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Arsenic liberation from mine wastes derived of skarn deposits at Sierra Madre Oriental, México

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Abstract

This work focuses on the evaluation of magnitude of arsenic release into the Xichú River from mine wastes at La Aurora mine, located in Sierra Madre Oriental at Guanajuato state, Mexico. Approximately 1 million tons of sulfur-rich tailings were deposited on the banks of the river after the extraction and processing of skarn ore type deposits. A total of 47 water samples were collected and analyzed at field and by atomic absorption spectroscopy. All samples contain As, Cd, Cu, Fe, Mn, Pb and Zn product of sulphide oxidation at mine wastes. Chemical composition diagrams (Piper and Stiff) were created with the obtained data with the software AQUACHEM to visualize the impact of arsenic leaching in the Xichú basin. At the base of one deposit, a small, localized and continuous liberation of leachates occur, with very high quantities of arsenic in solution and associated to suspended particles. In aqueous phase, at least migrates 2 kg of arsenic per year and great quantities of iron and sulfates. The affectation level is controlled by seasonal conditions. Is possible find Mn in all the analyzed samples and it seems that arsenic liberated from mine wastes affect a great area. The in-situ formation of oxides and oxi-hydroxides favor arsenic retention.

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Keywords: Arsenic; sulphides oxidation, leachates liberation

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1. Introduction

Xichu region was exploited for silver extractions at small scale since 1600, but more intensively during first half of XX century; activities finish in 1957. Unfortunately the generation and disposal of mine waste was neglected. At least five deposits of mine waste rich in sulphides were disposed at the riverside of the Xichú river that represent

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approximately 1 million tons. The exposure of these mine tailings to water oxidizes the sulphides and releases potentially toxic elements (As, Cu, Pb, Zn) in soluble and particulate forms with leachates.

Xichú is located in the NE of Guanajuato state, 353 km away north of Mexico city (Figure 1). This mining District is located at Sierra Madre Oriental physiographic region in Karst Huasteco sub-province. Drainage runs to Gulf of Mexico trough Santa Maria river, a sub-basin of Panuco river. The zone shows a great gradient elevation from 2,640 m above sea level (masl) until 1,040 masl which favors a very high climatic variability^1. Average annual rainfall is of 700 mm with a temperature difference between -4^o to 51^o C. This region has a summer drought between June to September.

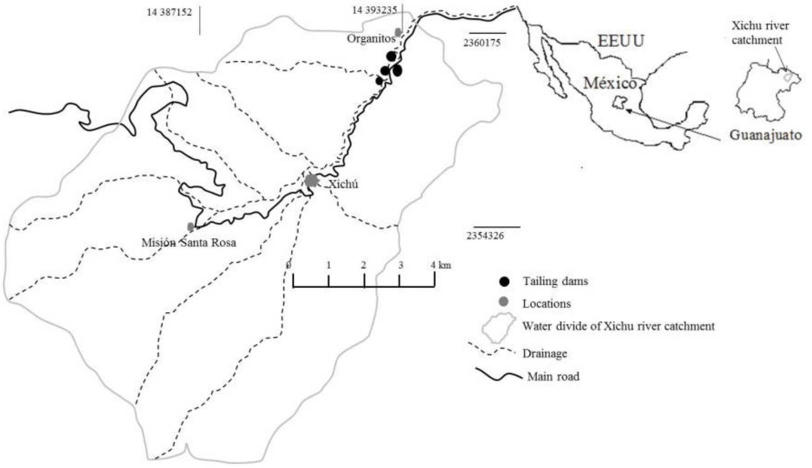

Fig 1. Location of Xichú mining district, at Sierra Madre Oriental.

Arsenic mobilization is a very complex issue to study in wastes produced by the mining of skarn deposits, mainly by the occurrence of arsenopyrite and pyrite in high quantities. Xichú tailings were recently characterized^2, contain extremely high As quantities as arsenopyrite and associated to oxides too. Field observations suggest that As can be migrate from these deposits in aqueous phase or associated to oxides and oxi-hydroxides. This work focuses on the characterization of leachates generated in piles of mine tailings and to dimension the potential liberated volume to Santa Maria river.

2. Methodology

2.1. Definition of a sampling strategy

The definition of a sampling strategy was paramount for a proper comprehension of how As is distributed in the Xichú basin. This was achieved as follows: a) definition of the study area in the Xichu river, b) identification of key points where different types of waters were found, c) sample collection and measure of field parameters. Samples were collected with clean polyethylene recipients previously washed with same collected sample. Samples were filtered by 0.22 µm Millipore membranes and acidified with concentrated nitric acid. At field, temperature, pH, electric conductivity, dissolved oxygen, redox potential, alkalinity, sulphides, ferrous and manganese was evaluated.

2.2. Sample analysis

Samples were analyzed at laboratory by atomic absorption spectroscopy (AAnalyst 100 Spectrometer), volumetric and photometric techniques. Chemical data were plotted in Piper and Stiff diagrams with the AQUACHEM software and geochemical simulations were made with the PHREEQC software to visualize the possible scenarios of As leaching.

3. Results and discussion

3.1. Variation of natural waters.

Most natural waters collected at the Xichú basin presented a carbonate-calcic hydrogeochemical facies. This is due to the presence of fractured rhyolite in the area where fresh water springs “pops-out”. Figure 2(a) shows the variation in the major anions and cations using Piper diagrams to identify leachates influence[3]. Only the most representative sites are highlighted. The bicarbonate-calcic character at stream "Charco Azul", located above the gradient of the waste deposits, is represented as a reference level of water quality at this basin.

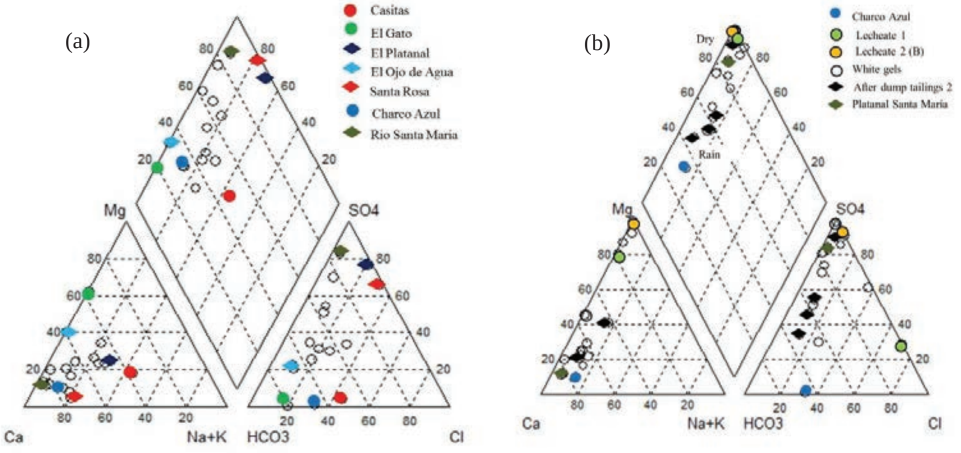

Fig. 2. Variation of water-types accord the influence of mine wastes.

Leachate 1, 2 and "White Gels" are sulfated, calcic or magnesic; product of sulphides oxidation and calcite and dolomite neutralization. Leachate 1 has very high concentrations of chlorides suggesting strong evaporation at the zone. Figure 2(a) represents water types of leachates and a mixing process with waters of Santa Maria river. The site "after tailings 2" (black diamond, Figure 2) shows a variation in chemical character according season sampling. It seems that the influence of leachate is higher in the dry season (December 2014) that during rains (September 2013); this influence is reflected because comes more sulfated.

Except for the spring "El Platanal", which has a sulfated character, every other sampled site has bicarbonate as dominant anion. The reason for this is that El Platanal spring has as hydrogeological basement Jurassic shales, rocks that contain FeS_2 and release SO_4^{-2} when are exposed to the atmosphere. The prevalent cation in all samples is Ca^{2+}. The spring "Casitas" also shows a calcium-sulfated character as the other sites, the presence of Cl^- and sodium suggests anthropogenic affectation. This spring is located in fractured rhyolite and is below the local cemetery, it remains highly vulnerable to contamination. Salinity is greater in the spring "El Ojo de Agua" which is the output of the hydrological Xichú basin, a tributary of the Santa Maria River. This spring has up to 20 mEq Ca^{2+}, when the others are in the order of 5 mEq.

Table 1 summarizes the percentages of samples that exceed maximum permissible levels (MPL) according Mexican Norm for drinkable water[4]. Significantly, 93.5% of the analyzed samples exceed the MPL for Mn. This element is linked to the weathering of a rhodochrosite ore and manganesiferous limestone. 49% of analyzed samples exceed the concentration range of sulfates and 34% has a concentration of more than 0.025 mg/L of As, the MPL. The high amount of As is partly due to the acidic drainage and heavy metals leaching released into the environment.

Table 2 shows correlation coefficients of metals, sulfates and electric conductivity. Correlations between metals and sulfates suggest a common origin: sulphides oxidation processes as pyrite, chalcopyrite, arsenopyrite, galena and sphalerite, founded at high quantities at tailings[2]. Tailings are cemented, with a crust of oxides, sulfates, oxi-hydroxides and hydroxi-sulfates of at least 1cm in all residue area. This cover decrease the potential of infiltration and the volume of material that oxidizes and liberates leachates is lesser accord age of atmospheric exposition. Water that infiltrates is only trough fractures.

Table 1. Percentages of samples that exceeds Maximum Permissible values for drinkable water accord Mexican Norm.

Parameter	MPL	% over (n=47)
As	0.025	34.0
Cd	0.005	8.5
Cu	2.0	12.8
Fe	0.3	23.4
Mn	0.2	93.6
SO_4	400.0	48.9
Zn	5.0	12.8

Table 2. Coefficient correlation of metals in all samples (n=47)

	CE (µS)	SO_4	Mg^{2+}	Ca^{2+}	Mn^{2+}	Zn^{2+}	Fe^{2+}	Cu^{2+}	Pb^{2+}	Cd^{2+}	As
CE (µS)	1.00										
SO_4	0.63	1.00									
Mg^{2+}	0.74	0.87	1.00								
Ca^{2+}	0.12	0.50	0.10	1.00							
Mn^{2+}	0.60	0.79	0.91	-0.03	1.00						
Zn^{2+}	0.56	0.90	0.90	0.12	0.90	1.00					
Fe^{2+}	0.47	0.77	0.84	-0.05	0.95	0.93	1.00				
Cu^{2+}	0.63	0.85	0.77	0.35	0.57	0.80	0.54	1.00			
Pb^{2+}	0.66	0.42	0.54	-0.02	0.48	0.46	0.50	0.29	1.00		
Cd^{2+}	0.49	0.78	0.85	-0.04	0.95	0.94	0.99	0.55	0.53	1.00	
As	0.45	0.33	0.63	-0.05	0.49	0.28	0.30	0.23	0.18	0.31	1.00

4. Conclusions

All analyzed samples contain arsenic, over detection limit quantification and in some samples at very high concentrations (until 2,000 mg/L); 16% of the samples exceeded the maximum permissible limit for arsenic concentrations in water according to the Mexican regulation (0.025 mg/L) while 8% of the samples exceed a concentration of 1.0 mg/L of arsenic. The leachate that comes from the mine tailings evidently affects the Xichú basin by releasing potentially toxic elements to the environment. A quantification of the arsenic liberated annually, based in annual rain and the evaluation of volume of leachates, suggest that at least 2,000 g of arsenic in aqueous phase is liberated each year.

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