ORIGINAL ARTICLE

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Assessment of the acid drainage neutralization capacity and the toxic metals lixiviation of tailing from Guanajuato mining district, Mexico

María Elena García-Arreola[1,3] · **Luisa María Flores-Vélez**[2] · **Marcos Loredo-Tovías**[1] · **Alfredo Aguillón-Robles**[3] · **Rubén Alfonso López-Doncel**[3] · **Irene Cano-Rodríguez**[4] · **Sonia Hortensia Soriano-Pérez**[2]

Abstract

In Mexico, many environmental problems are generated by large mining activities taking place in several mining districts. These mining activities produce great quantities of residues; large majorities of these have high sulfur content, which could generate acid drainage due to their interaction with the oxygen in the environment. The study area was located in the Mining District of Guanajuato, Mexico with abandoned tailings generated mainly by the gold and silver production. Two areas, called as Monte de San Nicolás (SN) and Peregrina (P) were selected for this study. The results study shows that there was no risk of production of acid drainage, since these tailings contained high amount of carbonates, which neutralized the generation of acidity and consequently decreased the possibility of leaching of some elements. However, not all elements leach in acid pH, as arsenic bound to oxyhydroxides, which is in a basic environment and its increased release by increasing the pH.

Introduction

The old mining city of Guanajuato in middle Mexico belongs to the most important historical cities of Latin America, which preserves one of the most important historical legacies in colonial activities in this region. The establishment of this city, which later would become one of the most important cities of the New Spain, was basically due to the discovery of important silver and gold ore deposits that initiated the mining industry in 1548, which resulted in the legal foundation of the town of Santa Fe de Guanajuato in 1570.

✉ María Elena García-Arreola
maria.garcia@uaslp.mx

1   Área de Ciencias de la Tierra, Facultad de Ingeniería, Universidad Autónoma de San Luis Potosí, San Luis Potosí, Mexico

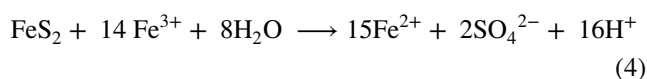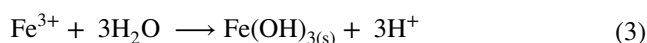2   Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, San Luis Potosí, Mexico

3   Instituto de Geología, Universidad Autónoma de San Luis Potosí, San Luis Potosí, Mexico

4   Departamento de Ingeniería Química, División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Guanajuato, Mexico

Because of the mining activities in Guanajuato as in many other mining places in Mexico, numerous environmental problems may be a potential risk of pollution in short and/ or long-term. A large majority of these residues are composed of sulfide minerals, as in the case of the tailings from the Guanajuato mining district, Mexico that contain sulfides and sulfates (Ramos-Arroyo et al. 2004). The oxidation of these metal sulfides may result in the generation of acid drainage, which are solutions characterized by low values of pH and high concentrations of potentially toxic elements (PTE) dissolved (Roussel et al. 2000; Moncur et al. 2005; Parbhakar-Fox et al. 2011). Mine drainage arises because of water percolating through various components of mining complex, such as tailings impoundments and waste rock piles (Plante et al. 2012). Besides, the release of SO_4^{2-} H^+, Fe^{2+}, and other metals by speed of the oxidation of sulfur were controlled, and therefore, their dissolution and precipitation of mineral phases of carbonates and oxyhydroxides in the tailings (Bain et al. 2000). Another important consideration is the potential long-term pollution problem, as production of acid mine drainage (AMD) may continue for many years after mines were closed and tailing dams are decommissioned (Johnson and Hallberg 2005). To solve the problem, some remediation proposals have been made, such as the biological treatment with sulfate-reducing bacteria to

neutralize the AMD (Sánchez-Andrea 2014; Neculita et al. 2007), as well as synthetic zeolites that reduce the concentration of Fe, As and Pb in the AMD, however, it is necessary to design and perform detailed experiments for each particular site (Rios et al. 2008).

## Mining tailings neutralization capacity

Tailings of the mining district of Guanajuato also contain high concentrations of PTE ranging from 37 to 429 mg/kg of Cu, 13–178 mg/kg Pb and 36 to 448 mg/kg Zn, which were determined as total concentrations (Ramos-Arroyo and Siebe-Garabach 2006). However, the total concentration of the elements that contain the tailings, are not sufficient to determine whether a waste is hazardous. The endangerment of the tailings is determined by the high reactivity that can generate the oxidation of sulfides contained, when they are exposed to the air or water (Plante et al. 2012), the pyrite oxidation reactions are represented by the following four equations (USEPA 2000).

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

$$Fe^{2+} + 1/4O_2 + H^+ \longrightarrow Fe^{3+} + 1/2H_2O \tag{2}$$

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_{3(s)} + 3H^+ \tag{3}$$

$$FeS_2 + 14\,Fe^{3+} + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$
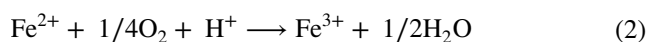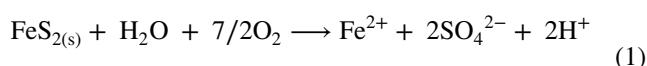
The pyrite oxidation reaction (1) causes an increase in the total dissolved solids and an increase in acidity causing a decrease of pH, unless a neutralization reaction could take place. If the environment is sufficiently oxidant, are oxidized ferrous ions to ferric ions as presented in reaction (2). Usually at pH around 3, the ferric ion formed is precipitated by hydrolysis as hydroxide reaction (3) reducing Fe^{3+} in solution, while the pH decreases simultaneously. Finally, some ferric cations, which are maintained in solution, can continue to oxidize pyrite and form Fe^{2+}, SO_4^{2-} and H^+ as presented in reaction (4).

The content of carbonates, hydroxides and aluminosilicates can neutralize the acidity that is generated, neutralizing the production of acid drainage. The ability to neutralize acidic or basic solutions is proportional to the amount of acid or base needed to achieve certain pH; this property is important to evaluate the environmental impact, long-term stability and possible incorporation in the environment of toxic elements contained in such residues (van der Sloot et al. 2001). The presence of calcite in the sulfur residues generated the following global reaction:

This reaction promotes the adsorption of the metals in the surface of the iron oxides, this characteristic has been considered in other studies as an alternative to remediation of acid mine drainage, using calcium carbonate to neutralize the pH (Kastyuchik et al. 2016; Romero et al. 2004). CO_2 beside HCO_3^- and CO_3^{2-} are distributed the species depending on the pH and on the conditions of saturation of $CaSO_4$ in solution. Although generally more common than carbonate phases, aluminosilicate minerals tend to be less reactive, and their buffering may only succeed in stabilizing the pH when rather acidic conditions have been achieved, as kaolinite (Ramos-Arroyo et al. 2004):

$$CaAl_2Si_2O_{8(s)} + 2H^+_{(aq)} + H_2O \longrightarrow Ca^{2+} + Al_2Si_2O_5(OH)_{4(S)} \tag{6}$$
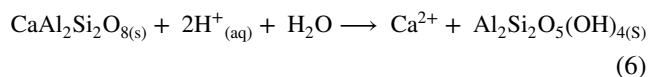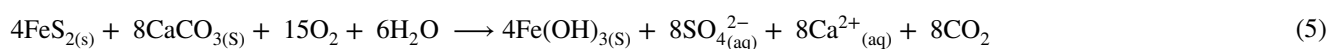
An additional component of any mineralogical evaluation is the assessment of the textures and abundances of any neutralizing mineral which will counteract the negative products of sulfide oxidation as acidity, sulfur species, total dissolved solids and metal(loid)s (Brough et al. 2013).

Several test methods in the research for the evaluation of mining waste, have been proposed; metals leaching include tests where the materials are in contact with a specific amount of lixiviation solution at a given time (Wastewater Technology Centre 1990). This test is a measure of the capacity of materials to neutralize the acid, which is a key variable for predicting the behavior of the material in the long-term, since it affects the precipitation of metals while maintaining the physical integrity of the material. The test involves using several portions of the homogeneous sample in which they had added various amounts of acid, all of these are in contact during 48 h.

The buffer capacity of the residues, determines the final pH of the leachate, and therefore, is one of the most important properties of the material (Bäverman 1997). To study the behavior in acidic waste; Coz-Fernández (2001), compared the results of a titration curve between sludge waste acid and casting a mixture of synthetic residue, which was prepared with two of the major components in the same proportion found in the actual waste, concluding that the pH buffering and the amount of ions in solution is given by the metal content of the sludge, mainly iron and zinc. In other behavioral studies in acid medium smelter dust waste was compared with a synthetic iron oxides and zinc, which were mainly responsible for the buffering of waste (Soriano-Pérez 2002).

The study area is located in the State of Guanajuato, Mexico, part of the Guanajuato mining district, the sites were tailings from Monte de San Nicolás and Peregrina (Fig. 1). These mining tailings had been abandoned for
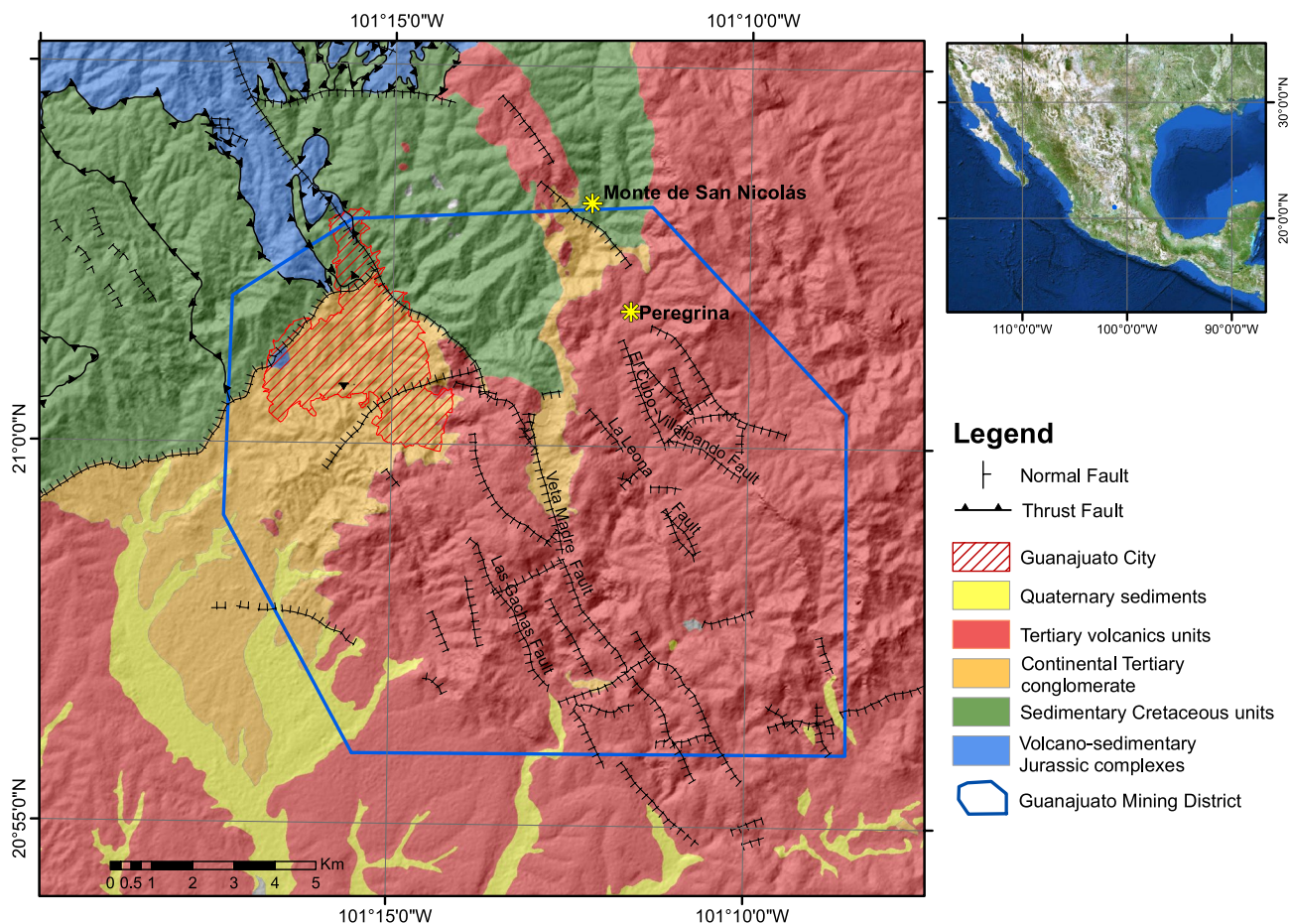
$$4FeS_{2(s)} + 8CaCO_{3(S)} + 15O_2 + 6H_2O \longrightarrow 4Fe(OH)_{3(S)} + 8SO_4^{2-}{}_{(aq)} + 8Ca^{2+}{}_{(aq)} + 8CO_2 \tag{5}$$

Fig. 1 Simplified geologic map form Guanajuato Mining District (Modified from Labarthe-Hernández et al. 1995)

70 and 50 years, respectively. The oldest residues such as Monte de San Nicolás could be more consolidated, considering the vegetation found on the tailings (Fig. 2). The tailings were deposited on the soil without any control to prevent its spread in the environment. Therefore, the main goals of the study are to determine if these residues had the capacity to generate and neutralize acid drainage, as well as to elucidate the behavior of As, Fe, Mn, Zn, Pb and Cu depending on the pH.

Guanajuato mining district geological settings

The Guanajuato mining district (GMD) is located in the Sierra of Guanajuato (Fig. 1), the geological record in the mining district begins with Mesozoic rocks that were deposited during the Jurassic and Cretaceous periods. The outcropped lithostratigraphic units are tonalite and diorite plutons, volcano-sedimentary complexes and dioritic dikes, which cross-cut the older units. This volcanic event was emplaced around 157–122 Ma (Echegoyen-Sánchez et al. 1970; Martínez-Reyes 1992; Labarthe-Hernández et al.

1995, 1996; Ortíz-Hernández et al. 2003). In the Cenozoic, began the deposit of continental conglomerates and sandstones with interbedded andesite lavas and pyroclastic flows around 49 Ma (Edwards 1955; Aranda-Gómez and McDowell 1998); later a volcanic sequence, composite by volcaniclastic deposits, andesitic and rhyolite lavas associated to faults and dome structures was extruded between 33 and 31 Ma, ending with rhyolitic domes around 29 Ma (Nieto-Samaniego et al. 2016). These volcanic units are known locally as Loseros, Bufa, Calderones, Cedro and Chichíndaro Formations. The Loseros and Bufa Formations are the main rocks used for the construction of the Guanajuato historic buildings (López-Doncel et al. 2012). The hydrothermal events that have generated the mineral deposit ranging between 30.7 and 28.3 Ma and probably related to pulses of a caldera-like event (Nieto-Samaniego et al. 2016).

The economic mineralization has been associated to diverse geologic structures among which are normal faults, veins, NW-SE trending rhyolite domes and dikes. Whereas in some segments of the fault systems occur horsts and grabens as well as secondary structures like faults and

Fig. 2 Sampling tailings sites. **a, b** Monte de San Nicolás shows abundant vegetation development due to low PTE leaching. **c, d** Peregrina tailing shows low vegetation due to high PTE leaching (the sites are marked by asterisk in Fig. 1)
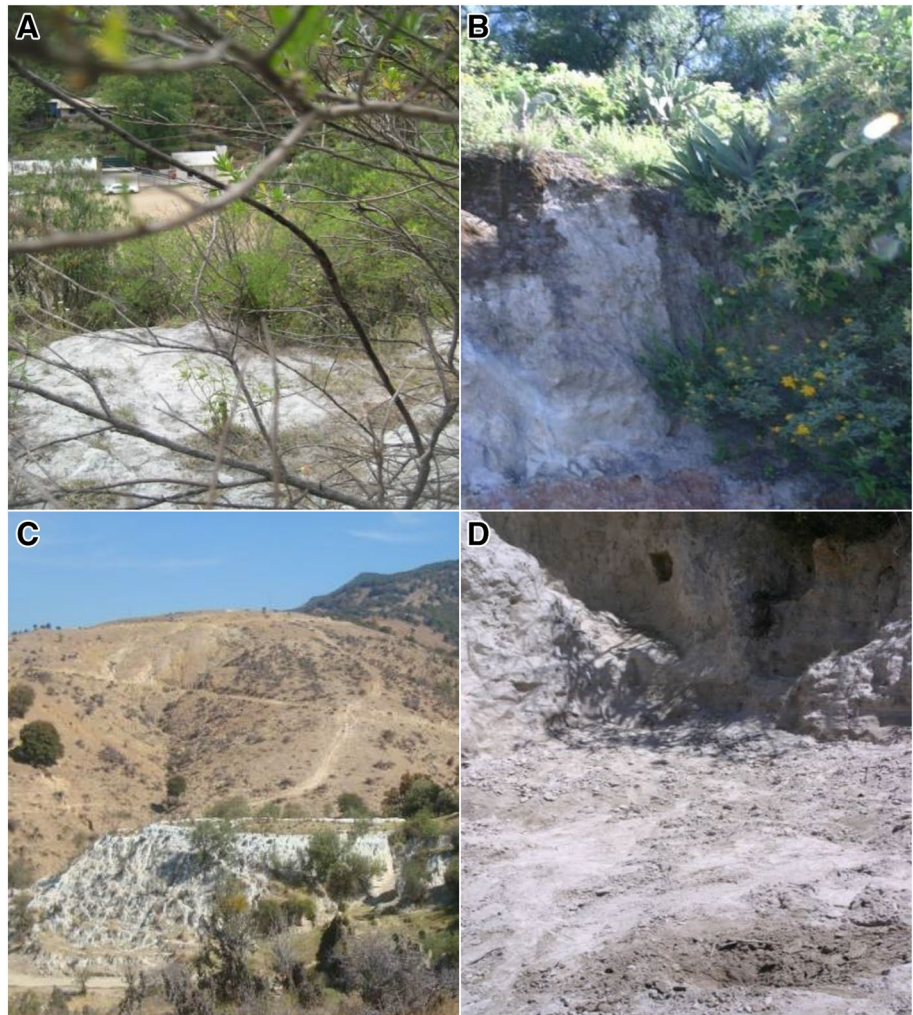
E-W, N-S trending fissures associated to the formation of a volcanic caldera (Randall et al. 1994; Nieto-Samaniego et al. 2016). The main faults were named as El Cubo-Villalpando, La Leona, Veta Madre and Las Gachas (Randall et al. 1994; Labarthe-Hernández et al. 1995; Nieto-Samaniego et al. 2016). The ore deposits are related to fluids of magmatic origin that generated Au, Ag, Cu, Hg, As, Sb sulfide and sulfosalts mineralization (Randall et al. 1994). The extraction of the mineralized rocks with different process methods in these structures inside the GMD, have originated, since 1548, around 95 million tons of residues. The extracted sulfides minerals are pyrite, marcasite, polybasite, sphalerite, chalcopyrite, galena, pyrargyrite, tetrahedrite, arsenopyrite and pyrrhotite. The gold and silver ore deposits are associated with selenium, silicates and carbonates. Ore deposits less economic are associated with quartz, chlorite and adularia (García-Arreola 2014). The Monte San Nicolás mine started the extraction at century XVIII, mainly by gold and Peregrina mine by silver. The GMD's mining output exceeds 37,000 metric tons of refined silver and 135 of gold, thereby making the district the second largest in the world.

Materials and methods

Three mining tailings samples at each site were taken, from Peregrina and from Monte de San Nicolás. Samples were taken at different depths, 5 cm from the top, called profile 1 (P1, SN1), another in the middle to 40 cm from the previous part called profile 2 (P2, SN2) and another one 40 cm from the profile 2, called profile 3 (P3, SN3). To determine the particle size, the tailing samples were sieved on different meshes (Mathieu and Pieltain 1998). The pH of tailings samples was determined according to NOM-021-RECNAT-2000 (Official Mexican Norm; SEMARNAT 2000). The mineralogical phases and composition was determined in the Institute of Metallurgy of the Autonomous University of San Luis Potosí (UASLP) with the help of an X-ray diffractometer (Siemens 5000D). The mineralogical phases at each site are
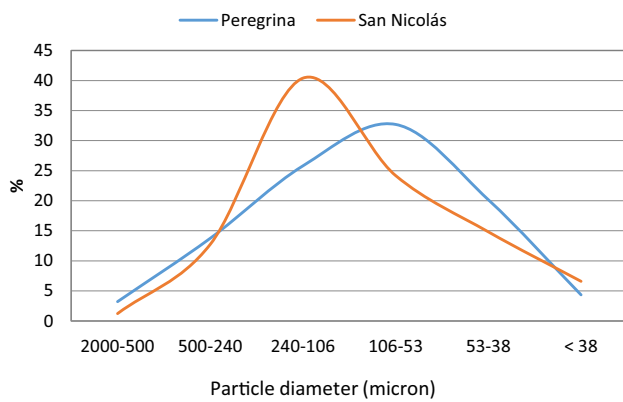
Fig. 3 Particle size distribution in waste of Peregrina and Monte de San Nicolás

(Fig. 3); in *Peregrina*, quartz (SiO_2), calcite ($CaCO_3$); albite ($NaAlSi_3O_8$); orthoclase ($K_{0.94}Na_{0.06}AlSi_3O_8$); sanidine ($K_{0.47}Na_{0.43}Ca_{0.10}Al_{1.1}Si_{2.9}O_8$); microcline ($KAlSi_3O_8$); gypsum ($CaSO_4 \cdot 2H_2O$); montmorillonite ($Ca_{0.5}Al_2Si_4O_{11}OH$); muscovite ($KAl_3Si_3O_{11} \cdot H_2O$). In *San Nicolás*, quartz, calcite, albite, microcline, orthoclase; muscovite, gypsum, clinochlore ($Mg_{2.96}Fe_{1.55}Fe_{0.136}Al_{1.275}Si_{2.622}Al_{1.376}O_{10}OH$); nontrolite ($Na_{0.33}Fe_2Al_4Si_4O_{10}(OH)_2 \cdot H_2O$).

X-ray Fluorescence (XRF) was used for the measurement of total major elements at the Institute of Geology of the Autonomous National University of Mexico, from tailings samples that were finely powdered in agate grinder; Lozano and Bernal (2005) reported the details of the analytical method. The samples were digested with the analytical technique described by Almaguer-Rodríguez (2010). To

Table 1 Leaching test to determine the neutralization capacity

L/S = 4 mL/g

No. tube	mL H₂O	mL HNO₃	meq/g	No. tube	mL H₂O	mL NaOH	meq/g
	Scheme with HNO₃ 1,5 N				Scheme with NaOH 0,1 N		
0	40	0	0	0	40	0	0
1	38	2	0.3	1	39	1	0.01
2	36	4	0.6	2	38	2	0.02
3	34	6	0.9	3	37	3	0.03
4	32	8	1.2	4	36	4	0.04
5	30	10	1.5	5	35	5	0.05
6	28	12	1.8	6	34	6	0.06
7	26	14	2.1	7	33	7	0.07
8	24	16	2.4	8	32	8	0.08
9	22	18	2.7	9	31	9	0.09
10	20	20	3.0	10	30	10	0.10
	Scheme with HNO₃ 2,0 N (Peregrina)			–	–	–	–
11	20	20	4.0	–	–	–	–
12	10	30	6.0	–	–	–	–
13	5	35	7.0	–	–	–	–
14	0	40	8.0	–	–	–	–

Table 2 Physical and chemical characteristics of Peregrina and San Nicolas samples

	pH	Conductivity mS/cm	ST	OM %	Carbonates %	As mg/kg	Cr mg/kg	Zn mg/kg	Pb mg/kg	Mn mg/kg	Cu mg/kg
P1	8.4	2.73	L	0.47	19	6329	6.1	1668	2759	348	1538
P2	8.08	0.5	SAL	0.45	20	7057	7.9	2015	3584	387	1942
P3	8.28	1.32	SAL	0.46	20	6163	5.2	1593	2810	363	1413
SN1	7.7	2.27	SL	0.5	11.8	10,201	45.9	2811	4585	716	2430
SN2	7.6	2.1	SL	0.5	5.3	9186	38.4	2362	3938	559	1993
SN3	7.7	2.21	SL	0.48	7.8	10,844	44.8	3048	4781	648	2429

pH hydrogen potential, *ST* soil texture, *L* loam, *SL* silt loam, *SAL* sandy loam, *OM* organic matter, *EPT* As, Cr, Zn, Pb, Mn, Cu in mg/kg (ppm)

Fig. 4 Diffractogram that shows main mineral phases in the tailings at the site of Peregrina and San Nicolás. **a** Mineral phases of the tiling at Peregrina, samples P1, P2, P3, PN. **b** Mineral phases at the site of Monte San Nicolás, samples SN1, SN2, SN3, SNN
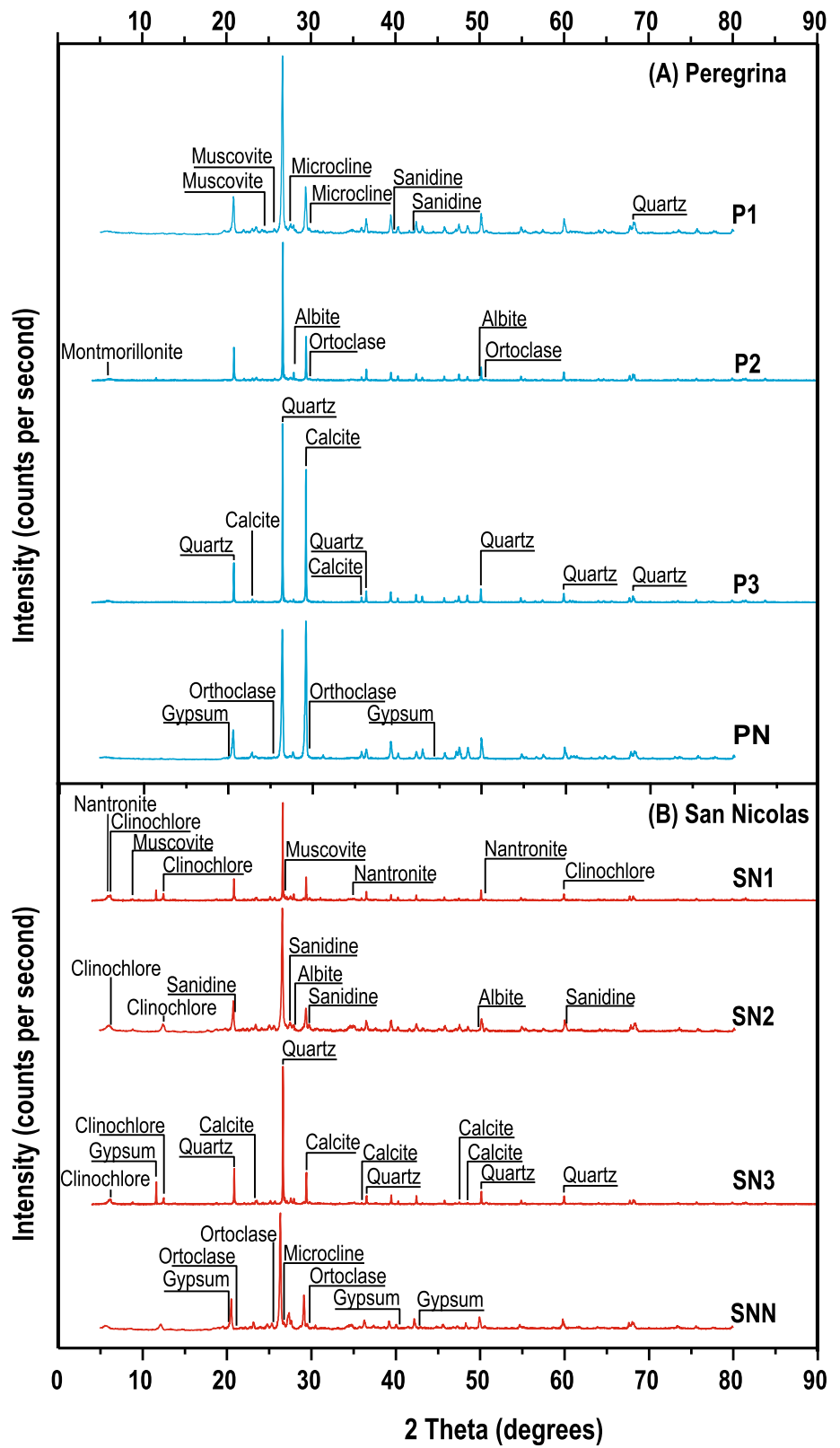
Table 3 Major element constituents in tailings (wt%)

Sample	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$
P1	66	0.14	8.4	1.9	0.10	0.7	10.0	0.73	2.8	0.04
P2	56	0.06	4.4	1.2	0.12	0.5	20.1	0.32	1.2	0.02
SN1	61	0.62	11.9	5.5	0.26	2.7	6.8	0.68	3.3	0.12
SN2	59	0.53	11.2	4.8	0.25	2.8	8.1	0.83	3.1	0.13

P1, P2 Peregrina tailing, *SN1, SN2* San Nicolas tailing
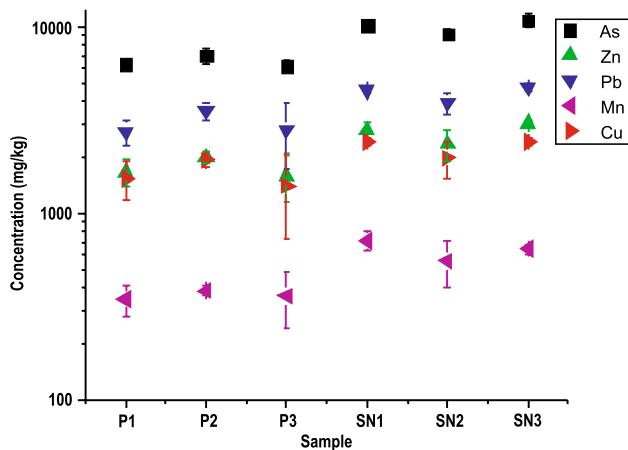

Fig. 5 Total element concentrations in mg/kg of waste

determinate, the PTE total concentration, was used an inductively coupled plasma optical emission spectrophotometer (ICP-OES).

Mining tailings neutralization capacity

To determine the mining tailings neutralization capacity, a metal pre-leaching test was performed to estimate the concentration of nitric acid and sodium hydroxide that could be used in the metal extraction test, to obtain a pH range of 2–12 in the tailings samples by adding acid or base. The normality was determined using solutions, 10 g of each sample was weighed in polyethylene tubes and added the amount of nitric acid or hydroxide sodium (Table 1); tubes were placed on a rotary shaker for 24 h at 30 ± 2 rpm, the tubes were centrifuged and the solid part separated; the pH of the solution was registered and adjusted to pH less than 2 with nitric acid and the metals concentration was determined by ICP-MS. All tests were performed in every sample for triplicate.

To understand the waste buffer capacity, the following experiment was performed; adding acid and base to artificial mixture made with the major components of the waste. Residues consist mainly of Si, Fe, Al and Ca oxides (Table 3); considering these percentages; the mixture was prepared with 65% SiO$_2$, 15% Al$_2$O$_3$, 9% of Fe$_2$O$_3$ and 11%

Table 4 Results of pH as a function of the meq aggregates of HNO$_3$ and NaOH in Peregrina and Monte de San Nicolás sites

Peregrina				San Nicolás			
meq HNO$_3$/g	pH	meq NaOH/g	pH	meq HNO$_3$/g	pH	meq NaOH/g	pH
0.0	8.48	0.00	8.48	0.0	7.52	0.00	7.52
0.3	6.45	0.01	8.62	0.3	6.08	0.01	7.58
0.6	6.19	0.02	10.93	0.6	5.89	0.02	7.66
0.9	5.96	0.03	11.39	0.9	5.50	0.03	9.07
1.2	5.89	0.04	11.58	1.2	5.48	0.04	10.36
1.5	5.76	0.05	11.81	1.5	5.36	0.05	11.55
1.8	5.72	0.06	11.89	1.8	5.28	0.06	11.69
2.1	5.55	0.07	11.96	2.1	5.19	0.07	11.84
2.4	5.50	0.08	12.10	2.4	4.88	0.08	11.84
2.7	5.39	0.09	12.15	2.7	1.86	0.09	11.95
3.0	5.28	0.10	12.27	3.0	1.85	0.10	12.03
4.0	5.18						
6.0	4.80						
7.0	2.10						
8.0	1.31						

The pH values were the average of three measurements independent samples, whose coefficient of variation was of maximum 3%

of $CaCO_3$. The homogenization of the chemical compounds was used in a porcelain mortar, afterwards 10 g were taken and added different volumes of nitric acid or sodium hydroxide (Table 1), the pH was measured after each addition.

Results

Mining tailings characterization

The pH of the tailings at the site of Monte de San Nicolás varies between 7.6 and 7.7, and at the Peregrina site was between 8.08 and 8.4 (Table 2). The tailings of Peregrina have finer particle size than Monte de San Nicolás (Fig. 3). The samples from Monte de San Nicolás site, 40% of particle size were between 106 and 240 μm and from Peregrina, 32% were between 53 and 106 μm.

XRD analyses show that the samples from Peregrina site (Fig. 4a), are composed of quartz (SiO_2), calcite ($CaCO_3$), clinochlore [$(Mg, Al, Fe)_6 (Si, Al)_4 O_{10} (OH)_8$] and sanidine ($KAlSi_3O_8$). From Monte de San Nicolás site, in addition to the previous compounds, muscovite [$KAl_2Si_3AlO_{10}(OH)_2$] was also found (Fig. 4b). Unlike Peregrina, San Nicolás presents mineralogical phases of low angles such as clinochlore and nantronite. The tailings samples analyzed by XRF in the two sites contain mostly silicon oxides, in addition to a large amount of calcium oxides, 8% in Monte de San Nicolás and 20% in Peregrina, and high percentages of aluminum, iron, potassium and magnesium (Table 3).

The concentrations of metals are higher in Monte de San Nicolás than in Peregrina. The highest values were 10,844 mg/kg for As, 4781 mg/kg Pb, 3048 mg/kg Zn, 2430 mg/kg Cu, 716 mg/kg Mn and 46 mg/kg Cr. The Cu, Pb and Zn (Fig. 5). The concentrations shown in Table 2, have higher values than those reported by Ramos-Arroyo and Siebe-Grabach (2006), 387 mg/kg Cu, 75 mg/kg Pb and Zn 136 mg/kg. This disagreement could be due to a partial digestion and in consequence several metals were not dissolved, principally elements that are bonded to silicates and were dissolved with hydrofluoric acid (Alloway 2013). Figure 5 also shows the dispersion found between replicates of the analyzed samples, the variation coefficient was 10%, with the exception of the sample maximum P3 which reached up to 27%, proving to be the most heterogeneous.

Leaching acid/base results

By the samples from Monte de San Nicolás, the results obtained by neutralization capacity were 2.5 meq of lixiviate solution per gram of tailings, since with 3 meq of nitric acid, pH 1 is obtained (Table 4). Neutralization capacity of the Peregrina site, was greater than Monte de San Nicolás site, because by adding up to 6 meq of nitric acid, the pH

was still around 5 (Fig. 6). Therefore, the acid neutralization capacity in Peregrina site was greater due to its high content of carbonates (Johnson and Hallberg 2005).

After the pH measurement of each meq of leaching added solution (NaOH or HNO_3) the concentration of lead, zinc, arsenic, manganese, iron and copper was analyzed (Tables 5, 6). At the beginning of the experiment, only with addition of 40 mL of water in each sample, a pH of 7.5 and 8.5 was obtained in tailings from Monte de San Nicolás and Peregrina, respectively. The results of the leaching of the elements as a function of pH are described below.

Leaching element results

Figure 7 shows the leaching of lead and the pH dependency. Pb lixiviation was greater at pH 2 and Pb lixiviation decreased rapidly, until a leachate minimum value between pH 5 and 6. Other studies have shown that Pb is adsorbed strongly on aluminum and iron oxyhydroxide, which limits its leaching (Hsu 1977, Schwertmann and Taylor 1989). At pH higher than 6, lead can be precipitated as hydroxide.
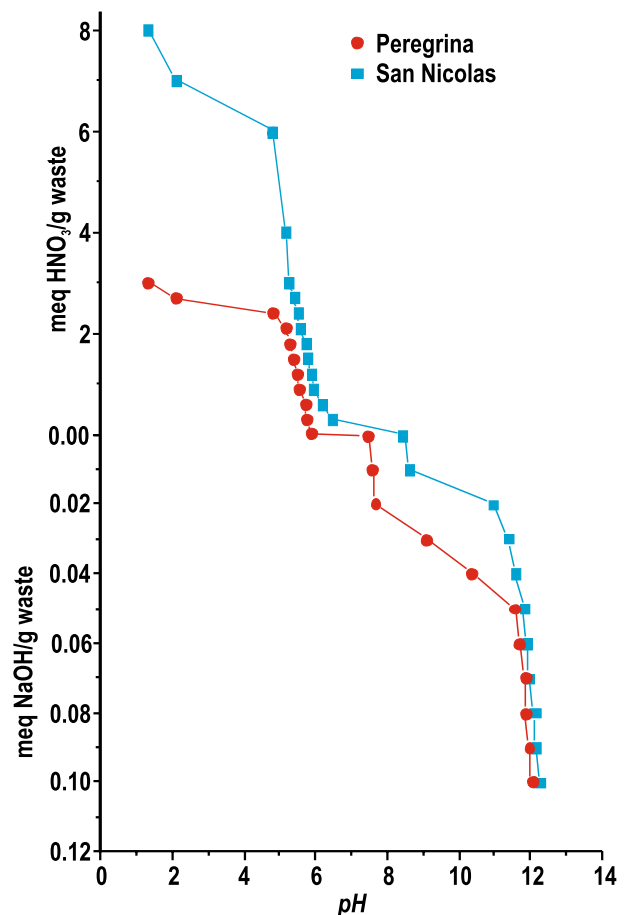

Fig. 6 Acid/base addition data in tailing of Peregrina and Monte de San Nicolás

Table 5 Leaching concentrations of EPT as a function of pH in Peregrina

pH	Peregrina, mg/kg					
	Mn	Fe	Cu	Zn	As	Pb
1.31	419.60	2344.40	5.63	108.36	3.08	37.96
2.10	532.40	1214.40	1.07	107.08	0.04	1.90
4.80	397.08	792.40	0.80	86.80	0.03	0.74
5.18	319.56	581.20	0.82	70.76	0.04	0.39
5.28	104.43	80.08	0.22	25.51	0.02	0.14
5.39	230.63	170.08	0.20	33.92	0.02	0.11
5.50	196.60	133.32	0.18	29.69	0.02	0.11
5.55	76.07	58.16	0.16	18.32	0.02	0.11
5.72	130.52	87.64	0.13	19.79	0.03	0.12
5.76	59.04	47.22	0.15	14.41	0.04	0.25
5.89	84.24	64.18	0.09	11.61	0.04	0.08
5.96	28.76	24.62	0.09	7.19	0.04	0.04
6.19	40.38	34.78	0.07	5.87	0.06	0.05
6.45	13.46	14.69	0.03	2.22	0.08	0.01
8.48	2.22	14.51	0.23	7.28	0.23	2.14
8.59	0.13	1.01	0.03	0.33	0.11	0.08
8.62	0.86	5.69	0.20	4.28	0.22	1.62
10.93	1.79	13.14	0.51	10.54	0.36	3.56
11.39	2.12	16.47	0.40	7.10	0.31	1.97
11.58	1.64	9.64	0.37	8.17	0.42	2.87
11.81	1.14	9.50	0.54	7.12	0.45	2.50
11.89	2.75	14.76	0.52	8.31	0.48	2.20
11.96	0.39	3.67	0.41	2.95	0.54	0.73
12.10	0.64	4.81	0.45	3.14	0.62	0.85
12.15	0.17	1.79	0.35	0.76	0.68	0.15
12.27	0.03	0.25	0.34	0.21	0.65	0.08

The concentrations of the elements were the average of three measurements independent samples, whose coefficient of variation was of maximum 5%

The zinc has shown greater leaching at the range from pH 2 to 5, obtaining a minimum leaching value between pH 8 and 12 (Fig. 7). The leaching of Zn to pH 5 begins to decrease because in this pH it is mostly adsorbed to iron and aluminum oxides (Hsu 1977, Schwertmann and Taylor 1989).

Copper leaching was greater at acid pH, 10 mg/kg (Fig. 8). This element from pH 5 to 6 can be adsorbed to the aluminum and manganese oxyhydroxides (Hsu 1977; McKenzie 1977), consequently reducing its leaching, afterwards continued to increase as pH increased.

Arsenic leaching behavior was independent of pH, leaching continued even at high pH values, still leaching approximately the same amount even in basic pH (Fig. 8). For both sites leaching decreased as pH increases up until neutrality; subsequently As, increases with increasing pH, even in a basic environment. At basic pH, As leaching is attributed to the presence of bicarbonates, which are generated by the presence of carbonates in contact with rain or intense moisture (De la Peña-Torres et al. 2012). The decrease in arsenic leaching may be due to the precipitation of calcium arsenates, however, these carbonates are also dissolved as pH increases by releasing the arsenic up to 80% at pH 11 (Jing et al. 2003).

The manganese showed high leaching values until pH 5, at higher pH values leaching decreased substantially (Fig. 9). This behavior could be mainly due to its precipitation with iron. Mn is adsorbed between pH 6 and 8 to this oxyhydroxides (Schwertmann and Taylor 1989), reducing the leaching of this element.

Greater leaching of Fe is produced from a pH of 1 up to a pH of 6 and above this its leaching kept constant in tailings from the site of Monte de San Nicolás, this fact can be explained due to the adsorption of Mn as mentioned above. At the site of Peregrina, Fe decreased since pH around 12 (Fig. 9), which can be attributed to its adsorption on silicates (Schwertmann and Taylor 1989).

Table 6 Leaching concentrations of EPT as a function of pH in San Nicolás

pH	San Nicolás, mg/kg					
	Mn	Fe	Cu	Zn	As	Pb
1.35	494.99	683.11	10.59	101.13	1.82	20.71
1.86	534.21	199.38	9.26	97.03	0.13	15.31
4.88	504.40	134.93	0.27	24.83	0.07	0.03
5.19	431.45	158.13	0.29	12.51	0.20	0.50
5.28	358.53	94.61	0.13	9.25	0.07	0.01
5.36	305.31	83.46	0.12	6.72	0.07	0.04
5.48	234.94	75.71	0.14	5.94	0.09	0.13
5.5	163.72	58.17	0.12	3.82	0.07	0.14
5.89	78.76	34.54	0.07	1.63	0.03	0.05
6.08	24.43	15.18	0.03	0.70	0.02	0.01
7.52	3.33	20.21	0.05	0.43	0.03	0.10
7.53	1.28	9.06	0.04	0.11	0.01	0.03
7.58	1.28	8.83	0.02	0.13	0.01	0.01
7.66	1.21	10.17	0.08	0.29	0.02	0.04
9.07	0.23	9.05	0.11	0.22	0.04	0.02
10.36	0.03	8.03	0.20	0.08	0.09	0.01
11.55	0.90	13.61	0.37	0.58	0.11	0.07
11.69	0.96	13.86	0.30	0.38	0.09	0.06
11.84	0.28	7.96	0.28	0.12	0.05	0.02
11.84	3.33	26.47	0.37	0.95	0.14	0.23
11.95	2.35	21.23	0.37	0.71	0.12	0.19
12.03	1.19	13.71	0.33	0.57	0.09	0.09

The concentrations of the elements were the average of three measurements independent samples, whose coefficient of variation was of maximum 5%

Discussion

The higher leaching of Pb and Zn were to pH 1 but decreased leaching as pH increased, until pH 8 where leaching increased in Peregrina mining tailings samples (Fig. 6). This behavior can be justified due to the high carbonate content of soluble Pb and Zn compounds (Table 2). The higher variable in reactivity in Peregrina, is also due to mixed tailings that comprised blend of coarser sand and the fine-grained silt (Brough et al. 2013). Several authors proposed the addition of calcium carbonate or calcium oxides to prevent acid drainage (Jing et al. 2003; Catalan and Yin 2003; McDonald et al. 2006), however, pH should be controlled around 5.5, since the increase in pH does not guarantee the stability of As and Cu. Possibly this occurs due to sulphosalts such as enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$) commonly found in mining waste (Liu and Huang 2016), occurring primarily in hydrothermal and magmatic ore deposits in association with a variety of sulfide minerals (O'Day 2006). As in the GMD, the mineralogical assemblage was associated to magmatic and hydrothermal fluids events during the volcanic caldera formation (Randall et al. 1994).

To reduce leaching of elements like Cu and As in tailings pH should be adjusted around 6, because at this pH, precipitation of those elements causes less leaching. However, 330 000 tons of waste are generated daily in Mexico (Vite et al. 2007) therefore, adjusting the pH would be very difficult. Another way to rehabilitate impacted sites through revegetation, as National Parks from Australian which were mined areas and then rehabilitated (Roe and Tinney 2002). It has been shown that the establishment of vegetative cover is limited by the chemical and physical properties of the tailings, such as poor moisture availability, pH toxic metal concentrations, poor soil/root aeration in low moist area, low nutrient levels and potentially ionic stress from high solute concentrations (Renault et al. 2002, 2003). Treating the tailings may overcome some of these limitations allowing for increased plant growth and establishment by increasing the soil organic carbon, promoting soil structural development, as well as increasing the nutrient holding ability (Renault

Fig. 7 Concentration of Pb and Zn leaching in pH function. The blue arrow on the points indicate ascending direction of pH in water addition only, in the left direction the addition of acid, and in the right direction the addition of NaOH
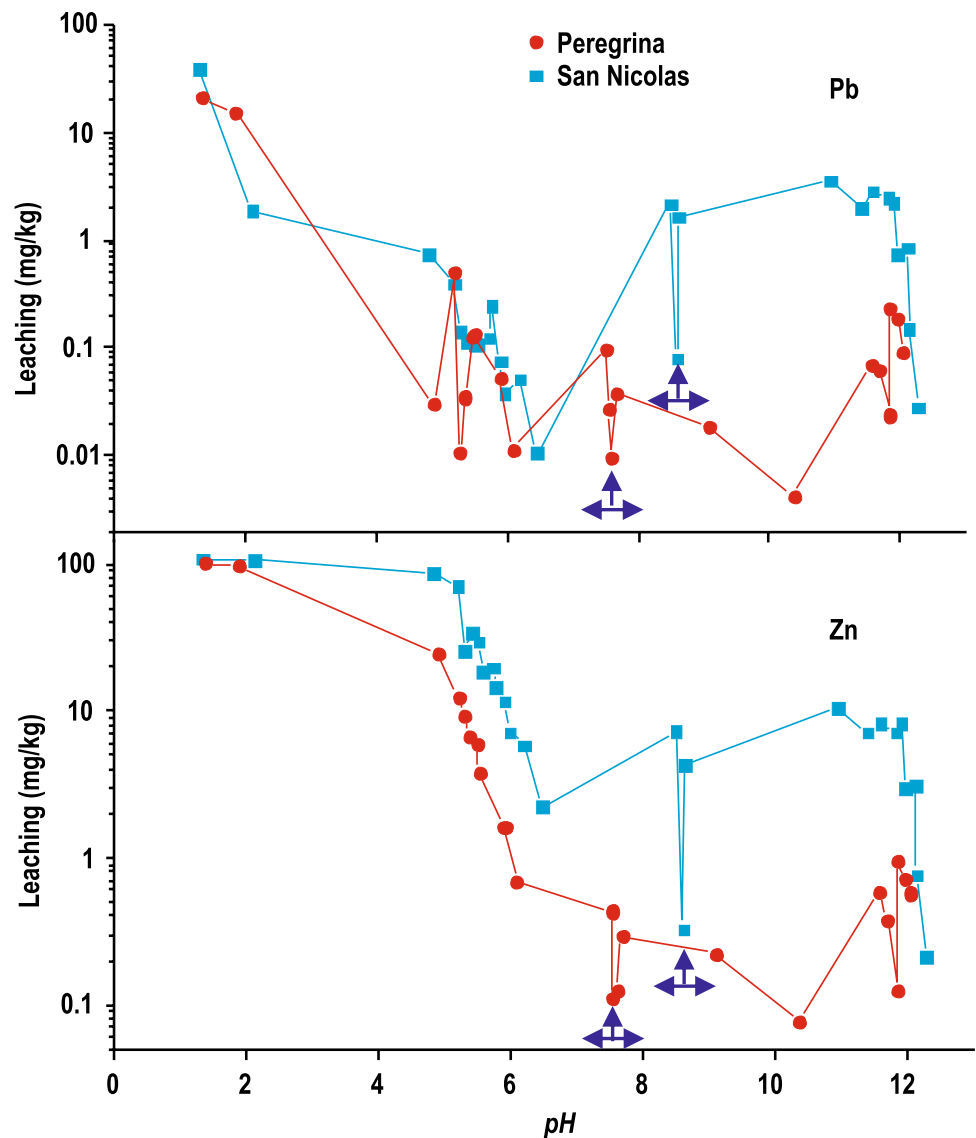
et al. 2004), favoring the phytostabilization of the elements (Fellet et al. 2014; Hernández-Acosta et al. 2009).

The plant canopy serves to reduce aeolian dispersion, whereas plant roots prevent water erosion, immobilize metals by adsorption or accumulation (Conesa et al. 2007), and provide a rhizosphere wherein metals precipitate and stabilize. Unlike phytoextraction, or hyperaccumulation of metals into shoot/root tissues, phytostabilization primarily focuses on sequestration of the metals within the rhizosphere but not in plant tissues (Mendez and Maier 2008).

Results of pH obtained from the synthetic matrix, were plotted against to the meq additions (Fig. 10). The same process was performed using 10 g of each component individually, the results show that the behavior of the synthetic mixture prepared with pure reagents was similar to actual

tailings sample, the buffer effect over pH was due to the amount of present calcium carbonate, as the pure reagent continues until pH 5–3 leaching meq per gram of residue.

The individual reactives of Fe_2O_3, SiO_2 and Al_2O_3 and the pH decrease dramatically. Other studies have shown that silicates and aluminum ions are not involved in neutralizing acidic (Yan et al. 2000).

Conclusions

The studied tailings had high acid neutralization capacity, due to the large content of present calcium carbonates. The San Nicolás mine waste, contain mineral phases more consolidated because it has more time of exposure to the

Fig. 8 Concentration of Cu and As leaching in pH function. The blue arrow on the points indicate ascending pH in water addition only, in the left direction the addition of acid, in the right direction the addition of NaOH
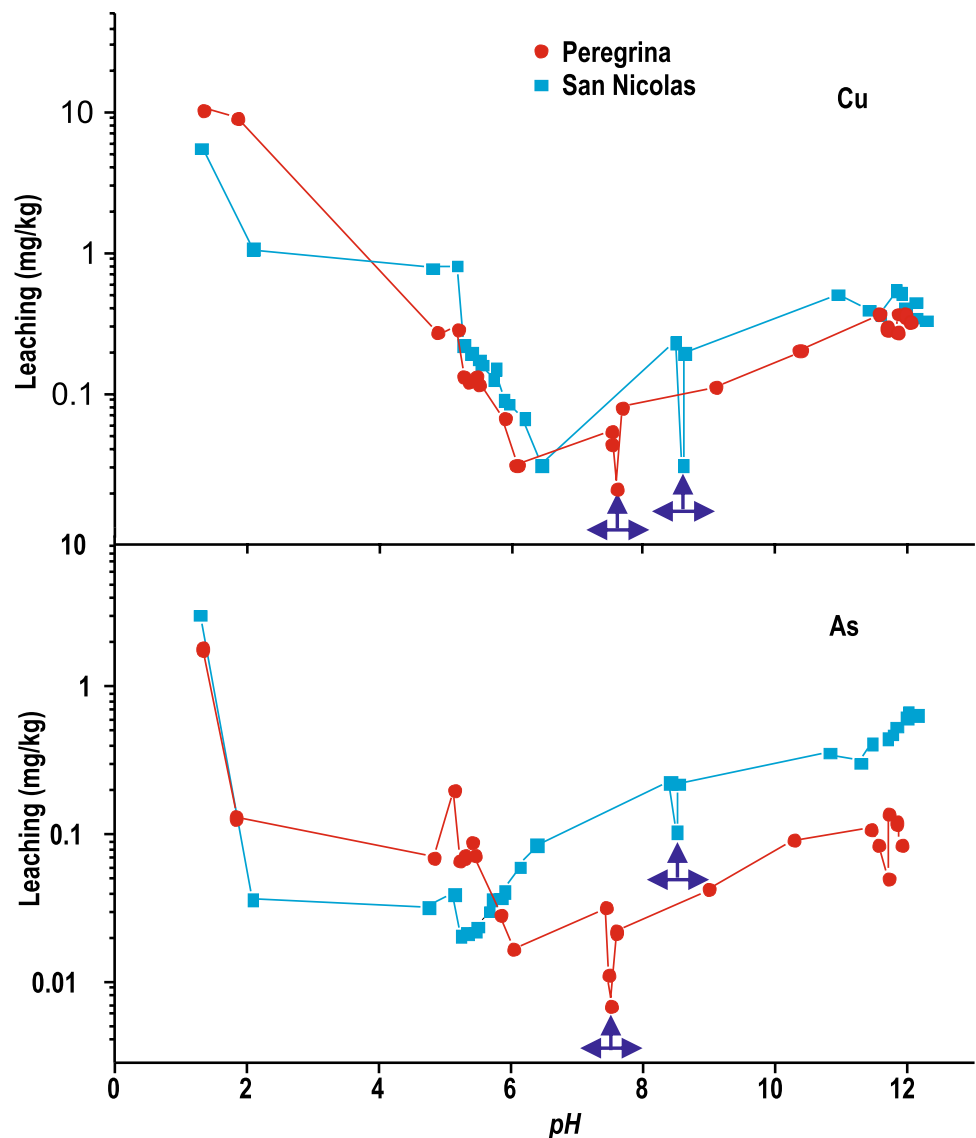
environment than Peregrina tailings. The Peregrina site had high neutralization capacity since it contained higher amounts of carbonates. The analyzed elements had greater leaching around pH 2, the minimum leached concentration was around pH 6, at this pH these elements were adsorbed in other tailings constituents. Although, Pb and Zn increased their leaching in Peregrina site, they decreased at pH 12, nevertheless Cu and As continued to be released even in basic environments, due to possible sulfosalts present.

The behavior of these elements showed a need to carry out the neutralization capacity study of tailings, even though they did not generate acid drainage; leaching of Cu and As continued even in the basic medium which was the main characteristic of this site.

These results implied, with the purpose of avoiding the formation of acid drainage, to increase the pH of tailings by calcium carbonates, to maintain a basic environment, but arsenic and copper continued to be released even in a basic environment. Results showed besides that the pH buffering action was due to the calcium carbonate present as the pure reagent continued to pH 5 into 3 meq per gram of residue. To reduce leaching of elements like Cu and As in tailings, pH should be adjusted to around 6, because at this pH leaches less concentration of these elements. The adjustment of pH could be difficult in solid wastes, therefore, an option might be the implementation of forest systems with tailings, to reduce the environmental impact by providing long-term benefits.

Fig. 9 Concentration of Mn and Fe leaching in pH function. The blue arrow on the points indicate ascending direction of pH in water addition only, in the left direction the addition of acid, in the right direction the addition of NaOH
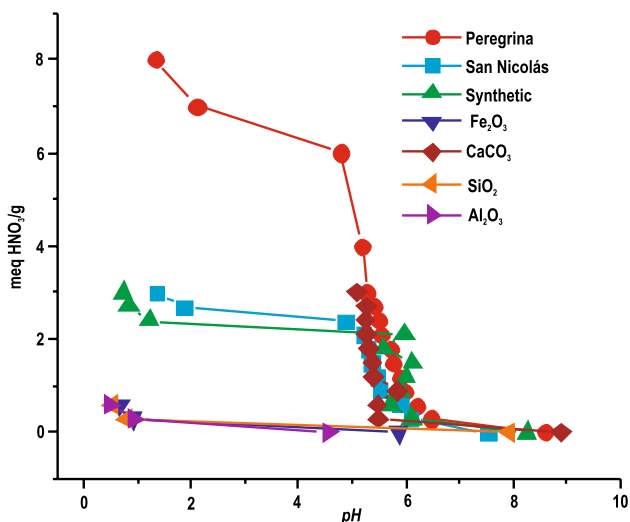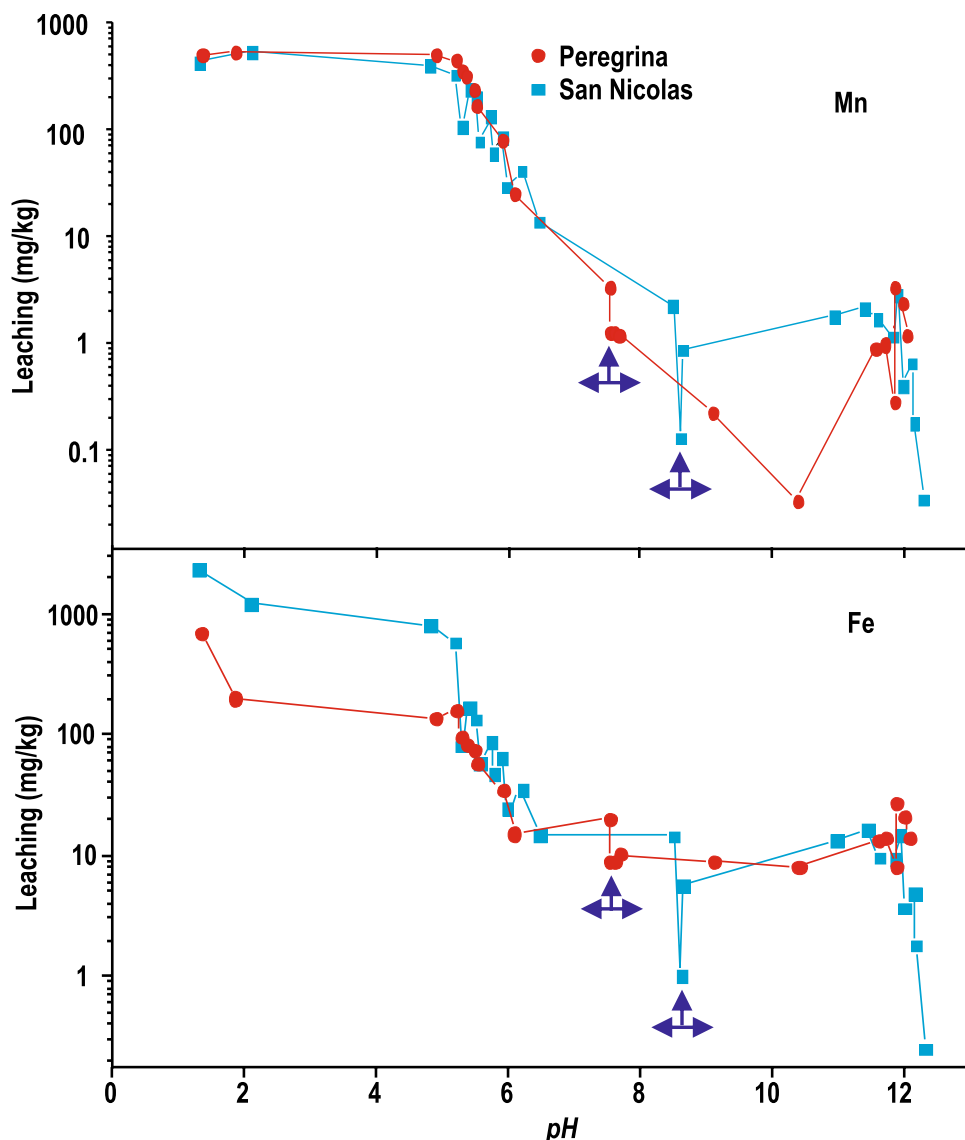

Fig. 10 Element leaching in function of pH in synthetic matrix

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