Factors controlling the release of arsenic from mining tailings

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Abstract

Some mine tailings pools in the Mine District of Guanajuato, Mexico, present a varied distribution and temporal and spatial concentration of elements that are potentially toxic, such as manganese, cadmium and zinc. These elements were detected in majority concentrations, and arsenic was present in the two major oxidation states As(III) and As(V). The highest arsenic concentration in the surrounding surface water reservoirs was detected when a rainy seasons occurred, which in turn is mainly a function of pH and the presence of bicarbonate ions. The conceptual model to describe the mobilization of arsenic from mining tailings towards the aqueous systems proposes a scenario where oxidation, the neutralization of acid drainage by carbonates, and arsenic desorption by bicarbonates takes place in different steps and at different times.

Keywords: mining tailings, potentially toxic elements, arsenic release.

1 Introduction

The mining district of Guanajuato is located 475 km from Mexico City. It is considered one of the largest worldwide. However, large amounts of mining tailings, which result from crushing and milling ore, once they have been recovered through commercial metal physical or chemical processes, have been generated over time [1]. These can be transported and become a severe environmental problem in relation to soil, sediment, surface water and groundwater pollution [2].

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Mining Tailings of *San Nicolas* Mine (*JSN*) and mining tailings of *Peregrina* Mine (*JP*) are both located in this district and are already abandoned. Under certain physico-chemical, geological and biological conditions they can promote the leaching and transportation of metals to aqueous systems. Several studies have been carried out aimed at different purposes: the identification of potentially toxic elements in leaching experiments of mining tailings [3]; geological and mineralogical characterization of mining tailings [4]; and the arsenic potential release from mining tailings [5]. In this context and in order to explain the presence of arsenic and other toxic elements in water from *Presa de Mata*, it is important to locate and characterize the source of the pollution and the factors that are controlling this event.

2 Methodology

2.1 Sampling and characterization of mining tailings in this study

2.1.1 Sampling, preservation and transportation of mining tailings in this study

Mining tailing samples of 2 k were collected from the surface and from 10 cm deep [6]. The choice of the place and sampling sites carried out depended on local conditions and ease of access to sampling points. Once in the laboratory all samples were air dried and sieved to homogenize them. Sampling was performed at three different seasonal times, corresponding to an abundant precipitation season (August 2007), a dry cold season (February 2008) and a dry season (July, 2009). The sampling of mining tailings of *Peregrina* mine was carried out only in the dry season (July, 2009).

2.1.2 Physico-chemical analysis of samples of mining tailings in this study

Granulometric analysis was performed. Subsequently, the physico-chemical properties – humidity percent, real density, bulk density, porosity and pH – were measured. For the determination of arsenic (As), cadmium (Cd), lead (Pb), manganese (Mn), and zinc (Zn), the mining tailing samples were digested in a microwave oven (Perkin Elmer, Multiware 3000) [7]. Element analyses were determined by flame atomic absorption spectroscopy (FAAS) (Perkin Elmer, AAnalyst 100). The hydride generation technique was coupling to FAAS for arsenic determination.

A speciation spectrum of arsenic by X-ray Absorption Spectroscopy was obtained. The collected samples of *JSN* packaged subsequently were analyzed beamline 7-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) in Menlo Park, CA.

2.1.3 Mineralogical analyses of samples of mining tailings in this study

Four samples of 10 g of mining tailing samples in this study were dried and sieved (*JSN* and *JP*); later the samples were concentrated using a solution of sodium dodecyl sulfate (SDS) in order to eliminate the high silica content. Two of these samples' mineralogical composition were obtained using an X-ray diffractometer (Siemens D-500) with a copper anode (λ=1.5418 Å) operated at 30 kV and 20 mA. Another two samples were determined by elemental qualitative analyses by X-ray fluorescence, using an X-ray spectrometer (Siemens SRS-200) operated at 40 kV and 30 mV.

2.1.4 Acid-base balance of samples of mining tailings in this study

The potential of acidity (PA) of the mining tailings was obtained, quantifying sulfides as the difference between total sulphur and sulfates. The potential of neutralization (PN) was obtained by the reaction of the mining tailings with sequential additions of HCl and pH after 2, 22 and 24 h. Finally the net potential of neutralization (PNN) was calculated by:

$$PNN = \frac{PN}{PA} \tag{1}$$

When the relationship (1) is less than 1.2 the tailings are generators of acid rock drainage, otherwise they do not generate acid rock drainage.

2.2 Sampling and characterization of aqueous samples of the main tributaries to *Presa de Mata*

2.2.1 Sampling, preservation and transport of potentially toxic elements from aqueous samples of the main tributaries to *Presa de Mata*

Collection containers (1 l approximately) were rinsed two or three times with the liquid to take as a sample [8]. Aqueous samples were acidified with nitric acid until a pH of less than or equal to 2.0 was obtained for metal analyses. The aqueous samples for anions determination were refrigerated until the analyses (sulfates, chlorides, carbonates-bicarbonates).

2.2.2 Physico-chemical analyses of potentially toxic elements in aqueous samples from the main tributaries to *Presa de Mata*

The pH and temperature of water samples *in situ* were measured using a Corning Checkmate II Modular Meter System, in accordance with the instructions of the manufacturer. Element concentration of water samples were determined by FAAS. The hydride generation technique was coupled for each arsenic determination. The following anions, sulfates, chlorides, carbonates and bicarbonates were also determined.

2.3 Leaching of potentially toxic elements of mining tailings in this study

2.3.1 Leaching of potentially toxic elements of mining tailings in a batch system

Samples of *JP* were used and contacted with different leachate solutions, in order to simulate different conditions that may be carried out. The leachate solutions employed were: acidified water pH 4, 9K culture medium, and bacteria growing in 9K cultured medium [9]; the final concentration of each array was 20 mg mining tailings/ml solution. For each experiment, 40 ml of each array were placed in conical polypropylene tubes in triplicate. The tubes were incubated for 1, 3, 5, 7 and 14 days in agitation at room temperature. Metals in the solution were determined. The metals analyzed were: As, Cd, Mn, Ag, Pb and Zn.

2.3.2 Leaching of potentially toxic elements of mining tailings in a continuous system

Samples of mining tailings, *JSN* and *JP*, were dried at room temperature previously, sieved (< 0.5 mm) and packed in glass columns of 4 cm in diameter and 16 cm high. Nitric acid solution (pH 4 ± 0.1 – maximum 2 ppb of metal impurities) was introduced in an up stream flow using a peristaltic pump at 12 and 9 ml/min for packed columns with samples of *JSN* and *JP*, respectively. Five fractions of leachate of each column by triplicate were collected at different times [10]. Each fraction was collected over the top of the column. The parameters in the leachate: pH, oxide-reduction potential, electrical conductivity were registered. The concentration of elements was determined by FAAS and As was determined by hydride generation coupling to FAAS.

3 Results and discussion

3.1 Sampling and characterization of mining tailing samples in this study

3.1.1 Sampling, preservation and transportation of mining tailing samples in this study

A map of microwatershed *Peregrina-Presa de Mata-Monte de San Nicolas* is displayed in fig. 1. This was created with Arcview GIS version 3.2 and shows

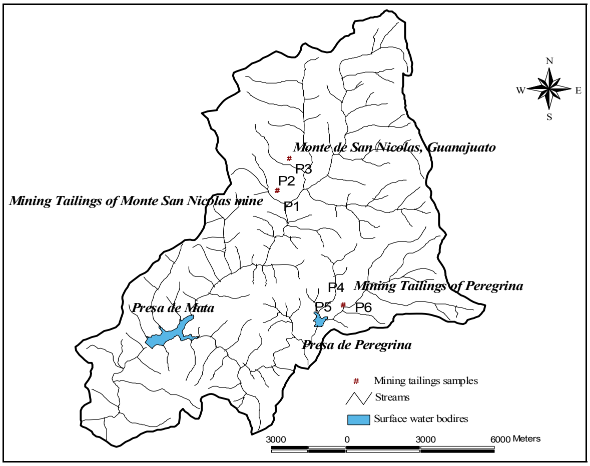

Figure 1: Microwatershed *Monte de San Nicolas-Presa de Mata-Peregrina*, Guanajuato. Mining tailing sampling points are located in (P) places.

the main surface water bodies towards *Presa de Mata*, as well as the points of the mining tailing samples. Georeferenced points: P1, P2, P3 and P4, represent sampling sites of *JSN* and P5 and P6 represent sampling sites of *JP*.

3.1.2 Physico-chemical analysis of mining tailing samples in this study

The physico-chemical parameters of the mining tailing samples determined are displayed in table 1.

Samples of *JP* showed a fine particle size. This feature is important for oxidation processes because it allows better oxygen diffusion, water conduction and interaction with other reactive phases.

Element concentrations in *JSN* and *JP* and their respective standard deviations are shown in tables 2 and 3, respectively.

Table 1: Physico-chemical parameters determined in mining tailing samples.

Sample (P)	Real density (g/cm^3)	Bulk density (g/cm^3)	Porosity	Humidity (%)	pH
1	2.97	1.01	0.79	0.274	7.60
2	2.86	1.38	0.52	0.102	7.21
3	3.22	1.01	0.68	0.274	6.08
4	2.87	0.92	0.67	0.288	7.08
5	2.22	1.05	0.52	0.110	6.00
6	2.20	1.03	0.50	0.103	6.03

Table 2: Concentration of elements in mining tailings *JSN*.

Sampling season	As (mg/k)	Mn (mg /k)	Zn (mg/k)	Cd (mg/k)	Pb (mg/k)
August 2007	4.8±0.004	638.9±0.025	219.11±3.25	No detected	34.82±0.04
February 2008	21.7±0.020	1030.1±0.001	266.77±3.1	2.58±0.006	63.85±0.11
July 2009	11.1±0.011	1960.3±0.001	278.52±1.2	3.33±0.003	101.8±0.005

Table 3: Concentration of elements in mining tailings *JP*.

Sampling season	Pb (mg/k)	As (mg/k)	Mn (mg/k)	Zn (mg/k)	Cd (mg/k)
February 2008	86.99±0.15	14.0±0.005	1388.2±0.001	484.19±0.9	2.21±0.004
July 2009	75.04±0.25	17.22±0.017	1165.3±0.001	379.12±1.5	2.57±0.009

The total As contents ranged between 4.8 and 11.1 mg/k. This concentration does not exceed the permissible maximum limit (*LMP*) for As, which corresponds to 22 mg/k [11], but the potential risk is presented because there are variations of arsenic concentrations over time and space. Concentrations of Mn show diversity in time and space. The Zn contents in all concentrations exceed the Canadian Standards [12]. The Pb contents ranged between 34.8 and 101.8 mg/k. In rainy seasons the presence of Cd was not detected. The concentration of elements in *JSN* occurs in the following sequence: Mn > Zn > Pb > As > Cd.

The major elements in *JP* were Mn and Zn. The As contents ranged between 14 and 17.22 mg/k, showing a greater concentration in the dry season. Therefore, the concentration of elements in *JSN* presents the same sequence of that in samples of the *Monte de San Nicolas* mine, but in a higher proportion.

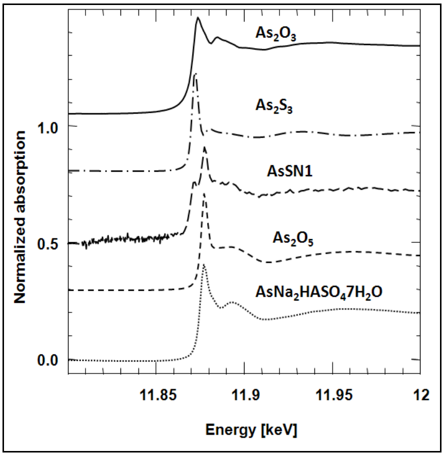

Figure 2: Spectra of X-ray absorption for sample of *JSN* for As (*AsSN1*). Model compounds: As_2O_3, As_2S_3, As_2O_5 y $AsNa_2HAsO_4\ 7H_2O$.

Table 4: Mineralogical analyses of mining tailings samples in this study by X-ray diffraction.

JSN		*JP*	
Phases identified	Possible phases	Identified phases	Possible phases
Quartz SiO_2 Calcite $CaCO_3$ Plagioclase $NaAlSi_3O_8$ Clinochlore $Mg_5Al(Si_3Al)O_{10}(OH)_8$ Muscovite $KAl_2Si_3AlO_4(OH)_2$	Smectite Fe_2O_3	Quartz SiO_2 Calcite $CaCO_3$ Ortoclase $KAlSi_3O_8$ Plagioclase $NaAlSi_3O_8$ Smectite (montmorillonite) Kaolinita $Al_2Si_2O_5(OH)_4$	Hematite Fe_2O_3

Spectra of several model compounds for As and *JSN* are shown in fig. 2. This figure shows displacement in absorption energy for As(V) and As(III). The As from mining tailing samples (*AsSN1* in the spectrum) displays two absorption energies for the same element. The first line threshold occurs at 11,867 keV and the second at 11,875 keV. This corresponds to the presence of As(III) and As(V), respectively.

3.1.3 Mineralogical analyses of mining tailing samples from *Monte San Nicolas* and *Peregrina* mines

The results of the X-ray diffraction are displayed in table 4. This table shows that the materials present a typical mineralogical composition of mining tailings. It was not possible to identify the presence of metal sulfides, given such high levels in the content and crystallization of the quartz and calcite minerals present.

Elemental qualitative analyses by X-ray fluorescence show that *JSN* and *JP* are constituted by Fe, Ca, Sr, Zn and Rb. Both samples contain Fe as the majority element, which is typical of mineral composition; also these samples consist of calcium, which reflected the high content of carbonates and that contribute to neutralize the degree of acidity, reducing the acid rock drainage.

3.1.4 Acid-base balance of mining tailings samples in this study

The determination of the acid rock drainage of tailings due to their reactivity can be determined by the oxidation of sulfide. The results are presented in table 5. These results suggest that the mining tailings in this study are not acid generators of acid rock drainage; this is possibly due to the high amount of carbonates containing mining waste and that they somehow contribute to neutralize the degree of acidity that is generated or generated since the age of abandonment of the mining tailings and processes that could have been carried out.

Table 5: Determination of acid rock drainage in the mining tailings.

Sample	PN (Kg $CaCO_3$/ton mining tailings)	PA (Kg $CaCO_3$/ton mining tailings)	(PNN)
P1	77.0	7.75	9.93
P2	76.0	7.7	9.87
P3	82.5	7.06	11.69
P4	80.8	7.02	11.42
P5	175.0	4.86	36.04
P6	185.0	4.13	44.75

3.2 Sampling and characterization of aqueous samples in the main tributaries to *Presa de Mata*

3.2.1 Sampling, preservation and transport of potentially toxic elements from aqueous samples in the main tributaries to *Presa de Mata*

A map of microwatershed *Presa de Mata, Guanajuato* and its main tributaries is presented in fig. 3, where sampling points are indicated for various seasonal times. The sampled surface water bodies are located "downstream" from deposits of mining tailings, which are considered as sources of pollution.

The results of potentially toxic elements corresponding to three seasons of sampling in the stream from *Monte de San Nicolas* to *Presa de Mata* showed that the As contents ranged between 0.012 and 0.015 mg/l, which is within Mexican Standards [13], but is not within the limit recommended by international guidelines, since chronic exposure to As causes toxic effects to human health. These results suggest that detected elements can be leachated from mining tailings and transported by main streams to *Presa de Mata*. In the case of the dry season and abundant rainfall, samples have higher concentrations of As. High concentrations of Mn are detected. Pb and Zn were only identified in the dry season (July, 2009) and rainy season (August, 2007), respectively. The Pb contents exceeds the *LMP*, while the Zn content is lower than this standard. Water samples from *Peregrina to Presa de Mata* corresponding to July 2009 presented high values of both As and Mn.

Variation of pH in the study sites for sampling in the dry season ranged between 7 and 8; this indicates a neutral environment to slightly alkaline, which can be explained by the presence of carbonates in samples of tailings that neutralize the degree of acidity that could occur. The temperature registered ranged between 19 and 24 °C.

Concentrations of anions were determined by following established guidelines in the Mexican Standards. The results are displayed in table 6, which

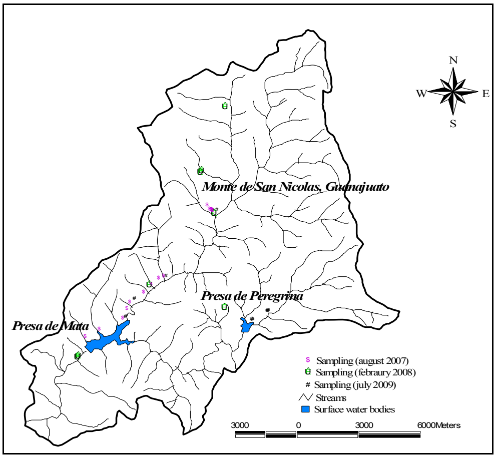

Figure 3: Microwatershed *Monte de San Nicolas-Presa de Mata-Peregrina, Guanajuato.* Sampling points are shaded in gray.

Table 6: Anions in water samples (July, 2009).

	Sample	Cl^- (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)
Stream from *Monte San Nicolas* to *Presa de Mata*	1	38.67±7.4	162.7±3.7	85.1±1.8
	2	38.67±3.7	162.7±3.7	128.6±1.5
	3	32.23±3.7	162.7±3.7	98.2±1.4
	4	32.23±7.4	122.0±3.7	311.4±1.3
	5	38.67±7.4	122.0±3.7	387.5±1.9
Stream from *Peregrina* to *Presa de Mata*	6	32.23±3.7	122.0±0.005	447.3±1.8
	7	38.67±3.7	203.3±0.005	154.7±1.5
	8	38.67±3.7	203.3±0.005	190.5±1.4
	9	32.23±3.7	122.0±0.005	447.3±1.3
	10	38.67±3.7	203.3±0.005	190.5±1.9

correspond to streams from *Monte San Nicolas* and *Peregrina* mining tailing sites, respectively.

3.3 Leaching of potentially toxic elements of mining tailing samples from *Monte San Nicolas* and *Peregrina* mines

3.3.1 Leaching of potentially toxic elements of mining tailings from *Peregrina* mine in the batch system

Fig. 4 shows the concentration of As leachate depending on the time, for different leachate solutions. In this figure, As was leachated in low amounts when a 9K medium and bacteria type *Thiobacillus ferrooxidans,* previously selected from mining tailings and grown in a 9K culture medium, was used as a leachate solution. The continuous line represents the initial concentration of total As in the sample of mining tailings.

The leaching kinetic of Cd is displayed in fig. 5. Cd was leachated efficiently, since more than 90% of mining tailings were detected in the solution. The continuous line represents the initial concentration of the total Cd in the sample of mining tailings.

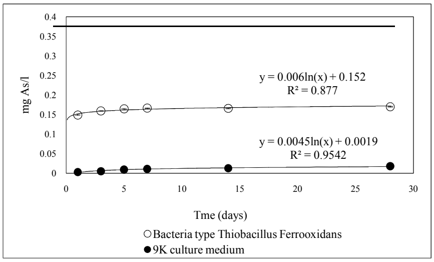

Figure 4: As leaching mining tailings in batch system.

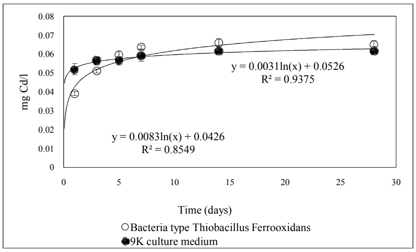

Figure 5: Cd leaching from mining tailings in the batch system.

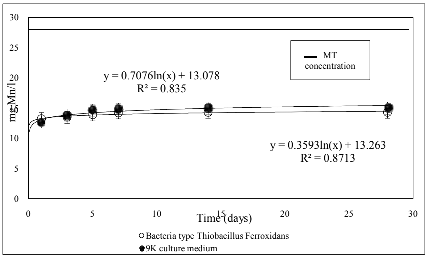

Figure 6: Mn leaching from mining tailings in the batch system.

For Mn, the leachate solution with bacteria was fitted to a logarithmic function as shown in fig. 6, where the trend line represents this behavior and points to the experimental data. The continuous line represents the initial concentration of total Mn in the sample of mining tailings.

The Pb leaching kinetic using 9K medium was fitted to a logarithmic function, while for Zn with bacteria type *Thiobacillus ferrooxidans* it was fitted to a linear function (these data are not shown). These results suggest that there are special sceneries that promote the leaching of potentially toxic elements and when these are combined in the natural system, their concentrations are higher in aqueous systems.

3.3.2 Leaching of toxic potentially elements of mining tailing samples in this study

The kinetics of As leaching in continuous systems as a function of time are displayed in fig. 7.

Each point represents the As released from mining tailings estimated by the difference between the total As concentration in the mining tailings and the As concentration detected in solution. In both cases the observed trend is logarithmic.

The variation of Mn concentration in the leachated solution and the fitted functions are shown in fig. 8. This figure shows that the concentration of Mn released from *JSN* is less than Mn from *JP*.

The Zn content in the solution and the fitted function are displayed in fig. 9. This element was obtained in higher concentration in comparison with other potentially toxic elements detected in the same system.

4 Conclusions

Mining tailing deposits from *Monte San Nicolas* and *Peregrina* showed a wide distribution and temporal and spatial concentration of potentially toxic elements, such as Mn, Cd and Zn in majority concentrations, as well as As. Arsenic is present in the two oxidation states (III) and (V).

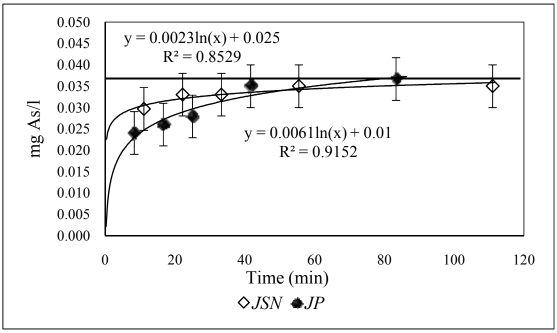

Figure 7: As leaching from mining tailings in a continuous system.

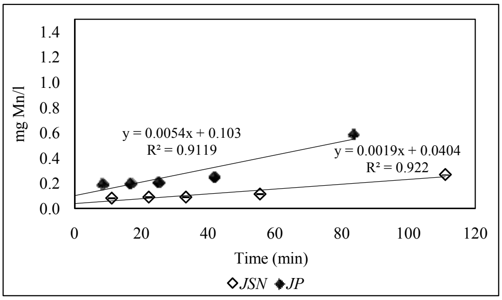

Figure 8: Mn leaching from mining tailings in the continuous system.

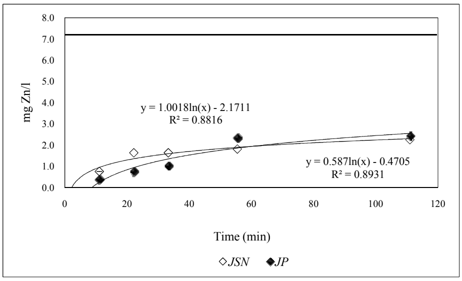

Figure 9: Zn leaching from mining tailings in the continuous system.

During rainy seasons, arsenic was obtained in higher concentration as a product of leaching of this element, which is a function of pH and the presence of bicarbonates in the system.

The pH of mining tailings in this study ranged between 6 and 8, which demonstrated that mining waste possesses a high amount of carbonates that reduce the degree of acidity that could generate the due porosity and granulometry of mining tailings.

Microbial activity can leach considerably potentially toxic elements, mainly those such as Cd.

The kinetics of leaching obtained in batch tests showed linear and logarithmic tendencies for Zn and As in continuous tests, respectively.

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