

# X-RAY DIFFRACTION AND INFRARED SPECTROSCOPY OF MILL TAILINGS IMPOUNDMENTS AND ACID SULPHATE MINE WATERS FROM ALGARES (ALJUSTREL), PORTUGAL

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## INTRODUCTION

Ore mining exploration produces huge amounts of waste materials all over in the world. Large volume of mine wastes occurs in the south of Portugal as a result of ore extracted from metalliferous mining works during the last 100 years. Approximately, 280 Mt of massive polymetallic sulphides were extracted mainly for sulphur, from about 60 mines (Strauss and Madel, 1974). Mill tailings constituted of residual material resulted from sulphide concentrate steps were retained in impoundments near the mining plant. The aim of this work is to study the mineralogy and geochemistry of mill tailings impoundments from Algarés, Aljustrel (Portugal). Particular attention is given to the precipitated mineral phases which occur either in oxidation zones of mill tailings or decantation lakes, in order to determine the type of sulphate coordination with bivalent metals (Me).

## SITE DESCRIPTION

### Regional geology and metallogenesis

The Iberian Pyrite belt extends about 230 Km along strike-faults with a width ranging from 35 to 50 km, which forms a roughly back-arc through southern Portugal and Spain (Fig.1). Metallogenesis of the Aljustrel mine area was described by Barriga et al., (1997). The Aljustrel mine area

is a Late Devonian – Early Carboniferous polymetallic volcanogenic massive sulphide deposits, which commonly shows an overall metal zoning from a zinc-rich zone near the hanging wall and a copper-rich zone near the footwall, separated by low grade to barren massive pyrite. The massive sulphide horizon in the Aljustrel mine area occurs at or near the top of the Lower Rhyolite unit in two linear belts that trend from northwest to southeast.

### Mill tailings impoundments

The mining area of Algarés has several tailings deposited in the impoundments, located in the vicinity of the decantation lakes. Tailings were deposited directly on clastic sediments without any impermeable layers and operated from 1963 to 1971. The decantation lake contains acid waters rich in heavy metals. Around the tailings, no vegetation is observed.

### Materials and techniques

Dry samples collected from mill tailings were sealed in plastic bags and stored at room temperature. Wet samples and acid waters collected from the decantation lake were stored in polyethylene containers. During the field campaign a pH- electrode was successfully used for pH-measurements (Sørensen scale), electric conductivity ( $\mu\text{S}/\text{cm}$ ) and temperature of acid mine waters. The pH ranges

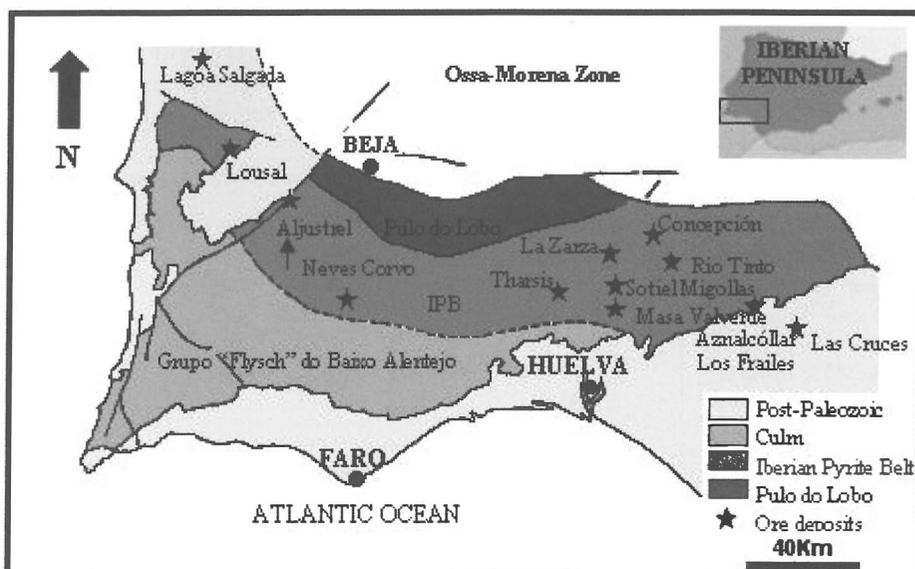


Figura 1: Geological map of the South Portuguese Zone (adapted from Carvalho et al., 1976). Arrow indicates the zone study.

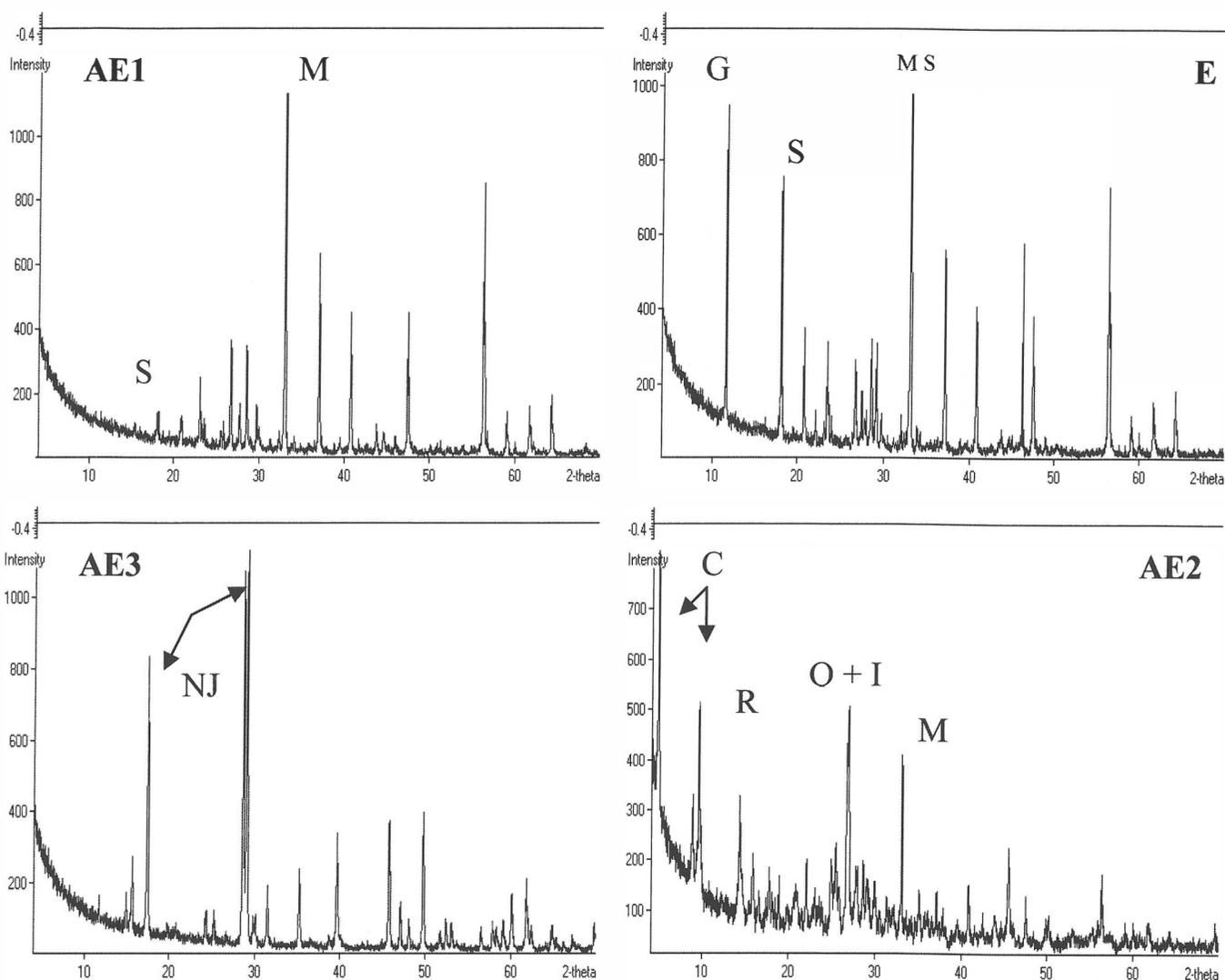


Figura 2: X-ray patterns of samples collected from mill tailings (S: siderotil; M: marcasite; N: natrojarosite; G: gypsum; C: copiapite; R: rhomboclase; Q: quartz; I: illite).

between 1.4 – 2.1 and electric conductivity between 28.000 – 30.000  $\mu\text{S}/\text{cm}$ .

Selected samples were sieved and particle-size distribution was measured using a laser particle-size analyzer. Separation of the aggregate fractions from acid waters was carried out by high-speed ultracentrifugation. Millipore filters ( $<0.45 \mu\text{m}$ ) were used for acid waters filtration. The residue obtained was immediately submitted to XRD and IR analyses. The XRD patterns of randomly oriented aggregates were obtained with a Philips X'Pert MPD machine equipped with  $\text{CuK}\alpha$  radiation, graphite monochromator, automatic divergence slit and 0.5-receiving slit. A step size of  $0.05^\circ 2\theta$ , a scan setting of  $2 - 70^\circ 2\theta$ , and a 10 s counting time were chosen. Infra-Red spectra in absorption technique were recorded in the  $4000 - 400 \text{ cm}^{-1}$  frequency region using a Bruker Tensor-27 Infra-Red spectrometer equipped with a room temperature TGC- detector and a horizontal ATR unit. A  $45^\circ$  horizontal ZnSe ATR crystal was mounted in a 30-ml rectangular cell made of polypropylene.

**RESULTS**

By a careful mineralogical analysis were separated two distinct zones in the mill tailings: primary and oxidation.

No cementation zones were found. Less abundant sulphide minerals (pyrite, chalcopirite, sphalerite, galeña) were found in the primary zone. XRD patterns of minerals identified in whole samples are shown in Fig.2. Fine fractions from mill tailings impoundments and filtrated material from acid mine waters consist of secondary ferric sulphate minerals, amorphous to poorly crystalline minerals formed, by oxidation of Fe in surface and in aqueous solution. XRD pattern of amorphous to poor Fe oxy-hydroxide is characterised by a very broad

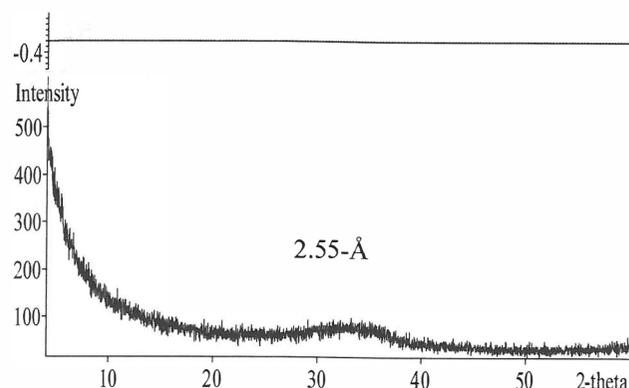


Figura 3: X-ray patterns of amorphous Fe oxy-hydroxide

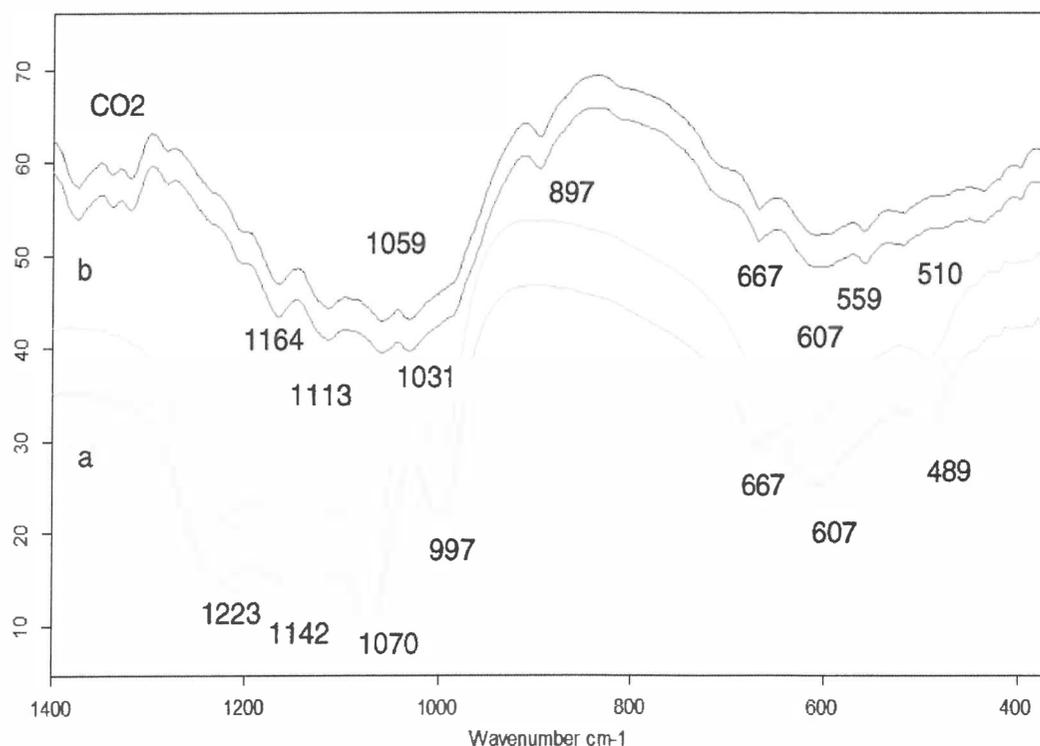


Figura 4: ATR - IR patterns of fine fractions (a) and filtrated waters (b)

reflection centred at about  $\sim 2.5\text{\AA}$  with a raw intensity of about  $150\text{ counts s}^{-1}$  (Fig.3). These mineral phases are of great interest due to their high specific surface areas and chemical reactivity.

The ATR-IR patterns of fine fractions separated from the oxidized zone of mill tailing impoundments are shown in Fig.4a. The frequencies of interest occur in the range  $900 - 1300\text{ cm}^{-1}$ , where the stretching modes of the S - O bonds show characteristic absorption bands. The undisturbed  $\text{SO}_4^{2-}$  tetrahedron displays usually one strong band ( $\nu_3$ ) occurring at  $1104\text{ cm}^{-1}$ . The splitting of the  $\nu_3$  band at  $\text{pH} \sim 3$  (our samples) indicates the presence of an inner-sphere sulphate surface complex.

For this inner-surface complex the  $\nu_3$  band was split into three peaks at  $1223$ ,  $1142$  and  $1070\text{ cm}^{-1}$ . The  $\nu_1$  band of lesser importance at  $997\text{ cm}^{-1}$  is assigned to the inner-sphere sulphate surface complex, which improved the fit pattern. Most probably, the  $1223\text{ cm}^{-1}$  band should be related to ferric hydrous oxides adsorption on sulphate. The  $\nu_4$  ( $\text{SO}_4$ ) band occurs at  $604\text{ cm}^{-1}$ . These band vibrations which yield features at  $1223$ ,  $1142$  and  $1070\text{ cm}^{-1}$  have been shown to be typical for schwertmannite (Bishop and Murad, 1996).

The ATR-IR patterns of filtration phases from acid waters are shown in Fig.4b. The bands at about  $1300\text{ cm}^{-1}$  correspond to carbonates. The splitting of the  $\nu_3$  band at  $\text{pH} \sim 1.8$  is characterized by four bands at:  $1164$ ,  $1113$ ,  $1059$  and  $1031\text{ cm}^{-1}$ . The  $\nu_1$  ( $\text{O}_3\text{S} - \text{OH}$ ) vibration occurs at  $897\text{ cm}^{-1}$  is assigned to an outer-sphere complex. This indicates that the symmetry of sulphates is lower.

## DISCUSSION AND CONCLUSION

Sulphide minerals from the mill tailings impoundments are subjected to oxidation in an acid-producing reaction to form  $\text{SO}_4$  and  $\text{Fe}^{2+}$ , which are transported in acid mine drainage as dissolved species. Metals associated to

sulphide minerals were also released into solution during oxidation. High  $\text{SO}_4$  and Me ions concentrations at  $\text{pH} < 3$  do occur either mill tailings deposits or decantation lakes. The oxidation front from mill tailings impoundments, sharply delimited from the dark grey zone, is characterized by smaller grains size than those found in the primary zone.

The mineralogy of secondary phases identified in the oxidation zone is characterized by ferric sulphate minerals (type  $\text{Fe}^{2+}\text{SO}_4 \cdot n\text{H}_2\text{O}$ ,  $n$  ranges from 7 to 1), ferrous and ferric sulphates (mixed-valence type) or ferrous sulphates and schwertmannite. Poorly ordered oxides and hydroxy sulfates resulted during mine drainage and identified in mill tailings impoundments of Algares, are excellent sorbents of toxic metals.

Sulphates analysed by ATR-IR form inner-sphere surface complex. The split into three peaks at  $1142$ ,  $1070$  and  $997\text{ cm}^{-1}$  indicates that sulphate exists in a bidentate coordination (Bigham et al., 1990). The strong  $\text{Fe}^{3+} - \text{SO}_4$  and  $\text{H} - \text{SO}_4$  interaction result in a relatively large splitting of the  $\nu_3$  bands. The ATR-IR pattern of filtration phases (Fig. 3b) from acid waters shows distorted  $\text{SO}_4$  tetrahedra with monodentate-like symmetry ( $\text{C}_{3v}$ ). This implies that the strong  $\text{H} - \text{SO}_4$  is replaced by a relatively weak  $\text{Me} - \text{SO}_4$  bond. The adsorption of Me is affected by the presence of  $\text{SO}_4$  sorbed in outer or inner sphere of schwertmannite or even of ternary surface complexes ( $\text{FeOHMeSO}_4$ ). Therefore, the formation of  $\text{Me} - \text{SO}_4$  complexes result either in bidentate or monodentate coordination, which is consistent with the data collected.

## REFERENCES

- Barriga, F.J.A.S., Carvalho, D., Ribeiro, A. (1997). Introduction to the Iberian Pyrite Belt. Society of Economic Geologist, Guidebook Series, 27, 1-20.  
 Bishop J.L., Murad, E. (1996). Schwertmannite on Mars?

Spectroscopic analyses of schwertmannite, its relationship to other ferric minerals, and its possible presence in the surface material of Mars. In: «Mineral Spectroscopy: A tribute to Roger Burns», Dyar, M.D., McCommon, C., Scafer, M.W. eds. Spec. Publ. 5, Geochem. Soc., 337 – 358.

Bigham, J.M., Schwertmann, U., Carlson, L., Murad, E.

(1990). *Geochim. Cosmochim. Acta*, 54, 2743 – 2758.

Carvalho, D., Conde, L., Enrile, J.H., Oliveira V., Schermerhorn, L. (1976). Livro - Guia das excursões geológicas na Faixa Piritosa Ibérica. *Comun. Serv. Geol. Portugal*, 6, 271 – 315.

Strauss, G.K., Madel, J. (1974). *Geol. Bunds.*, 63, 191 – 211.