

# Arsenic solubility, mobility and speciation in the deposits from a copper production waste storage

N. Lihareva

*Bulgarian Academy of Sciences, Central Laboratory of Mineralogy and Crystallography Acad.G. Bonchev Str. bl.107 1113 Sofia, Bulgaria*

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## Abstract

The sediments in large pond for discharge of waste products of metallurgical activity were studied with respect to the valence forms of arsenic and its mobility. A sequential extraction procedure for arsenic compounds was applied and optimized according to the nature of analyzed products. During the first stage, the content of water-soluble arsenic compounds was determined, during the second—HCl-soluble forms and during the third—compounds soluble in sodium hydroxide. The optimum conditions for leaching arsenic from sediments (sample weight, concentration and volume of extractants, time of treatment) were established for each fraction.

Speciation studies for determining As(III) and As(V) were carried out in the obtained arsenic extracts. The ability of the proposed sequential extraction procedure to specify the valence forms of inorganic arsenic was evaluated using model samples with added As(III) and As(V) and the recovery of spikes has been assessed. It was found that oxidation of As(III) and processes of sorption and sedimentation of As(V) proceed upon dissolution. A depth profiling was performed of the content of diverse forms of As in two sites. The content of water-soluble As does not exceed 7.4% of total As in the sediments, As(III) being lower than 7.4% of that of the extracted As. The bulk of arsenic compounds (above 78% As) is dissolved in 2M HCl, and As(V) was found to be more than 94% of extracted arsenic. The analytical features of the procedure are as follow: precision, evaluated through the repeatability  $w > 0.96$  and accuracy, estimated by the recovery above 93%, calculated on the basis of a twice repeated analysis of a series of 9 samples.

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## 1. Introduction

The presence of toxic metals in sediments, soils and sludge samples is an environmental problem resulting from the possibility of their transfer into aquatic media and absorption by vegetation. This holds especially for regions of metallurgic activity, in which there are ponds for storage of waste matter from ore processing. To determine the potential toxicity of such materials under real environmental conditions, the methods of sequential extraction procedure (SEP) are used, when particular phases are selectively affected using reagents with an increasing dissolving possibility. This makes it possible to determine the manner

of attachment of toxic elements contained in different phases or chemical compounds [1–6].

Separation of different chemical phases is by no means an easy task and the results obtained using SEP are operationally defined. In spite of such limitations, these methods are a tool for obtaining important information on the metal fractionation in soils and sediments. There exist a lot of SEPs and single extractions, the majority of which are variations of the method, developed by Tessier [1].

In order to generalize and harmonize the various methods used, the European Community's Bureau of References has proposed a method [2], which gives the possibility to compare the experimental results.

Concerning environmental pollutants, arsenic is one of the elements recognized as a powerful toxic substance suggested to be a human carcinogen [7]. Dissolved As may be absorbed by vegetation and in this way to enter the food

*E-mail address:* [nlihareva@abv.bg](mailto:nlihareva@abv.bg).

chain of humans. Arsenic is detected at a level of several hundred micrograms per liter in ground waters under the contaminated uppermost soil layer [8]. On the other hand, arsenic can be found in various chemical forms, differing in their toxicity. The main species of inorganic arsenic, arsenite and arsenate, are the most toxic ones (the LD50 value for As(III) and As(V) are 14 and 20 mg/kg, respectively [9]). That is why the determination of the total arsenic concentration does not provide enough information for evaluating the environmental risks or for developing remediation strategies. Speciation of arsenic forms is necessary, and can be realized using various methods. Extraction methods are based on different properties of the compounds of As(III) and As(V) with acids or complex-forming reagents. After the separation, spectral photometric methods of determination are applied [10]. Speciation of arsenic forms is frequently achieved by sensitive and selective chromatographic methods, such as GC, HPLC, IC with detection by AAS, ICP-MS, ICP-AES [11,12].

The problem to be taken into account during samples treatment and separation of different phases or chemical compounds; is the possibility for changing the arsenic valence. This is a general problem when using such methods because of the reactions' complexity and their, in many cases, unknown kinetic under real conditions [13]. That is why the selection of an appropriate method for fractionation is defined not only by the matrix, but also by the subsequent speciation scheme in order to minimize the possible changes in oxidation state.

The content of arsenic in copper ores is a problem from the viewpoint of its elimination during the ore processing and production of copper, as well as in storing wastes from the metallurgical activities. The copper and gold deposit "Chelopech" is known to be rich in arsenic (up to about 4%), which is included either as intrinsic minerals, associated with ore minerals or in high amounts in ore minerals. Metallurgical activity in this region has been carried out since a long time. The area around is highly polluted and includes a large pond for collecting the wastes [14]. They are products from the treatment of acidic wastewaters by lime milk ( $\text{pH} > 12$ ). The solid phase of the obtained pulp is a complex mixture of different calcium compounds—gypsum, calcium arsenates and calcium arsenites, iron-containing arsenic compounds, oxides, hydroxides and carbonates of heavy metals. This pulp is transferred to discharge pond, where after a time, the solid particles settle and fill the pond. The clarified water is periodically ejected via a canal into rivers. In order to decide some technological and ecological aspects of the pond, it was necessary to determine its physical and chemical parameters and to propose a consideration on the base of scientific data [14]. In the autumn of 1999, a drill probing was performed of sediments and collected samples were analyzed chemically. A total of 225 samples were collected for investigating and characterizing the distribution of heavy metals and arsenic in depth and horizontal profiles of pond sediments.

The present paper is part of this project, concerned with arsenic. Our main purpose was to develop an adequate sequential extraction procedure for studying the arsenic bound to the solid phase fractions, taking into account the nature of deposits. As a second aim, keeping in mind the toxicity of arsenites and arsenates, we intended to specify the content of As(III) and As(V) in arsenic-containing extracts. Thus, one can obtain information on the potential mobilization of As and to assess the environmental risk.

Many research articles [12,15–19] have dealt with the design, study and application of schemes for solubilization of arsenic, bound to specific phases in contaminated sediments and soils. The determination of arsenic in soils heavily contaminated by metallurgical or other industrial activity is considered in [12,15]. Tests with a wide variety of extractants, aiming at the study of their extraction efficiency for As and their selectivity and specificity for target phases in soils have been reported in [16,17].

The solubility of arsenic species at various pH for analyzing industrial products, is described in [18]. A detailed review of the recent publications concerning arsenic speciation is given in [11,12].

The applicability of the sequential extraction procedures, commonly used for As fractioning, has been tested by Gruebel [19] using pure minerals and their mixtures. They have found that, in dissolving mineral phases, corresponding to reductive and oxidative dissolution stages, one observes a strong re-absorption onto other phases and subsequent desorption of As in the next extraction step.

Owing to the specificity of the samples analyzed (wastes from metallurgical processing after additional chemical treatment), we chose to test the procedure described in [20]. It concerns the determination of As in ores and products of their processing—polymetallic ores, dusts from oxidation roasting and melting.

We optimized the parameters of the different stages, namely duration of treatment, temperature and extraction volume. Obtained results include information on the potential mobility of As in products and its valence forms. That makes possible to evaluate the potential environmental risk.

## 2. Materials and methods

### 2.1. Reagents

The solutions of all reagents were prepared using distilled water. The stock standard solution of As(III) (1000 mg/l) was prepared by dissolving 1.320 g of arsenic trioxide (Riedel-de-Haen, Germany) in 20 ml of 2 mol/l solution of NaOH, then diluting with water and acidifying with HCl. The volume was adjusted to 1 l in a volumetric flask. For preparing As(V) solution (1000 mg/l), 4.16 g  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Aldrich) were dissolved in water and diluted to 1 l. Standard solutions of other elements,

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