

Field methodology for the stabilization of arsenic species in AMD

Sarmiento Aguasanta⁽¹⁾, Sánchez-Rodas Daniel⁽²⁾, Oliveira Vanesa⁽²⁾, Nieto José Miguel⁽¹⁾ & Gómez-Ariza José Luis⁽²⁾

⁽¹⁾Department of Geology, University of Huelva, Campus "El Carmen", E-21071, Huelva, Spain.

E-mail address: aguasanta.miguel@dgeo.uhu.es

⁽²⁾Department of Chemistry and Material Sciences, University of Huelva, Campus "El Carmen", E-21071, Huelva, Spain.

Keywords: arsenic speciation, preservation, mine waste, cationic exchange.

ABSTRACT

The Iberian Pyrite Belt (IPB) is one of the largest metallogenic provinces of volcanic-hosted massive sulphide deposits in the world. The oxidative dissolution of these sulphides releases to the Odiel and Tinto rivers (Southwest Spain), acidic water characterized by elevated concentration of sulphates, metals and metalloids. From these metals and metalloids, arsenic is probably one of the most toxic. In the Odiel river arsenic is found mainly as arsenite and arsenate but the mobility of these species is influenced by the Fe species. In this type of waters the iron is in elevated amounts, for the most part as Fe(III), so the stabilization of arsenic species is especially necessary. In this work, several reagents were evaluated for sample stabilizing such as EDTA, hydrochloric acid, and acetic acid. A cation-exchange resin was used too. Clean and brown vials and different storage temperatures were used to evaluate the effects of photochemical reactions. Arsenic species were analysed by mean of HPLC-HG-AFS. From the obtained results, we describe a new technique for the stabilization of arsenic species in AMD.

INTRODUCTION

Arsenic is one of the most important inorganic pollutants of the aquatic system. The behaviour of As in natural waters is well known. Depending on pH and redox conditions, As forms oxyanions of the oxidation states +III and +V. Biological processes may also produce methylated As (Shorin *et al.*, 1997). As(III) and As(V) represent the main species usually found in natural waters, As(III) being more toxic than As(V).

Acid Mine Drainage (AMD) represents a form of water pollution characterised by high acidity and high metallic and sulphate content that originates in mining areas containing sulphide ores. The arsenic comes from the oxidation of As sulphides like arsenopyrite and As-rich pyrite. These minerals can be oxidized by O₂ and Fe³⁺. The rate of arsenopyrite oxidation by Fe(III) is about 10 times faster than the rate of pyrite oxidation by O₂ (Rimstidt *et al.*, 1994). The overall reaction of arsenopyrite oxidation with O₂ as electron acceptor is expressed as:

$$\text{FeAsS} + 3.5 \text{O}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + \text{H}_3\text{AsO}_4^0 + 2\text{H}^+ + \text{SO}_4^- \quad (1)$$

The preservation of the distribution of As species in water samples is a difficult task, as the sample matrix can produce quick changes in the oxidation states. Redox conditions and the availability of possible carrier phases determines both the mobility and toxicity of As. It has been shown that Fe(III)-oxyhydroxides are a main carrier phase of sorbed As and play an important role in the diagenetic cycle at the sediment water interface. In acidic oxidizing environments, arsenate or As(+V) is present in the form of H₂AsO₄⁻. In reducing environments, arsenite in the form of H₃AsO₃⁰ is present at pH values less than 9.2. The ionized form of As(+III), H₂AsO₃⁻, occurs only at pH >9.2. Adsorption affinity is higher for As(V) at lower pH values and for As(III) at higher pH values (Stollenwerk & Coleman, 2003). There is generally a period (<5 min) of initial rapid adsorption followed by continued uptake for at least 8 days because As diffuses to adsorption sites on Fe(OH)₃ surfaces (Fuller *et al.*, 1993). When pH increases, As is desorbed from Fe(OH)₃, and the rate of desorption for As(+V) can be quite high. Other potential adsorbents of As include Al oxides and hydroxides, Mn oxides and clay minerals (Stollenwerk & Coleman, 2003). The AMD represents a potential source of contamination for the superficial water courses that receive it. This is the case of the Odiel river, in the province of Huelva (SW Spain), which crosses on its upper course the Iberian Pyrite Belt, one of the most important metallogenic regions in the world (Ollás *et al.*, 2004). The AMD originated by mining activity represents a pollutant load for this river of at least 50 tonnes/day of metals, along its course to its estuary (Sarmiento *et al.*, 2004).

The literature reports the capability of the organic matter both to oxidise As (III) to As(V) and to reduce As(V) to As(III), even after sample filtration (Hug *et al.*, 2001). The most common approaches to preserve the As species include the addition of acidic solutions of HCl, HNO₃, H₂SO₄, H₃PO₄, nitriloacetic acid, ascorbic acid (Gabarino *et al.*, 2002; USEPA, 2001) and complexing agents (EDTA) (Huang & Ilgen 2004) in combination with temperature control (room temperature or refrigerated).

In this work, a new preservation method for arsenic speciation in AMD samples has been studied. It is based on the acidification of the sample and *in situ* cleanup using a cationic exchange resin. We have investigated the influence of several parameters on the arsenic species stability, in a period of time from a few hours to one week, such as the material of the sample containers (opaque brown or filmy clear bottles), the temperature (ambient and refrigerated), and the addition of reagents (acids, EDTA).

The study area is located in the Cueva de la Mora Mine, within the so called Iberian Pyrite Belt, a volcanogenic massive sulphide province in exploitation since pre-historical times (Sáez *et al.*, 1999). For this study, samples of

AMD were taken from a leaching that drains out of one of several shafts connected to underground galleries of the old mine.

METHODOLOGY

Two sampling campaigns were undertaken in July and October of 2004. In all of them pH, electrical conductivity, and redox potential were measured *in situ*. The pH was measured using a portable MX 300 measurer (Mettler Toledo). The redox potential was also measured in the field using a HANNA measurer with Pt and Ag/AgCl electrodes (Crison). In each campaign, 250 mL portions of the leaching were filtered in the field using 0.2 µm pore size filters, and divided into several smaller samples for the different preservation methods tested. In the lab, the arsenic speciation analysis of the samples was undertaken by HPLC-HG-AFS. In order to study the samples stability between collection and analysis, the samples were analysed at time intervals of three hours during the first 12 hours, then hereafter at 24, 48 hours and one week.

The preservation of the arsenic species was also studied as a function of the recipient used, the preservation temperature, and the chemical reagents added. Initially, 50 mL opaque brown and clear bottles were used. After collection, the temperature of the samples was maintained either at 4 °C or maintained at ambient temperature. When samples were preserved with EDTA, the standard procedure was to add 2 mL of a 0.25 mol/L EDTA solution to 20 mL of filtered sample. Two acidification procedures for preservation were tested: 60 µL of 6 mol/L HCl or 200 µL of 8.7 mol/L AcOH were added to 20 mL of filtered sample. Ion exchange cleanup of the samples was also tried to remove metallic cations in the samples: 30 mL aliquots of filtered sample (not acidified or acidified with HCl 6 mol/L) were eluted at a flow rate of ca. 2 mL/min through a 10 g cationic exchange resin placed in a glass column (25 cm height, 1.5 cm width). After elution of the first 10 mL of sample, the remaining 20 mL were collected.

RESULTS AND DISCUSSION

The physiochemical parameters are shown in Table 1. In both campaigns the pH was similar. The high dissolved metallic content of the samples is related to the high conductivity measured in both of them. Sarmiento *et al.* (2005) determined up to 455 µg/L of As and 307 mg/L of Fe in this effluent, ca. a 90% of the Fe being present as Fe (III). Concentration of other metals has also been measured: 99.5 mg/L Al, 4.5 mg/L Cu, 24 mg/L Mn, 97.5 mg/L SiO₂, 399.6 mg/L Zn and 4117 mg/L of sulphate.

In July of 2004, six samples were taken and filtered. 0.25 mol/L EDTA was added to four of them and collected in brown bottles or clear bottles. Some samples were stored at ambient temperature and others were refrigerated.

Table 1. Physiochemical parameters of the leaching in both campaigns

Campaign	pH	Eh (mV)	E.C. (mS/cm)
July-04	3.30	390	4.8
October-04	3.34	368	4.0

The two remaining samples were also filtered, but instead of adding EDTA, the metallic content was eliminated *in situ* by cleanup using glass columns filled with a cationic exchange resin and collected in a brown bottle and a clear bottle respectively. Both were refrigerated. The results corresponding to arsenic speciation analysis of this first campaign are shown in Figure 1.

It can be observed, for the samples whit added EDTA, that if we compare them under the same conditions of temperature (Figure 1a and 1b at ambient temperature, Figure 1c and 1d refrigerated) the material of the container does not affect the results. In this case, the brown bottles were preferred to the clear ones for further sampling campaigns, as the literature recommends to avoid light that may cause undesirable photochemical reactions (McCleskey *et al.*, 2004).

The results corresponding to preservation experiences with EDTA at ambient temperature (Figure 1a and 1b) were not satisfactory. They show that the concentration of As(III) decreased continuously during the whole experience (brown bottle) or remained fairly constant (clear bottle), but in both cases the concentration of As(V) increased quickly. The use of refrigeration in combination with EDTA (Figure 1c and 1d) did not improve the preservation. The As(III) concentration did not showed great changes during the first two days, but the As(V) concentration increased with time in both experiences.

A certain amount of trivalent iron may be also present within mineral colloids (Olivie-Lauquet *et al.*, 1999; Dupré *et al.*, 1999). The increment in the As(V) in these samples may be due to adsorption/desorption processes of this specie on the Fe oxyhydroxide colloids present in the filtered samples, onto which arsenate easily bounds (Zänker *et al.*, 2002; Stollenwerk & Coleman, 2003). We can conclude from the results with EDTA that the samples seem not to be stable for more than a few hours. These results are in apparent contradiction with other studies in which the AMD samples treated with EDTA were stable for 3 months (Bednar *et al.*, 2002). This could be explained considering that the AMD samples of our study are characterized by the fact that high concentration of Fe (hundreds of mg/L) is present mainly (ca. a 90%) as Fe(III) (Sarmiento *et al.*, 2005), thus representing a serious source for alteration of the distribution of arsenic species due to redox reaction and co-adsorption on the Fe oxyhydroxides. This situation is not common in AMD samples from other mining areas where the Fe content is usually very low, and mainly as Fe(II), and samples are analysed within the first 24 h. without any chemical treatment (Cassiot *et al.*, 2003).

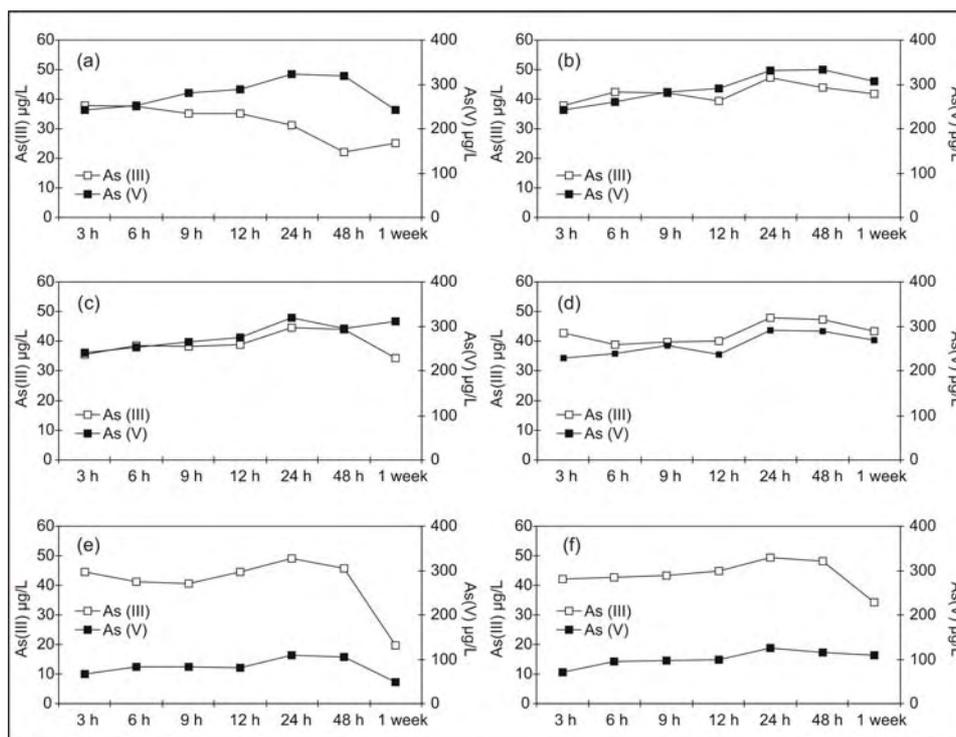


Figure 1. Speciation of arsenic in AMD samples of the first sampling campaign (July 2004). (a) EDTA added, brown container, ambient temperature, no resin clean up. (b) EDTA added, clear container, ambient temperature, no resin clean up. (c) EDTA added, brown container, refrigerated, no resin clean up. (d) EDTA added, clear container, refrigerated, no resin clean up. (e) No EDTA added, brown container, refrigerated, resin clean up. (f) No EDTA added, clear container, refrigerated, resin clean up.

In order to eliminate *in situ* the Fe interference, a cationic exchange resin (Amberlite IR-120) was used. This resin retains the metallic cations species, but not the arsenic ones (arsenate is negatively charged, whereas arsenate is neutral at a pH of 3.3). This resin has been previously reported for the reduction of the metallic content in water samples (Sánchez-Rodas *et al.*, 2005). It can be seen in Figure 1e and 1f that the As(III) concentration was similar to the values found in the samples treated with EDTA, but the As(V) was partially retained in the column, as the As(V) concentration found since the first analysis was very low in comparison to the estimated mean. This is most probably due to the retention of As(V) on the Fe oxyhydroxide colloids. Apparently, the cationic resin would be able to retain or co-adsorb colloids and Fe precipitates because these have a superficial positive charge at low pH.

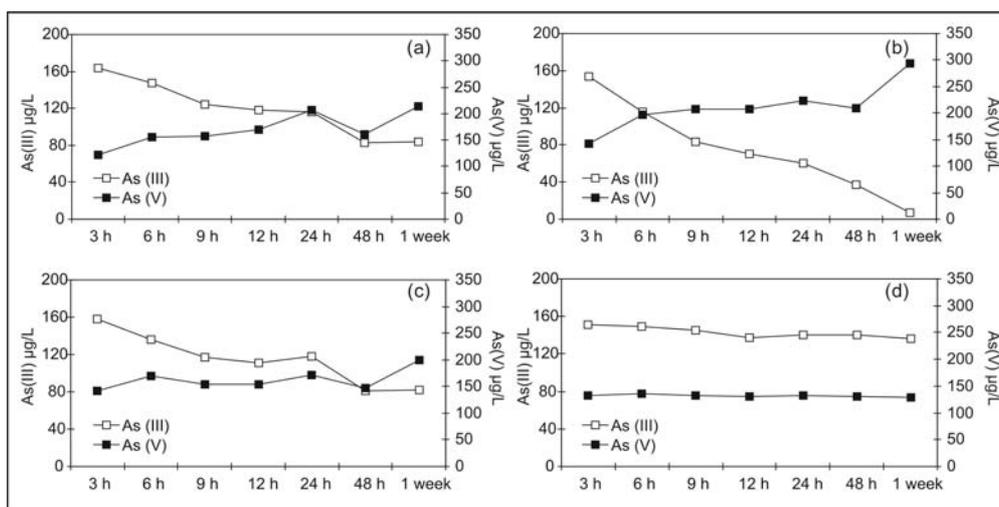


Figure 2. Speciation of arsenic in AMD samples of the second sampling campaign (October 2004). (a) EDTA added, brown container, refrigerated, no resin clean up. (b) EDTA and Hydrochloric acid added, brown container, refrigerated, no resin clean up. (c) EDTA and Acetic acid added, brown container, refrigerated, no resin clean up. (d) No EDTA added, brown container, refrigerated, Hydrochloric acid added and resin clean up.

In the second sampling campaign (October 2004), a new sample preservation strategy was tested in order to try to eliminate the colloids interferences. It was based on the acidification of the samples before the resin clean up. HCl was chosen for acidification (USEPA, 2001). AcOH was also tried, as it has been described to prevent iron-arsenic coprecipitation (Gallagher et al., 2004). A sample not acidified and with EDTA 0.25 mol/L, as in the first campaign, was also taken for comparison. All samples were taken in opaque brown containers and refrigerated. The results corresponding to the arsenic speciation analysis are summarized in Figure 2.

The sample with EDTA 0.25 mol/L (Figure 2a), showed the same trend as in the first campaign: a diminution of the As(III) concentration, and an increase of As(V) with time. When samples are acidified with HCl and EDTA is added (Figure 2b), the results are even worse; the oxidation of As(III) is faster. Also, As(V) concentration in solution increased at a higher rate. The acidification of the samples with HCl lowered the pH, thus reducing the capability of the EDTA to preserve the sample, as the complexing capacity of EDTA with metals is pH dependent. If HCl is replaced by acetic acid (Figure 2c), no improvement is obtained, which is not surprising, as the pH of the samples is already below the acidity that can provide AcOH, a weak acid. From the results of this set of samples, we can conclude that a high EDTA concentration helps to stabilize the arsenic species in AMD samples, although it is not enough for short preservation times of a few hours.

Sample of Figure 2d was first acidified with HCl and then passed through the resin. The results were satisfactory both for As(III) and As(V) for at least 48 h. After 1 week, a small loss in the As(III) was found. This is the best result obtained in this work, and it is due to the fact that Fe(III) precipitation is inhibited at low pH (Parnell, Jr. R. A. et al., 1983) and colloids redissolution is possible.

CONCLUSIONS

In this study, different methodologies for the arsenic species preservation in acid mine drainage samples were carried out. Different containers, temperatures, acids and cationic exchange resin were used for preserving the samples until the analysis. The best result was obtained with a method consisting in filtration of the samples to 0.2 µm pore size, acidification with HCl, and *in situ* cleanup with a cationic exchange resin. The use of opaque containers and refrigeration is necessary. This method will allow the sample preservation for As speciation for at least 48 h.

ACKNOWLEDGEMENTS

This study has been financed by the Spanish Ministry of Education and Science through project REN2003-09590-C04-03.

REFERENCES

- Bednar, A.J. et al., 2002. Preserving the distribution of inorganic arsenic species in groundwater and acid mine drainage samples. *Environmental Science and Technology*, Vol. 36, 2213-2218.
- Cassiot, C. et al., 2003. Geochemical processes controlling the formation of As-rich waters within a tailings impoundment (Canoulès, France). *Aquatic Geochemistry*, Vol. 9, 273-290.
- Dupré, B. et al., 1999. Major and traces elements associated with colloids in organic-rich river waters: ultrafiltration of natural and spiked solution. *Chemical Geology*, Vol. 160, 63-80.
- Fuller, C.C. et al., 1993. Surface chemistry of ferrihydrite: part 2. Kinetics of arsenate adsorption and coprecipitation. *Geochimica et Cosmochimica Acta*, Vol. 57, 2271-2282.
- Gallagher, P.A. et al., 2004. Preservation of As(III) and As(V) in drinking water supply samples from across the United States using EDTA and acetic acid as a means of minimizing iron-arsenic coprecipitation. *Environmental Science and Technology*, Vol. 38, 2919-2927.
- Huang, J.H. & Ilgen, G. 2004. Blank values, adsorption, pre-concentration, and sample preservation for arsenic speciation of environmental water samples. *Analytica Chimica Acta*, Vol. 512, 1-10.
- Hug, S.J. et al., 2001. Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environmental Science and Technology*, Vol. 35, 2114-2121.
- McCleskey, R.B. et al., 2004. Preservation of water samples for arsenic (III/IV) determinations: an evaluation of the literature and new analytical results. *Applied Geochemistry*, Vol. 19, 995-1009.
- Olías, M. et al., 2004. Seasonal water quality variations in a river affected by acid mine drainage: The Odiel river (south west Spain). *Science of the Total Environment*, Vol. 333, 267-281.
- Olivie-Lauquet, G. et al., 1999. Chemical Distribution of Trivalent Iron in Riverine Material from a Tropical Ecosystem: A Quantitative EPR Study. *Water Research*, Vol. 33(11), 2726-2734.
- Parnell, Jr. R. A. et al., 1983. Weathering processes and pickeringite formation in a sulfidic schist: a consideration in acid precipitation neutralization studies. *Environmental Geology*, Vol. 4, 209-215.
- Rimstidt, J.D. et al., 1994. Rates of reaction of galena, sphalerite, chalcopyrite and arsenopyrite, with Fe(III) in acidic solution. In: *Environmental Geochemistry of Sulfide Oxidation*, 2-13.
- Sáez, R. et al., 1999. The Iberian type of volcano-sedimentary massive sulphide deposits. *Mineralium Deposita*, Vol. 34, 549-570.
- Sánchez-Rodas, D. et al., 2005. Arsenic speciation in river and estuarine waters from southwest Spain. *Science of the Total Environment*, Vol. 345, 207-217.

Sarmiento, A.M. *et al.*, 2004. The contaminant load transported by the river Odiel to the Gulf of Cádiz (SW Spain). *Applied Earth Science*, Vol. 113(2), 117-122.

Sarmiento, A.M. *et al.*, 2005. Variación estacional en la especiación y movilidad de Fe y As en aguas afectadas por Drenaje Ácidos de Mina en la cuenca del río Odiel (Huelva). *Geogaceta*, Vol. 37, 115-118.

Shorin, Y. *et al.*, 1997. Arsenic biogeochemistry affected by eutrophication in lake Niwa, Japan. *Environmental Science and Technology*, Vol. 31, 2712-2720.

Stollenwerk, K.G. & Coleman, J.A., 2003. Natural remediation potential of arsenic-contaminated ground water. In: *Arsenic in Ground Water: Geochemistry and Occurrence*, Boston, 351–379.

U.S. Environmental Protection Agency, 2001, Method 1632.

Zänker, H. *et al.*, 2002. The colloid chemistry of acid rock drainage solution from an abandoned Zn-Pb-Ag mine. *Applied Geochemistry*, Vol. 17, 633-648.