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## **OPERATIONAL FRACTIONATION OF ARSENIC IN A MINING SOIL**

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## OPERATIONAL FRACTIONATION OF ARSENIC IN A MINING SOIL

### ABSTRACT

The environmental assessment of historical mining sites contaminated with various inorganic species, as also the determination of remediation targets require a better knowledge of pollutant-bearing phases. The objective of this paper was to investigate the operational fractionation of arsenic (As) in an As contaminated (ca. 3 wt%) soil collected from a gold mining site in France, where mining activities and smelting processes of gold ores took place until 2004.

Single and sequential chemical extraction procedures were performed to evaluate the potential mobility of As according to the fractions to which it was associated in the contaminated soil, and also the part of As sorbed onto soil particles.

These procedures used provided information on the nature of arsenic fixation processes in the mining soil studied. Results showed that As appeared mainly sorbed (ca. 72%) with iron on the soil particles, in particular amorphous iron oxyhydroxides. These results confirmed a potential risk of arsenic mobilization under acidic and/or reducing conditions, which frequently occur in mining environment.

This research evidenced the importance of the knowledge of As-bearing phases to better predict the mobility of this pollutant and in turn improve the management of arsenic contaminated sites.

### KEYWORDS

Arsenic, Mining Soil, Bearing Phases, Fractionation

### INTRODUCTION

Arsenic (As) is a toxic metalloid naturally present in the environment from various sources such as volcanism and weathering of the bed rock. Arsenic content in natural soils typically ranges from 0.1 to 50 mg.kg<sup>-1</sup> (Backer & Chesnin, 1975). Anthropogenic activities also contribute to the geochemical cycling of As in a variety of ways (Tamaki & Frankenberger, Jr., 1992; Yan-Chu, 1994; Smedley & Kinniburgh, 2002). As is used in agriculture as a component of pesticides and also used in wood preservation and glassmaking. It is also dispersed into the environment through the burning of fossil fuels. Additionally, due to its geochemistry, As is used as an indicator element in geochemical prospecting for various types of mineral ores (gold, silver, copper, uranium, etc.) (Boyle & Jonasson, 1973).

Soils near mining sites receive significant inputs of As and heavy metals during mining operations and minerals processing (Azcue & Nriagu, 1995; Hudson-Edwards et al., 1999; Savage et al., 200). As concentrations in tailing piles and tailing-contaminated soils can reach up to several thousand mg.kg<sup>-1</sup> (Smedley & Kinniburgh, 2002). However, unlike organic contaminants, As in soils cannot be decomposed chemically or biologically.

Environmental assessment of contaminated sites requires the determination of pollutants leaching potentials. Although a wide variety of leaching tests are available in the literature to determine the potential mobility of pollutants (Van Der Sloot et al. 1997; Kosson et al. 2002), very few have been designed to provide information on the nature of their fixation processes in studied matrices.

In this context, an approach was developed based on the use of leaching tests (single and sequential chemical extraction procedures) in conjunction with a mineralogical study. Indeed, knowledge of the pollutants operational fractionation in the studied matrix is required to better understand mechanisms regulating the leaching behavior of inorganic contaminants of interest.

The objective of this paper was to investigate the nature of As distribution and association to the soil constituents. The correlation between mineralogy and leachability of As was examined in a contaminated soil collected from a French gold mining site. Mineralogical analyses were performed following leaching tests to characterize the studied matrix.

## MATERIAL AND METHODS

### Sampling and preparation of soil

A contaminated soil collected from a gold mining site located in France was used for the study. The site was characterized by its geological heterogeneity and the utilization of a large variety of mining processes for ores extraction and gold purification until 2004. It was already known to present high concentrations of As (Clozel et al., 2002; Chatain et al., 2003; Chatain, 2004; Chatain et al., 2005a and b; Bayard et al., 2006).

Prior to characterizations and liquid-solid partitioning experiments, the soil samples was air-dried at room temperature ( $20 \pm 3^\circ\text{C}$ ) for one day, sieved through a stainless steel 2 mm mesh sieve to remove coarse debris and gravel, homogenized, and finally stored at  $4^\circ\text{C}$  in darkness.

### Soil characterization

#### Chemical characterization

A contaminated soil collected from a gold mining site located in France was used for the study. The site was characterized by its geological heterogeneity and the utilization of a large variety of mining processes for ores extraction and gold purification until 2004. It was already known to present high concentrations of As (Clozel et al., 2002; Chatain et al., 2003; Chatain, 2004; Chatain et al., 2005a and b; Bayard et al., 2006).

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#### Mineralogical characterization

##### *X-ray diffraction*

Mineralogical characterization was carried on three replicates of the less than 2 mm soil fraction grounded to powder ( $<50\mu\text{m}$ ) using a SIEMENS® D500 advance x-ray diffraction (XRD) instrument equipped with a copper anticathode. The samples were scanned from  $3^\circ$  to  $70^\circ$   $2\theta$  at a scan rate of  $0.02^\circ$   $2\theta/\text{second}$ . The results obtained were processed using the DIFFRAC<sup>Plus</sup> EVA<sup>®</sup> software (BRUKER AXS<sup>®</sup>) and the ICDD<sup>®</sup> database (International Centre for Diffraction Data).

##### *Scanning electron microscopy equipped for energy dispersive spectroscopy*

Mineralogical investigation was also performed on two replicates of the less than 2 mm soil fraction by scanning electron microscope (SEM) (JEOL<sup>®</sup> 840A LGS) using the backscattered electrons (BSE) mode, a voltage of 20 kV, coupled with an X-ray energy dispersive spectrometer (EDS). Samples for SEM-EDS analyses were prepared by attaching the soil particles on an adhesive tape placed on a stub (sample holder of the SEM). No coating of the samples with a conductive material was required prior to the analysis.

### Leaching tests

### Sequential chemical extractions

A sequential chemical extraction procedure adapted from Tessier et al. (1979) was carried out in triplicates to determine the major arsenic binding phases.

The chemical fractionation used includes the following five fractions:

- F1: exchangeable fraction (magnesium chloride solution 1 mol.L<sup>-1</sup> adjusted to pH 7.0);
- F2: carbonate fraction (sodium acetate solution 1 mol.L<sup>-1</sup> adjusted to pH 5.0 with acetic acid);
- F3: Fe-Mn oxide fraction (hydroxylammonium chloride 0.04 mol.L<sup>-1</sup> in 25 % (v/v) acetic acid at 96 °C);
- F4: sulfide and organic matter fraction (nitric acid 0.02 mol.L<sup>-1</sup> and hydrogen peroxide 8.8 mol.L<sup>-1</sup> at 85 °C followed by ammonium acetate solution 3.2 mol.L<sup>-1</sup> in 20 % (v/v) nitric acid); and,
- F5: residual fraction. This fraction was estimated from the total content obtained using acid digestion.

### Single extraction techniques

Single extraction techniques using 1 mol L<sup>-1</sup> sodium hydroxide (NaOH) solution, and 0.1 mol L<sup>-1</sup> dipotassium hydrogen orthophosphate (K<sub>2</sub>HPO<sub>4</sub>) solution were also performed to verify that an As adsorption on Fe oxyhydroxides was the major process of arsenic trapping in the soil (Clozel et al., 2002).

These single extractions were carried out in triplicate using an LS ratio of 10 mL/g and a contact time of 48 hours.

### **Leachates analyses**

All leachates were filtered through 0.45 µm pore size acetate-cellulose Whatman<sup>®</sup> membranes. They were subsequently analyzed for concentrations of constituents of interest using ICP-AES.

Sulphates and chlorides were analyzed using IC (ion chromatography, DionexDX320 HPIC<sup>®</sup>).

Total organic carbon (TOC) in solution was measured using a TOC analyzer (Total Organic Carbon analyzer, Shimadzu TOC-5000A<sup>®</sup>) (Clozel et al., 2002; Chatain et al., 2003; Chatain, 2004; Chatain et al., 2005a and b; Bayard et al., 2006).

## **RESULTS AND DISCUSSION**

### **Chemical characterization**

The major physicochemical characteristics and the elemental total contents as determined by acidic digestion of the studied soil are summarized in Table 1.

The soil was mainly characterized by a moisture content of ca. 10 %, ca. 3 wt% arsenic, ca. 9 wt% iron and ca. 1.9 wt% total organic compounds. Its natural pH and ORP measured after 48 hours of contact with deionized water at a L/S ratio of 10 mL/g, were ca. 6.5 and ca. +400 mV vs. NHE, respectively.

Moreover, a very low soluble (ca. 0.016 %) fraction of arsenic were obtained from the single extraction procedure using deionized water as the extractant.

Table 1 – Physicochemical characteristics (LS ratio: 10 mL/g; contact time: 48 hours) and total content of trace elements as determined by acid digestion of the studied soil

<b>Moisture content (%)</b>	10
<b>pH (H<sub>2</sub>O)*</b>	6.5
<b>ORP (mV vs. NHE)*</b>	400
<b>Si (%)</b>	20.3
<b>Fe (%)</b>	8.9
<b>Al (%)</b>	4.3
<b>Ca (%)</b>	3.7
<b>As (mg kg<sup>-1</sup>)</b>	27,700
<b>Cu (mg kg<sup>-1</sup>)</b>	1,700
<b>Pb (mg kg<sup>-1</sup>)</b>	800
<b>Zn (mg kg<sup>-1</sup>)</b>	400

### Mineralogical analysis

The methodology used scanning electron microscopy coupled with energy dispersive spectroscopy analyzer and X-ray diffraction analysis. Results from XRD analysis (Table 2) indicated that the soil was mainly constituted of quartz, gypsum, feldspars, muscovite, calcite, and dolomite.

Table 2 – Mineral composition by XRD analysis (Abundance: +++++ very abundant; +++ abundant; ++ present ; + traces)

<b>Mineral</b>	<b>Abundance</b>
Quartz	+++++
Micas	++
Feldspar	++
Chlorite	+
Kaolinite	+
Calcite	++
Dolomite	++
Calcite	++
Dolomite	++
Gypsum	+++
Jarosite	++

XRD analyses indicated the presence of traces of hematite and jarosite, which are the common pyrite weathering products with which As can be typically bound (Clozel et al., 2002). The absence of residual mixed sulfide phases in the soil can be due to the weathering and oxidation of pyritic minerals during the post-mining period.

Microscopy analyses performed using the BSE images by SEM coupled with EDS spectroscopy microanalysis can be used to complement the XRD analysis. The major minerals that were identified are quartz, gypsum, and particles containing Fe and As, with a composition in accordance with XRD results. A close similarity between the arsenic and iron cartography was observed in SEM results (Figure 1).

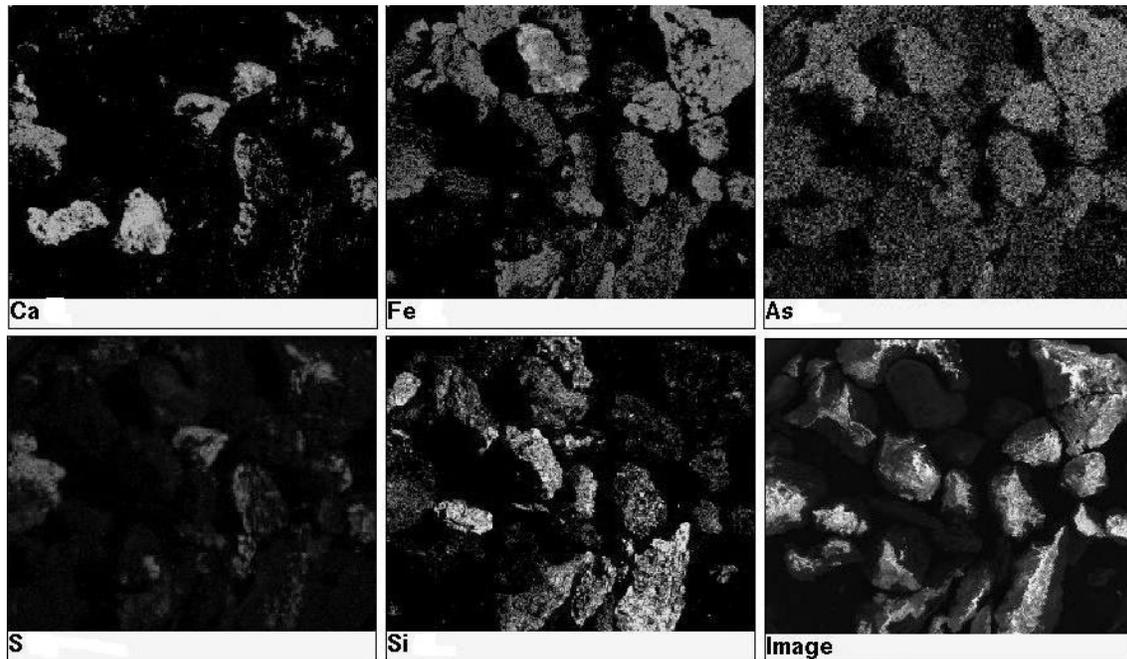


Figure 1 – SEM-EDX mapping of the 200 µm- 2 mm fraction of the arsenic contaminated soil (12X)

Fe and As, highly present in the soil (ca. 3% and ca. 9%, respectively), were not located in any of the main crystallized phases. As seemed to have been sorbed with Fe on the soil particles. The presence of amorphous As-bearing phases, such as amorphous Fe oxyhydroxides, was therefore assumed (Chatain et al., 2003; Chatain, 2004; Chatain et al., 2005a and b; Bayard et al., 2006) and thought to be the major process of arsenic trapping in the soil.

### **Leaching behavior**

#### Sequential chemical extraction

Results of sequential extractions are summarized in Figure 2. As and Fe appeared to be strongly bound to the soil matrix (ca. 80 wt% were concentrated in the residual fraction). A very low fraction of As and Fe (i.e., ca. < 1 wt%) was extracted as exchangeable and bound-to-carbonates fractions. These results confirmed that As and Fe were strongly bound on soil amorphous oxyhydroxide particles as shown already with the results from the XRD and SEM study.

Moreover, Al appears as the least mobile metal because of its high presence in the residual fraction (F5 – ca. 97 wt%). No correlations with As or Fe can be established.

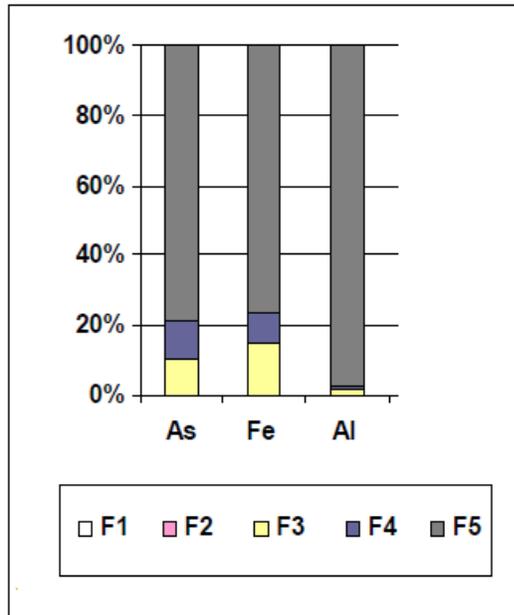


Figure 2 – Results from sequential chemical extractions performed on the fines < 2 mm of the soil (conc. in wt%)

#### Single extractions

Results obtained from single extractions, using 1 mol L<sup>-1</sup>NaOH solution, and 0.1 mol L<sup>-1</sup>K<sub>2</sub>HPO<sub>4</sub> solution, are summarized in Table 3. They are compared with those acquired during single extraction using demineralized water (natural).

Table 3 – Results from single extractions (LS ratio: 10 mL/g; contact time: 48 hours)

Extracting solution	As (conc. in wt%)	Fe (conc. in wt%)	pH	ORP (mV vs. NHE)
Deionized water	0.0016	0.0001	6.5	+400
1 mol L <sup>-1</sup> NaOH solution	73.51	0.17	13.8	+60
0.1 mol L <sup>-1</sup> K <sub>2</sub> HPO <sub>4</sub> solution	4.89	0.0034	7.5	+430

Concerning NaOH extraction, about 74 % of the total content in As was extracted within these extreme conditions of pH (ca. 14) achieved. A mechanism of As desorption from Fe oxyhydroxide surface by competition with OH<sup>-</sup> ions might explain the abruptly increase in As extractability (Carbonell-Barrachina et al., 1999). On the opposite, Fe solubility remained very low (ca. 0.2% of the total Fe content). Fe solubility may have been controlled by Fe oxyhydroxide precipitates.

These results suggest that most of As present in the soil is sorbed onto Fe-oxyhydroxides, which is consistent with mineralogical analysis. The remaining fraction (ca. 26% of the total As content) would represent the part co-precipitated with Fe and/or bound to resistant compounds (i.e., silicates or sulfides).

Results of extraction of As from the contaminated soil by K<sub>2</sub>HPO<sub>4</sub> solution are also shown in Table 3. The addition of this solution was found to have no significant effect on pH and ORP conditions and Fe release, as compared to those obtained under “natural conditions” with deionized water. However, a drastic increase in As solubilization (as much as 400-fold at pH ca. 7), and in phosphates adsorption onto

Fe oxyhydroxides (ca. 76%) was evidenced. These results are consistent with studies performed by Alam et al. 2001 and Clozel et al. 2002, that confirmed that As is for the most part reversibly sorbed onto Fe oxyhydroxides.

## CONCLUSIONS AND PERSPECTIVES

In this research, an As contaminated soil collected from a gold mining site has been considered. The assessment of the operational fractionation of As present in this soil has been performed by using leaching tests in conjunction with mineralogical characterization.

The first results shown in this study indicate that despite a high total concentration of As in the studied soil, this release with deionized water is very limited. This was principally explained by its low solubility and by the stability of its bearing solid phases under natural slightly acidic conditions.

The multiple approach (leaching and mineralogy) used in this work provided information on the nature of As fixation processes in the mining soil studied, and a better understanding of geochemical processes that control As reactivity in the subsurface environment.

Indeed, results showed that most of As appeared reversibly sorbed (ca. 72%) with Fe on the soil particles, in particular Fe oxyhydroxides. These results confirmed a potential risk of As mobilization over the long term under specific leaching conditions (i.e. pH or ORP gradient, chelation effect, etc.) which frequently occur in mining environment.

This initial study will lead to further research aimed at answering or confirming the processes considered. Metal speciation must be investigated further to provide the data needed for a better knowledge of As-bearing phases to better predict the mobility of this pollutant and in turn improve the management of arsenic contaminated sites.

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