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Monitoring study of the mine pond reclamation of Mina Concepción, Iberian Pyrite Belt (Spain)

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Abstract Mining of massive (Cu, Pb and Zn) sulphide bodies in the Iberian Pyrite Belt (SW Spain) has generated a great number of abandoned waste deposits such as mine ponds. These represent large accumulations of reactive minerals and subsequently, emission sources of trace elements and formation of acid drainage. Even if they have been restored, monitoring studies are required to evaluate the corrective effects and how they may change over time. This work presents the results of a monitoring study carried out at Mine Concepción mine pond, based on mineralogical (XRD), geochemical (INAA, X-ray fluorescence, ICP-MS) and geophysical (electrical resistivity tomography) techniques. In it, a series of relevant parameters have been well delimited, such as the infilling thickness and its variation and, the position, geometry and absence of water leakages through the base of the mine pond. Additionally, the existence of an internal, remnant flow of acid waters that tends to come out through the pond dyke has been

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J. Lillo-Ramos e-mail: javier.lillo@urjc.es identified. Chemistry of these waters indicates that oxidation processes affecting the Mina Concepción mine tailings are generating acid drainage waters which could potentially release substantial amounts of trace elements to the river Odiel. Thus, giving that not complete sealing is accomplished by the restoration capping and rainfall water infiltrates into the pond materials, at least the sealing of the dyke through which leakages occur should be revised.

Keywords Mine reclamation \cdot Monitoring \cdot Acid mine drainage \cdot Electrical resistivity tomography \cdot Iberian Pyrite Belt · Spain

Introduction

The Iberian Pyrite Belt is a geological unit of about 250 km length, within the South-Portuguese zone of the Iberian Massif. It is made up of an acid, volcano-sedimentary complex of later Devonian-Carboniferous age, where numerous bodies of massive sulphides were formed in response to hydrothermalism and tectonics related to the Variscan Orogeny (Tornos [2006](#page-9-0)). Exploitation of these massive (mainly Cu, Pb or Zn) sulphide bodies has generated a great number of structures, cavities and mining waste deposits, such as slag heaps and mine ponds, as a consequence of the extraction and metallurgic processes (Fig. [1\)](#page-1-0). In these mine ponds, watery sludge composed of medium-to-fine-grained material, resulting from grinding and mineral processing (e.g. pyrite, chalcopyrite, arsenopyrite), pile up. They entail both an accumulation and subsequent emission source of trace elements and formation of acid drainage due to oxidation of the sulphides present in the mine tailings, either because they were not sufficiently benefited or due to the existence of a deficient

Fig. 1 Location of the Mina Concepción mine pond, the different metalogenic domains and the main massive sulphide deposits of the Iberian Pyrite Belt. Modified from Tornos ([2006\)](#page-9-0). Metalogenic domains: I Western domain, II Puebla de Guzmán domain, III Sotiel-Aznalcóllar domain, IV Río Tinto domain, V Paymogo domain, VI Northern domain

extractive technology by the time they were exploited. Mine ponds in this area are, therefore, an important envi-ronmental problem (López et al. [2008](#page-8-0); Pérez-López et al. [2007\)](#page-9-0), all the more if they constitute abandoned deposits. In this sense, several recent works dealing with contributions of acid waters derived from mining activity in the province of Huelva to the watercourse of the river Odiel have been carried out (e.g. Sánchez-España et al. [2006,](#page-9-0) [2008\)](#page-9-0). The river Odiel presents a major contribution of acid waters in its sections located downstream from the studied area, as these sections are affected by the mining extractions of Riotinto.

Mina Concepción is a restored mine pond located to the west of Minas de Riotinto town, in the heart of the Iberian Pyrite Belt, that has not had virtually any monitoring over the 10 years already elapsed after the end of its reclamation works.

In this work, we have applied mineralogical and geochemical characterisation techniques (X-ray diffraction, X-ray fluorescence, INAA and ICP-MS) and shallow, nondestructive geophysical techniques (electrical resistivity tomography) to get a detailed picture of the mine pond geometry, composition and thickness of infilling, possible existence of water flows within it and occurrence of acid

mine drainage leaks. Thus, the study has been carried out in order to (1) characterise the present condition of the pond after 10 years of the restoration works, and (2) estimate if the reclamation will require any subsequent action.

This type of study is essential as a base for prevention of environmental disasters such as the one that occurred in 1998 in the mine pond of Aznalcóllar, Sevilla (Aguilar et al. [2004,](#page-8-0) [2006\)](#page-8-0).

Location of the study area and field survey of reclamation condition

The Mina Concepción restored mine pond is located on the SE of the Almonaster la Real municipal district, to the NW of the Minas de Riotinto town. It has 180 m \times 60 m \times 8 m maximum dimensions, corresponding to a surface extension of 10,000 m² and a volume around 30,000 m³ (Fig. [2a](#page-2-0), b).

In the surroundings of Mina Concepción, sulphides occurred in alternating crystal-rich and vitriclast-rich breccia deposits underlying pumice, as well as in vitriclastrich mass flows overlying dark shale intruded by felsic dykes (Tornos [2006\)](#page-9-0).

The mine tailings are flotation deposits of fine-grained, sand size material. They were produced from the metallurgical extraction and benefit of pyrite performed by the company Electrólisis del Cobre S.A. (IGME [1986](#page-8-0)), and were piled up on volcanic lithologies (basic tuffs) on the slope of the Cerro de la Corta hill (Fig. 2b, c). The contention dyke retaining them is 8 m high (Fig. 2d), and drainage is provided by three collector pipes going through the dyke. The drainage system includes an overflow channel that deflects a small watercourse.

The area affected by the mine was restored, under the quadrennial plan of 1993–1996, by the Environmental Council of the Junta de Andalucía, with a total budget of 300,000 € (Consejería de Medio Ambiente [1997](#page-8-0)). In the first stage, the physical restoration of the mine pond was carried out including the correction of zones with pollutants contributions. In the second stage, the landscape integration of the mine pond was achieved by sealing and reforestation of 20,000 $m²$ of ground with pine trees that substituted the original scrub vegetation.

Our first field survey, carried out in Mina Concepción in February 2007, showed that the pond infillings had a fairly homogeneous appearance overall, showing no signs of subsidence, cracks, slides or surface erosion forms such as ravines. However, vegetal covering was reduced to one-fourth of the mine pond surface (Fig. 2a, b). Up to 30– 50 cm of detritic material derived from erosion of surrounding slopes overlaid the mine tailings at the peripheral areas. These detritic sediments are gravels and angular pebbles on the most superficial part, grading into sandy clays with boulders directly overlying the mine tailing deposits. The latter clearly showed oxidation signs on their

first 5 cm. As part of the remediation works, a ditch skirting round all

mine pond perimeter was dug in order to facilitate lateral drainage of rainfall waters and avoid their infiltration. Water that comes from the mine pond through the dyke and drainage pipes flows down to a small watercourse running into the river Odiel (Fig. 2b–d). In the field surveys it was observed that the water leaking through the dyke was associated with precipitated sulphates. This water showed an intense red ochre colour, and stagnated in paddles downslope. The lateral drainpipe in this zone was also pouring out water with the same characteristics to the aforementioned small watercourse. Samples of these waters, as well as samples from the drainage system were taken and analysed

Fig. 2 a General view of the restored Mina Concepción mine pond. b Satellite image of the mine pond and its surroundings (<http://www.goolzoom.com>); the sampling location is marked as S. c Aspect of the volcanic substrate of the mine tailings, in this point covered exclusively by gravels. d Acid waters flowing through the dyke from the mine pond deposits. e Detail of the most superficial capping materials of the reclamation

with a multiparametric probe for temperature, pH, conductivity, redox potential, TDS and dissolved oxygen.

Methodology

Samples from the mine tailings were collected with an Eijkelkamp soil core sampler for undisturbed samples with a known volume and diameter, and a sampling depth of 1 m. Sampling was sequential with a vertical constant spacing of 5 cm. It was carried out by deepening down from the mine pond surface, casting aside the part corresponding to superficial sealing and avoiding the fall of the perforation wall material. With this procedure, seven samples were collected between 70 and 100 cm depth.

Geochemical techniques applied in the present study are the usual ones for this kind of residues. Mineralogical characterisation of the mine tailings was performed by X-ray diffraction (XRD), using a Philips X'Pert powder device with Cu anticathode and standard conditions of speed 2° 2θ / min between 2° and 70° at 40 mA and 45 KV. The study of the total sample was made by crystalline powder diffraction (non-oriented powder) on a side-loading sample holder. XRD analyses have been performed on the Centro de Apoyo Tecnológico (CAT Universidad Rey Juan Carlos). Minor and trace elements were analysed by Instrumental neutron activation analysis (INAA) at Activation Laboratories Ltd. (1428 Sandhill Drive, Ancaster, Ontario, Canada, [http://www.actlabs.com\)](http://www.actlabs.com). Cu and Pb were analysed by X-ray fluorescence (XRF) with a SHIMADZU EDX-900HS equipment at the Escuela Universitaria Politécnica de Almadén (Ciudad Real). NIST2711 was used as the certified reference standard. Five water samples were taken both from leakages of the dyke and from the basal and lateral drainages of the mining pond. Waters were collected in 250 ml bottles. They were kept in refrigerador at 4° C and, prior to analysis, were filtered with 45 µm pore spacing. Samples were analysed for a suite of major and trace cations by ICP-MS at Activation Laboratories Ltd. (see above).

The applied geophysical technique was electrical resistivity tomography (ERT). ERT employs the measurement of resistivity values of underground geologic materials to determine their thickness and depth (Telford et al. [1990](#page-9-0); Reynolds [1997\)](#page-9-0). In the mine ponds there is a strong resistivity contrast between the infilling materials themselves and those defining the base of the mine pond, which allows obtaining good results on the geometry, thicknesses and structure of the infilling mine tailings and the base morphology (Faz Cano et al. [2006](#page-8-0); Gómez Ortiz et al. [2006](#page-8-0); Martínez Pagán 2006; Gómez-Ortiz et al. [2007](#page-8-0); Martín-Crespo et al. [2007\)](#page-8-0). For this technique, a Syscal Junior Switch 48 equipment with Wenner-Schlumberger configuration was used. In order to characterise the mine pond fully, six ERT profiles were performed: one longitudinal and five transverse ones. Their lengths range from 47 to 188 m, with an electrode spacing from 1 to 4 m, respectively, and a maximum penetration depth of 16 m. The software used for obtaining the resistivity models was RES2DINV (Loke and Barker [1996](#page-8-0)).

Results

In this section, mineralogical and geochemical characterisation of the mine tailings sampled in location S is presented (Fig. [2b](#page-2-0)). Also included are the results derived from the ERT profiles concerning the geometry and structure of the pond and the possible presence of acid water flows circulating from surface to deep waters.

Mineralogy and chemical composition of the mine tailings

A mineralogical composition made up of pyrite and quartz as main minerals, and illite, Na–Ca feldspar, chloritesmectite and sphalerite as accessory mineral phases, can be defined from the XRD study in all the studied samples (Table 1). Gypsum has also been identified in most of the

Sample	Deph (cm)	Qtz	Ш	Fsp	Chl-sme	Ro	Gp	Me	Py	Sp	Apy	Mag	Tur
$MC-1$	70	45	$5 - 10$	$5 - 10$	$5 - 10$	$\qquad \qquad -$	$1 - 5$	$\qquad \qquad -$	20				
$MC-2$	75	40	15	$1 - 5$	5	$\qquad \qquad -$	$1 - 5$	$\overline{}$	30	$1 - 5$			
$MC-3$	80	35	$1 - 5$	$1 - 5$	$1 - 5$	5	$5 - 10$	$1 - 5$	45	$1 - 5$	$1 - 5$	$1 - 5$	$\qquad \qquad -$
$MC-4$	85	20	$1 - 5$	$1 - 5$	$1 - 5$	10	$1 - 5$	$1 - 5$	65	5.	$1 - 5$	$1 - 5$	$1 - 5$
$MC-5$	90	20	$1 - 5$	$1 - 5$	$1 - 5$	15	$\overline{}$	$1 - 5$	50	$1 - 5$	$1 - 5$	$1 - 5$	$1 - 5$
$MC-6$	95	35	15	5	$5 - 10$	-	5.	$\qquad \qquad -$	20	$1 - 5$			
$MC-7$	100	60	$1 - 5$	15	5	$\overline{}$	-	$\overline{}$	15	$1 - 5$			

Table 1 Semi-quantitative mineralogical composition (wt%) of the studied samples from the mine tailings

 Q tz quartz, Ill illite, Fsp feldspar, Chl-sme chlorite-smectite, Ro rozenite, Gp gypsum, Me melanterite, Py pyrite, Sp sphalerite, Apy arsenopyrite, Mag magnetite, Tur tourmaline

samples (MC-1, MC-2, MC-3, MC-4 and MC-6). Although sulphide phases are typically present in this type of mine tailings, only pyrite and sphalerite have been identified in significant amounts, whereas arsenopyrite has been detected at the trace level and neither galena nor chalcopyrite have been detected. Regarding Fe-oxides, only traces of magnetite could be identified on samples MC-3–MC-5. It is important to highlight that, in these same samples (taken at 80, 85 and 90 cm depth, respectively) rozenite has been identified in noteworthy amounts, and it could be even considered as an essential mineral, together with pyrite and quartz, in sample MC-5. Rozenite is a tetra-hydrated Fe sulphate (Fe²⁺SO₄·4H₂O), and its presence in these levels could be related to a higher concentration of metals and important water flows at those depths. Also in this sample (MC-5) tourmaline, and another sulphate associated with rozenite and melanterite $(Fe^{+2}SO_4 \cdot 7H_2 O)$ have been identified, both in minor quantities.

Fe₂O_{3total} and trace element concentrations at different sampling depths are shown in Table 2. Elements displaying the highest values are As (up to 1,080 ppm), Cu (up to 3,215 ppm), $Fe₂O_{3total}$ (up to 24.1 wt%), Pb (up to 475 ppm) and Zn (up to 970 ppm). These are important amounts in all cases, although predictable due to the type of mineralisation that was exploited, which was fundamentally composed of pyrite $(F \in S_2)$, calchopyrite $(CuFeS₂)$, sphalerite (ZnS) and galena (PbS) (Vázquez [1976\)](#page-9-0). All analysed elements show significant variations in their contents as a function of depth (Fig. [3\)](#page-5-0). Such variation defines a pattern with three depth intervals showing different metal contents. Thus, the lowest metal content occurs between 70 and 75 cm and between 95 and 100 cm depth, whereas the highest contents are located between 80 and 90 cm. Within the latter depth interval, preferential concentration of total ferric iron at 85 cm depth is accompanied by the highest concentrations in cobalt, arsenic and antimony (shaded area labelled A in Fig. [3](#page-5-0)), as well as gold (see Table 2), whereas at 90 cm depth the same occurs for copper, lead and zinc (shaded area labelled B in Fig. [3](#page-5-0)). Cr, however, displays an inverse concentration pattern to that of all the rest of elements, with its lowest concentration occurring on the central depth interval (80– 90 cm).

The geochemical data are also defining the occurrence of two groups with high significant correlations between elements. The first group includes positive correlation coefficients from 0.97 to 1.00 between elements described in zone A (i.e. total iron, As, Sb and Co; Table [3\)](#page-5-0). The second group, in turn, shows slightly lower significant positive correlation ranging from 0.84 to 0.95 between Cu, Pb and Zn (elements described in zone B in Fig. [3](#page-5-0)). Additionally, Cu also shows a strong interdependence with zone A elements, such that its correlations with As, Sb and Co are 0.97, 0.95 and 0.93, respectively (Fig. [3\)](#page-5-0), and Au is clearly linked mainly to As and Sb, whereas Pb and Zn show moderate interdependence with zone A elements. As expected from distribution-with-depth profiles, Cr shows negative (between -0.70 and -0.80) correlation with virtually all the rest of elements.

Geometry of the mine pond base

ERT has allowed determining the general shape of the bedrock over which the mine materials were deposited, as well as their maximum depth (Figs. [4](#page-6-0), [5](#page-6-0)). The mine tailings display low resistivity values $\left(\langle -1-30\right\rangle$ ohm m) that strongly contrast with the elevated values for the rocky substratum $(>1,000$ ohm m). Lower resistivity values have been interpreted as the silt and clay materials conforming the infilling of the mine pond, whereas the higher resistivity values represent the metamorphic rocks defining the base of the mine pond. The latter interpretation is supported by the obtained resistivity values, which range from 30 to more than 2,000 ohm m, in good agreement with the average of published data for both weathered and fresh tuffs (e.g. Reynolds [1997](#page-9-0)). On the other hand typical mean resistivity values for medium to fine-grained sediments range from 50 to 150 ohm m (e.g. Reynolds [1997\)](#page-9-0), thus being higher than the ones obtained in this study. Nevertheless, it must be taken into account that the infilling of the mine ponds is commonly water saturated and that it contains a great abundance of different types of sulphides with

Table 2 $Fe₂O_{3total}$ and trace elements content in the Mina Concepción mine tailings

	Sample Prof. (cm)	Au (ppb)					As (ppm) Co (ppm) Cr (ppm) Cu (ppm) Fe ₂ O _{3total} (%)	Pb (ppm)	Sb (ppm)	Sc (ppm)	Zn (ppm)
$MC-1$	70	32	238	37	118	1.071	6.11	210	20.4	7.4	240
$MC-2$	75	51	517	90	160	1.912	10.3	279	36.9	8.9	390
$MC-3$	80	80	831	161	12	3.030	15.8	282	52	4.6	680
$MC-4$	85	86	1.080	262	20	2.963	24.1	310	67.5	2.7	660
$MC-5$	90	59	932	214	32	3.215	21.2	475	54.7	4	970
$MC-6$	95	44	472	87	176	1.646	10.6	222	32.7	10.3	440
$MC-7$	100	22	223	41	114	924	7.06	71	16.2	12.9	200

Fig. 3 Distribution-with-depth profiles for total ferric iron and trace elements from Mina Concepción mine tailings. Shaded areas A depth of preferential concentration of As, Co, $Fe₂O_{3tot}$ and Sb, and B depth preferential concentration of Cu, Pb and Zn

Table 3 Correlation matrix between elements of the Mina Concepción mine tailings ($n = 9$; significance $P < 0.05$)

Bold values indicate $r \geq 0.75$

highly variable resistivity values (e.g. the resistivity value of pyrite ranges from 2.9×10^{-5} to 1.5 ohm m). Thus, both factors (water and sulphide occurrence) may satisfactorily justify the measured decrease of resistivity values in the infillings of the studied mine pond, to values lower than 1 ohm m (Figs. [4b](#page-6-0), [5](#page-6-0)). The resistivity values obtained in this work are similar to the ones obtained by different authors: e.g. Martínez-Pagán et al. [\(2009\)](#page-9-0) and Faz Cano et al. ([2006](#page-8-0)) for similar abandoned sulphide mine ponds located in La Unión (Murcia, Spain), where they found resistivity values of $\&$ ohm m for mine tailings and >150 ohm m for bedrock (composed by Paleozoic schists and quartzites).

The longitudinal profile (profile 1, Fig. [4](#page-6-0)b) reached at the seventh iteration a minimum root mean square (RMS) error of 10.9%. This profile shows that the base of the mine pond describes a step in its middle zone that separates two

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sectors with different filling thickness. The shallowest sector is 5 m thick and is located on the western part of the mine pond (from 8 to 100 m of ERT profile 1). The deepest sector is situated towards the eastern part (from 100 to 175 m of ERT profile 1) where a depth of 8 m is reached. Regarding the transverse profiles (Fig. [5](#page-6-0)), the minimum RMS errors obtained during the inversion procedure for profiles 2–6 were of 2.2, 4.4, 2.9, 5.4 and 4.3% at iterations sixth, seventh, eighth, sixth and sixth, respectively. In these profiles, a step in the base of the pond is also clearly visible, such as greater infilling thicknesses found near the dyke and at the northern part of the mine pond. The maximum thickness of the infilling materials is >8 m in most of the profiles near their northern end.

In summary, the infilling materials of the mine pond as deduced from the ERT profiles are heterogeneous, with

Fig. 4 a Location of ERT profiles in Mina Concepción mine pond. b Longitudinal ERT profile (profile 1). White dashed line represents the location of the mine pond base

Fig. 5 Transverse ERT profiles (profiles 2–6). White dashed lines indicate the position of the mine pond base. Yellow dashed lines represent the boundaries of the zones with resistivity values lower

than 1 ohm m, interpreted as due to acid water flow. The location of the profiles can be seen in Fig. 4a

maximum thickness values at the northern and eastern zones, due to the presence of clear, longitudinal and transverse steps, located at the central part.

Acid water flows

By means of ERT, we have been able to define the presence of zones with resistivity values lower than 1 ohm m (Figs. [4](#page-6-0)b, [5\)](#page-6-0). The low resistivity values are related to watersaturated silt and clay materials with abundance of sulphides, mainly pyrite. The low resistivity zones show slightly elliptical, extended geometries, the initial position of which represents the site of influx of surface waters into the mine pond, whereas their farthest end coincides with the leakage of the acid water flowing through the masonry dyke delimiting the mine pond in its eastern part (Figs. [2d](#page-2-0), [5\)](#page-6-0). It is for this reason that such zones have been interpreted as indicative of the presence of an acid water flow within the mine tailings, due to acidification of meteoric water when it goes through the materials with high pyrite contents.

The results of water sampling shown in Table 4, indicate these waters represent acid mine drainage, as reflected by their very low pH $(2-3)$, high redox potentials $(550 \text{ mV}$ on average) and, in general, high conductivity and TDS. Concentrations of trace elements are very high for Cu and Zn $(>=2,000 \mu g/l)$, both going beyond the EPA's maximum recommended limits of these elements in irrigation waters $(0.2 \text{ mg/l}$ for Cu and 2 mg/l for Zn; EPA 2004). This is also the case for Co ($>2,000 \mu$ g/l) and As (1,350 to $>2,000 \mu$ g/l) in samples leaking from the dyke wall (MCW-1) and samples from the puddle (MCW-4, MCW-5). Although samples leaking through the basal (MCW-2) and lateral (MCW-3) drainage pipes show moderate-to-high Co contents (134 and 940 μ g/l, respectively) and much lower As (1.1 and 5 μ g/l, respectively), they also still surpass or get very close to the maximum recommended limits of these elements (0.05 mg/l for Co and 0.1 mg/l for As; EPA [2004\)](#page-8-0). Lead, in turn, also surpasses the legislation limits as much in the sample leaking from the dyke wall (MCW-1) as in both samples from the drainage pipes (MCW-2, MCW-3).

Discussion

Mineralogically, the Mina Concepción mine tailings are fundamentally composed of quartz, pyrite, chlorite-smectite, illite, gypsum and hydrated Fe sulphates, and chemically they present important contents of toxic elements such as As, Cu, Fe, Pb and Zn. The alternation of different stages of operation of the mine has been revealed. Periods in which mineral benefit was higher, were probably due either to improvement of metallurgic processes or to higher grade. These periods alternated with others in which a greater proportion of ore mineral particles were not conveniently well-exploited and ended up within these residual mine tailings. Positive correlations could also be established between As, Au, Co, Fe, Sb and Zn, as well as negative correlations between them and Cr. This means that an association exists between these elements, linked to a common origin and metallurgic behaviour for all of them.

The occurrence and concentration of the iron sulphates rozenite and melanterite at relatively shallow levels $(around 1 m depth)$ in the Mina Concepción mine tailings is strongly indicative that pyrite has been chemically weathered mainly by O_2 . Doménech et al. ([2002\)](#page-8-0) proposed a three-step dissolution mechanism for pyrite chemical weathering by O_2 in sludges of the Aznalco^{fllar} mining district and also in SW Spain. The step two, oxidation of sulphide to sulphate, is the main process affecting to the Mina Concepción mine tailings. Concomitant surface weathering of Na–Ca feldspars would, in turn, provide the calcium for neoformed gypsum in samples MC-1–MC-4.

Pb and Cu contents in the Mina Concepción mine tailings range from significant, for the former, to fairly high for the latter, in spite of the fact that no galena or chalcopyrite was recognised on XRD. In the original mineralisation, galena was only reported to be in trace amounts (Vázquez [1976](#page-9-0)), whereas chalcopyrite was described as present in drops within pyrite. In our data, Pb shows a strong positive correlation coefficient with Zn $(0.91; \text{ see Table 3}; \text{Fig. 3})$ $(0.91; \text{ see Table 3}; \text{Fig. 3})$ $(0.91; \text{ see Table 3}; \text{Fig. 3})$, which could indicate its presence as impurities in sphalerite. Taking into account that

Sample Colour $T (^{\circ}C)$ pH Conductivity $(\mu S/cm)$ Redox potencial (mV) TDS (ppm) Dissolved oxygen (%) MCW-1 Deep ochre red 16.7 2.20 16,780 418.0 8,348 39.1 MCW-2 Colourless 16.7 2.55 1,059 543.8 530 47.3 MCW-3 Colourless 15.9 2.25 4,361 602.6 2,178 47.4 MCW-4 Deep ochre red 16.0 2.15 8,297 628.0 4,153 50.6 MCW-5 Deep ochre red 18.2 2.00 10,580 636.3 5,290 40.2

Table 4 Parameters measured in water samples from Mina Concepción water (MCW) drainage in February 2007

TDS total dissolved salt, MCW-1 water leaking through the dyke wall, MCW-2 basal drainage, MCW-3 lateral drainage, MCW-4 surface of deep ochre red puddle, MCW-5 bottom of deep ochre red puddle

both Cu and Zn are relatively soluble elements at a wide range of pH $(2-6)$ and $O₂$ concentrations (Doménech et al. 2002), oxidation processes affecting pyrite and sphalerite in the mine tailings would have released them into solution. This would explain their high contents, as well as those of lead, in drainage waters from Mina Concepción. Arsenic, in turn, seems to have been also mobilised from oxidation of pyrite and arsenopyrite, and its highest concentrations are associated with deep ochre red colours in the waters (Table [4](#page-7-0)).

A shallow, non-destructive geophysical technique such as ERT has proved very useful in this kind of studies dealing with restoration monitoring of mine ponds. ERT has delimited very well the position, the in-steps geometry and the good waterproofing of the mine pond's base, as well as the infilling thickness and its variation. Additionally, the technique has identified the existence of an internal, remnant flow of acid waters that tend to come out through the dyke of the mine pond. Chemistry of these waters indicates that oxidation processes affecting the Mina Concepción mine tailings are generating acid drainage waters which could potentially release substantial amounts of trace elements to the river Odiel. Thus, given that complete upper sealing is not accomplished by the reclamation and that rainfall water infiltrates into the pond materials, we consider that, at least, waterproofing of the dyke, through which leakages occur, should be revised. An aspect that must be emphasised is that the measured resistivity values $\langle 1 \rangle$ ohm m are confined to the mine tailings. This, together with the homogeneous resistivities of the bedrock, shows that there are no acid water leakages through the base of the mine pond that could reach groundwater, and that at least its waterproofing condition is correct.

Conclusions

As much the mineralogical composition as the contents in potentially toxic geoavailable elements from the mine pond (As, Cu, Fe, Pb and Zn) made its monitoring necessary. The high sulphide content makes this mine pond a potential source of acid drainage that is leaking to the outside, producing serious contributions of acid waters to the watercourse of the river Odiel. Consequently, this is one element of the Mina Concepción mine pond restoration that would need an improvement of waterproofing.

The used combination of geophysical and geochemical techniques allows first the characterisation and then monitoring of storage structures of mining wastes, such as are mine ponds. Thus, this type of monitoring studies also allow determining if past reclamations are still effective or if, on the contrary, these zones require additional measures in order to avoid they could become an environmental problem.

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