# Hydrochemistry of pit lakes in the Portuguese sector of the Iberian Pyrite Belt

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**Abstract.** The Iberian Pyrite Belt (IPB) is a world-class metallogenic province with volcanogenic massive sulphide ore deposits. Most ore exploitation occurred since pre-Roman time, creating extensive galleries, wells, waste-dumps and pit lakes. These last structures are a concern for their potential environmental impact because they accumulate large volumes of mine water affected acid mine drainage. The present work classifies the pit lakes based on the surface water hydrochemistry. Using the Ficklin diagram for classification, pit lake waters vary from acid, high-metal to high-acid, extreme-metal and exhibit similarities with other pit lakes from the Spanish sector of the IPB.

## 1 Introduction

Mining activities generates environmental impact, especially by the presence of reactive minerals such as sulphides. As a consequence, water can become acidic, with high concentrations of metals and sulfates. Ore exploitation in the IPB dates back to pre-Roman times and was intensified with the beginning of the Industrial Era. After mine operation closure, surface and rain water transforms open cut mines into pit lakes [1]. Acid mine drainage (AMD) is a typical feature of these structures, which typically are abandoned without environmental remediation measures.

The present study focused on acidic lagoons from two major sulphide mines in the IPB, namely São Domingos and Lousal. Their water properties were analysed in order to interpret hydrochemical relationships, classified in terms of acid and metallic contamination, and potential risks to aquatic ecosystems examined. Results were compared with data from similar pit lakes in the Spanish sector of the IPB [2].

## 2 Study area

The study area includes the mining complexes of São Domingos and Lousal, located in the Portuguese sector of the IPB (Fig. 1). This region is part of a geological region characterized by a high density of polymetallic sulphide deposits consisting predominantly of pyrite, sphalerite, galena, chalcopyrite, and associated many minor phases [3]. It is one of the driest regions of southwestern Europe, with precipitation

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occurring mostly in the winter months, and droughts frequently occurring during the summer [4].

In São Domingos, the pit lake is one the main features that define the mining landscape, which has been developed since pre-Roman time, but especially during the XIX century. The mine working took place in galleries and wells, as well as creating an open-cut that reaches 120 m depth with a perimeter of approximately 2 km [5]. A similar scenario occurred at the Lousal mine, which has two pit lakes. This complex was exploited between 1900 and 1988 for pyrite, with mining works developed to a depth of about 500 m. The pit lake, Lagoa Azul, comprises about 0.7 ha and has a perimeter of approximately 320 m. There is also the so-called Lagoa Vermelha, a feature flooded by acid water associated with an acidic spring [5, 6]. Both mining complexes were subject to environmental remediation, but the pit lakes were not subject to such intervention.
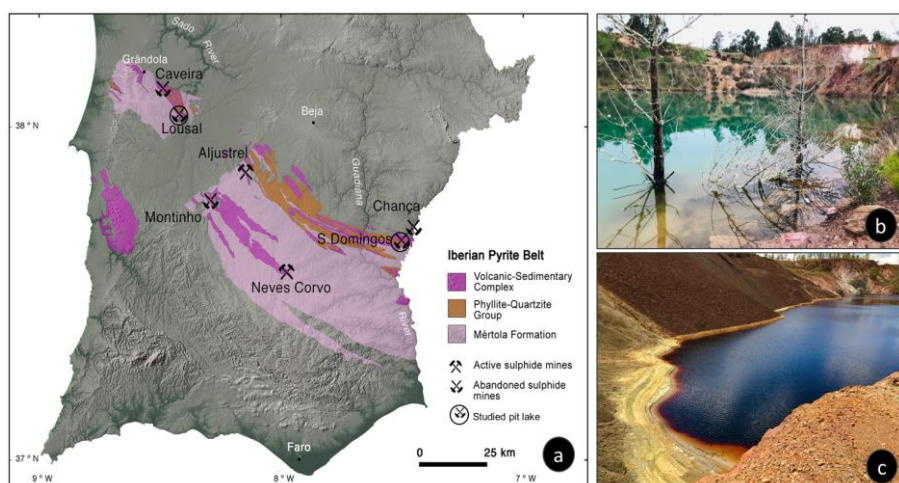


**Fig. 1**. (a) Geological characteristics of the Portuguese Iberian Pyrite Belt, including locations of the mines with the pit lakes studied; (b) Image of the Lousal pit lake Lagoa Azul; (c) São Domingos pit lake.

## 3 Materials and methods

Pit lakes were sampled for surface water, but at different times and frequency. Specifically, monthly sampling was undertaken at São Domingos during the hydrological year of 2016-17. Furthermore, in order to compare behaviour in rainy and dry conditions, summer (July) and winter (February) measurements were made for the three lagoons. Physicochemical parameters as pH, Electrical Conductivity (EC) and Redox Potential (Eh) were obtained in the field. An aliquot of sampled waters was filtered (with 0.45 µm disposable syringe) and acidified, with ultrapure $HNO_3$ (until pH~ 2), for later analytical determination. Another aliquot was obtained for sulfate and acidity. Metals and arsenic contents were analysed by inductively coupled plasma-mass spectrometry at the Activation Laboratories Ltd., Canada (ISO 17025 accredited and certified to ISO 9001).

## 4 Results and discussion

Table 1 presents the water properties of the São Domingos and Lousal pit lakes. The three pit lakes reveal typical conditions of an AMD environment [7, 8]. A strong level of

contamination is documented by electrical conductivity, acidity, sulfate, and other constituents as described for other pit lakes in the Spanish sector of the IPB [2]. There is no clear distinction between the two mining areas examined in this study in terms of acidity, sulfate, Al and Mg, which reflects the common effect of the oxidative dissolution of the sulphides and weathering of host rock minerals. However, the two areas are distinguished from the specific metals associated with the paragenesis of the two deposits. Thus, concentrations of Cu and Zn, for example, are considerably higher at the São Domingos site, while Pb, Co, and Ni dominate the hydrochemistry at the Lousal site.

**Table 1.** Hydrochemical properties. São Domingos annual average (n = 12) and summer and winter values for the three lagoons.

| Pit lakes | São Domingos | | | Lagoa Azul | | Lagoa Vermelha | |
|---|---|---|---|---|---|---|---|
| Campaigns | Annual average | Summer | Winter | Summer | Winter | Summer | Winter |
| pH | 2.7 | 2.9 | 2.7 | 3.9 | 3.5 | 3.3 | 2.4 |
| EC (mS/cm) | 7.852 | 8.850 | 8.460 | 4.430 | 4.784 | 8.630 | 9.517 |
| Eh (mV) | 552 | 555 | 539 | 373 | 410 | 405 | 503 |
| Acidity (mg/L $CaCO_3$) | 3707 | 4150 | 3980 | 197.5 | 143.0 | 1865 | 2545 |
| $SO_4$ (mg/L) | 5873 | 6070 | 6707 | 2095 | 2715 | 5433 | 6753 |
| Al (mg/L) | 215.5 | 221.0 | 219.2 | 11.76 | 16.22 | 96.83 | 196.6 |
| Cu (mg/L) | 66.91 | 70.30 | 75.44 | 0.051 | 0.037 | 0.069 | 0.082 |
| Fe (mg/L) | 725.4 | 709.0 | 1186 | 1.070 | 1.209 | 3.318 | 3.286 |
| Mg (mg/L) | 686.1 | 670.0 | 675.7 | 1.498 | 7.488 | 380.4 | 288.9 |
| Mn (mg/L) | 141.8 | 137.0 | 146.1 | 4.740 | 5.520 | 4.167 | 4.720 |
| Ni (mg/L) | 1.463 | 1.910 | 1.924 | 46.23 | 57.11 | 184.9 | 168.6 |
| Co (mg/L) | 3.599 | 3.770 | 3.590 | 138.9 | 196.3 | 269.4 | 378.2 |
| Zn (mg/L) | 141.7 | 149.0 | 133.9 | 0.226 | 0.522 | 1.045 | 1.409 |
| Cd (mg/L) | 0.831 | 0.875 | 1.003 | 0.173 | 0.201 | 0.087 | 0.011 |
| Pb (mg/L) | 0.155 | 0.200 | 0.309 | 20.74 | 24.90 | 82.32 | 79.93 |

Considering the two pit lakes at Lousal, the most extreme conditions of AMD occur in the Lagoa Vermelha, which exhibits the highest concentrations of most elements. Also, some seasonal effect may be present, with water having higher acidity and metals during the winter. However, this may in fact be a particular condition of the 2016-17 hydrological year. Although there was a severe drought [9], the winter sampling was undertaken after the first rains of the year. Therefore, dissolution of sulfate salts may have generated an increase in the sulfate and metallic contents.

In São Domingos pit lake this seasonal influence is not so clear probably due to the higher resilience associated with the larger volume. Figures 2 and 3 represent some elemental correlations for São Domingos pit lake, with Figure 2 illustrating elemental relationships with EC and acidity. For example, the sum of metals presents a good correlation with acidity, reflecting the process of hydrolysis, with liberation of $H^+$. Also, the results indicate the contribution of acidity to EC. According to [10], EC appears closely linked to the presence of dissolved solids and metal load.
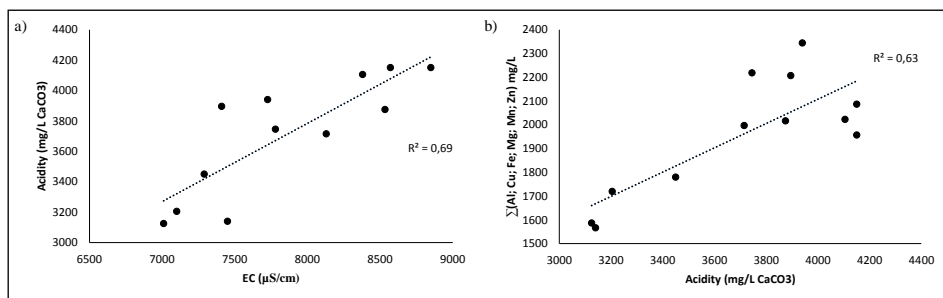


**Fig. 2.** Correlation between pit lake acidity and EC (a) and metal contents and acidity (b).

Figure 3 illustrates the strong correlation between elements from the ore paragenesis (Fe, Cu, Zn) and from the host rock (Al, Mg), suggested by Pearson coefficients >0.70. The metals resulting from dissolution of sulphide minerals correlates with Al and Mg, reflecting the effect of acidity associated with sulphide oxidation over the aluminosilicates that compose the host rock. The strongest relation is observed for Fe and Mg, with Fe mobilized from sulphides and Mg from silicates. So, this relationship reflects the acidic dissolution of minerals that mobilize iron (e.g. from pyrite) and Mg (e.g. from chlorite), two of the most abundant elements in this system. The same assumptions are valid for the other elements such as Al and Cu, also with high correlations, indicating the same derivation from both host rock and ore minerals.
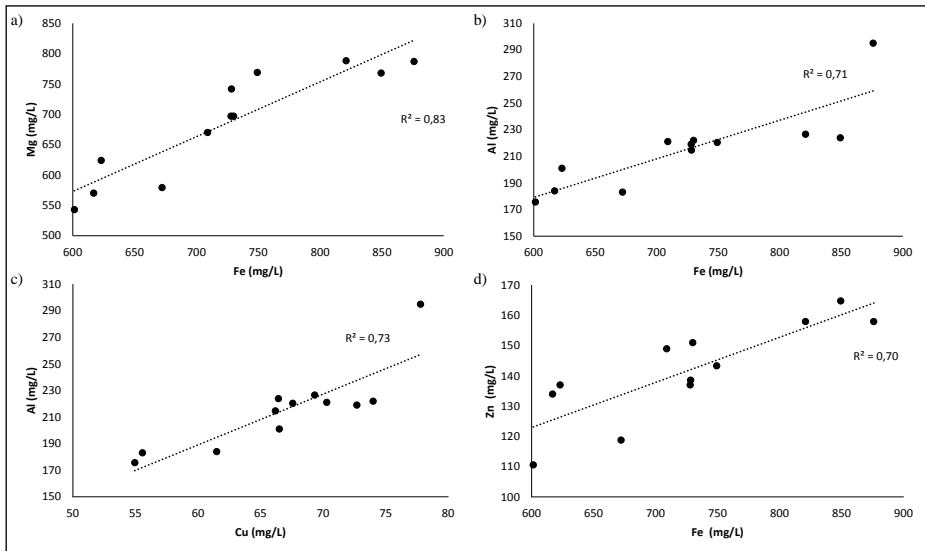


**Fig. 3.** Elemental correlations in waters of São Domingos pit lake: Mg versus Fe (a), Al versus Fe (b), Al versus Cu (c), and Zn versus Fe (d).

Figure 4 presents a Ficklin diagram [11, 12] for the pit lakes of the Portuguese sector of the IPB. For comparison, some representative pit lakes from the Spanish sector of the IPB are also shown on the diagram. The figure shows that São Domingos and Atalaya (Riotinto mine, Spain) fall in the same classification domain: High-acid, Extreme-metal. They are relatively near geographically (only 81 km apart), and have similar paragenesis and exploitation history.
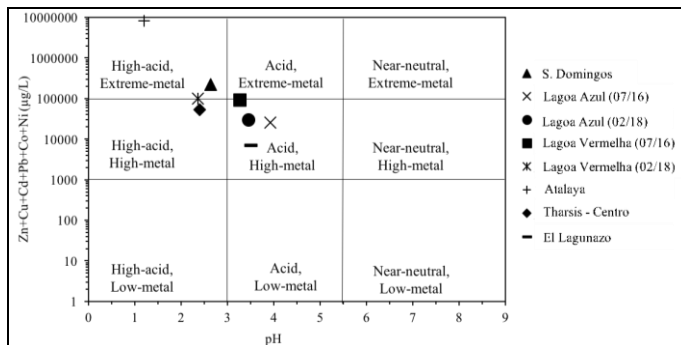


**Fig. 4.** Projection of pit lake in Ficklin diagram. Data of Spanish pit lakes are from [2].

Lagoa Azul and El Lagunazo are classified as Acid, High-metal. Both are characterized as having the least acidic character and lowest metal contents of the study. Another characteristic common to these two pit lakes is their bluish water color, distinctive by comparison to most pit lakes in the IPB, that have a strong characteristic red color. This fact may be reflective of lower dissolved solids content and presence of aluminium [2].

## 5 Conclusions

As a consequence of cessation of water extraction in the open-cuts, groundwater levels in the São Domingos and Lousal pit lakes have risen to an apparently stationary level. Our results indicate slightly lower levels of contamination in Lousal, especially in Lagoa Azul. Also, seasonal influence is more noticeable at Lousal. São Domingos is a high-acid, extreme metal pit lake having the same chemical character as that Atalaya in Spain.

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