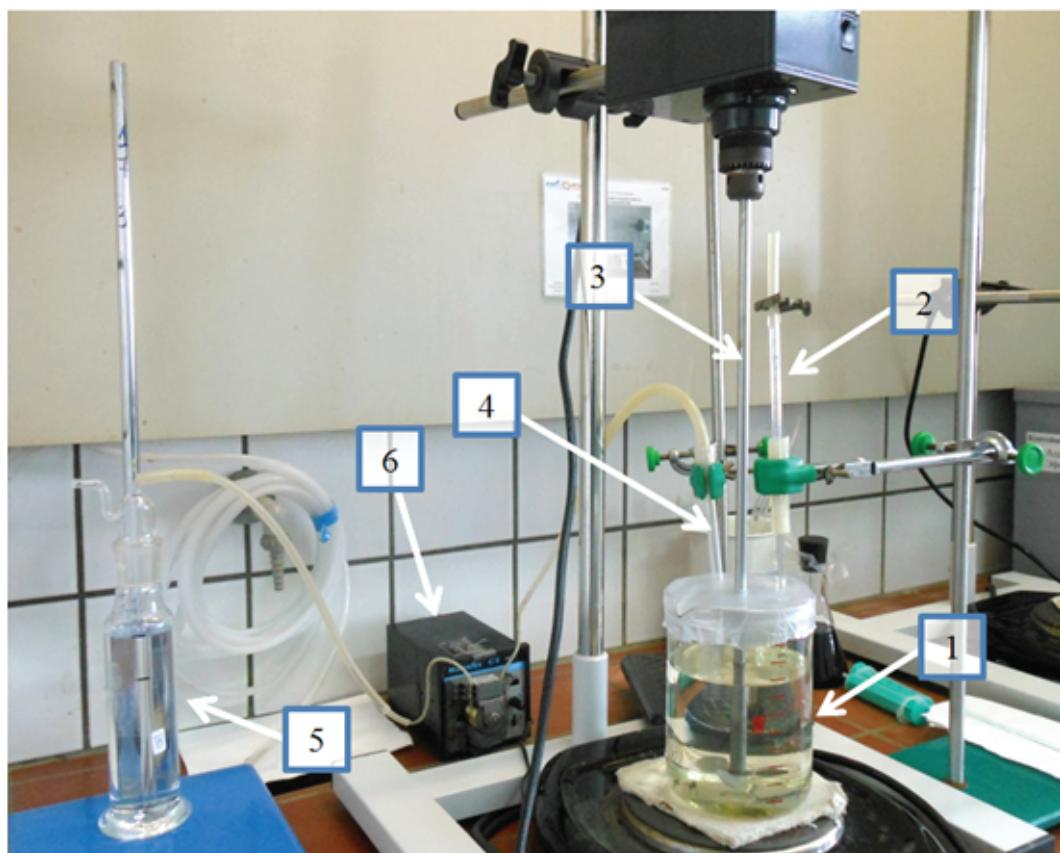


Figure 1: Laboratory unit for arsenic sulphide precipitation. Author's own work. 1 – reaction beaker insulated with polyethylene film; 2 – a tube for dosing the reagent deep into solution; 3 – a mechanical stirrer; 4 – tube for emitted gas withdrawal; 5 – Drexel bottle; 6 – peristaltic pump.

were treated with sodium sulfide ($100 \text{ g/dm}^3 \text{ Na}_2\text{S}$, consumption $230.4 \text{ cm}^3/\text{dm}^3$). The experimental results (see Table 2) showed that the consumption of sodium pyrosulfite solution, equal to $220.8 \text{ cm}^3/\text{dm}^3$, allows transferring up to 97% of arsenic (V) to arsenic (III). During the subsequent precipitation of arsenic (III) with sodium sulfide about 95% turns into an insoluble form.

After conducting an enlarged laboratory experiment with the acidic solution treated with solutions of sodium pyrosulfite ($220.8 \text{ cm}^3/\text{dm}^3$) and sodium sulfide ($230.4 \text{ cm}^3/\text{dm}^3$) the precipitate of arsenic trisulfide of the following composition was obtained, %: 42.58 As, 46.87 S, 4.11 Se, 0.021 Te, 0.019 Fe, 0.005 Cu, 0.085 Sb, 0.37 Na, 0.012 K, 0.004 Mg, <0.02 Ca, <0.1 Sn. The yield of the precipitate was $\sim 25.7 \text{ kg}$ (dry weight) out of 1 m^3 of the initial solution. The chemical compositions of acidic solution at different treatment stages are given in Table 2.

TABLE 2: The composition of the acidic solution at different treatment stages. Author's own work.

Name	As(III), g/dm ³	As(V), g/dm ³	Σ As, g/dm ³	H ₂ SO ₄ , g/dm ³	Se, g/dm ³	Na, g/dm ³	Na ₂ S, g/dm ³
<i>Initial solution</i>							
Initial acidic solution	2.09	11.31	12.8	85.65	1.3	88.9	–
<i>Treatment with sodium pyrosulfite (consumption $110.4 \text{ cm}^3/\text{dm}^3$)</i>							
Solution filtrate after treatment with sodium pyrosulfite	9.85	1.95	11.80	68.35	–	–	–
1) Treatment with sodium pyrosulfite (consumption $220.8 \text{ cm}^3/\text{dm}^3$); 2) subsequent treatment with sodium sulfide (consumption $230.4 \text{ cm}^3/\text{dm}^3$)							
Solution filtrate after treatment with sodium pyrosulfite	8.43	0.69	9.49	47.04	1.04	–	–
Solution after precipitation of arsenic sulphide from filtrate after treatment with sodium pyrosulfite	–	–	< 0.01	2.37	0.097	89.8	< 1
An enlarged experiment: 1) treatment with sodium pyrosulfite (consumption $220.8 \text{ cm}^3/\text{dm}^3$); 2) subsequent treatment with sodium sulfide (consumption $230.4 \text{ cm}^3/\text{dm}^3$)							
Solution filtrate after treatment with sodium pyrosulfite	9.69	0.31	10.0	45.65	1.0	–	–
Solution filtrate after treatment with sodium sulfide*	–	–	0.56	5.57	0.095	82.6	<1

* other impurities, g/dm³: Te – 0.008; Fe – 0.009; Cu <0.0005; Sb<0.004; Sn <0.01; K – 0.24; Ca – 0.12; Mg – 0,07.

Based on the conducted studies, the following conclusions should be made:

1. processing of acidic As-containing solutions with the use of sulfide reagents provides the formation of sparingly soluble, low-toxic precipitate of arsenic sulfide, herewith the volume of solid waste is significantly low in comparison with other methods of arsenic removal from solutions;

2. to convert arsenic to an insoluble trisulfide form with sodium sulfide solution, preliminary reduction of pentavalent arsenic As(V) to trivalent state As(III) with sodium pyrosulfite solution is advisable;
3. the direction of further research is the arsenic removal in the form of trisulfide from alkaline As-containing solutions, including the assessment of the possibility of joint processing of alkaline and acidic solutions which contain arsenic.

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