

# **Arsenic Iron Crust Developed within Tailings of a Former Metallic Mine**

By

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## **Abstract**

Arsenopyrite-rich dumps of a former metallic mine were spread out by rainfalls and acidic waters originating from the abandoned mine galleries. This intensive leaching involved formation of arsenic-iron crusts onto the tailings surface. The thinly layered “ferri-crust” frequently constitute massive coatings of mineral grains, and locally cement the dump grains. The crusts are composed of jarosite, mangangordonite, arsenate iron hydroxides and iron hydrous oxides (identification by XRD, SEM, microprobe). Jarosite deposition is favoured by the acidic and oxidant conditions present in the mine’s site.

## **1 Introduction**

Arsenic mobilisation, in metallic mine spoils or tailings, is known to be induced by oxidation of As bearing sulfides. As mobility and stability conditions in groundwater and surface water have been extensively studied in numerous mining areas (Pierce and Moore, 82; Mok & al., 88; Azcue & al., 94; Daus et al., 98). The authors emphasise the importance of sulphates and As-bearing oxides precipitation and As-absorption onto iron oxihydroxides. The knowledge of As speciation and successive oxidation states is thus required for predicting the later release of soluble arsenic in waters. This study aims at characterising As-rich iron cements (ferri-crusts) developed onto the dumps of a former metallic mine and forecasting As releases induced by the leaching of the tailings surface.

## **2 Locations and Material**

In the southern part of the French Massif Central, the former exploitation of arsenopyrite-rich metallic ores generated about 300 000 metric tons of wastes. The resulting tailings were spread out along a steep slope ( $\approx 35^\circ$ ) and dug out by rainfalls and by very acidic surface waters ( $\text{pH} \approx 3$ ) coming from the former mine galleries. Within twenty years only, the wastes leaching involved development of decimetric indurated layers which even well developed in most recently-dug gullies. These are iron rich materials, coloured from the yellow-brown to the red, and named “slope sandstones” according to their position in the slope or « ferri-crust » by reference to their composition and by analogy with similar formations of tropical countries. These ferri-crusts are composed of hardly cemented millimetric to centimetric fragments of quartz, other silicates or micaschists resulting from the crushing of the ore gangue and surrounding metamorphic rocks.

Three samples of various granulometry and colours were collected at different locations in the tailings : a red fine cement (99E103), a red cement (1E312), and a ochre cement (99E53). Chemical and micro-morphological analysis were performed by ICP-MS (CNRS, Nancy),

AAS (LSEE, Limoges), optic lens and microscopy on both (i) bulk cemented dump material (minerals grains + cement), and (ii) isolated Fe-oxides hand-picked after magnetic separation. Scanning electron microscopy (SEM) and electron microprobe analysis (EMPA) were used to characterise every microscopically recognised phases.

### 3 Results

#### *Bulk material characterization*

Whole rock samples are rich in iron (up to about 40%) and contain significant quantities of arsenic (1.3 to 3.9% As).

Binocular lens examinations indicate that the crushed quartz grains are frequently coated by the red or the ochre cement. According to thin sections microscopic observations, five different types of cements were defined in all samples (Figure 1) : (1) resinous cement, (2) fleecy cement (3) yellow cement (4) red cement, and (5) dark-reddish cement; (1), (4) and (5) being the most abundant. The two later often present collomorph textures while the resinous and yellow cements both show well developed desiccation cracks.

This optical classification was confirmed by the microprobe analyses. Cements characteristic are as follows (average values expressed in atomic weight %) :

- 1) The resinous cement is the As-richest cement (*212 analyses*): As  $\approx$  16.7 %, Fe  $\approx$  23.2 %; mean heat loss : 32.8%.
- 2) The fleecy cement (*56 analyses*) As  $\approx$  5.7 %, Fe  $\approx$  27.5 %; mean heat loss : 35.9%.
- 3) The yellow cement appears generally zoned and more heterogeneous in composition (*20 analyses*): As  $\approx$  1.4 %, Fe  $\approx$  39.9 %. Mean heat loss : 25%
- 4) The red cement (*176 analyses*) : As  $\approx$  3 %., Fe  $\approx$  44.7 %.
- 5) The dark reddish cement (*75 analyses*) : As  $\approx$  1.4 %, Fe  $\approx$  46.9 %. Heat loss  $\approx$  28%.

SEM cartography (Figure 1) show the different chemical compositions in between above mentioned cements and a strong As / Fe association, particularly in the resinous cement. Different morphology of As-Fe bearing phases could also be seen by SEM observations :

- As-rich acicular crystals of jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  are present in the red fine cement of 99E103.
- Same acicular crystals are also observed in the red cement of the 1E312 sample. These crystals are agglomerated and form “spherolites”.
- Two phases can be identified in the ochre sample (99E53) : one amorphous gel showing dessication cracks mainly composed of Fe; only few amounts of As and S are noted. As-bearing spherolites grow as epitaxial crystals on this Fe-rich gel.

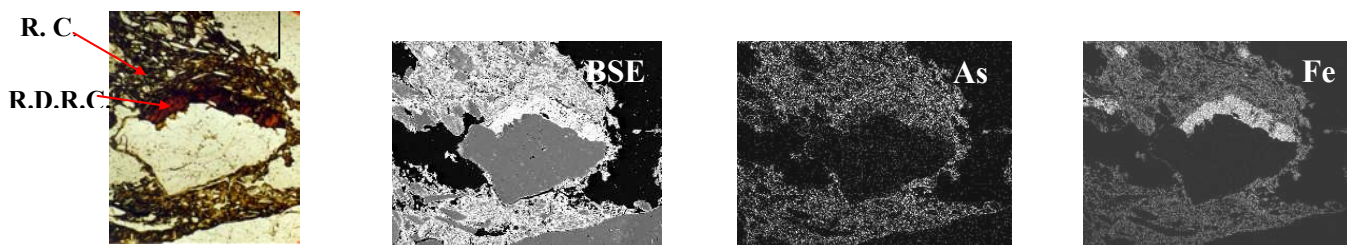


Figure 1 : From the left to the right, thin section under optical microscope (black scale bar = 0.1 mm; R.C. = resinous cement; R.D.R.C. = red and dark-reddish cement) , SEM cartography (BSE = back scattered electrons, As and Fe contents). This figure shows differences in chemical composition between three defined cements and the strong association of As with Fe especially in resinous cement.

Population density repartition of the Log Fe/As for the microprobe analyses (Figure 2) indicate that only three kinds of cements are chemically well-defined (resinous cement, fleecy cement and red cement). The two others (yellow cement and dark reddish cement) present more scattered composition and their chemical identity is more controversial.

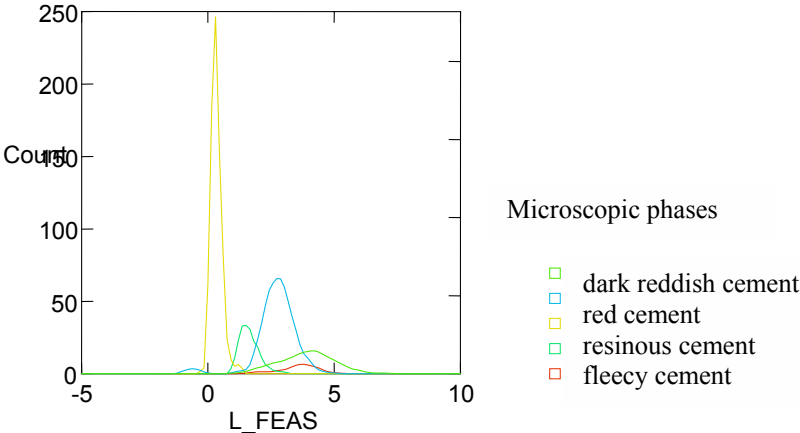


Figure 2 : Population density function of log Fe/As for 464 microprobe analyses

*Separated material*

DRX spectra of the three selected samples (Figure 2) show the presence of primary minerals such as quartz, muscovite, tourmaline (schorl) and clinochlore which are known constituents of ore gangue and surrounded rocks. The other peaks, which can be attributed to the authigenic cements, appear to be composed by amorphous phases, seen in all samples (dome between 7-15°2θ), by jarosite  $[KFe_3(SO_4)_2(OH)_6]$  and mangangordonite  $[(Mn^{++},Fe^{++},Mg)Al_2(PO_4)_2(OH)_2.8(H_2O)]$ . These two minerals are present only in the two red cements (samples 99E103 and 1E312).

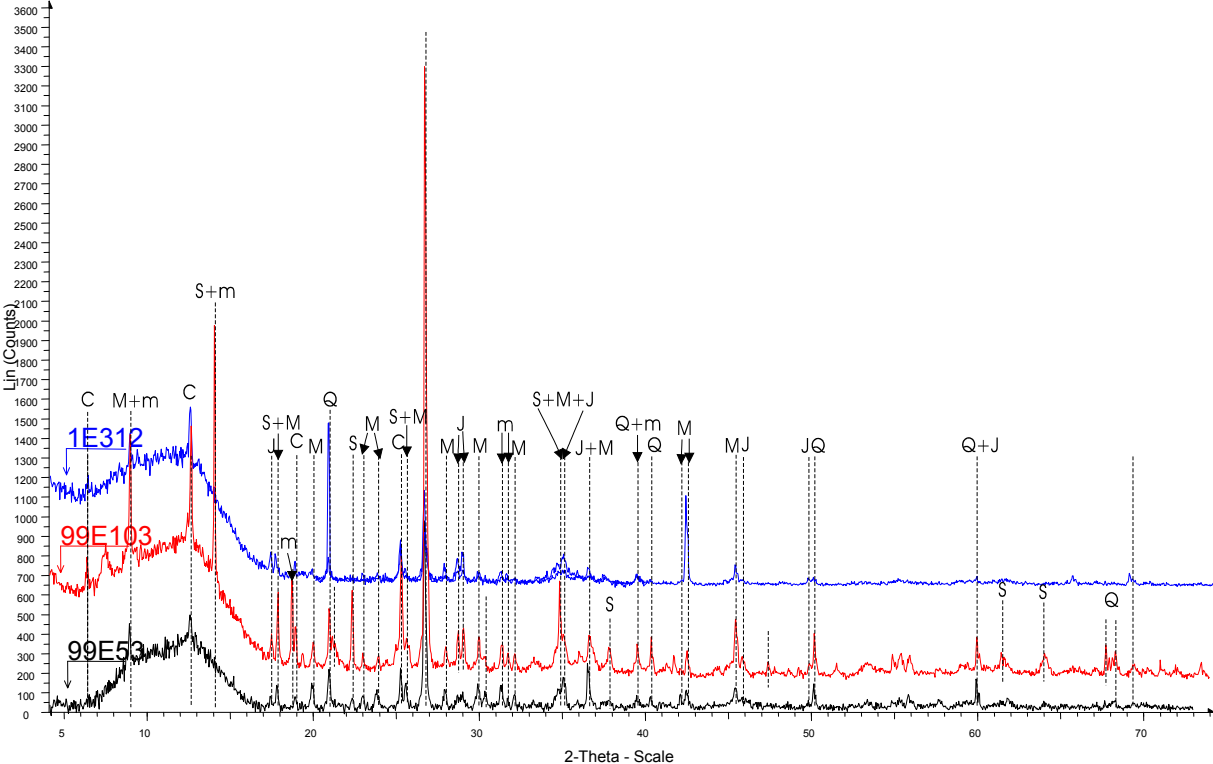


Figure 3 : Compared DRX spectra of the samples 99E103, 1E312, and 99E53 showing the presence of Q = quartz, M = muscovite, S = tourmaline (schorl), C = clinochlore, J = jarosite :  $KFe_3(SO_4)_2(OH)_6$ , m = mangangordonite :  $(Mn^{++},Fe^{++},Mg)Al_2(PO_4)_2(OH)_2.8(H_2O)$ ; the dome between 7-15°2θ is due to the presence of an amorphous phase. Step : 0.04, step time : 10 sec, from 4 to 74 °2θ

## 4 Discussion

Sulfide oxidation allows the release of the greatest part of arsenic, iron and other heavy elements contained in the primary ore. A part of these elements is exported by surface waters coming out from the mine galleries. The major part is immobilised as secondary ferri-crusts onto the tailings.

Although presenting obvious Fe / As associations, these crusts differ widely in their mineralogical and chemical composition. The main recognized phases are authigenic sulfates and phosphates (in only two samples), and well developed low-crystalline forms :

- amorphous or low crystalline phases are always iron-dominant but can present very different As concentrations (as seen in the resinous cement);
- jarosite is the only As bearing crystalline phase. As suggested by Scott (1987) for the alunite-jarosite family; As is probably substituted by S in  $XO_4$  sites. The presence of jarosite is in agreement with actual pH-Eh conditions in the dump (2.8 – 481 mV).

The morphological analysis suggest that the low crystalline As-rich forms correspond to an early stage of cement precipitation. The later stages of cement precipitation correspond to more stable and more crystalline forms presenting greater Fe contents and smaller As contents. Indeed, according to its cracked muddy texture, the resinous cement probably represent the first step of As-Fe immobilization (Roussel et al., 1999). Its homogeneity in composition could be due to rapid precipitation of homogeneous leachates.

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