Water Air Soil Pollut (2019) 230:158
https://doi.org/10.1007/s11270-019-4190-1

Oxidation Dynamics and Composition of the Flotation Plant Derived Tailing Impoundment Aquisgrana (Spain)

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Received: 17 January 2019 / Revised: 14 May 2019 / Accepted: 27 May 2019

Abstract A tailing impoundment situated in the mining district of La Carolina (Spain), which stores waste resulting from the washing of Pb and Ag sulphides, was studied 30 years after it was abandoned. Fibre optic sensors were installed to record humidity, temperature, electrical conductivity and oxygen content in the pores down to a depth of 35.5 m. The oxygen profiles show an oxidised thickness of 5 m, meaning that the speed of the advancing oxidation front is estimated as 15 cm year^{-1}. Sediment samples were obtained from different depths, and parameters such as pH, carbonates and metal(loid)s, among others, were analysed. High concentrations of As (> 500 mg kg^{-1}), Fe (> 34,000 mg kg^{-1}), Mn (> 900 mg kg^{-1}), Pb (> 8000 mg kg^{-1}) and Zn (> 5000 mg kg^{-1}) were found. A piezometer was installed to enable the water inside the tailing pond to be sampled, and this presented high contents of SO_4^{2-} (> 2400 mg L^{-1}), Fe (> 28,000 μg L^{-1}), Mn (> 7800 μg L^{-1}) and Zn (> 7000 μg L^{-1}), suggesting that the mineral leaching was related to the oscillations in the water table. The water from two drainage adits situated at the foot of the impoundment was also analysed, as well as surface water both upstream and downstream from it. The speciation-saturation models applied for these water samples indicated that in spite of the contamination potential of the impoundment, the deterioration in the quality of the river water is mainly due to the discharge from mining drains and the dissolution processes of precipitates accumulated along the riverbanks.

Keywords Tailing impoundment · Sulphide ore · Fibre-optic oxygen sensor · Mine drainage · Surface water quality

1 Introduction

The La Carolina mining district contains great amounts of copper and lead sulphide vein deposits. Its exploitation dates back to pre-Roman times, increased between the nineteenth and twentieth centuries, and came to a halt at the end of the last century. The remnants of concentration plants and tailing impoundments scattered throughout the area are witnesses of major mining development (Gutierrez 2007).

Tailing impoundments are areas for the storage and deposit of residues that result from the process of mineral extraction via flotation. These structures are one of the biggest environmental problems concerning the mining industry (Kossoff et al. 2014; Amos et al.

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2015). Residues from the treatment of metal sulphides are highly reactive in the presence of oxygen. This gas determines various reactions that occur in the interior of tailing impoundments, particularly for sulphide containing minerals under aqueous phase oxidation. Sulphide oxidation results in the formation of SO_4^{2-}, a decrease of water pH and in the release of metal(loid)s, such as As, Fe, Mn, Pb and Zn into solution. This process generates a major environmental issue (Nordstrom et al. 2015; Lindsay et al. 2015), and the speed of the advancing oxidation front was estimated by several authors (Dold and Fontboté 2001; Bussière et al. 2003; Salmon and Malmström 2006; Schuwirth et al. 2007; Kohfahl 2003; Kohfahl et al. 2010; Hayes et al. 2014).

According to Aachib et al. (2004) and Kohfahl et al. (2010), the concentration of oxygen in mine waste heaps depends on several factors. On the one hand, the water saturation of the tailings affects the oxygen concentration, due to the fact that diffusivity is much greater in ground air than in water. Other important factors are (i) the grain size distribution, with lower penetration depths of oxygen in fine-grained sediments; (ii) the content of sulphides in the waste, since their oxidation results in oxygen consumption; and (iii) the presence of cemented layers that act as a barrier for oxygen transport.

Numerous modelling approaches have been carried out obtaining very different results about oxygen consumption rates. For instance, in a humid climate region, Romano et al. (2003) obtained that the oxidation front penetrated 1 m after 100 years, under flooded conditions in an impoundment located in Tasmania (Australia). Kohfahl (2003) studied heaps in Lusatian (Germany) with 10 m of oxidised tailings after 30 years and obtained in column test oxidation rates around 2 m year^{-1}. Moncur et al. (2005) propose a model whereby the oxidation front would advance 50 cm after 70 years under a hardpan horizon in tailings from Sherridon (Canada). Schuwirth et al. (2007) studied tailing impoundments with high content in S^{2-} at Rhineland-Palatinate (Germany), with the zone of active oxidation at a depth of 0.7 m after 45 years. Alakangas et al. (2010) considered tailing impoundments under humid conditions in Laver (Sweden) and obtained rates of the oxidant front progression of 2.8 cm year^{-1}. In temperate and semi-arid areas, Dold and Fontboté (2001) estimated an oxidation rate of 1 m in 40 years in tailing impoundments located in Cauquenes (Chile). In mining sludges from Arizona (USA) with an average content of 10% in S^{2-}, the zone of oxidation has penetrated the tailings to a depth of 55 cm after 50 years (Hayes et al. 2014).

In the specific case of fine tailing impoundments under Mediterranean climate, high rates of evaporation lead to efflorescent metal salts to precipitate into the pores. During the rainy months, these secondary minerals may be dissolved and incorporated to the percolating water (Hammarstrom et al. 2005; Smuda et al. 2007). These processes have also been identified at the mining district of La Carolina, and it has been confirmed that they are associated with a significant environmental risk, especially with regard to the conditions of the chemical quality of surface water resources (Hidalgo et al. 2010). In particular, the progression of the oxidation front and the precipitation-dissolution phenomenon of secondary minerals in tailing dumps are processes that are determined by the semiarid Mediterranean climate, and they are of great environmental significance in terms of metal mobilisation (Navarro et al. 2008; Redwan and Rammlmair 2012; Root et al. 2015).

In the case of the mining district of La Carolina, previous studies of one of the largest tailing impoundments, known as La Aquisgrana, highlighted the presence of high concentrations of certain metal(loid)s (Martínez et al. 2016). The results obtained indicate that As, Fe, Mn, Pb and Zn are the elements with the highest concentrations, with average contents of 150 mg kg^{-1}, 19,746 mg kg^{-1}, 722 mg kg^{-1}, 1534 mg kg^{-1} and 1833 mg kg^{-1}, respectively. Furthermore, electrical resistivity profiles were carried out which, combined with hydro-geochemical data, made it possible to identify three levels in the deposit which were particularly enriched by these elements, coinciding with the top part (1–5 m), the deepest part (35–39 m) and an intermediate zone at a depth of 10 to 15 m.

Due to the scarcity of field studies measuring the real speed of the oxidation advancement front, this tailing impoundment was chosen for the installation of a network of fibre optic sensors which make it possible to monitor in situ the dissolved oxygen content inside these sediments. Additional sensors were positioned to measure the variation of temperature, electrical conductivity and humidity according to depth. Thus, the main goals of this study are (i) to determine the progression of the oxidation front in tailing impoundment at the La Carolina mining district, (ii) to evaluate the water quality affections and (iii) to assess the contamination potential of the tailings under semi-arid conditions.

2 Study Area

From a geological point of view, the mining district of La Carolina is located on the SE limit of the Hesperian Massif, and two great groups of materials can be distinguished: a Palaeozoic basement and a post-Hercynian sedimentary cover (Lillo et al. 1998; Rey et al. 2005). The Palaeozoic basement is constituted essentially by shales and quartzites. A granitoid massif was placed at the end of the Hercynian orogeny and constitutes the origin of the dyke network in the La Carolina mining district (Lillo 1992). The hydrothermal veins are made up mainly by galena, sphalerite, chalcopyrite, pyrite, baryte, quartz, ankerite, and calcite, and hosted by the Palaeozoic basement and the granitoids. For the most part, the dykes present lengths of several kilometres with a strong dip.

The impoundments were constructed to hold the residues produced from the extraction of minerals (mostly galena) obtained through the technique of flotation. The activity was developed during the 1950s and 1960s, and the mine was definitively closed in 1983 (Gutiérrez 2007).

The tailing impoundment under this study, La Aquisgrana, is located on top of Palaeozoic phyllites, in a depression created by the Boticario creek, which is channelled by a drainage pipe at the bottom of the impoundment (Fig. 1). The site was made by the construction of a dyke to contain the tailings. Afterwards, the upstream dyke containing the flotation residues was enlarged. These structures were conducted without first making the basin impermeable (Martínez et al. 2012).

Currently, the impoundment measures 200 m in length, 180 m in width and 39 m in thickness at most, and it is found along the right bank of the La Campana River (Fig. 1). Its capacity is around 1 hm^3. The top is on a slight south-westward facing slope, and during the rainy season, it gathers a small sheet of water. The dump present steep slopes, affected by surface erosion and local landslides, mainly at the lower section of the structure. Average precipitation in the area is around 500 mm year^{-1}, with much of the rain falling during the winter season. The average temperature of the area is 15 °C, ranging from − 1 °C in winter to 42 °C in summer, characteristic of Mediterranean climate.

The La Campana River has an average flow of 175 L s^{-1}, with seasonal variations from more than 800 L s^{-1} during the winter to less than 10 L s^{-1} during the summer. Metamorphic rocks which constitute the substratum are considered impervious materials, with a scarce capacity of storing or transmitting water. However, mining operations have resulted in the generation of a network of shaft and galleries, flooded at present. Two drainage adits of the La Aquisgrana mine (M1 and M2, Fig. 1) are situated at the foot of the study heap, and discharge in the La Campana River. These adits provide a constant discharge of around 10 L s^{-1} as a whole. On the other hand, leachates have not been detected at the bottom of the tailing impoundment, so presumably they infiltrate into the underlying phyllites. In fact, geophysical studies indicate that the phyllitic bedrock is strongly altered and fractured, and could be acting as a lateral infiltration zone for subsurface flow (Martínez et al. 2012, 2016).

3 Material and Methods

3.1 Borehole Drilling and Installation of Sensors

Three boreholes were drilled in October 2012, one for sampling undisturbed sediments by dry core drilling and the other two for installing measurement sensors. The first was made until a depth of 40.3 m, reaching the phyllitic basement (G1, Fig. 1). Afterwards, it was coated with 63-mm PVC pipe and slotted at the bottom 6 m, to be used as a piezometer. The installation of sensors took place in the other boreholes, at 2 m of distance from the first one. The deeper borehole recorded a depth of 37.55 m, where contact with the Palaeozoic phyllites occurred. Sensors for measuring the humidity, temperature, electrical conductivity and oxygen in pore gas were installed at seven different depths, with the intention of integrating data from the entire vertical profile, but with the greatest representation at the uppermost section, where the highest dynamics of oxygen levels were expected. The measurements of these variables were taken on a daily basis for 10 days, then on a weekly basis for two months and then on a monthly basis.

The Decagon GS3 soil moisture, humidity, temperature and electrical conductivity sensor (hereinafter referred to as FD sensor device) was used, comprising of a connector for each of these parameters. The precision of these sensors is ± 3% for humidity, ± 10% for electrical conductivity and ± 1 °C for temperature. It should be indicated that the electrical conductivity registered by

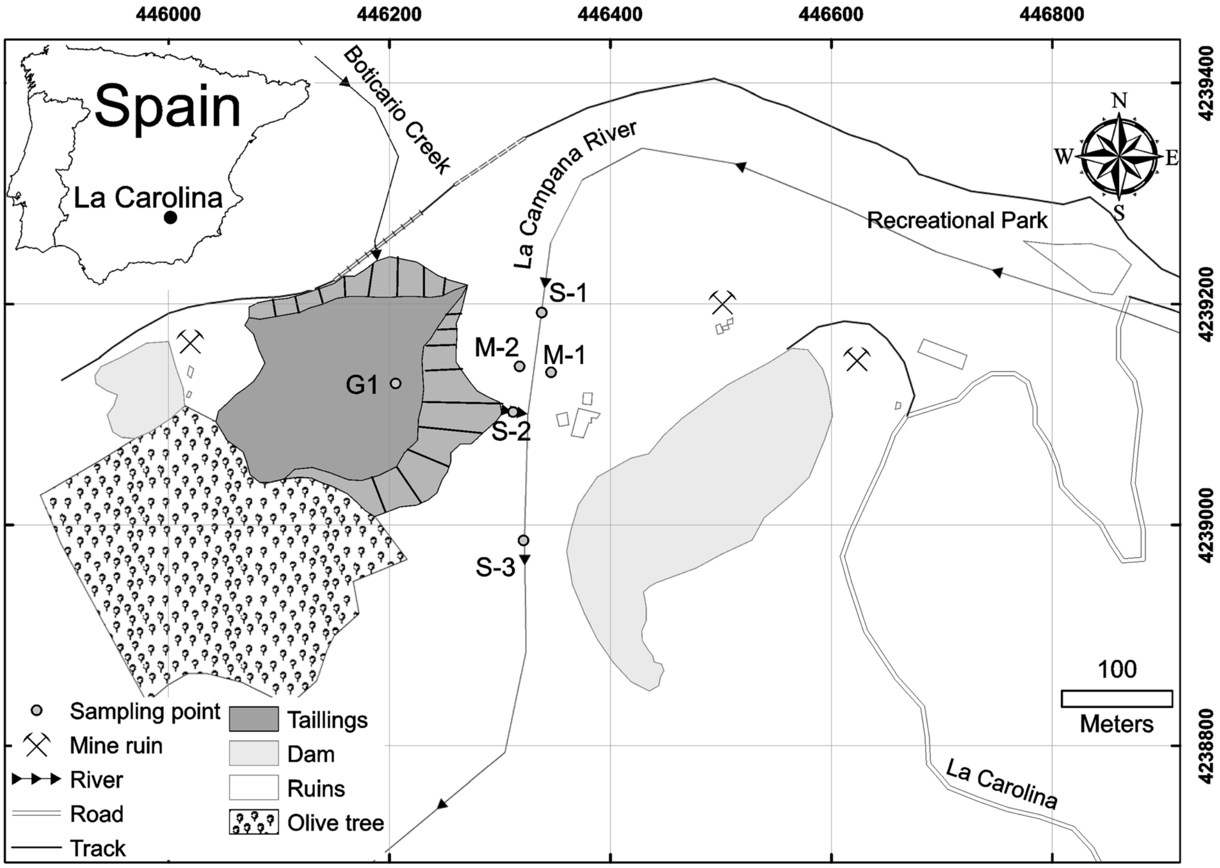


Fig. 1 Study area: sketch of the La Aquisgrana tailing impoundment and location of the sampling points

the sensors is the bulk E.C. or apparent electrical conductivity, which corresponds to the electrical conductivity of the whole soil mass (minerals, air and water). The E.C. of porewater (E.C.p.) can be calculated from this and corresponds to the concentration in soluble salts present in the solution found in the sediment porewater. The E.C.p. has been calculated according to Amente et al. (2000) as:

$$\text{E.C.p.} = \text{E.C.b.}/0.94 \cdot (\text{WC})^{1.514}$$

where E.C.p. = porewater E.C. in mS cm^{-1}

E.C.b. = bulk E.C. in mS cm^{-1}

WC = water content in percent

The fibre optic oxygen meter, model PreSensFibox 3 LCD, was used to measure gaseous oxygen in the field using PSt3 sensor foil. Fibox 3 LCD has one measurement connector with a 99% level of precision. The installation was made in pairs, so that each pair contained a FD sensor and an oxygen sensor, and the selected depths were 1, 3, 5, 6, 13, 23 and 35.5 m.

3.2 Sediment Analysis

Undisturbed samples were obtained from the core drilling covering the entire thickness of the impoundment. A total of 21 samples at 1-m to 2-m intervals were analysed. The selection criteria were based on (i) the position where the sensors would be located, (ii) the presence of moisture and water in the borehole, and (iii) change of colour and texture.

The samples were stored in the field at a temperature below 20 °C and isolated from the atmosphere. For each sampling depth, two sub-samples were obtained for moisture determination and sulphide analysis. The rest of the sample was dried at room temperature and sieved using a 2-mm mesh in order to determine pH, total carbon (T.C.), organic matter (O.M.), $CaCO_3$, clay and total metal contents.

Table 1 indicates the methods used for the different parameters analysed.

3.3 Water Analysis

Water samples were collected from the piezometer (G1), in order to characterise the saturated zone of the tailing impoundment, and at different points in the surrounding area (Fig. 1). Samples of surface water were taken from the La Campana River and Boticario creek. In the former, these were taken at two points: one upstream (point S1) and the other downstream (point S3) from the impoundment, whilst in the latter, the samples were taken from the exit from the vaulted zone below the impoundment (point S2, Fig. 1). Sampling campaigns also included mine waters from two drainage adits of La Rosa vein, located below the heap and discharging in both banks of the La Campana River (M1 and M2). Sampling campaigns were made since the completion of the boreholes, from November 2012 to June 2015, under different seasonal conditions. Measurements were taken in the field for both electrical conductivity (E.C.) and temperature, using a WTW LF92 meter with automatic compensation temperature, and for pH, Eh and O_2 with a Hach Lange HQ20 meter. Samples for the analysis of minor and trace constituents were filtered in the field (0.45 μm), acidified with reagent-grade HNO_3 at a pH lower than 2.5 and stored in a refrigerator until their arrival at the laboratory.

Mixing calculations were carried out using the surface water and that draining from the mining adits (M1 and M2) for the sampling campaign implemented in February 2014. In order to do so, it was necessary to measure the flow rates at each of these points. Stream discharge in the selected channel cross sections was measured with a Flow Probe current meter model FP111, whereas the flow rate in the mining adits was measured using volumetric gauging. The mixtures were calculated using the program Phreeqc, version 3.1.7. The input file is presented in Sect. 4.3, which includes the analytical determinations of the sampled waters at points S1, M1, M2 and S2. These four entry solutions were mixed using the command MIX, and estimating the percentages of mixture from the flow rates 540, 6, 5 and 32 Ls^{-1}, respectively. The theoretical mixture calculated (S3 calculated) was compared with the analytical results obtained from the river downstream from the mixing zone. This hydro-chemical data was also included in the Phreeqc input file (S3 measured), in order to obtain the distribution of dissolved species and the saturation index in certain mineral phases for this sample.

4 Results and Discussion

4.1 Sediment Chemistry

The results obtained from sediment analysis are presented in Fig. 2, which shows the variation of the parameters with depth.

Table 2 shows the results obtained for carbonate and sulphur contents, and those metal(loid)s more abundant in the levels where the sensors are installed.

The pH values were between 6.5 and 8.3, with an average value close to 8, directly related to the carbonate content in the tailing impoundment (Fig. 2a, b). These carbonates are related to the carbonated gangue (calcite and ankerite) and to the additives introduced into the solution where galena was found, to increase pH and facilitate its extraction (Martínez et al. 2012).

As regards texture, it is important to note that the first 15 m contains fewer clays than the rest of the tailing impoundment, where the amount of fines is higher (Fig. 2c). On the other hand, the concentration in organic matter is very low and high concentrations are only observed in the pelitic substrate due to the soil having developed prior to the deposit of sediments from the tailing impoundment (Fig. 2d).

Turning to the metal(loid)s, it can be seen that Fe has the highest concentration, being several times greater than the other elements analysed. Pb is also present in high concentrations, as well as As, exceeding the levels permitted by the Junta de Andalucía [Andalusian regional government] for industrial soils (D18/2015), which are 2750 mg kg^{-1} and 40 mg kg^{-1}, respectively. Another element found in high concentrations is S^{2-}, which exceeds the limits established by European law (2006/21/CE), the limit being 0.1% sulphide content in order for the residue to be considered inert.

A clear relationship between Fe and As can be appreciated from the data obtained, these presenting fairly similar distribution profiles at depth. This relationship is probably linked to the absorption capacity of the Fe oxyhydroxides. Furthermore, at a depth of 13 m, a simultaneous increase in the content of Fe, S^{2-} and Zn was recorded, which could be related to the presence of sphalerite and arsenopyrite in the processed materials.

Table 1 Methods used for sediment and water analysis

Parameter	Method	Error
pH	ISSS Rule	0.01
Organic matter	Anné 1982 (Walkey-Black modification)	5%
Total carbon	Elemental AnalizatorThermoFinnigan FlashEA1112 CHNS-O	0.01%
$CaCO_3$	Bernard'scalcimeter	5%
Texture	Bouyoucos'sdensimeter	2–5%
Moisture	Gravity (heater)	1%
Sulphide	UNE-EN 1744-1 Rule	
Total metals	X-Ray Fluorescence (NITON XLt 792)	5%
Major constituents in water	Chromatography (Dionex DX 120)	5%
Metals in water	ICP-Mass Agilent 7500a	5%

On the other hand, an increase in the concentration of metal(loid)s was observed, both in the zone nearest the surface and at the base of the tailing impoundment (Fig. 2e–g). In the latter case, just above the phyllites, this could be due to the oxidation of sulphides which occurs at the limit of the saturated zone. As can be seen in Fig. 2h, a fall in the concentration of S^{2-} occurs at a depth of 35.5 m, coinciding with the zone where the

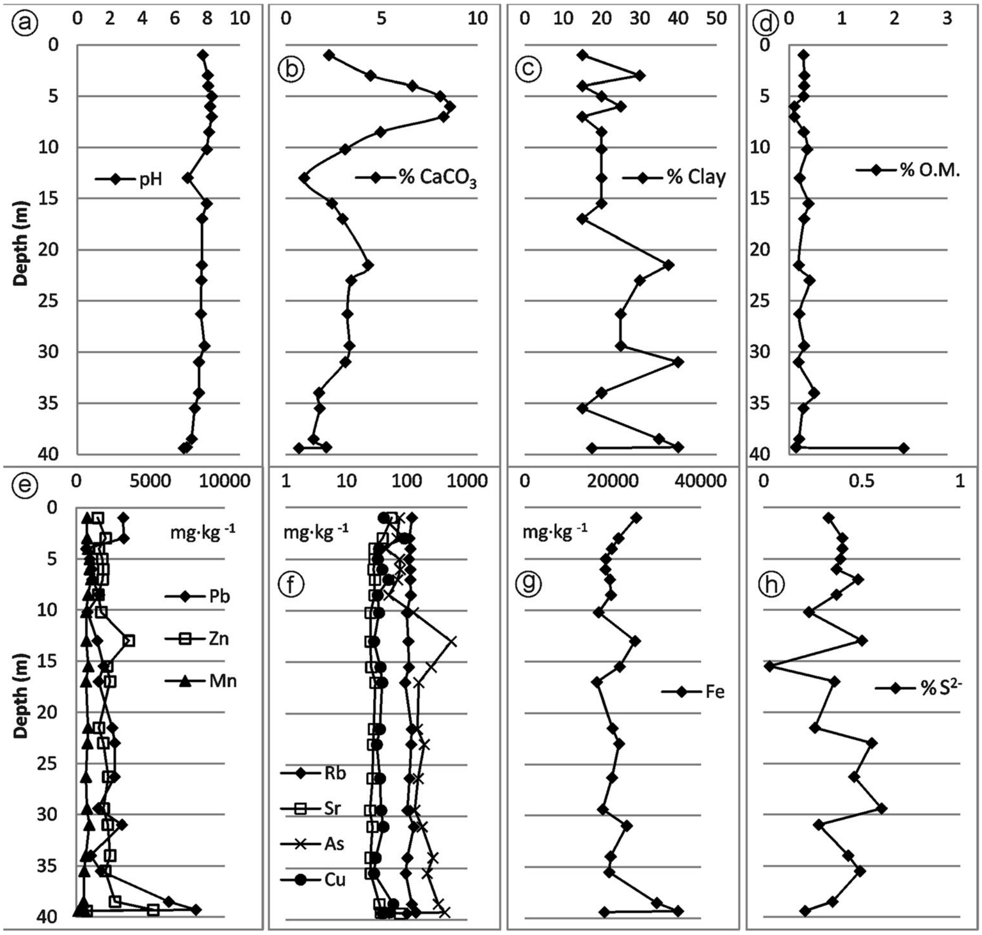


Fig. 2 (a-h) Variation of pH, $CaCO_3$ content, clay, organic matter (O.M.), metal(oid)s and S^{2-} with depth

Table 2 Distribution of contents of $CaCO_3$, S^{2-}, As, Fe, Mn, Pb, and Zn in the tailing impoundment

Sample depth (m)	$CaCO_3$ (%)	S^{2-} (%)	As (mg kg^{-1})	Fe (mg kg^{-1})	Mn (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
1	2.2	0.33	76	25,279	728	3153	1442
3	4.4	0.40	69	21,267	722	3195	1977
5	8.1	0.39	76	18,384	900	916	1747
6	8.6	0.23	78	18,284	888	1033	1812
13	0.9	0.26	544	25,015	676	1412	3540
23	3.4	0.43	194	21,401	751	2591	1821
35.5	1.7	0.21	218	19,152	537	1655	1956
Minimum	1.0	0.03	45	16,350	492	674	1442
Maximum	8.6	0.6	544	34,790	987	8065	5186

water table oscillates. The increase observed at a depth of 1 m could be due to the evaporation and re-concentration processes that give rise to the formation of secondary minerals which accumulate near the surface during dry spells.

Other than at these two depths, no other evident correlations are apparent among the parameters analysed. This lack of correlation in the distribution of the metal(loid)s reflects the absence of mobility in the heart of the tailing impoundment, suggesting that these elements are still in their original position.

4.2 Oxygen and FD Sensors

Since October 2012, oxygen and FD sensors have been monitoring humidity, temperature, electrical conductivity and oxygen in pore gas in the entire profile of the impoundment. Figure 3 presents the values obtained in seven campaigns of measurements from 2013 to 2015, which include both humid and dry season.

The first group of sensors was placed at the greatest depth (35.5 m) and was located at 1 m below the water table, in the saturated zone of the tailing impoundment. Volumetric water content was 50%, with a value of 3500 μS cm^{-1} for E.C.p., null presence of oxygen, and a temperature of 18 °C that has remained constant in time (Fig. 3a–c). E.C.p. value indicates that the sediment provides a large amount of salts to the water, and the temperature is characteristic of an area that is not affected by atmospheric variations.

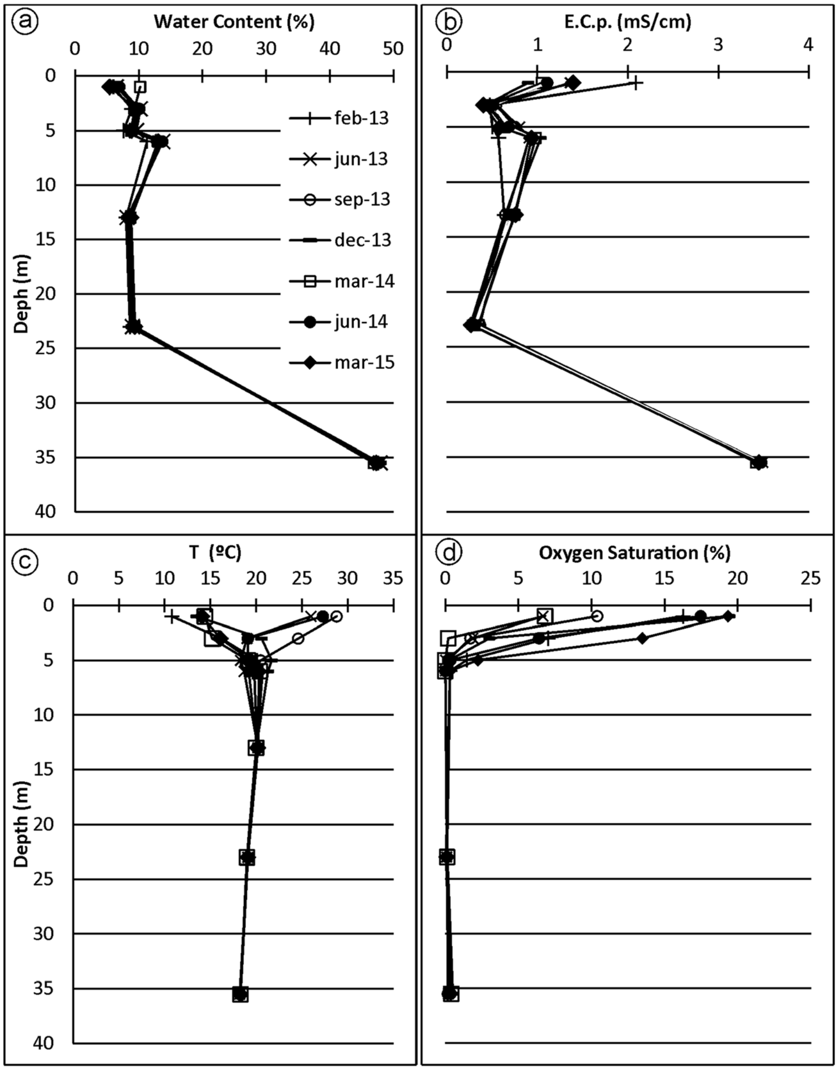
Outside the saturated zone, a sharp decrease in humidity in the central part of the tailing impoundment is apparent, corresponding to a reduction in the E.C.p. value. However, it is important to note that in spite of showing humidity values that are very similar between the depths of 23 and 13 m, this is not so for the E.C.p., which displays an increase at 13 m. This could be due to the presence of levels with higher content in metal minerals, consistent with the enrichment of As, Fe, Zn and S^{2-} identified at a depth of 13 m.

In the area between the surface and 6 m down, a direct relationship can again be observed between humidity and E.C.p. It is worth pointing out, however, that at the sensor nearest the surface (at a depth of 1 m), the range of variation in the E.C.p. associated with the increases in humidity is much greater than in the rest of the profile (Fig. 3a, b). This could be due to the fact that this level functions as an area of re-concentration and formation of highly soluble saline precipitates, in such a way that the variations in humidity cause sharp variations in the E.C.p.

As a whole, dissolved oxygen starts to diminish in the tailing impoundment at a depth of 3 m, such that at 5–6 m, its presence was rarely detected. Given that the pore water content is scarce in this dump, the advance of oxygen towards the interior of the tailing pond would have been expected to be faster. However, the high content in S^{2-} leads to the oxygen which enters the sediment being consumed, and thus, 30 years after it was abandoned, only the top 5 m has been oxidised, suggesting an average oxidation advance of 15 cm year^{-1}.

As can be appreciated in Fig. 3d, a wide variation is recorded in the oxygen saturation in the sensors nearest the surface, with values which oscillate from 1 to 5 to 15–20%. These variations do not show a seasonal tendency, leading us to analyse the influence of other factors in the variations in O_2 content

Fig. 3 (a-d) Variation of the water content, pore water electrical conductivity (E.C.p.), oxygen saturation and temperature with depth



for the most superficial levels. Figure 4 represents the evolution in time of O_2 values measured in the fibre optic oxygen meter situated at a depth of 1 m from October 2012 to March 2015. Temperature and humidity values have also been included in this graph, measured by the FD sensor at the same depth, together with the values of atmospheric pressure and precipitation recorded on the sampling days. The results obtained show no apparent correlation between the variables recorded that could explain the changes in the percentage of atmospheric oxygen. Therefore, these oscillations must be produced by other factors that have not been determined, but work will continue to be able to explain this phenomenon.

4.3 Water Chemistry

The impoundment has a saturated zone of 4 m in thickness. Water samples obtained from the piezometer (G1) were characterised by a mean E.C. value near 3100 μS cm^{-1}. The water pH was around 6.4, the temperature ranged from 16 to 21 °C, with dissolved O_2 contents from 2 to 6 mg L^{-1}, and Eh values were close to 250 mV (Table 3).

The chemical composition of the water in the tailing impoundment is of a calcium sulphate type, as can be seen in the Piper diagram in Fig. 5. It has an average sulphate concentration of over 2000 mg L^{-1} (Table 3), with very high contents of Fe (> 14 mg L^{-1}), Mn (> 4.5 mg L^{-1}) and Zn (3 mg L^{-1}).

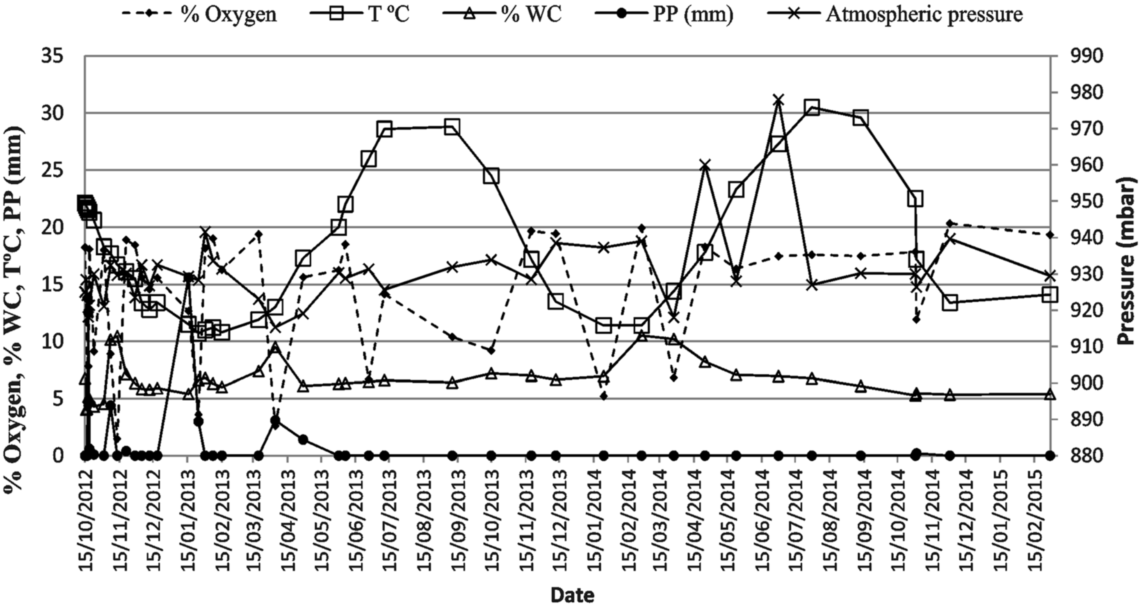


Fig. 4 Oxygen saturation, volumetric water content (WC), and temperature (T °C) reported on the sensor installed at 1 m in depth. Atmospheric pressure and precipitation (PP) recorded at the station of Santa Elena (AEMET)

This hydro-chemical facies is characteristic of an oxidation process of sulphides contained in the tailing impoundment, which could be accompanied by a mobilisation of metals. Although the O_2 sensors installed in the unsaturated zone indicate its total absence in the sediment pores above the water table, the water in the saturated zone has average values of dissolved oxygen of around 4 mg L^{-1}. Using electrical resistivity imaging (ERI), Martínez et al. (2016) identified the existence of a very fractured and mylonitised zone in the south-western sector of the tailing pond, which could function as a zone of preferential infiltration of the sub-surface flow. This fractured zone is in contact with the mining residues and could give rise to a lateral recharge of the saturated zone of the tailing impoundment with water that has a higher content in dissolved oxygen. This oxygen contribution would facilitate the transformation of S^{2-} to SO_4^2, leading to its heightened concentration in the water of the tailing pond as well as an increase in metal(loid)s. However, the pH of these waters is never net acid, always being above 5.9, suggesting that the acidity generated by the oxidation of the sulphides may be accompanied by a neutralisation reaction associated with the $CaCO_3$ present in the sediments of the tailing impoundment. This interpretation is consistent with the low $CaCO_3$ content obtained in the deepest part of the tailing pond.

Although no visible drainage was observed coming from the tailing impoundment to the river, there are two mining drains located at the foot of the fines pond which correspond to the La Rosa (M1) and La Aquisgrana (M2) adits. With a discharge of around 5 L s^{-1}, both drain the same vein, meaning that their chemistry is very similar, although each flows into different banks of the La Campana River. Just like in the saturated zone of the tailing impoundment, the hydrofacies are calcium sulphate (Fig. 5), but with an average calcium and sulphate content much lower than in the latter case (600 mg L^{-1} and 190 mg L^{-1}, respectively, Table 3). The presence of abundant carbonated gangue in the veins leads to an alkaline pH of around 6.6 (Table 3) and means that the water from the mine contains dissolved HCO_3^- with average values of around 260 mg L^{-1}. Once again, the high concentrations in Fe (16 mg L^{-1}) and Mn (2 mg L^{-1}) are of note, although in this case, there is also an important mobilisation of As (nearly 1 mg L^{-1}). This could be related to the presence of arsenopyrites in the mineralisations of the vein.

On the other hand, the drainage from the Boticario stream (S2) has a calcium sulphate-bicarbonate hydrofacies, although in some of the samples taken during drier seasons, a notable sulphate character can be appreciated. The content in Fe, Mn and Zn also varies considerably, being higher in dry spells (Table 3). This

Table 3 Physical-chemical characteristics of the water samples. *S1* La Campana River upstream the impoundment, *S2* Boticario creek, *S3* La Campana River downstream the impoundment, *M1* La Rosa adit, *M2* La Aquisgrana adit, *G1* saturated zone of the tailing impoundment

	S1			M1			M2			G1			S2			S3		
	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
E.C. (μS cm^{-1})	147	370	840	1300	1379	1534	1420	1508	1760	2990	3086	3300	222	654	1566	231	767	1470
T (°C)	8.1	12	16.9	20	22.9	24	21.3	22.5	23.1	16	18.4	21	8.6	13	17	6.8	15.3	23
pH	7.1	7.9	8.3	6.3	6.7	7	6.2	6.6	7.6	5.9	6.4	6.9	7.2	7.7	8.3	6.9	7.6	8.4
Eh (mV)	258	286	367	208	190	201	170	188	208	157	252	329	197	271	406	161	240	354
O_2 (mg L^{-1})	6.1	9.7	11.8	2.4	4.1	7.3	2.7	2.5	7.7	2	3.97	7	5.5	9.2	11.6	4.6	8.6	12.5
Q (L s^{-1})	0	160	820	4	5	11	3	5	7	–	–	–	–	16	75	9	174	848
Ca^{2+} (mg L^{-1})	12.2	19.9	23.8	115	190	222.3	217.2	245.3	169.7	480	542	609	17.9	56	202	24.5	73.5	197.8
Mg^{2+} (mg L^{-1})	6.4	8.5	10.1	49	63	71.9	66.2	74.1	83.3	111	129	152	8.7	25	87	10.3	25.2	62.9
Na^+ (mg L^{-1})	5.1	5.4	5.7	23.1	30	65	24.8	27.3	29.5	45	52	56	5	9.4	21	5.8	11.5	23.4
K^+ (mg L^{-1})	1.9	2.1	2.3	1	10.7	13.2	12.6	13.7	15	122	142	164	2	8	29	2.2	5	11.9
Cl^- (mg L^{-1})	5.9	6.6	7.5	11.1	14.7	28.4	11.3	11.9	12.9	26	46	75	7	9.7	16	7.4	9.8	12.1
SO_4^{2-} (mg L^{-1})	34	48	64.9	355.6	559.1	695.7	635	704.5	830.9	1937	2109	2495	41	198	780	58.4	209.7	584.9
HCO_3^- (mg L^{-1})	36.6	50.8	67.1	192	262	347.7	231.8	300.6	378.2	16	61	92	36.6	62	79	54.9	122.6	262.3
As (μg L^{-1})	27	36	74	437	722	1057	515	823	1213	5	22	38	–	18	39	34	151	341
Cu (μg L^{-1})	–	4	7	–	2	4	2	1	3	2	13	69	–	2	4	1	4	9
Fe (μg L^{-1})	265	782	1860	10,232	15,894	25,389	13,028	17,713	27,567	2200	14,298	28,973	275	1114	3402	486	3671	8245
Mn (μg L^{-1})	31	112	315	1171	1950	3020	1389	1945	2859	1800	4708	7888	41	1150	4223	91	890	1968
Ni (μg L^{-1})	3	7	9	6	11	17	7	9	12	38	92	353	2	18	58	5	12	23
Pb (μg L^{-1})	13	35	59	4	21	60	2	20	62	2	25	45	5	20	79	1	33	92
Zn (μg L^{-1})	188	329	437	200	413	735	–	200	505	1087	2994	7134	–	678	1348	191	512	1193

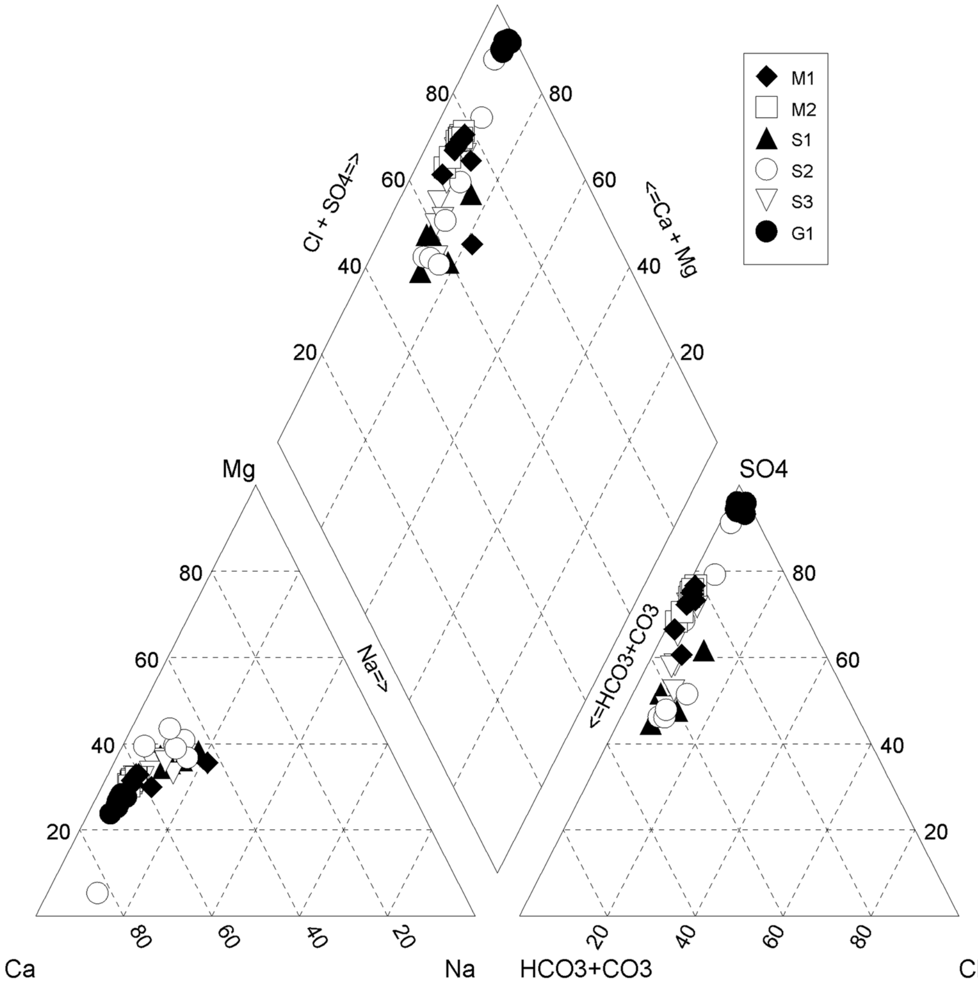


Fig. 5 Piper diagram and hydrochemical types of the water samples analysed. M mine drainage, S surface water, G saturated zone of the tailing impoundment

increase in mineralisation is related to the existence of filtrations originating in the saturated zone of the tailing impoundment. During the dry season, when water flow is minimal, the E.C. has maximum values and O_2 content is close to 5 mg L^{-1}, similar to those recorded in the saturated zone of the tailing impoundment. At this time of year, the area where the drain flows into the river is reddish in colour, due to the precipitation of Fe oxyhydroxides.

In order to analyse the effect of these discharges into the surface waters, the river La Campana was sampled upstream (S1) and downstream (S3) from the tailing impoundment. The river water at S1 exhibits low mineral content and a calcium sulphate-bicarbonate facies (Table 3 and Fig. 5). As regards dissolved metal(loid)s, the most significant are Fe, Mn and Zn, characteristic of mineral paragenesis, although here they are always lower in value than in the water from the mine (Table 3).

As already mentioned in Sect. 3.3, the calculation of the mixtures was made with Phreeqc for the campaign of February 2014. The input file (Table 4) includes the analytical determinations of the sampled waters at points S1, M1, M2 and S2. In addition to these calculations, several mixing calculations have been carried out with Phreeqc to consider the uncertainty of defining mixing ratios based on the measured flow rates of the different inputs. These simulations all gave very similar results without significant modifications in the concentrations for Fe, Mn and Zn.

As expected, the river has a higher mineral content at S3 (E.C. > 700 µS cm^{-1}), mainly due to receiving discharge from the mining adits M1 and M2. However, the results obtained from the simple mixing calculations of river, stream and adits seem to indicate lower metal(loid) contents than those analysed in S3. Table 5 sets out the results obtained from the theoretical water mixture (S3 calculated) and those analysed in the river water (S3 measured), together with those measured in the saturated zone of the tailing impoundment and the other sampling points.

If we consider that this increase could be associated with a contribution from the saturated zone of the tailing impoundment, an increase in the concentrations of sulphate and chlorides should also appear. Therefore, to substantiate this increase in the concentration of metal(loid)s with respect to the calculated sample, the speciation results obtained using Phreeqc were considered, as well as the Eh/pH diagrams, which make it possible to establish the distribution of the main mineral phases considered.

Of the metal(loid)s found in highest concentrations in these waters, As is the one which causes the greatest environmental risk, as it always appears in concentrations much higher than the limits of the current quality regulations. Due to its strong relationship with Fe, it was necessary to consider both. The speciation diagrams for Eh/pH were therefore focussed on Fe and As, with the aim of analysing their mobility in the medium (Fig. 6).

A marked difference between the surface waters (S1, S2 and S3) and the ground waters corresponding to the saturated zone of the pond (G) and the mining adits (M1 and M2) can be appreciated (Fig. 6). In the Fe diagram (Fig. 6a), the ground waters were found to be very close to the stability field of Fe^{2+}. This is because these waters have a low dissolved oxygen concentration, meaning that the Fe is in a reduced state. Once they reach the surface, they come into contact with atmospheric O_2 and mix with the surface water, such that the Fe^{2+} is oxidised and gives rise to the formation of oxyhydroxides, such as ferrihydrite $Fe(OH)_3$. This mineral phase has a very high specific surface, enabling the adsorption of other elements such as As, Mn and Zn (Jackson and Miller 2000).

In the case of the Eh/pH diagram for As, all the water samples are in the stability field of As (V). However, the waters from the mine are in the area characteristic of $H_2AsO_4^-$, whereas the surface waters are in the stability field of $HAsO_4^{2-}$ (Fig. 6b). It is worth pointing out that the pH conditions of around 7 favour the adsorption process of As (V) species into the Fe oxyhydroxides, such as ferrihydrite and goethite, but when pH is above 8, the charges found on the surface of these oxyhydroxides can begin to invert, such that a release of adhered anions can occur (Pierce and Moore 1982). This process could explain the increase in As observed in sample S3 (measured).

On the other hand, the speciation calculations carried out with Phreeqc indicate that the water from sample S3 (measured) is oversaturated in Fe mineral phases, such as ferrihydrite (saturation index 4.0) and goethite (saturation index 9.4). Under these saturation conditions, the predominant reaction in the river water could be considered to be the precipitation of ferrihydrite and goethite, a process which would take Fe, Mn and Zn out of the aqueous phase. This is clearly contrary to the increase in Fe, Mn and Zn observed in the river sample.

However, in spite of the water being oversaturated in these mineral phases, the differences in kinetics of the precipitation and dissolution processes could lead to the precipitates deposited in the riverbed or its banks being dissolved in the water. Therefore, if Mn and Zn were found adhered to ferrihydrite and goethite, they would also be carried into the river water in the same dissolution process.

In addition, the increase in Fe and Mn observed in the river sample with respect to the calculated mixing could be associated with the dissolution of some mineral phases rich in Fe and Mn, such as melanterite and $MnSO_4$. Both mineral species have been identified by De la Torre et al. (2010) as secondary precipitates appearing on the river banks in this mining area. According to the speciation calculations, the water in S3 is undersaturated in melanterite (saturation index −8.1) and Mn sulphates (saturation index −12), and a dissolution reaction of these phases could be considered to explain the increase in Fe and Mn measured in S3.

5 Conclusions

The analyses of the flotation fines show that the tailing impoundment has a high total carbon content (of which most is calcium carbonate), metal(oid)s and S^{2-}. The latter two make it potentially highly contaminating as a result of the oxidation processes of these mineral phases and of the mobilisation of metal elements. The position of the oxidation front indicates that after over 30 years since the mine was abandoned, the oxidised depth corresponds to the 5 m nearest the surface, meaning that the average speed of the oxidation front is around

Table 4 Data entered in the input file Phreeqc to calculate a conservative mixing in La Aquisgrana area

	Solution 1	Solution 2	Solution 3	Solution 4	Solution 5	
Sample point	S1	M1	M2	S2	S3 (measured)	
temp	10	22.7	21.6	10.8	9.7	
pH	7.86	6.9	6.8	8	8.4	
pe	4.6	3.28	3.47	3.7	4.2	
Redox	pe					
Units	mg·L^{-1}					
Density	1					
Alkalinity as HCO_3^-	48.8	244	232	36.6	54.9	(mg·L^{-1})
Ca	23.57	190	234	17.87	24.5	
Cl	7.517	11	12	7.3	7.3	
K	1.947	11.7	13	2.3	2.1	
Mg	9.02	61	70	8.7	10.29	
N(5)	3	2.7	2.7	4.2	3.2	
Na	5.36	23	27	5.2	5.8	
O(0)	11	3.7	1.7	11.1	10.8	
S(6)	44.97	551	650	41	58.5	
Al	42	33	34	22	20	(ug·L^{-1})
As	59	1057	1213	11	118	
Ba	107	54	42	120	72	
Fe	398	1833	2057	276	1624	
Mn	62	235	238	62	412	
Ni	7	16	12	3	9	
Pb	39	32	31	39	9	
Sr	123	643	747	59	207	
Zn	290	547	359	470	337	
-water 1 # kg						
END						
MIX 1						
1	0.926					
2	0.0102					
3	0.0085					
4	0.055					
END						

15 cm year^{-1}. One of the factors slowing down the advance of the oxidation front is the high sulphide content, which consumes all the oxygen penetrating the dump. If the results are compared with those recorded in tailing impoundments in similar conditions from other studies, it can be seen that the oxidation speed occurring in this one is greater than in others from semiarid climates. The acidity that could be generated by this oxidation process is neutralised by the carbonates present, such that the pH values remain above 7.5 throughout the oxidised zone of the dump. The oxidised zone, in spite of the time exposed, still contains very considerably amounts of metal(oid)s that have not been mobilised. This is probably due to a very efficient neutralisation process, meaning that the relationship S^{2-}/CO_3^{2-} minimises the contaminating potential because the mobilisation of metals in a hydric medium is relatively low.

In spite of the semiarid climate typical of this region, the existence of a permanently saturated zone in the

Table 5 Physical-chemical characteristics of the water samples (February 2014). *S1* surface water upstream of La Aquisgrana, *M1* La Rosa adit, *M2* La Aquisgrana adit, *G1* saturated zone of the dam, *S2* Boticario creek, *S3* (measured) surface water downstream of La Aquisgrana, *S3* (calculated) results for mixing calculations

	S1	M1	M2	G1	S2	S3 (measured)	S3 (calculated)
E.C. (μS cm^{-1})	199	1344	1504	3230	184	244	221
T (°C)	10	22.7	21.6	17.5	10.8	9.7	10
pH	7.8	6.9	6.8	6.6	8	8.4	7.6
Eh (mV)	260	193	203	264	212	237	–
O_2 (mg L^{-1})	11	3.7	1.7	3.5	11.1	11	–
Q (L s^{-1})	540	6	5	–	32	583	–
Ca (mg L^{-1})	24	190	234	570	17.8	25	27
Mg (mg L^{-1})	9	61	70	135	8.7	10	10
Na (mg L^{-1})	5	23	27	51	5.2	6	6
K (mg L^{-1})	2	12	13	137	2.3	2	2
Cl (mg L^{-1})	8	11	12	32	7.3	7.3	7.6
SO_4^{2} (mg L^{-1})	45	551	650	2058	41	58	55
HCO_3 (mg L^{-1})	49	244	232	85	36.6	55	52
As (μg L^{-1})	59	1057	1213	16	11	118	76
Cu (μg L^{-1})	5	2	1	2	1	3	5
Fe (μg L^{-1})	398	18,334	20,573	7922	276	1624	749
Mn (μg L^{-1})	62	2356	2386	6765	62	412	105
Ni (μg L^{-1})	7	16	12	92	3	9	7
Pb (μg L^{-1})	39	32	31	20	39	9	39
Zn (μg L^{-1})	290	547	359	4109	470	337	303

nucleus of the dump was identified, about 4 m in depth, in which the sensors situated at 35.5 m record the highest values of E.C., being over 3 mS cm^{-1}, and a high volumetric water content of nearly 50%. For its

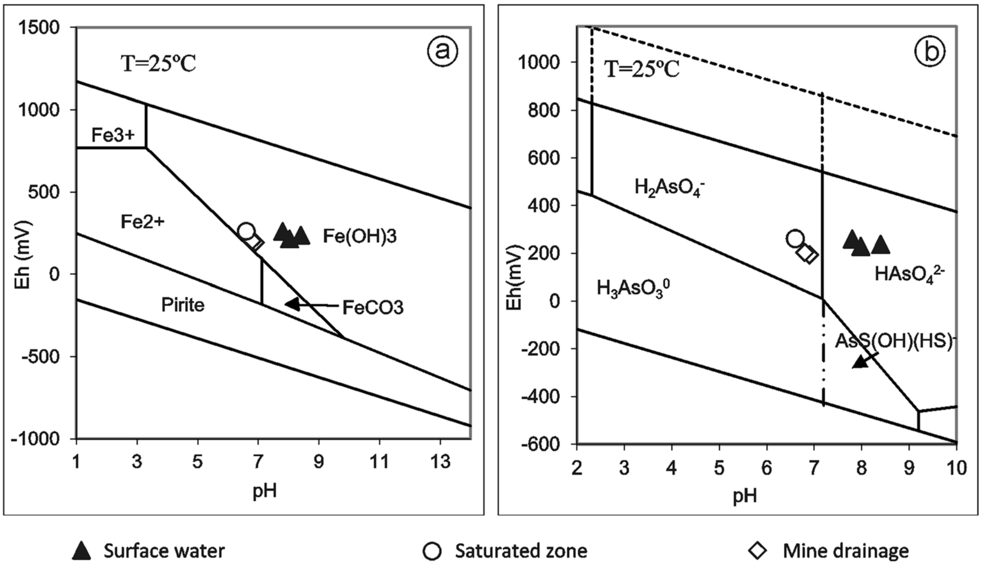


Fig. 6 (a-b) Eh/pH speciation diagrams (of the reference system H_2 for Eh), for Fe and As in water of the tailing impoundment and its surroundings

part, the unsaturated zone is characterised by low humidity, although at certain levels, such as at depths of 1 and 13 m, an increase in the E.C. can be seen, which could be associated with the zones of soluble secondary mineral formation. Furthermore, these coincide in many cases with an increase in the concentration of metal elements. On the other hand, although lixiviates were not observed on the surface at the foot of the tailing impoundment originating from the saturated zone, a high charge of metal(oid)s and dissolved sulphates exists in the nucleus of the pond.

The results obtained from the mixing calculations from the surroundings of the tailing impoundment of La Aquisgrana show that the water from this stretch of the river is mainly influenced by the discharge from the mining adits, which causes considerable increases in its sulphate and metal(oid) contents. Although the contaminating potential of the dump is high, its final contribution to the river water is minimal compared with that associated with the discharge from the mining adits and processes of dissolution of other types of oxyhydroxides that accumulate on the river banks.

Funding Information This research was funded by the Government of Junta de Andalucía (Project RNM 05959) and by the Spanish Ministry of Economy and Competitiveness (Project CGL2013-45485-R, co-financed FEDER).

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