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DISTRIBUTION OF ARSINE IN THE PROCESS OF COPPER CEMENTATION

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ABSTRACT: The paper presents results of the of arsine distribution in the process of cementation of copper from the underground mining water and waste metallurgical solutions and the possibility of appearance of toxic gas arsine. Investigations were conducted on synthetic solutions similar to the solutions used in copper cementation. It was found that the more rigorous conditions than the limit (the acidity of water at the entrance to the cementation plant of pH = 1.5 and arsenic content of 1 g/dm³) arsine does not separated from the processes of cementation. Investigations have been showed that there no conditions for toxic arsine emissions into the atmosphere, during the copper cementation from underground mine water and waste solution. Investigation is necessary to be continued for determining maximal content of arsenic and acidity of cementation solution, which should not be exceed, with aim to prevent arsine emissions into the atmosphere. In the same time it was explained, that presence of arsenic in the cement-copper is a result of arsenic ions cementation on iron scrap.

KEYWORDS: copper cementation, arsenic, underground mining water

INTRODUCTION

Based on theoretical and experimental data [1,2], it should be expected the release of the arsine in the cementation process of copper from underground mining waters and metallurgical waste solution and waste waters, for the defined boundary conditions. Starting from this conclusion, it was laboratory investigated possibility of extraction arsenic paired solution from plant for copper-sulfate; underground mining water and prepared solution with the desired acidity and arsenic content. Next phases of work were investigated:

- Change the content of arsenic in water cementation with decreasing acidity.
- Release arsenic for these boundary conditions cementation.
- Cementation of arsenic on the iron scrap.

CHANGES OF ARSENIC CONTENT IN CEMENTATION WATER - Characteristics of water for cementation

Department of cementation in the service mining shaft processed underground mining water in a quantity of 130 m³/h, with the content (g/dm³): Cu = 0.1-0.2; As = 0.001; Fe = 0.2; pH = 2.9-3.1 and metallurgy waste solution in a quantity of 1.5 m³/h, with copper and harmful content of impurities (g/dm³): Cu = 1.0-4.5; H₂SO₄ = 20-35; As = 0.01-0.07. Those results are obtained by measuring flow rate by Thomson's spillway at the entrance to cementation. Waters are mixed and put in the process with acidity pH = 2.3-2.6 and the arsenic content of 0.002 g/dm³. The maximum arsenic content in the entrance at the cementation is 0.004 g/dm³ and it can be achieved when the arsenic content in the waste solution electrolysis reached a value of 0.2 g/dm³.

Change the content of arsenic in arsenic salt solution - Usage of sodium-arsenate solutions

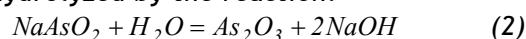
For experimental work synthetic arsenic solution has been prepared. For the preparation of 0.25dm³ aqueous sodium, C_{As} = 2.0g/dm³ As, 0.66g As₂O₃ is used. Arsenic trioxide was dissolved in water in the presence of 0.40g NaOH at temperature of 50°C, by the reactions:



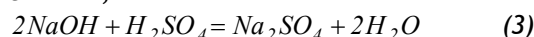
By this way aqueous solution of sodium arsenic concentrations 2 g/dm³ As was prepared. It was used as the initial solution for laboratory experiments.

Change the content of arsenic in solution with decreasing acidity

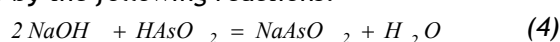
Sodium-arsenate, with the concentration of As 2.0g/dm³, was used for getting solution with a concentration of arsenic of 0.50g/dm³. The initial alkalinity of pH = 9.8 was reduced to pH = 2, with the addition of sulfuric acid solution. Sodium arsenate hydrolyzed by the reaction:



Reaction (2) is dependent on the pH of the solution, and the reaction of the arsenic acid is followed by the release of OH ions, which are neutralized:



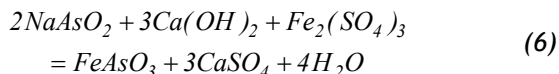
But for the acidity and concentration of Arsenic in the solution, arsenic acid is stable and As₂O₃ does not precipitate. Acidity of the resulting solution is then reduced by addition of sodium-hydroxide solution in the first stage to pH = 4.5 and in the second stage to pH = 7.5 by the following reactions:



In both cases a hydrolytic precipitate does not existed.

Change the content of arsenic in solution with increasing Ferro ion concentration

By the addition of sulfuric acid, pH of the solution is reduced to 2.5, which is the acidity of input waters in copper cementation plant. Decopperised water from cementation was added to the solution and acidity was adjusted to pH = 3.5. Solution with 0.125 g/dm³ As was obtained. Arsenic compounds were not precipitated. With addition of Ca(OH)₂ at the same time with Fe₂(SO₄)₃ pH is adjusted to 9.8. The content of arsenic after neutralization was 3.0mg/dm³. Arsenic from synthetic solutions is precipitated by the following reactions:



Arsine extraction in cementation of copper

Boundary conditions for arsine release are defined in the works related to the cementation of copper underground mining water (to which is added waste electrolysis solutions) [3,4]. The first boundary condition refers to the minimum acidity of the solution at the entrance of cementation which is pH = 1.5, for the existing content of arsenic in water with copper. The other condition is the maximum allowed concentration of arsenic of 1 g/dm³ for the acidity of water with copper about pH=2.3-2.6, at the entrance to cementation.

In the aim to check these settings, in laboratory conditions, cementation of copper from the copper solution experiments were performed. The realization of these experimental three samples was used. Table 1 shows the list of these samples. The content of released arsine in cementation products, for each tested sample, is shown in Table 2.

Table 1. The tested copper solutions

Sample	pH	C _{As} (g/dm ³)	C _{Cu} (g/dm ³)
Underground mining water with sulfuric acid	1.4	0.02	0.2
Underground mining water with arsenic	2.4	1.14	0.2
Solution from CuSO ₄ production plant	3.0	1.12	25

Table 2. Results released arsenic

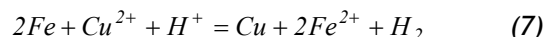
Sample	C _{As} (g/dm ³) in sample	Release of arsenic (quantitatively)
Underground mining water with sulfuric acid	0.02	-
Underground mining water with arsenic	1.14	-
Solution from CuSO ₄ production plant	1.12	+

In the first experiment, a prepared sample of water from mining had 0.02 g/dm³ As, and acidity of pH=1.4, in the cementation with an iron plate, arsine was not detected.

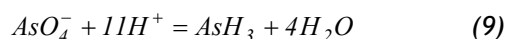
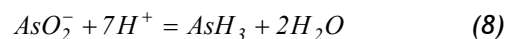
In the second experiment sample was prepared with 1.14g/dm³ As, acidity was pH = 2.4, and in the process of cementation arsine also was not detected. In the third experiment the original vaporized electrolyte from the copper sulphate production

plant with 300 g/dm³ H₂SO₄, 25 g/dm³ Cu and 12 g/dm³ As, in the cementation with iron staple, arsine was detected.

Copper cementation reaction is represented by the chemical reaction:



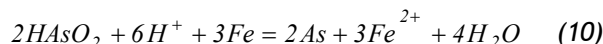
Reactions of arsine release reactions are presented by the chemical reaction:



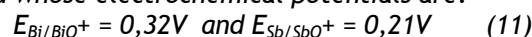
Elementary hydrogen that is released in the cementation has reductive properties, so that ions with AsO₂⁻ and AsO₄⁻ in contact with it realize arsine (5). Results of the analyze are presented in Table 2.

Cementation of arsenic from the solution

The solution prepared from 0.5 g/dm³ As acidity and pH = 5, cementation of arsenic was performed with iron staple. The relatively low acidity of the solution was taken for favoring arsenic cementation. After one hour of process, the acidity of the solution is slightly reduced at pH = 5.5 and the content of arsenic in solution to 0.34 g/dm³. On this basis, it may be adopted that the cementation caused by the reaction of arsenic:



This reduction is thermodynamically possible because in this case (as in the case of copper) electrochemical potential of the iron E_{Fe/Fe2+} = -0.41V, is more negative than of arsenic, which is E_{As/AsO+} = +0.25V. Similar reactions can be expected in the case of bismuth and antimony, whose ions are also present in copper water, and whose electrochemical potentials are:



CONCLUSIONS

This research has shown that there are no conditions for the release of toxic arsenic in operation of copper cementation from mining waste waters and the electrolysis solution. However, further research is needed to determine maximum allowed content of arsenic in water and its acidity, which should not be exceeded in order to prevent the occurrence arsine emission. At the same time it was explained that the presence of arsenic in cement slurries is the consequence of arsenic ions cementation on the iron staple.

ACKNOWLEDGMENT

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