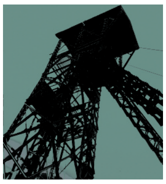

RELATIONSHIPS BETWEEN PHYSICO-CHEMICAL INDICATORS OF ACID MINE DRAINAGE

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ABSTRACT

Acid mine drainage (AMD) is an important focus of environment impact that supports the degradation of the ecosystems at global levels. São Domingos mine is a paradigmatic site in the Portuguese Iberian Pyrite Belt, known by strong contamination by AMD. The acidic waters drain into the Chança water dam, highlighting the importance of the mine regarding accomplishment of water quality compatible with human consumption.

The present study shows the variations between pH, Electrical Conductivity, Total Acidity and Sulphates in the rainy season (from October to March 2017) in the most affected areas, as well as the response of the receiving water dam to the changes induced by AMD.

The results indicated that the extreme values occur in one peculiar small dam (PAT 7), as result of AMD potential of the accumulations of very fine grain sulfide-rich wastes that drain into this dam. Here, strong reactivity is marked by water physical-chemical parameters as well as by the presence of mineralogical indicators, such as salt efflorescences. The correlation between parameters reflects water-mineral interactions involving the sulfides, which oxidative dissolution is responsible for the production of acid sulphate waters.

Key words: physical-chemical, total acidity, sulphates, acid mine drainage, São Domingos mine.

1. INTRODUCTION

Since pre-historic times, the humankind explores natural resources to obtain raw materials. The exploitation of mineral resources stimulates the economy, creates wealth, but generates impacts that may be the basis of some conflicts of interest with other uses of the territory. The mining industry is one of the most problematic activities in the primary sector. This impact is even superior in mines whose abandonment occurred in an uncontrolled manner, generating environmental focus that persists until today (Gomes, 2011).

Sulfide-rich waste-dumps, when exposed to weathering processes, promote a global environmental problem related with acid mine drainage (AMD) (Chockalingam and Subramaniam, 2009). In the rainy season, waters interact with sulfide materials in the waste-dumps and release acidity, sulphate and metals, forming acid sulphate-rich leachates (Grande et al., 2016).

In the Iberian Pyrite Belt (IPB) there are many abandoned mines that do not present any corrective or preventive measures for the aquatic system. São Domingos mine is located in the Portuguese sector of the IPB, and it was an important mining centre dating back to pre-Roman times remaining in activity until 1966, when it was definitely halted (Álvarez-Valero et al., 2008). It is characterized by an open pit exploitation of massive sulfide ores that are located near the top of the Volcanic Sedimentary Complex. Nowadays, the waste-dumps are spread along approximately 5.5 km in the margin of the Chança River, being the main contaminant focus of the water system. Inserted in the semi-arid climate of this area and considering the lack of water resources in this region (Alentejo), the study of AMD contamination is a relevant issue.

The specific objectives of the present work are focused on characterizing the variations between pH, Electrical Conductivity, Total Acidity and Sulphates in the rainy season (from October to March) and observing the response of the aquatic system to the changes induced by AMD. This will give indication about the degree of contamination in São Domingos and will allow preliminary understanding of the hydrochemical and hydrological relationships that are occurring in the receiving aquatic system (Chança reservoir, used human consumption). Sampling points were selected immediately upstream and downstream of São Domingos mine, in order to evaluate the effects of the leachates on the physical-chemical parameters of the system.

2. MATERIALS

Field sampling and laboratory analyses implied the use of diverse equipment, materials and reagents. Multiparameter portable meter CRISON MM40+ was used for in situ parameters. The following Orion probes were used: combined pH/ATC electrode Triode ref. 91-07WM and a conductivity cell DuraProbe ref. 013010. Potential redox (Eh) was measured using multiparameter porta-

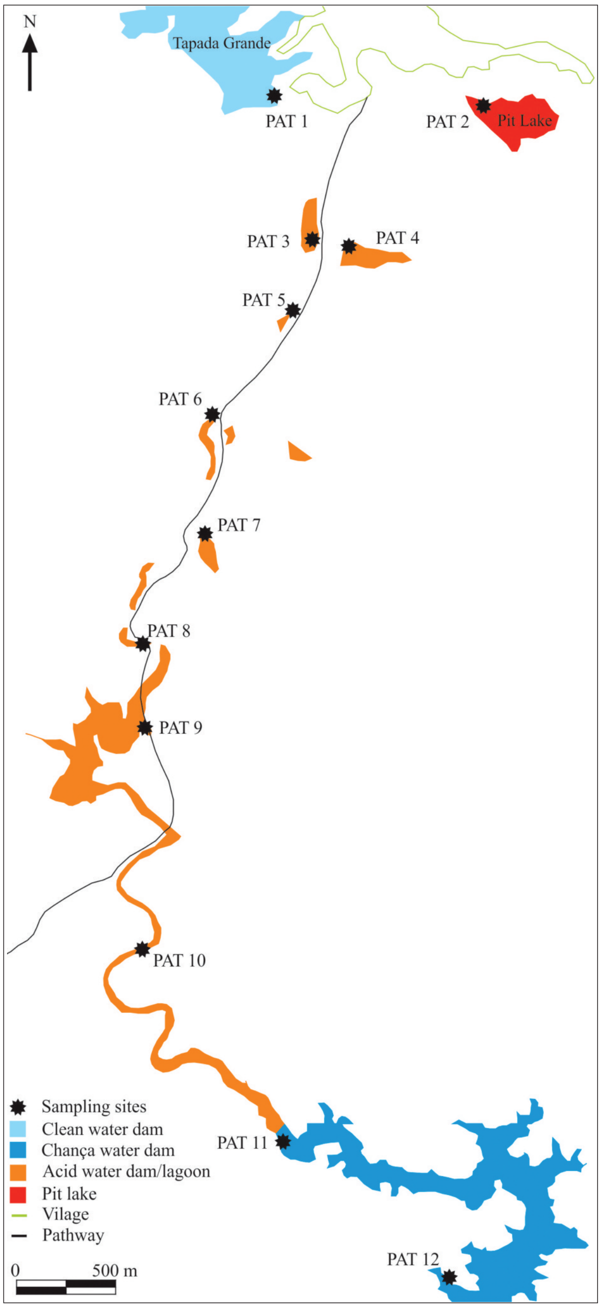

Figure 1 - Map location of water dams in São Domingos mine with sampling sites

ble meter Thermo Scientific Orion with a probe Orion triode low maintenance ref. 9179BN. Water samples were collected into high-density polyethylene containers and maintained in a portable refrigerator. In the laboratory, heating plates, glass calibrated material, and pro analysis reagent standard solutions were used for volumetric determinations in accordance with ASTM (1992).

3. METHODS

The samples were collected in different sites, as represented in Figure 1: water dam upstream the mine (PAT 1); pit lake (PAT 2); in water dams along the mining complex (PAT 3-PAT 9); upstream of the confluence in the Chança river (PAT 10); in the plume of AMD dispersion (PAT 11), and in the Chança water dam (PAT 12). Field determinations presented in this work consisted in the following parameters: pH, Electric Conductivity (EC) and Potential Redox (Eh). In the laboratory, Total Acidity was immediately measured by volumetric determination (ASTM, 1992), whereas sulphates were determined by turbidimetry (Standard Methods, 4500 E). Samples of efflorescent salts were collected in March with plastic spatulas in closed polyethylene bottles around de sampling point PAT 7 (Fig. 1). X-ray diffraction (XRD) and scanning electron microscopy were applied for their mineralogical analysis.

4. RESULTS AND DISCUSSION

Table 1 shows the results of water parameters.

The pH shows variability among water dams. As expected, the highest value (7.52) was found in the water dam referenced as PAT 1, in January 2017. This sampling point represents clean water, without influence of the acid leachates. Therefore, it has the highest pH range, from 5.18 to 7.52. In a similar way, PAT 12 presents also high pH values, showing the absence of contamination in a location already far from the mine. The lowest value was 1.44 (PAT 7), measured in October 2016, highlighting the effect of AMD from the sulfide wastes accumulated around the metallurgical complex. Furthermore, this dam (PAT 7) shows unique conditions regarding evidences of reactivity and mining pollution. This fact can be explained by the high contamination potential of several waste-dumps and piles that drain into PAT 7. From mineralogical and textural point of view, the analyses reflect the purity of these materials, which are mainly composed by milled pyrite and chalcopyrite, describing a typical scenario of polymetallic sulfides from volcanic-hosted massive deposits (Grande et al., 2013). Moreover, strong salinization is another evidence of reactivity. It is possible to observe over the waste dumps, pools and banks of the drainage channel, a variety of colours promoted by the blooms of salt efflorescences. Figure 2 shows the PAT 7 surrounding area and the soluble salts. In humid microenvironments, melanterite ($FeSO_4 . 7H_2O$) is the most abundant phase. Additionality, analysis performed by XRD allowed the identification of sulfate minerals, such as ferricopiapite ($Fe^{3+}_5(SO_4)_6O(OH) \cdot 20H_2O$), pickeringite ($MgAl_2(SO_4)_4\ 22H_2O$), coquimbite ($Fe^{3+}_2(SO_4)_3 \cdot 9(H_2O)$)), as well as sulphur. These minerals are known by their environmental importance in monitoring pollutants in contaminated environments (Valente et al., 2013).

Samples from PAT 2 to PAT 9 have always pH < 3 in the four initial campaigns. The lowest pH value was recorded in PAT 5 in October (2.33) and PAT 4 in November (2.54). These results represent the influence of waste dumps and meteorological conditions in the water quality.

EC behaves somewhat inversely to pH. So, the clear water dam had the highest pH of all samples, while the EC was one of the lowest (28.00 $\mu S/cm$ in January). The highest EC occurs in the AMD solutions, reaching 26200 $\mu S/cm$ (PAT 7), in November 2016. Thus, pH and EC present the expected pattern taking in account the environment of each sampling point. Downstream, from the point of the plume dispersion of AMD in the river, there is a tendency to incre-

TABLE 1- PHYSICAL-CHEMICAL PARAMETERS, TOTAL ACIDITY AND SULPHATE CONCENTRATION (N=6). NOT APPLICABLE= N.A

	Samples	pH	EC (µS/cm)	Eh (mV)	Acidity (mg/L $CaCO_3$)	SO_4 (mg/L)
PAT 1	Average	6,54	227,6	239	n.a.	6,6
	Median	6,54	264,8	271	n.a.	6,5
	Min	5,18	28,00	49	n.a.	2,2
	Max	7,52	308,0	352	n.a.	12,5
PAT 2	Average	2,55	6597,2	537	3704,2	5792,6
	Median	2,56	7440,0	541	3820,0	5768,4
	Min	2,42	741,00	506	3125,0	4742,0
	Max	2,67	8572,0	565	4150,0	6520,2
PAT 3	Average	2,67	2414,7	521	1067,5	1379,7
	Median	2,69	2550,0	519	938,8	1160,9
	Min	2,40	228,00	501	530,0	661,5
	Max	2,79	4251,0	543	1952,5	2661,1
PAT 4	Average	2,69	2266,2	550	1311,3	1714,0
	Median	2,63	2334,5	552	1335,0	1824,9
	Min	2,54	310,00	487	437,5	552,3
	Max	2,99	4230,0	605	1980,0	2600,4
PAT 5	Average	2,64	3018,5	5445	1847,6	2350,9
	Median	2,67	2880,0	535	1331,3	1606,3
	Min	2,33	251,00	497	640,5	865,7
	Max	2,84	6541,0	600	4970,0	6518,0
PAT 6	Average	3,02	1456,6	509	1055,8	1083,8
	Median	2,81	304,00	515	702,5	660,8
	Min	2,71	117,30	450	0,0	68,2
	Max	3,99	4320,0	541	3455,0	2955,1
PAT 7	Average	1,97	13387,8	531	79843,8	74077,0
	Median	2,13	12332,5	516	30468,8	25459,9
	Min	1,44	1252,0	447	11812,5	10123,7
	Max	2,29	26200,0	657	292500,0	282924,9
PAT 8	Average	3,10	2251,5	463	1415,8	1646,7
	Median	2,85	1917,5	480	791,3	951,0
	Min	2,45	181,90	288	0,0	58,5
	Max	4,71	6114,0	549	4485,0	5502,6
PAT 9	Average	2,98	1593,8	482	748,8	926,1
	Median	2,87	1436,5	478	842,5	1096,5
	Min	2,66	204,00	374	58,3	110,4
	Max	3,52	3186,0	561	1332,5	1641,5
PAT 10	Average	3,19	2106,5	470	735,9	1451,7
	Median	3,25	956,00	466	284,6	422,9
	SD	0,48	3217,3	65	1148,2	2608,0
	Min	2,54	185,70	363	92,3	151,3
	Max	3,74	8598,0	543	3037,5	6753,2
PAT 11	Average	3,95	544,9	386	165,7	324,6
	Median	3,72	370,3	426	81,3	124,4
	Min	2,92	168,7	85	0,0	98,4
	Max	5,09	1429,0	516	522,5	790,0
PAT 12	Average	5,90	252,3	297	n.a.	38,3
	Median	5,91	248,0	310	n.a.	39,0
	Min	5,34	26,50	174	n.a.	26,2
	Max	6,58	503,1	391	n.a.	48,2

Figure 2 – Image of PAT 7 surrounded by waste-dumps and piles and the presence of soluble salts at the banks of dam. Green color is due to melanterite (FeSO4 7H2O).

ase the pH and decrease of EC, due to dilution of the AMD and minor presence of waste dumps. The lowest EC value was found in the Chança water dam (26.50 μS/cm), in January 2017.
The Figure 3 highlights the inversely relationship between pH and EC, i.e., when the EC presents extreme high values, pH is found to have low values. In relation to sulphate concentrations, it is possible to notice a similar trend to parameters such as Total Acidity and EC. On the other hand, they decrease with the increase of pH.
As noticed for other parameters, sulphate is also highest at PAT 7, with 282925 mg/L. In the opposite, PAT 1 exhibited the lower concentration with 2.20 mg/L, followed by PAT 12 with 26.2 mg/L. Regarding the redox conditions, PAT 1 and PAT 12 present the lowest Eh values, in accordance with the highest pH measured in all campaigns.
According to Grande et. al. (2017), the solubility of substances is determined by the acidity of the channel, as the pollutant concentration follows the pattern defined by the values of pH, corresponding points with higher concentration of pollutants with those of lowest pH values.
The description of the process that happens along the system can be as following: rainfall promotes the release of elements in the

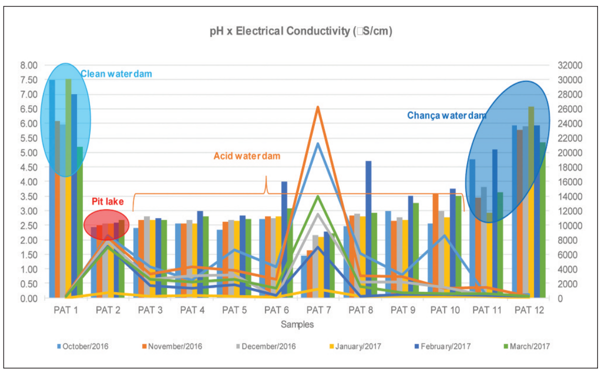

Figure 3 – Monthly variation of pH and EC.

waste dumps, generating AMD contaminated leachates causing a decrease of pH and an increase of sulphates' concentration in the receiving waters.
In terms of the degree and type of mining pollution, climate conditions especially precipitation, are the most significant external controlling factors (Santisteban et al., 2015).
Correlation analysis provides an effective way to reveal the relationships between physical parameters. Therefore, Figure 4 shows the correlation between pH x Total Acidity, pH x Sulphate and Total Acidity x Sulphate, suggesting a close association. Person correlation indicated strong positive correlation of 0,907; 0,862 and 0,998, respectively, highlighting the role of sulfides in the acidity production.

5. CONCLUSION

The preliminary results obtained for the São Domingos mining complex represent the influence of the mining infrastructures in the water contamination. The sampling point that has the lowest pH was PAT 7, contrarily to PAT 1, with higher values. In general, all the extreme values were observed in PAT 7 as result of AMD produced by the weathering of very fine grain sulfide-rich wastes dispersed around the area. The secondary paragenesis, represented by sulphate efflorescences are mineralogical indicators of such contamination.
The pH x Total Acidity, pH x Sulphate and Total Acidity x Sulphate are well correlated. This reflects the water-mineral interactions involving the sulfides, which oxidative dissolution is responsible for the production of acid sulphate waters.
It is possible to notice a dilution of AMD downstream, mainly from the confluence with the Chança River.
The meteorological conditions and the influence of waste-dumps had a massive effect on contamination. The abandoned waste-dumps and piles continue to product acid leachates when the structures are exposed to precipitation.
Further studies intend to characterize in more detail the correlations between the composition of the waste dumps, hydrological variations and the hydrochemistry of water, including the response of the

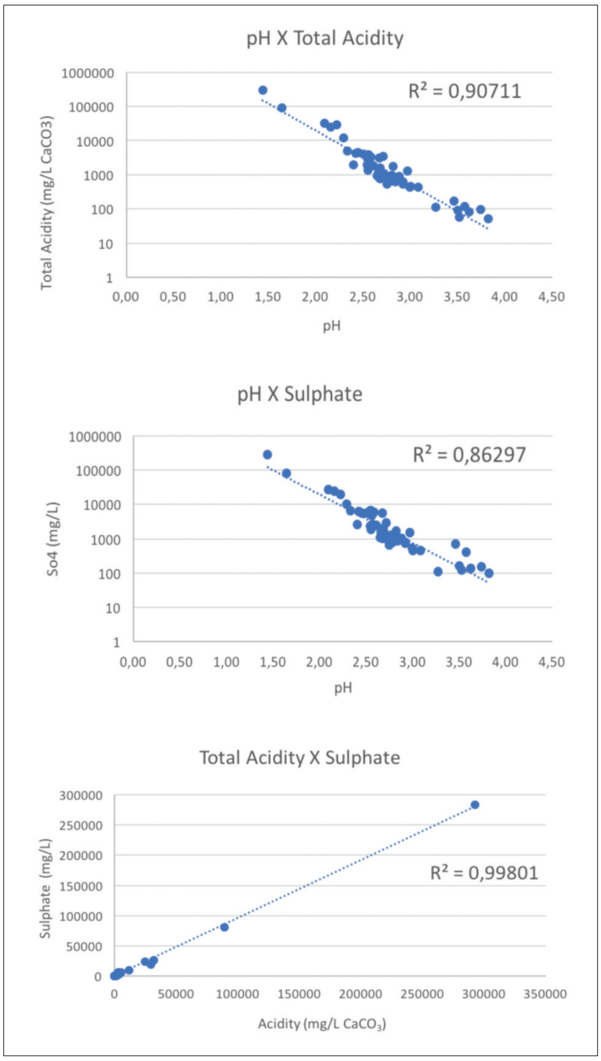

Figure 4 - Correlation between pH, Total acidity and Sulphate. Pearson correlation coefficients are provided in the graphs.

Chança River. These studies may help the establishment of preventive and rehabilitation measures for this mining complex.

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7. REFERENCES

- Álvarez-Valero, A.M., Pérez-López, R., Matos, J.X., Capitán, M.A., Nieto, J.M., Saez, R., Delgado, J., Caraballo, M. (2008). Potential environmental impact at São Domingos mining district (Iberian Pyrite Belt, SW Iberian Peninsula): evidence from a chemical and mineralogical characterization. Environ Geololgy. 55, 1797–1809.
- ASTM 5245. (1992). Standard practice for cleaning laboratory glassware, plasticware and equipment used in microbiological analysis. ASTM Committee on Standards. American Society for Testing and Materials, 5.
- AWWA, "Standard Methods for the Examination of Water and Wastewater", American Public Health Association, Washington DC, 18th ed., 1992.
- Chockalingam, E., Subramaniam, S. (2009). Utility of Eucalyptus tereticornis (Smith) bark and Desulfotomaculum nigrificans for the remediation of acid mine drainage. Bioresource Technology 100, 615-621.
- Grande, J.A., Valente T., de la Torre M.L., Santisteban, M., Ceron, C., Pérez Ostalé, E. (2014). Characterization of acid mine drainage sources in the Iberian Pyrite Belt: base methodology for quantifying affected areas and for environmental management. Environ Earth Sci 71:2729-2738.
- Grande, J.A., de la Torre M.L., Valente T., Pérez Ostalé, E. (2016). Spatial evolution of an AMD stream in the Iberian Pyrite Belt: process characterization and control factors on the hydrochemistry. Hydrological Sciences Journal. 61(8) 1503-1511.
- Grande, J.A., Santisteban, M., Valente T., de la Torre M.L., Gomes, P. (2017). Hydrochemical characterization of a river affected by acid mine drainage in the Iberian Pyrite Belt. Water Science & Technology. DOI: 10.2166/wst.2017.097.
- Gomes, P., (2011). Processos de reabilitação natural em escombreiras de minas abandonadas – Estudo de Casos. Tese de Mestrado. Univ. Porto, Porto, 121.
- Santisteban, M., Grande, J.A., de la Torre, M.L., Valente, T., Ceron, C. (2015). Acid mine drainage in semi-arid regions: the extent of the problem in the waters of reservoirs in the Iberian Pyrite Belt (SW Spain). Hydrol. Res. 46, 156e167.
- Pérez-Sirvent, C.; Hernández-Pérez, C.; Martínez-Sánchez, M.J.; García-Lorenzo M.L.; Bech, J. (2016) Geochemical characterisation of surface waters, topsoils and efflorescences in a historic metal-mining area in Spain. Journal of Soils and Sediments, 16:1238–1252, DOI 10.1007/s11368-015-1141-3.
- Valente, T.; Leal Gomes, C. (2009). Occurrence, properties and pollution potential of environmental minerals in acid mine drainage. Science of the Total Environment, 407:1135-1152.
- Valente, T.; Grande, J.A.; de la Torre, M.L.; Santisteban, M.; Cerón, J.C. (2013). Mineralogy and environmental relevance of AMD-precipitates from the Tharsis mines, Iberian Pyrite Belt (SW, Spain). Applied Geochemistry, 39:11–25.