

(5) RETENTION OF HAZARDOUS METALS BY SECONDARY IRON SULPHATES IN ACID MINE DRAINAGE PROCESSES: THE POSITIVE ENVIRONMENTAL CONTRIBUTION OF JAROSITE BY EFFICIENTLY SEQUESTERING LEAD

Maria-Ondina Figueiredo & Teresa Pereira da Silva

LNEG, Unidade de Recursos Minerais e Geofísica, Ap. 7586, 2721-866 Alfragide, Portugal.

Secondary iron sulphates formed in abandoned sulphide-ore mines as a result of mine wastes weathering - acid mine drainage (AMD) processes - have currently a negative environmental connotation because these secondary hydroxylated and/or hydrated minerals concentrate a large span of toxic elements, particularly the hazardous metals lead and thallium. This apparently negative feature may become a positive contribution, since immobilization of such elements under the form of stable minerals significantly reduces their spread in soils and aquifers. This is just the case of the mineral jarosite - ideally $KFe_3(SO_4)_2(OH)_6$, very common in AMD environments, recently identified in materials from Mars [1] and nowadays recognized as an important model *kagomé* antiferromagnet [2]. The analysis of the chemical exergy of jarosite in relation to the uptake of lead has highlighted the possibility of a positive role played by this mineral in mine wastes [3,4], confirmed by a subsequent minero-chemical study [5].

1. An Overview on the Mineral Chemistry of Jarosite

Jarosite (*s.s.*) belongs to the alunite mineral group [6] with general formula $AB_3(TO_4)_2(OH)_6$, where A represents a large cation with icosahedral coordination (coordination number CN = 12) - K^+ , Na^+ , NH_4^+ , H_3O^+ , Ag^+ , Tl^+ , Pb^{2+} , Bi^{3+} , plus minor Ca^{2+} , Ba^{2+} , Sr^{2+} and trivalent rare-earth ions, e.g., Eu^{3+} -, B stands for a smaller cation with octahedral coordination (CN = 6) - Fe^{3+} (jarosite *s.s.*) or Al^{3+} (alunite *s.s.*), plus minor V^{3+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , Mg^{2+} - and T represents a tetrahedral cation (CN = 4) - S^{6+} , As^{5+} , P^{5+} . The octahedral B cations are surrounded by two oxygen anions from the tetrahedral groups (TO_4) plus four hydroxyl ions (OH) shared between two neighbour octahedra; A cations are coordinated by six OH anions shared with the octahedral cations and six oxygen anions from the tetrahedral groups. The crystal structure of jarosite is depicted in figure 1.

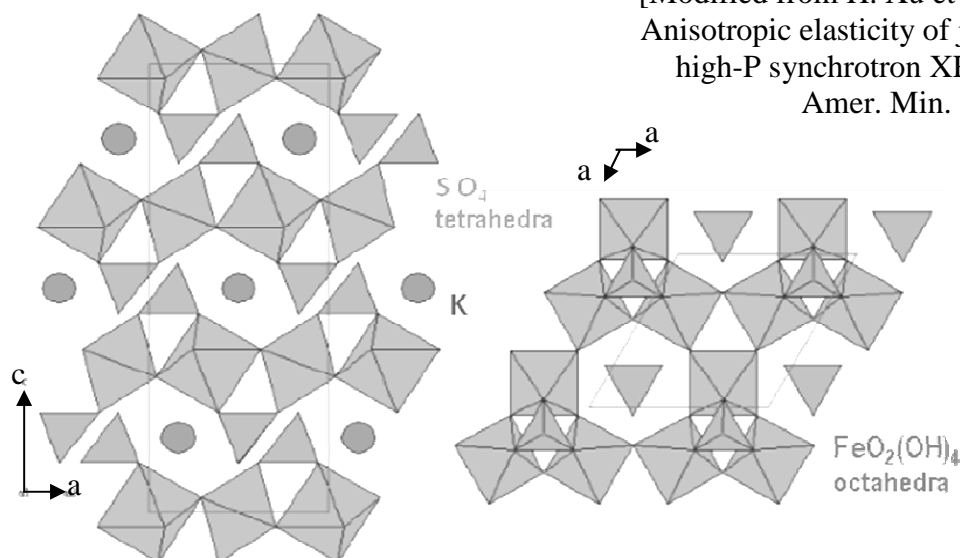


Fig. 1. Crystal structure of Jarosite
[Modified from H. Xu et al. (2010)
Anisotropic elasticity of jarosite: a
high-P synchrotron XRD study.
Amer. Min. 95, 19-23]

The alunite supergroup covers more than 40 distinct mineral species [7]. There is a limited solid-solution between end-members with respect to the octahedral B cations, jarosite (Fe) and alunite (Al), the same holding for the large icosahedral ions filling the A site - namely, K^+ and Na^+ , particularly for the ferric term.

In fact, the incorporation of lead within the crystal structure of jarosite by replacing the large icosahedral ion K^+ is quite limited [8], despite the recognized occurrence of a specific lead mineral - plumbojarosite, $Pb_{0.5}Fe_3(SO_4)_2(OH)_6$ - to which the same trigonal symmetry was attributed but with a double *c*-parameter of the hexagonal cell [9].

In view of this structural query, and with the purpose of clarifying the reduced but effective replacement of potassium by lead in jarosites from AMD wastes, X-ray absorption spectroscopy studies were undertaken using synchrotron radiation. First results concerning the analysis of Fe *K*-edge (fig. 2) clearly display the influence from the cationic population of the large icosahedral A site through the variation of pre-edge details [10].

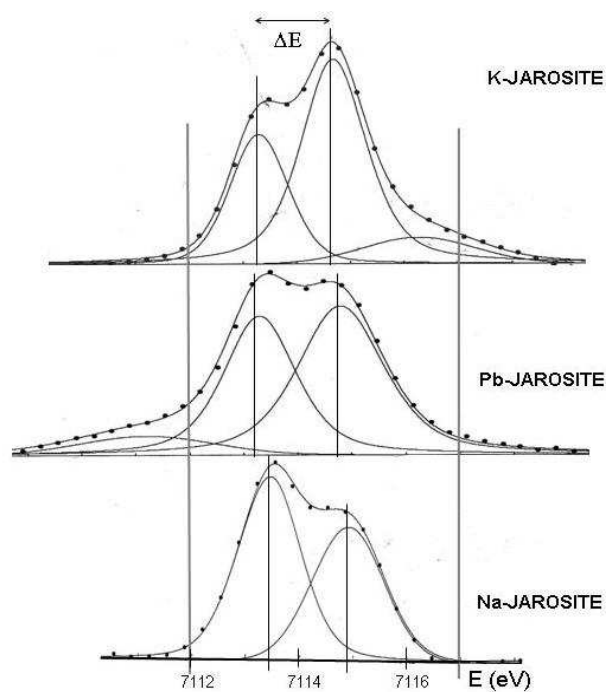


Figure 2. Pre-edge details of Fe *K*-edge X-ray absorption spectra (XANES) collected from jarosites with distinct A-site populations

2. Lead Retention by Jarosite in Waste Materials from S. Domingos Mine

The Portuguese sector of the Iberian Pyrite Belt (IPB) has been exploited since pre-Roman times and during the Roman occupation of Iberia, when gold and silver were extracted from extensive massive gossan caps, particularly the jarosite-rich layer at the base [11].

The modern exploitation of São Domingos mine in Alentejo (northern sector of IPB) started in 1859 for the extraction of copper along with these precious metals and since 1870 also for sulphur production until 1966, when the mine was definitely closed. Records on mine activity allow for estimating the extracted ore (mainly constituted by pyrite, chalcopyrite, sphalerite, galena, arsenopyrite and various sulphosalt minerals) at several million tons. It is nowadays envisaged to carry out a complete study of the potential sustainability of recovering scarce and valuable metals from abandoned mine residues (e.g. rhenium [12]), in line with EU recent efforts to promote new mineral resources through mining waste materials.

With the aim of ascertaining the role of jarosite as an efficient Pb-retainer, type-case materials of waste products sampled at São Domingos mine were analysed. Common laboratory techniques were applied to characterize the phase constitution of these samples: X-ray fluorescence spectrometry in wavelength dispersive mode (XRF-WDS) to assess the chemical constitution and to estimate comparative elemental contents, X-ray diffraction (XRD) for phase identification and thermo-analytical techniques – simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) – to complement XRD phase data.

A Philips PW1400 automated X-ray fluorescence spectrometer equipped with a rhodium tube and various analysing crystals was used to scan the angular intervals (2θ) suitable for element detection through the scanning of selected emission lines (Table 1).

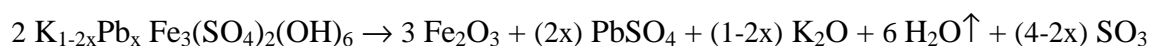
Table 1. Comparative elemental contents of a mining waste obtained by XRF-WDS

Element	K	Sn	Sb	Ca	Ba	Ti	Fe	Pb	Hg	Tl	Bi	Se	As
Line	$K \alpha$	$L \alpha 1$	$L \alpha 1$	$K \alpha$	$L \alpha 1$	$K \alpha$	$K \alpha$	LL	$L \alpha 1$	$L \alpha 1$	$L \alpha 1$	$K \alpha$	$K \beta 1$
$2 \theta^\circ$ (LiF 200 crystal)	136.7	126.77	117.34	113.1	87.17	86.14	57.52	39.17	35.91	34.90	33.01	31.89	30.45
Collimator	Large					Fine							
Amt. 3-5	x	x	x	x	vtg	x	x	x	vtg	vtg	x	x	x

A SETARAM 92-16.18 apparatus, incorporating a microbalance with a controlled gas flow of argon (inert atmosphere), was used to perform DTA-TG analyses. About 100 mg of milled sample were deposited in an alumina (α - Al_2O_3) crucible. The reference material was alumina powder and the heating temperature ranged from ambient to 650 C at a heating rate of 10 C.min⁻¹. The phase constitution of DTA-TG heated material was monitored by XRD and compared to the original mineralogical constitution in order to interpret the registered energy variations and mass losses.

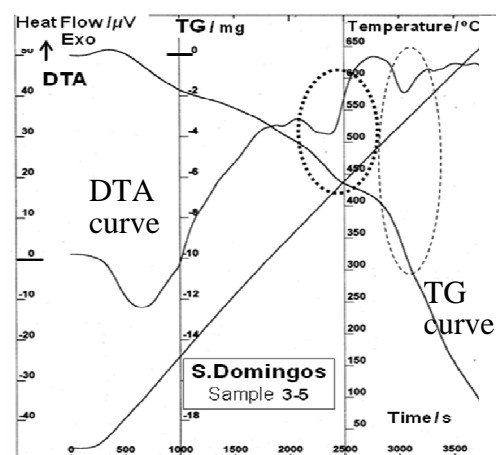
A powder diffractometer with Bragg-Brentano geometry operating at 50 kV and 40 mA and equipped with a large-anode copper tube and a curved graphite crystal monochromator was used to collect X-ray diffraction patterns from sampled wastes.

The thermal behaviour of mine waste materials was expected to match the decomposition of a lead-containing jarosite, $(K_{1-2x}Pb_x)Fe_3(SO_4)_2(OH)_6$ - with x much lower than 0.5, the value in the ideal formula of plumbojarosite, $Pb_{0.5}Fe_3(SO_4)_2(OH)_6$ - under normal atmosphere by gas release (water plus SO_2) and formation of anglesite ($PbSO_4$) according to the equation:



Sample 3-5 (a silty yellow-greyish material from S. Domingos mine wastes [13]) was selected to illustrate the minero-chemical study carried out with the purpose of ascertaining lead retention by jarosite. This sample displays a composite mineralogy that already includes anglesite as a primary component; accordingly, the phase constitution of DTA/TG heated material reflects the behaviour of both sulphates (anglesite and Pb-jarosite) under a thermal treatment in inert atmosphere – that is, the partial reduction of S^{6+} to S^{4-} with release of SO_2 (fig. 3) and to S^{2-} with formation of PbS .

Figure 3. Thermal analysis output. The regions corresponding to the decomposition of jarosite with liberation of water just above 450C and to the release of SO_2 at higher temperature are assigned in DTA plus TG curves.



X-ray powder diffraction pattern collected from sample 3-5 (fig. 4) reflects the composite mineralogy of this mine waste: jarosite and anglesite are the main constituting phases, along with minor hematite and quartz, plus vestigial anatase and anhydrite, in accordance with the chemical constitution noticed by X-ray fluorescence spectrometry (Table 1).

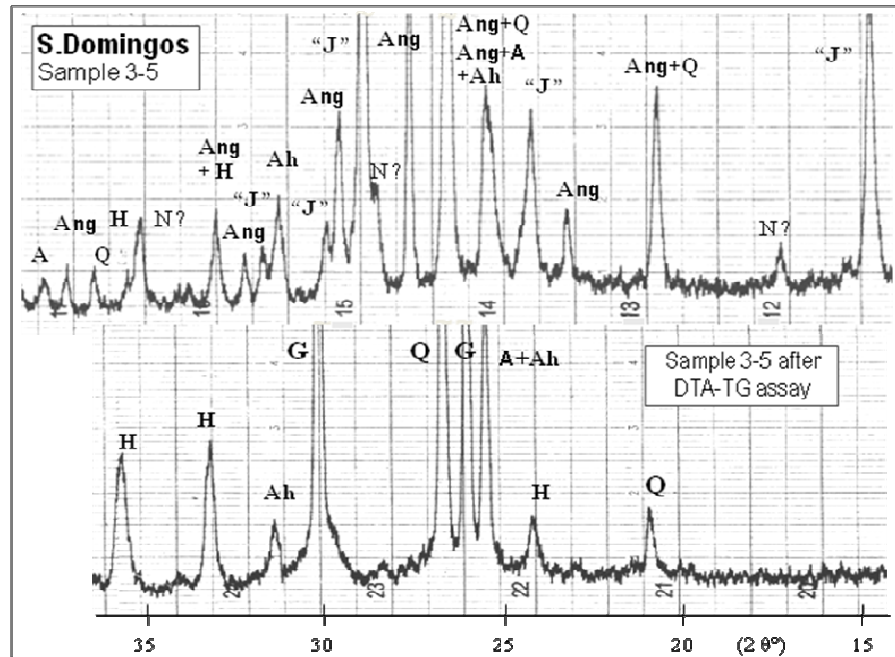


Figure 4. XRD pattern of sample 3-5: above, as collected; bellow, after the thermal assay. Ang - anglesite (PbSO_4); "J"- jarosite [$(\text{K}_{1-2x}\text{Pb}_x)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$]; Q - quartz ($\alpha\text{-SiO}_2$); Ah - anhydrite (CaSO_4); H - hematite ($\alpha\text{-Fe}_2\text{O}_3$); A - anatase (TiO_2); G - galena (PbS); N? Non identified minor phase.

Once anglesite was already present in the original waste material, and despite being much less representative in the heated material (as clearly seen by comparing the XRD patterns, fig. 4), an uncertainty may arise concerning the original incorporation of lead in jarosite crystal structure.

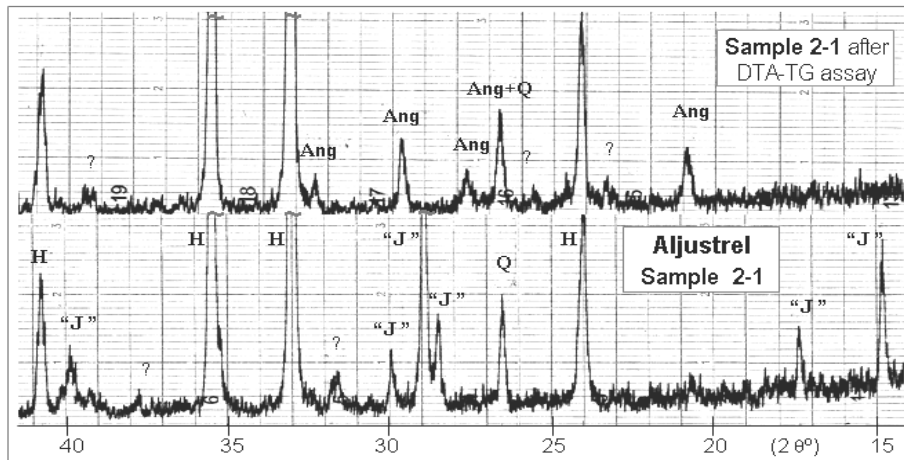


Figure 5.

Reproduced from ref. [5]

A similar minero-chemical analysis of a waste material from Aljustrel mine (sample 2-1), composed of jarosite, hematite and quartz [5], decisively contributes to clarify this doubt: the formation of anglesite (PbSO_4) in the heated product resulting from the DTA-TG assay (Fig. 5) can only be explained by the supply of lead from a Pb-rich jarosite, $(\text{K}_{1-2x}\text{Pb}_x)\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$.

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