

# Waste Management in the Process of Precipitation of Arsenic in the Form of Sulfide Cakes From Alkaline Sulfide Solutions

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## Abstract

One of the main problems in non-ferrous metals metallurgy is increase of arsenic content in the processed raw materials and correspondingly in production by-products. Today, there are many ways for processing arsenic-bearing by-products [1-5]. One of the possible methods for selective removal of arsenic from non-ferrous metals production circuits is leaching in alkaline sulfide solution [6-8]. At this, it becomes possible to separate copper, zinc, lead and iron into lead-copper cake and to transfer arsenic into alkaline sulfide solution.

Alkaline sulfide leaching of arsenic-bearing materials with subsequent precipitation of arsenic in the form of sulfide cakes inevitably leads to the formation of significant amounts of sodium sulfate aqueous solutions. In the context of metallurgical productions, that work in closed circuit of internal water circulation, where water balance of the system is strictly monitored, it is of a high importance to deal with the issue of sodium sulfate aqueous solution accumulation.

In the present work results of the laboratory tests on precipitation of arsenic from alkaline sulfide solution into sulfide cake and regeneration of alkaline sulfide solution from product sodium sulfate aqueous solutions are given.

According to the results of the experimental works:

- Process indicators were compared for precipitation of arsenic from alkaline sulfide solution into arsenite-arsenate and sulfide cakes;
- Parameters were determined that allow for the highest recovery of arsenic into sulfide cake, at this over 98% of arsenic transfer to sulfide cake that contains 17.42 % As;
- Possible regeneration of sodium hydroxide and alkaline sulfide reagent from the product sodium sulfate aqueous solutions were studied;
- The possibility for regeneration of alkaline sulfide solution by reacting sodium sulfate aqueous solution produced during arsenic precipitation into sulfide cake with calcium polysulfide solution was proved and process parameters were provided.

**Keywords:** Arsenic-Bearing By-Products; Waste Management; Regeneration of Alkaline Sulfide Solution; Sodium Sulfate Solution

## Introduction

Development of the complex technology for processing arsenic-bearing by-products using alkaline sulfide leaching method required finding solution for the following main tasks: determination of optimal method for arsenic precipitation from alkaline sulfide solutions and regeneration of initial alkaline sulfide reagent.

Arsenic content in the solutions depend from the alkaline sulfide leaching process parameters. Compositions of arsenic-containing solutions used in the present work are given in Table 1.

Description	Content, g/dm <sup>3</sup>			
	As	Sb	S	Na
Solution 1	8.05	2.8	66.14	27.00
Solution 2	10.9	3.5	83.51	49.50

- Solution 1 – arsenic-containing alkaline sulfide solution used for precipitation of arsenic to arsenite-arsenate residue.
- Solution 2 – arsenic-containing alkaline sulfide solution used for precipitation of arsenic to sulfide residue.

**Table 1:** Compositions of arsenic-containing solutions

In order to determine the optimal method for arsenic precipitation from alkaline sulfide solutions, precipitation into arsenite-arsenate and sulfide cakes were studied and compared.

## Experimental Techniques

- Precipitation of arsenic to arsenite-arsenate cake. During the tests on precipitation of arsenic into arsenite-arsenate cake, solution 1 was used. Its composition is provided in Table 1. Calcium hydroxide slurry of a certain target concentration (200 g/dm<sup>3</sup>) is added at the ratio of 10 g CaO to 1 g As to arsenic-containing alkaline sulfide solution that was preliminarily heated to 90-95 °C. The slurry is constantly agitated during specified time, and upon completion of the test is filtered to filtrate and solid residue. The content of the controlled elements in solutions and solid residues was determined using chemical and physical-chemical methods: atomic absorption, spectral emission with inductively coupled plasma.
- Precipitation of arsenic into sulfide cake. During the tests on precipitation of arsenic into sulfide cake, solution 2 was used. Its composition is provided in Table 1. Sulfuric acid solution was added by 1-2 cm<sup>3</sup> portions into arsenic-containing alkaline sulfide solution with the initial temperature of 25 °C and pH 11.77 at constant agitation until pH of the solution reached 1.5-2. Upon completion of the test, the formed slurry is filtered to filtrate and solid residue. The content of the controlled elements in solutions and solid residues was determined using chemical and physical-chemical methods: atomic absorption, spectral emission with inductively coupled plasma.

## Comparison of the Methods for Precipitation of Arsenic from Arsenic-Containing Alkaline Sulfide Solutions into Arsenite-Arsenate and Sulfides Cakes

The test was conducted on precipitation of arsenic from arsenic-containing alkaline sulfide solution into arsenite-arsenate cake. According to the results of the tests:

- Recovery of arsenic into arsenite-arsenate cake is 62.68%, residual concentration of as in the final solution – 3.45 g/dm<sup>3</sup>.
- Arsenite-arsenate cake contains 3.4% as and 0.22% Sb. Moisture grade – 39.14%.
- Filtrate after arsenic precipitation contains 54.05 g/dm<sup>3</sup> of total sulfur and 0.5 g/dm<sup>3</sup> of sulfur in sulfate form i.e. sulfur in the filtrate is represented only in polysulfide and thiosulfate forms.

Thus, recovery of arsenic into solution comprised only 62.68%. At this, arsenic content in cake is 3.4% As. This shows unfeasibility of using the method of arsenic precipitation from alkaline sulfide solutions into arsenite-arsenate cake.

Therefore, further tests were conducted using alternative method for precipitation of arsenic into sulfide cake by adding sulfuric acid into arsenic-containing alkaline sulfide solution.

The process of arsenic precipitation into sulfide cake from alkaline sulfide solution is based on the following reaction equation:



The results of the tests conducted according to the above-described procedures are as follows:

- Recovery of arsenic into sulfide cake is over 98%, residual concentration of as in the filtrate – 0.03 g/dm<sup>3</sup>.
- Sulfide cake contains 17.42 % as and 5.84 % Sb. Moisture grade – 56.56%.
- Filtrate after arsenic precipitation contains 41.82 g/dm<sup>3</sup> of total sulfur and 33.91 g/dm<sup>3</sup> of sulfur in sulfate form i.e. around 80% of sulfur in the filtrate are represented by sulfate form.
- Precipitation of arsenic using sulfuric acid leads to the formation of hydrogen sulfide (reaction equation 1). Therefore, implementation of the technology in industrial scale will require fully sealed gas duct system: maximum allowable concentration of hydrogen sulfide in work place is 10 mg/m<sup>3</sup> [9].

Description	As content in filtrate, g/dm <sup>3</sup>	As content in residue, % (mass)	Recovery, %	Content of S (total)/S(sulfate) in filtrate, g/dm <sup>3</sup>
Precipitation into arsenite-arsenate cake	3.45	3.4	62.68	54.05/0.5
Precipitation into sulfide cake	17.42	0.03	98.00	41.82/33.91

**Table 2:** Comparison of the methods for precipitation of arsenic from arsenic-containing alkaline sulfide solutions into arsenite-arsenate and sulfide cakes

According to the test results, given in Table 2, precipitation of arsenic into sulfide cake allows for obtaining residue with higher arsenic grade at higher recovery rate of arsenic and lower final concentration in the filtrate. The disadvantage of the method is formation of significant amounts of sodium sulfate solutions that will have a negative impact on the water balance of the metallurgical productions that work in closed internal water recirculation loops.

## Conversion of Sodium Sulfate Solutions from the Arsenic Precipitation Process

The results of the analytical review of the methods for conversion of sodium sulfate solutions, produced during the process of arsenic precipitation, for further recycling to alkaline sulfide leaching of arsenic-bearing by-products showed three possible methods: obtaining sodium hydroxide by reacting sodium sulfate with calcium hydroxide [6], electro dialysis of sodium sulfate into sodium hydroxide and sulfuric acid [10] and production of alkaline sulfide reagent by reacting sodium sulfate with calcium polysulfide.

The process of sodium hydroxide regeneration from sodium sulfate solutions is based on the following reaction equation:



Laboratory scale tests were conducted on regeneration of sodium hydroxide by reacting sodium sulfate solutions with calcium hydroxide in stoichiometric ratio and double stoichiometry. The criteria for evaluation of the test were the residual concentration of sulfate ions in the filtrate. Test results showed that sodium hydroxide regeneration extent does not go above 10%. It is assumed to be due to the lower solubility product (Ks) of calcium hydroxide ( $6.5 \times 10^{-6}$ ) compared to solubility product of gypsum ( $4.93 \times 10^{-5}$ ) i.e. because of gypsum being more soluble compound than calcium hydroxide equilibrium of the systems shifts to the sodium sulfate formation side [11,12].

Conversion of sodium sulfate by electro dialysis method is based on the following reactions on electrode:



During bipolar membrane electro dialysis, under applied electric current cations of  $\text{Na}^+$  and anions of  $\text{SO}_4^{2-}$  move across the monopolar ion exchange membrane and react with  $\text{OH}^-$  and  $\text{H}^+$  ions forming correspondingly sodium hydroxide and sulfuric acid.

Regeneration process of alkaline sulfide reagent from sodium sulfate solutions is based on the following reaction equation:



Results of the process on regeneration of alkaline sulfide reagent by reacting sodium sulfate solution, obtained by precipitating arsenic into sulfide cake, with calcium polysulfide are given in Table 3.

Test	Molar ratio Ca: S(sulfate form)	Content of S(sulfate form), g/dm <sup>3</sup>	
		Initial	Final
1	1.25	33.91	10.2
2	2	33.91	2.56

**Table 3:** Regeneration of alkaline sulfide reagent by reacting sodium sulfate solution with calcium polysulfide ( $\tau = 1$  hour;  $t = 90-95$  OC; calcium polysulfide solution contains:  $C_{\text{Ca}} = 65$  g/dm<sup>3</sup>,  $C_{\text{s(total)}} = 130$  g/dm<sup>3</sup>)

According to the results of the tests, when regenerating alkaline sulfide reagent at molar ratio of Ca: S = 2, regenerated solution contains 2.56 g/dm<sup>3</sup> of residual sulfate sulfur. Chemical analysis also showed 71.4 g/dm<sup>3</sup> of total sulfur in the regenerated solution that is represented in sodium polysulfide and thiosulfate forms. In addition, it was determined that the residual content of arsenic in solution is fully precipitated into gypsum cake (content of as in cake is 0.03%), at this regenerated alkaline sulfide solution does not contain arsenic.

## Conclusion

Processes for precipitation of arsenic from arsenic-containing alkaline sulfide solution into arsenite-arsenate and sulfide cakes were studied. The two methods were compared based on the criteria of arsenic recovery into precipitate and residual content of arsenic in filtrate. It was determined that the method of arsenic precipitation into sulfide cake by reacting sodium sulfate solution with sulfuric acid allows for recovering 98% of arsenic into precipitate, at this filtrate contains less than 0.03 g/dm<sup>3</sup> of arsenic. The disadvantage of the method is in obtaining sodium sulfate solutions that are undesirable when operating metallurgical productions with closed internal water circulation loop. Analytical review of the methods for conversion of sodium sulfate solution to sodium hydroxide or alkaline sulfide reagent was done in order to recycle regenerated solution back to the alkaline sulfide leaching of arsenic-bearing by-products. The possibility for regeneration of alkaline sulfide reagent by reacting sodium sulfate solution, produced during arsenic precipitation into sulfide cake, with calcium polysulfide solution was determined and process parameters provided.

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