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ORIGINAL ARTICLE

Stream water geochemistry from mine wastes in Peña de Hierro, Riotinto area, SW Spain: a case of extreme acid mine drainage

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Abstract In this work we have studied the geochemistry of stream waters arising from waste dumps at the Peña de Hierro mine (Iberian Pyrite Belt, SW Spain), and we have correlated them with the mineralogical and geochemical characteristics of the wastes to asses the source and factors affecting the release of trace elements. The mineralogical composition and geochemistry of 58 borehole samples of waste dumps were studied in the <2 mm fraction. Twenty-eight water samples collected in winter and summer from streams emerging from the waste dumps were analysed for pH, Eh, conductivity, temperature, sulphates and major and trace elements. The leachates from pyrite-rich volcanic tuffs produced very acidic waters, usually with pHs below 2 and reaching values as low as 0.7. The partial dissolution of gossan, which is mainly composed of Fe oxy-hydroxides and is rich in trace elements, released high concentrations of Fe_{tot} (up to 33 g/L), As (up to 72), Mo (up to 11 mg/L). On the other hand Cd, Zn and Pb reached up to 0.85, 142 and 0.42 mg/L, respectively, in the stream arising from roasted pyrite ashes and other pyritic wastes. Several elements such as Al, Fe, As, Co, Cu and Mo were strongly correlated with the pH, but Cd and Zn were not correlated under such acidic conditions. The precipitation of jarosite seems to be an important factor in the retention of Pb. The mobility sequence of trace elements shows that Co, Zn and Cd were among the most mobile elements; Cu, As and Mo had intermediate mobility, and Pb was the most immobile. This work shows that uncontrolled waste dumping increases the pollution potential, and a selective management could reduce the release of trace elements into stream waters and mitigate the contamination.

Keywords Acid mine drainage · Trace elements · Mine-waste dumps · Tinto River · Iberian Pyrite Belt

Introduction and aims

Acid mine drainage (AMD) is the major pollution problem associated with coal and metallic sulphide mining worldwide. The term "AMD" refers to acidic waters originating from the oxidation of pyrite and other sulphides. In the United States, AMD affects more than 19,000 km of rivers and streams (Kleinmann 1989). The main problems associated with AMD are its acidity and high concentration of trace elements (As, Cd, Cu, Co, Mo, Ni, Pb, Se, Zn, etc.) carried in solution.

The sources of AMD include tailings, mine adits, pit lakes or any material containing sulphides that is prone to oxidation. One of the most important sources of AMD is the waste rock piles, which usually are very heterogeneous in grain size, mineralogy and geochemistry. This makes very difficult to study the generation of AMD from them, since the water geochemistry is affected by all these waste characteristics (Pantelis and Ritchie 1991; Ritchie 1994; Nordstrom and Alpers 1999a; Lefebvre et al. 2001).

Extreme acid waters, with a pH below 1, have occurred in several mines such as Genna Luas (Sardinia, Italy), Iron Duke (Zimbabwe) and San Telmo (Spain) (Frau 2000; Williams and Smith 2000; Sánchez España et al. 2008, respectively). Trace element concentrations were also high in all these waters. For instance, up to 60 mg/L of Cd, 73 mg/L of As and 10,700 mg/L of Zn in Genna Luas, Italy (Frau 2000); 72 mg/L of As in Iron Duke, Zimbawe

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(Williams and Smith 2000); and 13.76 mg/L of Cd and 1.1 g/L of Zn in San Telmo, Spain (Sánchez España et al. 2008). But all these values were far from those found in Iron Mountain, California (Nordstrom and Alpers 1999b; Nordstrom et al. 2000), with pH values as low as −3.6, As as high as 850 mg/L, Cd up to 370 mg/L, and Zn up to 49 g/L.

In Spain, the contamination associated with AMD has been documented at several sites such as Galicia or Asturias (e.g. Monterroso and Macías 1998a; Loredo et al. 2005), but it largely occurs in the Iberian Pyrite Belt (IPB), which is one of the most important metallogenic provinces in the world. Most of the mines in this area have been abandoned and are discharging huge quantities of acidic waters and heavy metals into the Tinto and Odiel Rivers (González et al. 2004; Sánchez España et al. 2005; Cánovas et al. 2007). As a result, these rivers are among the most polluted in the world and have gained the attention of many researchers and studies (Fernández-Caliani et al. 1997; van Geen et al. 1997; Elbaz-Poulichet and Dupuy 1999; Hudson-Edwards et al. 1999; Braungardt et al. 2003; Galán et al. 2003). However, there is not enough information about the contribution that the different abandoned mine spoils have on those rivers. This is reasonable if we consider that the headwaters of both rivers receive leachates from huge quantities of mine spoils of the Riotinto mining district. The volume of these wastes has not been assessed, but it is known that at least 6.6 million tons of slags are from the Roman and pre-Roma period (Rothenberg et al. 1990). The intense exploitation of the Riontinto Mines, especially during the nineteenth century, has caused about 1,800 ha of land to be covered with dumps, tailings and open pits, making it difficult to characterize and remediate.

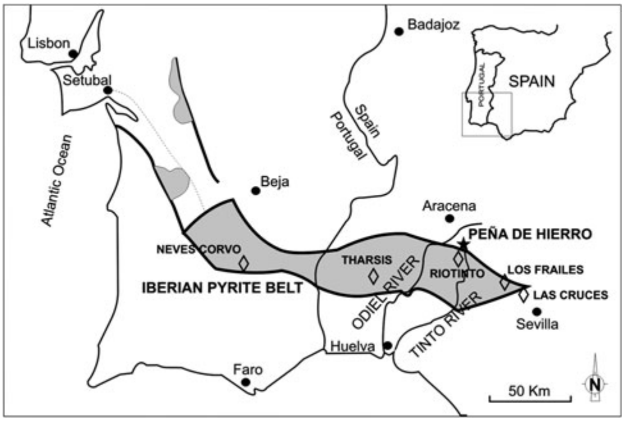

Fig. 1 Location of the Peña de Hierro mine in the Iberian Pyrite Belt (SW Spain)

Here, we have investigated the geochemistry of stream waters in the Peña de Hierro abandoned mine site, located in the catchment area of the Tinto River and being the first source of pollution to this river (Fig. 1). The deposit consists of a copper-bearing pyrite ore with variable concentrations of copper, usually comprised between 1 and 4 wt%, and lower concentrations of Zn and Pb (Pinedo Vara 1963; IGME 1982; Tornos 2008). The mine was working between the middle of the nineteenth century and 1966, and it produced about 3 million tons of waste rock and other residues that were dumped around the pit, covering 25 hectares. The characterization of the wastes and the mapping of the dumps have been carried out by Romero et al. (2006a). There are several streams that arise from these waste dumps, and thus, the geochemistry of the waters can be directly linked to the different waste rocks. The aim of this work was to correlate the trace element concentration in stream waters with the different mine-waste dumps, in order to determine the source and factors affecting the genesis of AMD. To achieve these objectives, we studied the geochemistry of the stream waters and the results were compared with the chemical and mineralogical characteristics of the waste dumps.

Materials and methods

Waste dumps

Waste rock samples were collected from boreholes drilled into the dumps by the company RIOTINTO S.A.L., at depths between 1.5 and 14.0 m. A representative sample was collected from each borehole, up to a total of 58 samples. Since the dumps consist of different wastes, the mineralogy and chemistry were analysed in the <2 mm fraction. The mineralogical characterization was carried out by X-ray diffraction (XRD) using a Bruker D8 Advance equipment with slit fixed at 12 mm and monochromatic Cu Kα radiation. Random powders were scanned at 40 kV and 30 mA from 3° to 70° 2θ at a speed of 0.3° 2θ/min.

Chemical analyses of major, minor and trace elements were made in the <2 mm fraction of selected samples. Nineteen elements were analysed at Activation Laboratories Ltd (1428 Sandhill Drive; Ancaster, Ontario, Canada) from 3 g of sample ground in agate mortar and sieved at 50 µ. Analysis methods included Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Infra-Red Spectroscopy (IR). The detection limits were 1 mg/kg for As, Co, Cu, Hg, Mn, Mo, Ni and Zn, 0.3 mg/kg for Cd, 2 mg/kg for Cr, 3 mg/kg for Pb, 50 mg/kg for Ba and 0.01% for major elements and S. The results were contrasted against certified materials such as DMMAS-14, G-2, SDC-1, DNC-1, SCO-1, GXR-1, GXR-2, GXR-4 and

GXR-6. Errors were always below 10%, except for Cd, Al and Mg, which could be higher.

Stream water

A total of 28 water samples were collected in PVC bottles from the streams arising from the waste dumps during two field trips (Fig. 2): the first one was carried out in winter (March 2002, 12 samples), 2 weeks after a period of continuous rain. The second was carried out in summer (July 2002, 16 samples), after more than 2 months of high temperatures and no precipitation. Water samples were collected from the headwaters of each stream next to the waste dumps, and several metres downstream from the confluence of different watercourses. After collection and filtration to 0.45 μ, samples were acidified below pH 2 when needed and kept at 4°C until chemically analysed.

The pH was measured in the field using a CRISON 507 portable pH meter equipped with a 52-00 electrode and automatic temperature compensation. Conductivity was measured using a CRISON 524 portable conductimeter equipped with a 52-90 cell and automatic temperature compensation. Temperature and Eh were measured (in July 2002) using a CRISON 52-61 platinum electrode coupled with the above-mentioned pH meter. All instruments were calibrated in the field before measurements were taken.

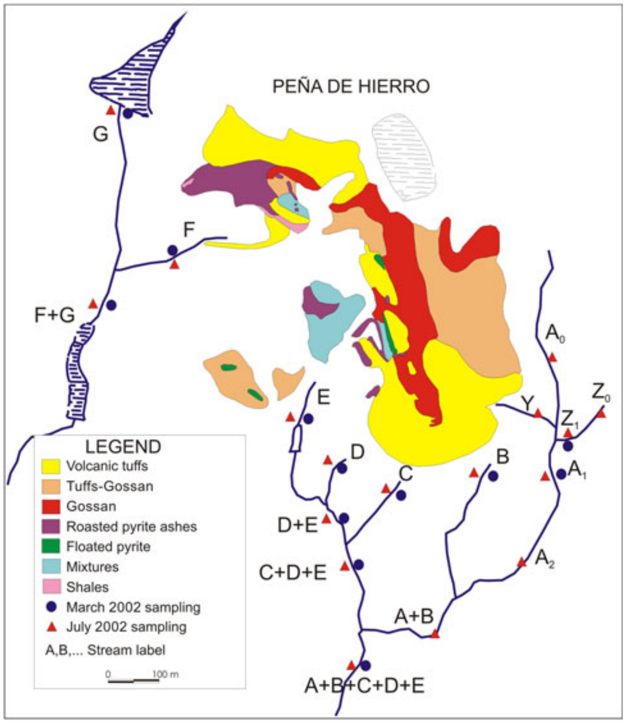

Fig. 2 Distribution of mine-waste dumps in Peña de Hierro and location of streams and sampling stations. *Blue circles* denote sampling in winter, and *red triangles* are for summer. Modified after Romero et al. 2006a

In the laboratory, the sulphate concentration was determined by turbidimetry on a Zuzi 4200/50 UV–vis spectrophotometer. Samples collected from the headwaters and some from the confluence of watercourses were selected to analyse the concentration of major, minor and trace elements (21 samples). All analyses were carried out at Activation Laboratories (http://www.actlabs.com) by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The detection limits for the analysed elements were 2 μg/L for Al, 50 μg/L for Ca and Si, 5 μg/L for Fe and Na, 10 μg/L for K, 1 μg/L for Mg, 0.03 μg/L for As, 0.01 μg/L for Cd, 0.005 μg/L for Co, 0.5 μg/L for Cr and Zn, 0.2 μg/L for Cu and 0.1 μg/L for Mn, Mo and Pb. The accuracy and precision of the analytical method was verified against the certified reference waters SLRS-4 for major elements and NIST 1640 for trace elements. Errors were always below 5% except for As and Pb (7.5%) and Ni (10%).

Results and discussion

Waste dumps

Waste dumps consist of a mixture of different materials such as volcanic rocks, gossan, shales, and mining residues such as roasted pyrite ashes or floated pyrite. A detailed description of the wastes is presented by Romero et al. (2006a). According to which of these materials predominates in the dumps, a mapping of the waste has been carried out, with the following being the most important units (Fig. 2, Romero et al. 2006a):

1. Tuff dumps are mainly made up of acid volcanic tuffs, but usually gossan and shales are mixed in the dumps. The mineralogy is mainly composed of quartz, muscovite, pyrite and jarosite (Table 1). Pyrite is common in blocks of volcanic rocks, and jarosite precipitates in the <2 mm fraction after the oxidation of pyrite. When gossan fragments are present, hematite and amorphous Fe oxy-hydroxides occur in the fine fraction of the dumps. The concentration of trace elements in the <2 mm fraction of this unit is low when compared with other residues. For example, As is below 263 mg/kg and Pb is below 628 mg/kg (Table 2). By contrast, the concentration of Co (64 mg/kg) was higher than that found in other materials.
2. Gossan dumps may also contain remains of tuffs and shales. They have a high content of hematite, goethite and X-ray amorphous iron oxy-hydroxides. The <2 mm fraction of these dumps displays high concentration in several trace elements such as As (538–1,710 mg/kg), Mo (143–331 mg/kg), Pb (318–

Table 1 Mineralogy of fraction <2 mm in different types of mine-waste dumps (in %)

Mine-waste dump	Qz	Ms	Py	J	Chl–Kl	Ba	Hem	Gt	Fe-OH
Volcanic tuffs ($n = 14$)	>50	10–30	0–5	5–10	5–10	tr	<10	–	–
Gossan ($n = 18$)	>25	10–20	–	tr	0–5	5	10–25	10–25	>5
Tuff–gossan ($n = 14$)	>35	10–25	–	tr	0–5	5	5–10	0–10	0–10
Roasted pyrite-ashes ($n = 5$)	10–40	<15	0–15	5	–	5–10	>35	–	>10
Mixture ($n = 4$)	30–50	15–25	0–15	5–10	–	5	5–10	–	<10
Pyrites ($n = 1$)	>40	<15	>20	–	–	5–10	–	–	–
Shales ($n = 1$)	>40	20–30	–	tr	10–15	5	–	–	–

Qz, quartz, *Ms* muscovite, *Py* pyrite, *J* jarosite, *Chl/Kl* chlorite + kaolinite, *Ba* barite, *Hem* hematite, *Gt* goethite, *Fe-OH* poorly-crystalline iron oxyhydroxides, *tr* traces, *n* number of samples analysed

989 mg/kg) or Cu (90–895 mg/kg). These concentrations can be higher in rock fragments of gossan. For example, Romero et al. (2006a) determined up to 2,330 mg/kg of As, 4,560 mg/kg of Pb, and 749 mg/kg of Mo.

3. Tuff–gossan dumps consist of a mixture of tuff, gossan and shales. Their mineralogical and geochemical characteristics are intermediate between the two units mentioned above.
4. Roasted pyrite ash dumps are characterized by a high content of hematite and X-ray amorphous iron oxides. They are also rich in trace elements such as Pb (2,000–3,460 mg/kg), As (303–971 mg/kg), Mo (81–351 mg/kg), Cu (419–527 mg/kg), Cd (2–3 mg/kg) and Zn (283–536 mg/kg).

Other dumps such as floated pyrite and mix dumps are rich in fine pyrite and may have high concentration of trace elements, but they are less important because their volume is relatively low (Romero et al. 2006a, Fig. 2).

Stream waters

Physical–chemical features

The pH was very acidic in most of the streams, ranging between 0.7 (site C, July) and 3.5 (site Z_1, March) (Table 3). Streams Y, B, C and D arising from the tuff dumps displayed the lowest pH values (always <2). Site G, located outside the mining area, showed neutral natural water. Stream Z was not affected by leachates from the waste dumps, but pH ranged between 3.1 and 3.5. The pH values recorded in summer were lower than those of winter in most of the streams.

Conductivity ranged between 1,000 and 47,000 µS/cm in the acidic streams, being of 130 µS/cm in the neutral stream G. The most acidic streams (Y, B, C, D) recorded the highest conductivity values, which were over or about 20,000 µS/cm. The values recorded in the summer field trip were higher than those of winter in most of the streams. The sulphate concentration, which correlates with the conductivity, ranged between 363 and 33,202 mg/L in the acidic samples, and it was about 6–7 mg/L in the neutral stream.

The Eh in the acidic streams ranged between 333 (site Z_0) and 563 mV (site Y), and it was of 202 mV for the neutral water. The Eh increased as water moved downstream.

According to the temperature values, stream Z displayed values of about 24°C, streams Y, A and B were about 28–30°C and the other streams ranged between 20 and 22°C. The temperature values recorded at the confluence of different streams, as well as pH, conductivity and sulphate concentration, showed intermediate values with upstream waters.

Stream water geochemistry

The chemical analyses of major and trace elements are shown in Table 4. Among the major elements, Fe displayed the highest concentration, up to 30 g/L at stream C, and many times it was over 10 g/L, especially in streams arising from the tuff dumps. Aluminium and Mg reached 3,730 and 1,680 mg/L, respectively. Calcium ranged between 21 and 470 mg/L. Sodium and Si were lower than 100 mg/L. Potassium displayed the lowest concentration, being in most of the samples below 3 mg/L.

Among the minor and trace elements, Mn, Cu and Zn displayed values over 100 mg/L in several samples (Table 4). Arsenic and Mo reached up to 72 and 11.3 mg/L, respectively (site C, July). Cadmium was usually over 0.1 mg/L and reached up to 0.85 mg/L in site F (July). Cobalt usually displayed a few mg/L, and it was over 10 mg/L in the most acidic streams. Among the most immobile elements was Pb, which was always below 0.5 mg/L.

Figure 3 shows the relative concentration of elements in the headwaters of every stream, corresponding to summer sampling. The element concentrations of every sample

Table 2 Chemical analysis of <2 mm fraction of borehole samples (Romero et al. 2006a)

Sample	Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)	P (%)	S (%)	As (ppm)	Ba (ppm)
Acid volcanic tuffs										
T1	4.0	0.03	10.9	1.6	0.7	0.5	0.01	4.2	263	4,600
T2	2.1	0.01	6.8	1.2	0.1	0.1	0.01	2.8	214	3,900
T3	3.5	<dl	6.9	2.3	0.1	0.1	0.01	7.2	46	11,000
T4	5.1	0.03	4.0	1.9	0.2	0.7	0.02	1.2	157	7,700
T5	5.5	<dl	8.2	3.9	0.2	0.2	0.01	5.3	119	5,800
Tuff–Gossan										
TG 1	3.5	<dl	16.6	1.3	0.1	0.1	0.02	0.4	371	14,000
TG 2	4.2	0.09	14.0	2.1	0.2	0.2	0.02	0.3	433	5,200
Gossan										
G1	0.8	0.02	30.8	0.6	0.1	0.2	0.02	1.3	1,450	36,000
G2	4.6	0.01	16.1	1.5	0.2	0.2	0.03	0.6	725	20,000
G3	2.4	0.02	21.3	0.7	0.1	0.1	0.01	0.1	570	32,000
G4	2.8	0.03	22.7	0.6	0.1	0.1	0.01	0.1	538	42,000
G5	1.9	<dl	20.8	0.7	0.1	0.1	0.02	0.2	896	30,000
G6	3.2	0.01	18.2	1.6	0.2	0.1	0.02	1.1	692	23,000
G7	2.8	0.06	26.5	1.4	0.1	0.1	0.02	0.7	1,250	71,000
G8	3.3	0.02	27.7	1.0	0.2	0.1	0.03	0.3	1,710	79,000
Roasted pyrite ashes										
PA1	1.2	0.07	49.8	0.6	0.04	0.1	0.01	1.5	720	21,000
PA2	0.3	0.04	52.1	0.1	<dl	0.02	0.00	0.5	303	110,000
PA3	1.2	0.03	36.3	0.6	0.1	0.1	0.01	0.6	971	44,000
Mixtures										
M1	3.4	0.72	11.0	1.5	0.2	0.2	0.04	4.8	231	19,000

Sample	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Hg (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Acid volcanic tuffs										
T1	<dl	22	28	1,487	2	113	21	10	201	392
T2	<dl	11	39	23	<dl	12	95	15	628	19
T3	1	64	29	16	1	7	58	13	179	27
T4	0.3	7	28	131	1	17	38	9	389	61
T5	<dl	35	15	51	<dl	16	65	5	113	35
Tuff–Gossan										
TG 1	<dl	5	<dl	75	3	35	161	<dl	212	59
TG 2	<dl	11	<dl	146	5	96	101	3	341	72
Gossan										
G1	4	3	37	264	22	79	210	18	467	238
G2	<dl	8	27	202	5	69	207	5	683	180
G3	1	4	34	101	2	39	207	11	381	90
G4	<dl	4	17	90	1	33	213	3	318	56
G5	2	4	20	211	11	58	251	8	593	164
G6	<dl	8	<dl	207	5	49	143	2	533	75
G7	1	6	38	895	53	72	204	13	764	434
G8	0.3	4	42	606	22	45	331	14	989	365
Roasted pyrite ashes										
PA1	3	58	28	527	4	44	156	14	2,660	283
PA2	2	18	<dl	419	11	27	81	<dl	3,460	536
PA3	2	32	32	476	16	41	351	18	2,000	303
Mixtures										
M1	3	20	65	234	3	387	45	29	1,700	379

<dl below detection limit

Table 3 Values of pH, conductivity, Eh, temperature and sulphate contents of water samples

Sample	March 2002			July 2002				
	pH	Conduc (µS/cm)	Sulphate (mg/l)	pH	Conduc (µS/cm)	Eh (mV)	T	Sulphate (mg/l)
Z_1	NA	NA	NA	3.2	5,280	333	24	3,262
Z_2	3.5	7,360	2,082	3.1	3,830	392	24	5,522
Y	NA	NA	NA	1.6	21,800	563	30	8,902
A_0	NA	NA	NA	2.6	7,610	423	28	2,544
A_1	1.8	10,820	3,035	1.7	17,050	530	28	5,026
B	1.5	19,150	5,505	1.5	25,000	485	28	11,566
C	0.8	36,800	12,380	0.7	47,080	496	22	33,202
D	1.7	20,080	10,417	1.2	31,200	475	21	15,235
E	2.1	8,340	3,665	1.8	12,030	499	21	5,858
F	2.3	3,550	363	2.7	6,320	375	20	1,876
G	7.3	130	7	7.8	1,002	205	22	6
A + B	NA	NA	NA	1.7	16,000	502	26	6,526
D + E	2.0	9,360	4,711	1.8	9,900	508	21	4,358
C + D + E	1.7	11,870	4,383	1.7	11,870	514	20	5,303
A + B + C + D + E	1.8	10,940	3,350	1.7	15,040	524	27	5,215
F + G	2.3	3,970	401	2.4	7,170	413	18	2,531

NA not analysed

were normalized with the maximum value found for each element. Thus, a value of 1 for a particular element points out the sample with the maximum concentration for this element. So, Fig. 3 shows that stream C had the lowest pH and the maximum concentration in sulphate, Fe, As, Co, Cu and Mo. High concentrations of these elements were also found in other streams arising from the tuff dumps (B, D, Y), and they correlated negatively ($r < -0.7$) with pH (Table 5). The maximum concentration of K was recorded in stream C, but the concentrations in the other streams were very low.

Other elements such as Ca and Mn showed low values in the most acidic streams, and the highest values occurred in streams Z, A and F. These streams flow over the bedrock constituted of shales that are rich in Ca and Mn (Fernández-Caliani and Galán 1991), suggesting that these elements can be leached from them into the stream water.

Cadmium and Zn displayed high values in stream F where pH was also high, and in streams B, C and D. The concentrations of Pb were very low in most of the streams, and the highest values were found in streams C and F.

These results show that the streams in Peña de Hierro are among the most polluted in the world (Table 6). For example, the minimum pH and maximum concentration of As (72 mg/L) were similar to those found in other mines such as Genna Luas, Italy, or Iron Duke, Zimbabwe (Frau 2000; Williams and Smith 2000). The concentration of Mo recorded in Peña de Hierro (up to 11.3 mg/L) was extremely high. This value is even higher than the maximum found in Iron Mountain (4.2 mg/L, Nordstrom and Alpers 1999b). A similar value of Mo (10.41 mg/L) has been measured in San Telmo, another mine of the IPB (Sánchez España et al. 2008).

Source of AMD and trace elements

One possible source of acidic waters in Peña de Hierro is the natural acid rock drainage produced by the bedrock, as other authors have suggested (González-Toril et al. 2003; Fernández-Remolar et al. 2004). In this sense, stream Z, which is located in the eastern part of the mine, does not seem to be affected by mine waters (Fig. 2), and its geochemistry is highly affected by elements leached from the bedrock, such as Ca, Na and Mn. Therefore, these waters can represent the natural acid rock drainage in the headwaters of the Tinto River. In any case, and in comparison with the geochemistry of streams arising from these waste dumps, the low content of trace elements in stream Z shows that the mismanagement of mine wastes and their subsequent abandonment have a very negative impact on the environment, since it causes the load of acid and trace elements in stream water to rise by several orders of magnitude.

The high acidity of the streams arising from the tuff dumps (Y, B, C, D) shows that these wastes, which contain pyrite and have no neutralizing minerals, are a very important source of AMD in Peña de Hierro. Although there are other pyrite-containing wastes that may generate AMD, the coarse grain size of the tuff dumps (Romero et al. 2006a) allows the air to enter easily into the dumps,

Table 4 Chemical analyses of water samples

Sample	Al (mg/l)	Ca (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	As (µg/l)	Cd (µg/l)
March (2002)									
Z	1	140	41	1.3	193	24	8	2	0.4
A_1	591	146	3,480	2.1	222	13	54	3,840	219
B	964	63	7,880	0.5	216	16	60	9,110	179
C	1,780	36	15,400	28.7	246	25	45	27,700	220
D	2,270	39	10,300	0.5	674	5	56	10,100	247
E	408	64	2,750	0.8	304	12	22	1,560	29
F	73	50	514	0.9	142	8	25	153	66
F + G	63	53	573	1.7	93	10	18	562	87
C + D + E	567	104	3,920	0.8	180	15	46	4,090	181
A + B + C + D + E	573	115	3,610	0.2	192	16	51	3,330	194
July (2002)									
Z	52	470	613	2.5	645	49	10	143	5
Y	3,250	21	18,700	0.2	1,680	4	54	13,800	119
A_1	1,980	205	10,800	0.8	1,430	37	44	7,080	71
B	3,810	79	16,300	0.2	1,040	7	52	19,600	488
C	3,730	86	30,200	10.7	628	42	40	72,200	512
D	2,070	139	16,900	0.9	465	25	57	28,200	433
E	574	203	3,800	0.2	310	21	42	4,840	259
F	173	283	1,290	1.7	251	30	22	249	849
F + G	71	330	915	0.7	281	30	30	28	738
C + D + E	525	142	3,610	0.4	201	18	39	4,310	226
A + B + C + D + E	1,780	192	7,880	0.3	675	25	52	7,930	275

Sample	Co (µg/l)	Cr (µg/l)	Cu (µg/l)	Mn (µg/l)	Mo (µg/l)	Ni (µg/l)	Pb (µg/l)	Zn (µg/l)
March (2002)								
Z	833	<0.5	139	44,500	<0.1	357	9	6,410
A_1	3,700	157	42,000	22,700	309	658	49	67,700
B	7,320	200	39,100	12,700	1,860	618	161	51,900
C	13,800	145	61,300	9,730	5,370	522	342	58,600
D	10,900	179	66,500	20,900	1,290	750	55	69,900
E	2,870	58	2,540	24,700	161	485	37	5,280
F	599	<0.5	6,990	10,100	29	177	143	26,700
F + G	666	<0.5	7,190	15,300	80	230	210	24,000
C + D + E	3,980	131	32,300	16,600	705	560	106	57,800
A + B + C + D + E	3,700	139	32,800	18,300	516	601	113	63,700
July (2002)								
Z	3,560	<0.5	1,140	152,000	6	866	12	26,500
Y	18,700	391	19,200	36,100	895	1,260	33	17,300
A_1	12,800	223	11,100	110,000	455	1,240	24	21,000
B	17,900	268	132,000	36,500	2,310	1,040	28	142,000
C	26,100	416	161,000	30,600	11,300	1,200	345	128,000
D	15,200	412	92,400	27,600	5,410	978	203	110,000
E	3,840	165	43,800	34,600	340	776	26	68,800
F	2,700	14	30,400	114,000	5	698	412	119,000
F + G	2,760	<0.5	16,200	138,000	5	872	55	116,000
C + D + E	3,430	124	34,000	20,400	761	561	37	64,100
A + B + C + D + E	9,010	174	61,000	49,600	929	830	27	85,600

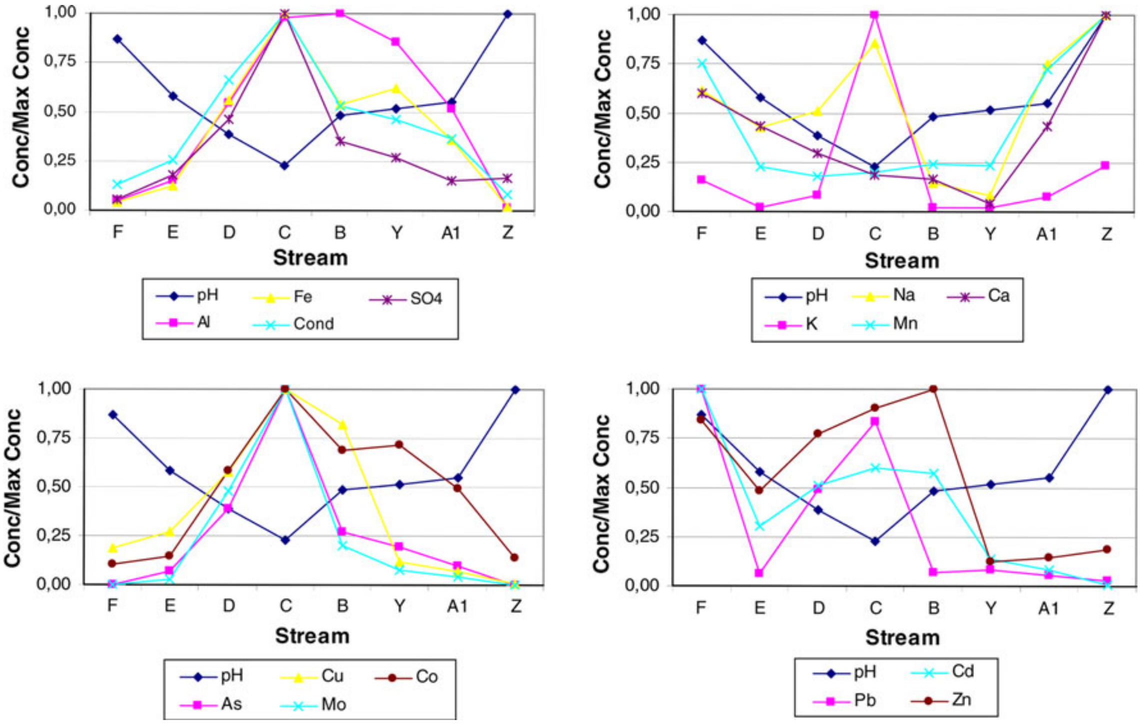

Fig. 3 Conductivity, pH, and concentrations of different elements normalized with the maximum respective value in streams sampled during July 2002 field trip

causing the oxidation of pyrite through the following reaction 1 (Ritchie 1994; Lefebvre et al. 2001; Nordstrom and Alpers 1999a):

$$FeS_{2(s)} + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

The tuff dumps are also an important source of trace elements to streams Y, B, C and D (Fig. 3). Some elements such as Co seem to come from pyrite oxidation, because this element is mainly present in the tuff dumps (Table 2), probably associated to pyrite. By contrast, other elements such as Fe, As and Mo displayed high concentration in gossan wastes, and their occurrence in the water may be influenced by the dissolution of this material. In fact, the Fe/SO_4^2 ratio is up to more than three times greater than that expected from pyrite dissolution alone (Fig. 4), which suggests that the dissolution of gossan is being accomplished. This process can occur easily if we consider that the gossan is mixed in the tuff dumps and acidic waters with $pH < 2$ can partially dissolve the Fe oxy-hydroxides and release Fe^{3+} through the following reaction 2 (Nordstrom and Alpers 1999a). Although we have not measured the Fe^{2+}/Fe^{3+} ratio, this hypothesis is consistent with the wide occurrence of Fe^{3+} rich efflorescent sulphates (coquimbite, rhomboclase, magnesiocopiapite) found in the banks of the streams (Romero et al. 2006b). The releasing of Fe^{3+} may also contribute to lower the pH to values down to 0.7, because it can react with pyrite and oxidize it rapidly through the following reaction 3 (Singer and Stumm 1970; Nordstrom and Alpers 1999a).

$$Fe(OH)_{3(s)} + 3H^+ \rightarrow Fe^{3+} + 3H_2O \qquad (2)$$

$$FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (3)$$

The dissolution of gossan does not only release iron but also trace elements, particularly As and Mo, which occur widely in these wastes. This explains their very high concentration in the stream water (Table 4). The strong correlation Fe–As–Mo in stream water samples ($r \geq 0.86$, Table 5) and wastes with variable concentrations of gossan ($r \geq 0.84$, Romero et al. 2006a) support this idea. These results have an important environmental impact because the gossan is stable in an oxidant environment, and a low mobility of trace elements is expected under these conditions. By contrast, when gossan wastes are mixed with high acid potential materials, the acidic leachates can dissolve them and release huge contents of trace elements into the water.

Other elements as K, Na and Pb were not correlated with pH, but they displayed high concentrations in stream C (Fig. 3b, d). The low values displayed by K in most of the water samples probably indicate that it is largely retained by the precipitation of secondary jarosite. When the physical–chemical conditions are unfavourable for the

Table 5 Statistical correlations for stream water chemistry

	pH	Al	Ca	Fe	K	Mg	Na	Si	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Zn
pH	1.00																	
Al	**−0.70**	1.00																
Ca	0.53	−0.40	1.00															
Fe	**−0.78**	**0.93**	−0.39	1.00														
K	−0.44	0.21	−0.20	0.40	1.00													
Mg	−0.23	**0.71**	−0.02	0.55	−0.12	1.00												
Na	0.13	−0.07	**0.73**	0.11	0.26	0.04	1.00											
Si	**−0.78**	0.60	−0.42	0.54	0.02	0.32	−0.35	1.00										
As	**−0.70**	**0.74**	−0.29	**0.91**	0.50	0.24	0.29	0.32	1.00									
Cd	−0.17	0.20	0.26	0.22	0.04	−0.06	0.22	0.15	0.29	1.00								
Co	**−0.73**	**0.96**	−0.31	**0.99**	0.35	0.66	0.13	0.53	**0.86**	0.23	1.00							
Cr	**−0.77**	**0.86**	−0.38	**0.90**	0.09	0.58	−0.04	**0.73**	**0.73**	0.15	**0.89**	1.00						
Cu	**−0.70**	**0.78**	−0.26	**0.81**	0.28	0.19	0.08	0.51	**0.84**	0.48	**0.78**	**0.71**	1.00					
Mn	0.50	−0.20	**0.89**	−0.23	−0.16	0.26	0.69	−0.43	−0.23	0.33	−0.12	−0.30	−0.27	1.00				
Mo	**−0.70**	0.65	−0.28	**0.86**	0.57	0.10	0.32	0.29	**0.98**	0.29	**0.79**	0.67	**0.82**	−0.25	1.00			
Ni	−0.40	**0.73**	0.22	0.69	−0.05	**0.81**	0.36	0.44	0.50	0.34	**0.76**	**0.73**	0.48	0.39	0.39	1.00		
Pb	−0.32	0.09	−0.16	0.32	0.57	−0.30	0.23	−0.04	0.49	0.49	0.24	0.10	0.35	−0.11	0.57	−0.09	1.00	
Zn	−0.40	0.41	0.15	0.41	0.08	−0.02	0.18	0.37	0.48		0.42	0.36	**0.77**	0.12	0.48	0.40	0.38	1.00

Concentrations below the limit of detection were considered as zero. In bold, values higher than 0.70

precipitation of jarosite (e.g. pH < 1, Dutrizac and Jambor 2000) K is leached into the water. Similarly, other authors have also measured high concentrations of K in waters with pH < 1 in other areas (e.g. Williams and Smith 2000; Frau 2000). In the same way, the release of Na and Pb into stream C suggests that they can be also retained by jarosite when this phase precipitates. Indeed, Na and Pb interexchange with K in the jarosite structure as other authors have previously reported (Dutrizac and Jambor 2000; Acero et al. 2006; Graupner et al. 2007).

Besides the tuff dumps and gossan wastes, the mixed dumps, which are rich in pyrite and the roasted pyrite ashes can be important sources of Cd, Zn and Pb to the water. For example, stream F, which receives leachates from both materials, showed high concentrations of Cd, Zn and Pb (Table 2) despite the fact that the pH was about 2–3, which is higher than the values recorded in other streams. With respect to Cd and Zn, there is a strong correlation between them ($r = 0.89$), but not with the pH (Table 5). These elements can be easily released into the water due to their high mobility and low pH dependence in very acidic environments (Nordstrom and Alpers 1999a; Plumlee et al. 1999). By contrast, Pb is a very immobile element, and its high concentration in stream F seems to be related to the low Eh values (375 mV), which are unfavourable for the precipitation of secondary phases such as jarosite (Bigham et al. 1996) or any other oxidized phase.

Element mobility

According to the above-discussed considerations, it is plain to see that the release of major and trace elements into the water depends on several factors such as their concentration in the wastes, the pH–Eh environment or the dissolution/precipitation of mineral phases. So, depending on these factors, the mobility of an element may change in different environments.

Considering the waste dumps as the source of elements and the stream water as the environment into which they are released, it is possible to asses their mobility by determining the ratio between their concentration in water versus wastes. So we have calculated the average concentration of major and trace elements in water and divided it by their average concentration in wastes (Table 7). The mobility of the major elements shows the following sequence:

$$\mathrm{Mg, Ca, S > Al, Fe, Na > K}$$

The minor and trace elements show the following mobility sequence:

$$\mathrm{Mn > Co, Zn, Cd > Cu, Ni >> As, Mo, Cr >> Pb}$$

Thus, Na and K are among the most immobile elements, because after their release from primary minerals, they can be largely retained by the precipitation of jarosite. With regard to trace elements, Cd and Zn are highly mobile,

Table 6 Comparison between some of the most polluted waters in the world with the results presented in this study (data in mg/L, except pH)

Location	Water type	pH	Fe	As	Cd	Cu	Mo	Pb	Zn
Iron Mountain, Richmond Mine, California[a, b]	Adit	(−3.6)–1.51	2,670–141,000	3–850	0.4–370	209–9,800	0.59–4.2	0.1–12	58–49,300
Genna Luas Mine, Sardinia, Italy[c]	Pool	0.6–3.5	3,443–77,250	0.23–73.11	3.2–60	0.1–220	0.0004–0.49	0.04–7.9	1,065–10,750
Iron Duke Mine, Mazowe, Zimbabwe[d]	Stream water	0.52–6.6	0.2–132,929	0.001–72	0.001–3.72	0.002–20.87			0.02–55.96
Cerro de Pasco Mine, Peru[e]	Stream water	2.78–5.10	1,632–5,640	1.98–7.99	0.57–6.60	1.08–161.1		0.14–1.28	1,218–3,000
Berkeley Pit, Butter, Montana, USA[f]	Pit lake	2.8–3.08	250–1,040	0.03–0.7	1.3–1.9	6.9–218			184–496
San Telmo Mine, Iberian Pyrite Belt, Spain[g]	Pool	0.82	74,215	0.3	13.76	1,945	10.43	0.11	1,096
Odiel River Basin, Iberian Pyrite Belt, Spain[h]	Several AMD discharges	1.4–5.4	0–5,848	1–39.7	0–8.24	0–440		0–0.73	0–1,437
Odiel River, Iberian Pyrite Belt, Spain[i]	River	2.5–6.3	0.03–263	0.0002–3.3	0.001–0.38	0.01–37.62		0.004–1.2	0.17–130.2
Tinto River, Iberian Pyrite Belt, Spain[j]	River	1.4–6.0	300–4,300	0.9–25		24–240		0.1–2.4	56–420
Peña de Hierro, Iberian Pyrite Belt, Spain[k]	Stream water	0.7–3.5	41–30,200	0.002–72.2	0.0004–0.85	0.14–161	0–11.3	0.009–0.4	5.3–142

[a] Nordstrom and Alpers (1999b)

[b] Nordstrom et al. (2000)

[c] Frau (2000)

[d] Williams and Smith (2000)

[e] Smuda et al. (2007)

[f] Davis and Ashenberg (1989)

[g] Sánchez España et al. (2008)

[h] Sánchez España et al. (2005)

[i] Olias et al. (2004)

[j] Hudson-Edwards et al. (1999)

[k] This study

while As and Mo are only moderately mobile and Pb is relatively immobile. Similar results were obtained in other AMD-affected areas by McGregor et al. (1998) and Monterroso and Macías (1998b).

Conclusions

Mining operations in Peña de Hierro have produced extremely acidic waters containing high concentrations of trace elements such as As, Cd, Cu, Mo, Pb, and Zn. Dumps composed of volcanic tuffs are the main source of AMD, and the partial dissolution of gossan mixed in these dumps is an important source of As and Mo. Roasted pyrite ashes and pyrite wastes are sources of Cd, Pb and Zn, and the bedrock leaches Ca, Na and Mn. Several elements such as Fe, As, Co and Mo are greatly affected by the pH, but others as Pb and Cd–Zn are conditioned by their low or high mobility, respectively.

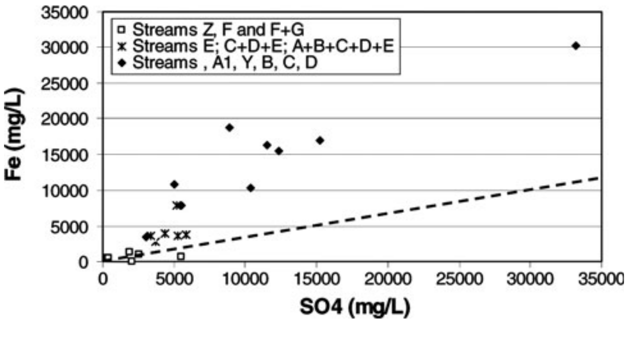

Fig. 4 Concentration of Fe versus SO_4^{2-} in water samples. The *dotted line* shows the Fe/SO_4^{2-} ratio expected from pyrite dissolution

This study has shown that the geochemistry of stream waters strongly depends on the characteristics of the materials drained. On one hand, the dumping of wastes increased the trace element concentration in streams compared with natural waters, both neutral and acid. On the other hand, the mismanagement of waste rocks when

Table 7 Relative mobility of some elements determined by means of the ratio “mean value in water”/“mean value in mine-waste dump” (B/A)

Major elements	Mg	Ca	Al	Fe	Na	K
A: Mean value in waste dumps (mg/kg)	1,500	595	27,950	235,700	1,650	12,600
B: Mean value in stream water (μg/l)	479,429	140,952	1,205,000	7,594,095	20,571	2,671
Ratio B/A	320	237	43	32	12	0.2

Trace elements	Mn	Co	Zn	Cd	Cu	Ni	As	Mo	Cr	Pb
A: Mean value in waste dumps (mg/kg)	62	17	194	1	319	10	584	149	25	859
B: Mean value in stream water (μg/l)	44,997	7,827	63,333	257	42,529	728	10,420	1,559	152,190	116
Ratio B/A	764	488	372	304	150	88	19	12	11	0.2

The data of the waste dumps is taken from Romero et al. (2006a)

mixing pyrite-rich spoils with others rich in trace elements (e.g. gossan) involved their release through dissolution of iron oxy-hydroxides, increasing the contamination of stream waters.

A selective management of these different mine spoils could be an easy way to control and mitigate the pollution, as it would avoid the leaching of potentially toxic wastes (e.g. gossan) practically without any corrective action, and it would reduce the volume of acid generating wastes. These results can be also applied to the management of waste dumps in new or reopened mines of the IPB.

Characterization studies of waste rocks are necessary for planning accurate remediation actions. Classification/selection of different wastes according to their acid/basic generating potential, concentration in potentially toxic elements and factors affecting their mobility or their harmlessness are necessary to control them. According to the waste potential hazard, specific management criteria can be established, such as insulation, covering, mixing, supervision and temporary control, abandonment, revegetating, etc.

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