

## XII CONGRESO NACIONAL Y XI IBÉRICO DE GEOQUÍMICA

Investigar los recursos cuidando el ambiente

# MAPPING MINING WASTES AND ANALYZING AFFECTED AREAS THROUGH EXPEDITIOUS PHYSICO-CHEMICAL PARAMETERS

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#### **ABSTRACT**

In the past, the large-scale exploitation of São Domingos mine, in the Portuguese sector of the Iberian Pyrite Belt, generated enormous reactive waste dumps. The sulphide- richness of these accumulations has been responsible for degradation of the entire ecosystem through the discharge of acidic leachates, very enriched in sulfate and metals. Pyrite is the most abundant mineral, from which oxidation results this acid mine drainage. Nowadays, there are numerous waste dumps, of different mining periods (from the roman until XX century), dispersed along the entire mining complex. The wastes present high variability in gran size and lithological composition, which controls their reactivity and consequently their contaminant potential. So, specifically, the present study shows a map of the wastes, at scale of 1:25,000, in order to analyze the nature of water changes induced by the solutions that are drained from the different types of waste accumulations.

Key words: acid mine drainage, mapping, mining wastes, reactive materials, São Domingos, SW Portugal

#### 1. INTRODUCTION

The mining complex of São Domingos is located in the northern part of the Iberian Pyrite Belt (IPB) and was mined between 1857 and 1966 for the production of pyrite, copper and sulfur (Matos et al., 2012). The intense mining activity produced considerable amounts of wastes, from which oxidation results extremely acid leachates with high content of sulphate, metals and metalloids, known as acid mine drainage (AMD) (Parker and Robertson, 1999; Younger et al., 2002; Grande et al., 2016; Valente et al., 2016). The presence of secondary minerals in the waste dumps and the drainage surfaces indicate that these materials are still reactive and have environmental importance with regard to the solubility and potentially toxic elements enclosing in its composition. The final discharge of acid leachates reaches the Chança river, main effluent of the Guadiana river, potentially affected by this pollution (Álvarez-Valero et al., 2008). This work presents

preliminary results on mapping of the mining wastes and in analyzing their properties, in order to understand the contribution of different types of wastes to the water degradation.

#### 2. MATERIALS

For mapping activities Garmin GPSMAP 76CSx was used. This activity was supported by the topographic map 559-Santana de Cambas (1:25000), aerial photographs and the QGIS 2.12 software. Measuring of field physico-chemical parameters was achieved through multi-parameter meter (Orion 5 Star). Mining wastes were collected and stored in plastic bags.

#### 3. METHODS

#### 3.1. SAMPLING

Water was collected once a month between October 2016 and June 2017 in the following locations of the system: (PAT 1) water from Tapada Grande, represents water that is not influenced by the mine; (PAT 2) water from the pit lake; (PAT 3), (PAT 4), (PAT 5), (PAT 6), (PAT 7) and (PAT 8) are sites directly influenced by AMD; (PAT 9) acid water dam; (PAT 10) immediately upstream of the confluence in the Chança river, (PAT 11) dispersion plume of AMD in the river; (PAT 12) Chança water reservoir. Wastes were collected in order to cover compositional variability.

#### 3.2. ANALYTICAL METHODS FOR WATER

The pH, electric conductivity (EC) and redox potential (Eh) of the water samples were measured in the field with a multi-parameter meter (Orion 5 Star).

#### 3.3. MAPPING AND ANALYTICAL METHODS FOR WASTES

The identification of the wastes and landfills in the field were coeval to the cartographic activity. For the waste characterization, the pH and EC of the paste were obtained in a suspension of 1:2.5, following the procedure described by Black (1965), X-ray diffraction was applied for mineralogical characterization of selected materials. Sulphur content was obtained by ICP-MS.

#### 4. RESULTS

The Figure 1 illustrates the mapping of the wastes, which accumulations were classified in two categories: waste dumps (Ex) were considered as piles of different types of materials derived from the mining and industrial activities, whereas landfills (Ax) represent accumulated materials that suffered transport, which

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WD E1	<b>Location</b> N from the PL	Area (ha) 1.87	<b>Drainage direction</b> PL and north	General properties  Horizontal surface, medium to fine granulometry, black and re-				
LI	IV HOITI THE FE	1.07	TE did north	colors, composed of old slags and gossan, very old wd and				
	NIM from the DI	0.07	DI .	partially re-vegetated.  Compacted volcanics and shales.				
E2 E3	NW from the PL  NE from the PL	0.86 2.02	PL PL	Group of small wd with heterogeneous granulometry and				
LJ	INE HOITI THE FE	2.02	I L	composition. Old slags mixed with material in process of				
				pedogenesis and material used in civil construction. Very old				
				wd and totally re-vegetated.				
 E4	E from the PL	0.51	PL	Volcanics and shales with heterometric granulometry.				
E5	SE from the PL	6.36	PL and stream	Wd from distinctive periods overlapped,				
LJ	SE HOM the FE	0.50	southwards	heterogeneous material (shales) of fine to gross granulometry				
			from the PL	re-vegetated.				
E6	E from the PL	0.08	PL	Very thin material, light color.				
E7	S from the PL	2.5	PL	Gossan with fine to medium particle size; re-vegetated.				
 E8	W from the PL	0.41	Stream southwards	Fine to very fine granulometry, great presence of secondary				
			from the PL	oxides and sulfates of green and yellow colors (Cp and Jrs).				
E9	SW from the PL	7.48	PL and stream	Major composition of cementation wastes (~ 80%). At the SW				
			southwards from	limit of this wd there are sulphide-rich materials and secondar				
			the PL	minerals resulting from their alteration, predominantly Cp and J				
E10	NW from the PL	0.49	PL	Washed Py, fine granulometry, there are also abundant				
				quartz, Jrs and Gth				
E11	W from the PL	2.1	PL	Fine material, composed predominantly of modern slags,				
				black color.				
E12	N from the PAT 4	3.1	PAT 4	Predominate fragments of shale, medium to gross				
				granulometry, sporadically occur large mineralized blocks				
				that show evidence of incipient oxidation and salinization.				
E13	NW from the church	1.5	Lagoon	Shale with medium to gross granulometry, re-vegetated				
				(planting of olive trees).				
E14	N from the PAT 6	2.11	AWS	Old slag, medium to thick granulometry, black color.				
E15	E from the PAT 6	5.93	AWS	Material very thin to fine, white to pale beige.				
E16	Between PAT 6 and PAT 7	6.28	AWS	Slag with granulometric variety, sand to pebble, black color ar with different degrees of roasting. There are portions where there is evidence of reactivity (gypsum) probably because the process was not complete, thus there were sulphides capable				
				origin these salts. Ordinary slag has an inert, vitreous characte however in some portions (more exposed areas), there are reactions.				
E18	E from the PAT 7	1.55	PAT 7 and AWS	Mixture of washed ore, Py ashes and Cp (the last can reach				
				thicknesses of up to 10 cm). Sometimes they are distinguished				
				in the field, by the type of salinization that develops on their				
				surface, in some cases white salts predominate, probably				
				gypsum and iron sulphate (rozenite); in other cases the green				
F10	CE ( DAT 7	0.07	0.47.7	salt Cp is the most common one.				
E19	SE from the PAT 7	0.07	PAT 7	Old slag, medium to thick granulometry, black color.				
E20	S from the PAT 1	16.89	AWS	Brownish shales, sometimes dark gray, with medium to thick				
F 2 4	CE feace the DAT 4	1.40	DATO	granulometry. This wd is partially re-vegetated.				
E21	SE from the PAT 1	1.42	PAT 3	Volcanics and clay shales with variable granulometry (medium				
	E f II - DI	0.24	D.	to thick) and light gray and light brown colors.				
E22	E from the PL	0.24	PL	Old slag, medium to thick granulometry, black color.				



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	LE 2 – DESCRIPTI						
LF A1	Location  Surrounding PAT 3	Area (ha) 14.6	Drainage direction PL and PAT 3	C or NC	pH paste 2.59 - 3.07	EC paste 6.92 - 7.21 mS/cm	General properties  Heterogeneous granulometry of various origins: tailings, residues from smelted ore, remains of old precipitates and iron oxides. There are strong evidences of acidity, like salinization (Al-Fe and sulphates, mainly at the landfill base) and filamentous algae. There is great abundance of Jrs as a cover over the rock fragments. Fragments of jasper were also identified.
A2	Stream southwards from the PL	2.15	Stream southwards from the PL	NC	-	-	Fine to very fine materials from metallurgical treatment.
A3	N from the stream southwards from the PL	1.37	Stream southwards from the PL	C	3.27	10.97 mS/cm	Very heterogeneous granulometry, predominance of highly oxidized material, very red color. Features characteristics similar to the oxidized material of E9.
A4	W from the PL	3.42	PL and PAT 3	NC	-	-	Very heterogeneous material (volcanics and shales) and granulometry, not calcined, very high degree of revegetation.
A5 S	SW from the PL	3.31	Stream southwards from the PL	С	2.71 - 2.86	2.05 - 2.32 mS/cm	At the western boundary of this landfill there is the formation of a depression where the accumulation of very fine sediments is observed, with fine, beige color, deriving from transport.
A6	W from PAT 4	1.92	PAT 4	C	2.51	7.70 mS/cm	Fine sediment deriving from the leaching of the surrounding landfills, providing the accumulation of fine material. Contaminant character evidenced by corrosion phenomena and the presence of supergenic neoformations, namely Jrs / Fe sulfate besides the pH of the paste and of the finer residue.
A7	E from PAT 1	7.71	PL and PAT 3	NC	-	-	Shale and gossan fragments with variable granulometry.
A8	NW from PL	2.71	Tapada Pequena and PL	NC	-	-	Fragments of volcanics and shales with variable granulometry.
A9	NE from PAT 3	3.49	PAT 3 and PAT 4	С	3.35	297 µs/cm	Predominantly fragments of shale nature, sporadically occur large mineralized blocks that show signs of incipient oxidation and salinization.
A10	S from PAT 3	10.09	PAT 5 and AWS	C	3.05 - 3.31	595 - 1525 μs/cm	Similar characteristics to A1: heterogeneous granulometry and diverse origins. There are also recent precipitates, but there are scattered accumulations of old slag and a greater proportion of rocks with iron oxides, variable granulometry and a greater proportion of shales.
A11	NE from PAT 5	0.28	PAT 5 and AWS	С			Washed Py, fine granulometry, occurs covering the debris deposited below (A10).
A12	N from PAT 6	1.76	AWS	NC	-	-	Shales, medium particle size, non reactive, without vegetation.
A13	NW from PAT 7	6.58	AWS	NC	-	-	Similar characteristics to A12, shale material, medium particle size, non reactive, without vegetation.
A15	NE from PAT 7	1.12	AWS	nd			Set of evaporation rafts used to recover Fe sulphate.

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TABL	E 2 – DESCRIP	TION OF L	ANDFILLS (CO	NT)			
LF	Location	Area (ha)	Drainage direction	C or NC	pH paste	EC paste	General properties
A16	E from PAT 6	6.31	AWS	nd			Leaching tank with very fine, white to pale beige, material.
A17	E from PAT 7	11.23	PAT 7 and AWS	NC	-	-	Areas affected by old mining processes. fragments of rocks yellowish to reddish with some evidence of oxidation - small portions of rocks with Fe oxide. Fragments of jasper, shale and volcanic. Incipient revegetation where there is water
A18	SW from PAT 9	0.41	AWS	C			Heterogeneous material, identified shales and gossan fragments. The water drained by this landfill reaches a water line where there is the presence of opaque and shiny white salts (gypsum), this water line shows no evidence of acidity.
A19	SE from PAT 9	0.72	AWS	NC	-	-	Heterometric non-reactive heterogeneous fragments of shales and volcanics.
A20	NE from PAT 3	2.17	PAT 3	NC	-	-	Heterometric fragments of volcanics and shales.
A22	S from PAT 7	6.25	AWS	-	-	-	Area around the infrastructures of the Achada do Gamo and railway, with small lenticules of heterogeneous material, namely washed Py (greater proportion), slag and oxidized materials.

Note: LF: Landfill; PL: pit lake, C: contaminant; NC: not contaminant; nd: not determined; AWS: acid water stream; Py: pyrite; Jrs: jarosite.

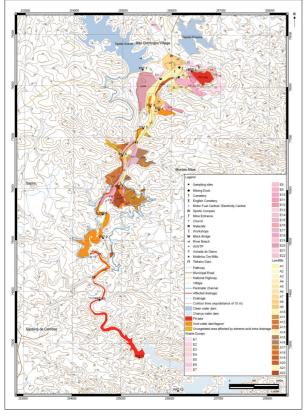


Figure 1 – Mapping of mining wastes.

present location results from some kind of the use of the waste dumps. Both present high variability concerning grain size and composition. The waste dumps and landfills were described according to their attributes, such as occupied surface area, particle size, color, main lithologies, physical stability, pH paste, EC paste and state of revegetation, among others. Table 1 is an extract of the waste dumps inventory and Table 2 is concerned to the landfills. The characterization of the landfills attended to their reactive nature, which is potentially responsible for AMD. So, criteria such as pH of the paste and presence of salinization were used as indicators of the respective contaminant character: Contaminant (C) or not contaminant (NC).

Figures 2 and 3 present average values of field parameters, illustrating the influence of the discharge of AMD along the river system. For effects of better illustration, the mining complex was divided in two sectors. The North sector (Fig. 2) includes the materials around the pit lake until the area of industrial treatment (Achada do Gamo), whereas the South sector shows the downstream area, until the confluence in the Chança reservoir. The lowest values of pH, and highest EC and Eh were presented by PAT 7 (Achada do Gamo), followed by PAT 2 (pit lake). Both sites are influenced by waste dumps, as shown in Figure 2, whose amount of sulphur is presented in Table 3. The most contaminated site, PAT 7, is surrounded by the waste dump E18, which were sampled in three different areas and presented the highest concentrations of sulphur. Regarding to the PAT 2, six waste dumps were analyzed, and some of the samples also showed elevated concentrations of sulphur.



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TABLE 3 – DESCRIPTION OF L	ANDFILLS				
Drainage direction	Waste Dump	Total S (%)	рН	EC (μS/cm)	Eh (mV)
PAT 2 - Pit lake	E1	0,28			
	E4	0,30			
	E5	0,50			
	E7	0,77			
	E10 (oxidised)	11,20			
	E10 (unoxidised)	1,26			
	E11	3,20	2.68	6939.22	550.10
PAT 7 - Achada do Gamo	E18	6,75			
	E18a	66,20			
	E18b	10,50	1.86	14132.44	521.47

#### 5. CONCLUSIONS

In general, waste dumps and reactive landfills are the main focus of the contamination in São Domingos. The pH of the paste, the sulphur content as well as evidence of salinization are indicators of the contaminant character. In accordande, drainage from these reactive sites is reponsible for the worst contamination scenario, observed in PAT 7. Thus, this point has an average pH of 1.86, EC of 14132.44  $\mu$ S/cm and Eh of 521.47 mV, followed by the pit lake (2.68 pH, EC 6939.22  $\mu$ S/cm, Eh 550.10 mV), both of them strongly influenced by discharge of acidic leachates emerging from different types of waste dumps, including piles of fine grain pyrite.

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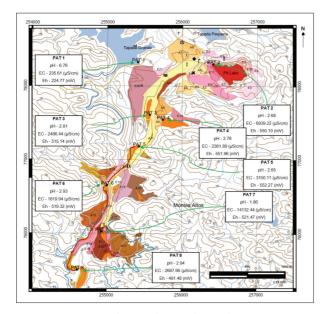


Figure 2 – Average values of physico-chemical parameters in representative sampling points in the northern area.

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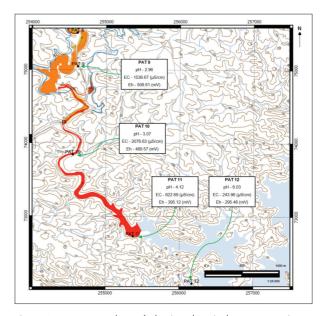


Figure 3 – Average values of physico-chemical parameters in representative sampling points in the southern area.

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