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Determination of Metals for Leaching Experiments of Mine Tailings: Evaluation of the Potential Environmental Hazard in the Guanajuato Mining District, Mexico

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Tailing deposits generated from mining activities constitute a potential risk to the environmental through leaching of potentially toxic elements hosted by a variety of minerals present in the mine-waste materials (Lin 1997; Craw 1999; Armienta et al. 2003). Leaching of metals in tailings involve numerous geochemical and transfer processes that control the concentration of extracted elements, such as mineralogy composition, mineral solubility, rates sulfide mineral oxidation, water content, oxygen and pH (Parson et al. 2001; Al 2000; Jourjovec et al., 2002). It is important to know the dissolution behavior of the heavy metals in order to predict the long-term reactivity of these source materials and their impact on surface, groundwater and/or soil in the natural environment. The most often used approach to asses metals mobility is laboratory extractions experiments, which include both leaching experiments (humidity cell test and column experiments), static test and extraction experiments (Manz 1997; Morin and Hut, 1998). These synthetic water leaching studies on solid tailing can simulate surface leaching of mine waste material to predict the natural weathering reactions of the tailings and to estimate the danger to the environment arising from this materials (generation of acid mine drainage and heavy metals in solution). Such leaching studies are conducted under experimental conditions that can be very different from the natural weathering environment, however the data provide some measurement of the relative dissolution kinetics of different waste materials.

Measurements of fraction compositions in the laboratory extractions test require of a accurate and rapid analytical method able to multi-elemental determination in a wide rang of concentration. Several analytical methods are available for this kind of determinations. In recent years, inductively coupled plasma mass spectrometry (ICP-MS) has aroused grate attention as a sensitive instrument for the measurement of trace and ultra trace elements in various kind of samples. The ICP-MS method also allows simultaneous multi-elemental determination in a wide range of concentrations with very low detection limits. This method is used to evaluate the leaching behavior of tailings from the Guanajuato mining district (Mexico). With this geochemical evaluation, the potential environmental hazard of the mine waste material in the region can be better constrained. These data will be helpful for the mine waste management and further environmental programs.

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MATERIALS AND METHODS

This ICP-MS analytical method to determine metals and metalloids in leaching experiments of mine tailings was established at the Instituto de Geofísica, Universidad Nacional Autónoma de México (UNAM). A PQ3 (VG-Elemental) Inductively Coupled Plasma Mass Spectrometer was used throughout this study. The leaching tests for the tailing material from the Guanajuato mining district were done using the established method for humidity cell tests (HCT) by Sobbek et al. 1978). Samples from the different materials were collected in double sealed plastic bags and transported to the Geosciences Center-UNAM Campus Juriquilla for total digestion with concentrated HNO_3 in microwave oven and for leaching experiments.

The humidity cell test is a kinetic method that tries to simulate the weathering conditions of the tailings in the field, especially acid-producing, acid-consuming processes and dissolution of mineral phases with liberation of heavy metals into the aqueous system, that occur in the natural environment (Sobbek et al., 1978). The HC are plastic containers with tight-fitting lids. Each cell is about 7 cm high and has about 50 cm^2 cross-sectional area. An air inlet feeds into the center of the top and a drain fitting is located in the bottom of each cell. Four individual cells were connected to a regulated source of compressed air (~5 l/min) using $^1/_2$ inch diameter Tygon tubing. Humidified air was generated using a 5 gallon glass carboy, which was half-filled with deionized water. Compressed air was fed directly to the HC (dry-air cycle for three days) or pumped to the carboy first and then routed to the HC (humidified-air cycle for four days).

At the end of the humidified-air cycle, the sample was treated with 200 ml of double-deionized water passed through a Milli-Q system and allowed to soak for one hour. The leachates were collected using glass beakers, filtered through 0.45 micron micro-pore membranes, and divided into two sub-samples. One was used for alkalinity titration and anion analysis by anion chromatography (AC), and the second was acidified to pH 2 for the trace metals determination using ICP-MS. The leachates were stored overnight at 4^0 C before analysis. All the glassware and plastic-ware were cleaned with detergent, 0.12M HCl, and rinsed with deionized water.

RESULT AND DISCUSSION

The humidity cell leachates samples were taken every week during a 20 week period. The 14 elements analyzed are: V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl and Pb. The relative concentration of these elements varied greatly in the leachates. Figure 1 shows the average concentration of the 14 trace elements during the 20 weeks of leaching. Zn is the element with the highest concentration,

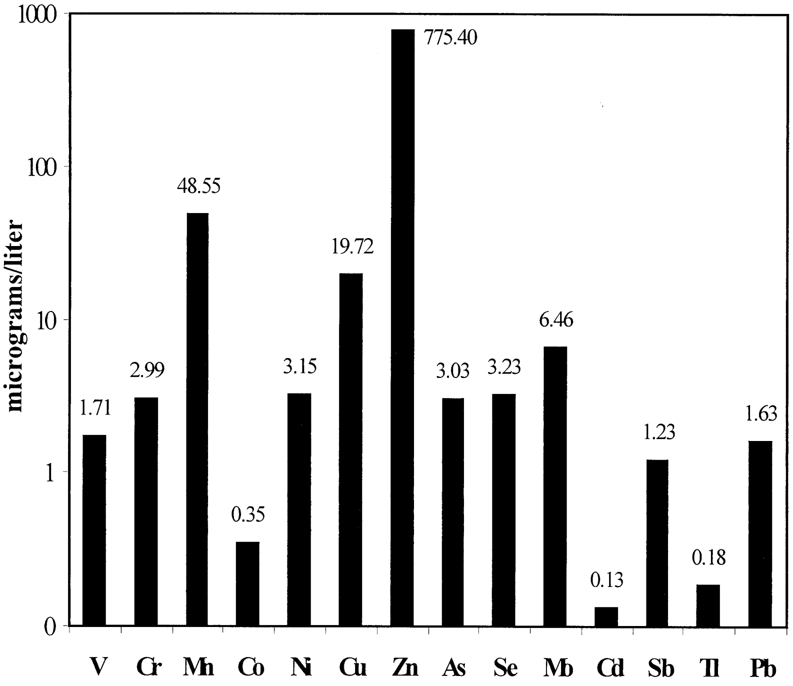

Figure 1. Average concentration of trace elements in the leachates of the HCT during 20 weeks. See Table 1 and text for discussion of the highest and lowest concentration, and comparison with drinking water standard (DWS) and average concentration in fresh waters (ACFW).

(between 0.003 to 13.73 μg/l and average of 0.775 μg/l). The elements that follow zinc in concentration in the leachates are: Mn (between 0.002 and 0.24 μg/l, average of 0.05 μg/l); Cu (between 0.001 and 0.17 μg/l, average of 0.02 μg/l); Mo (between 0.001 and 0.03 μg/l, average of 0.006); Se (between 0.001 and 0.02 μg/l, average of 0.003 μg/l), As (between <0.001 and 0.01 μg/l, average of 0.003 μg/l). The lowest concentration was on Cd (<0.001 μg/l). Figure 2 shows the variation of the leachates during the 20 weeks. From these results it can be concluded that elements that start leaching relatively high concentrations during the first weeks and decrease the concentration towards the week 10 or so, are very likely bounded to secondary minerals phases that easily dissolve and liberate the trace elements (V, Cr, Mn, Co, As, Se, Mo, Cd, Sb, Tl and Pb). For elements that started with low concentrations and then increased their concentration by week 10 or so (Cu, Zn), it is assumed that they are mostly bounded to primary minerals (carbonates, sulfides). Nickel has a behavior with relatively high concentration in early leachates, then decreasing and toward week 11-12, the high concentrations came back again. In this case, Ni very likely is bounded both to secondary phases and to primary minerals, so the concentration in the leachates first goes up (dissolution of secondary phases), then down (depletion of secondary phases) and then up again (beginning of dissolution of primary phases).

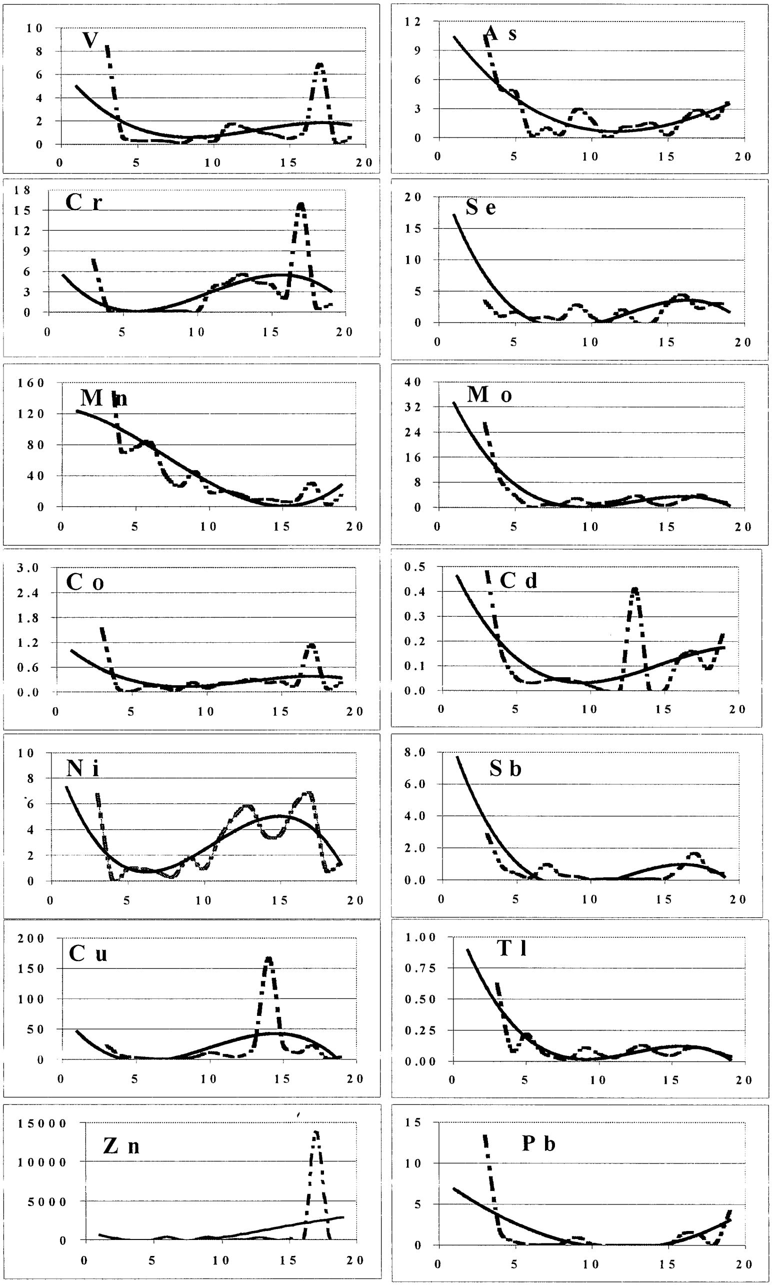

Figure 2. Concentration of trace elements in the leachates from the HCT during the 20 weeks. Note that the vertical scale (concentration in µg/l) is different for every element. The dashed line represents the real data. The continuous line is a tendency line obtained with a second order polynomic regression (best fit).

Table 1. Results for the 14 trace elements during the 20 weeks period of leaching the humidity cell and their average. For comparison, the drinking water standards (DWS; EPA, 1975; WHO, 1970; Freeze and Cherry, 1979), and the average concentration in fresh water are shown (ACFW; Cox, 1995; Emsley, 1998). The concentrations are in micrograms/liter (μg/l or ppb). See figure 3 for graphic display of results and text for discussion.

Week	V	Cr	Mn	Co	Ni	Cu	Zn	As	Se	Mo	Cd	Sb	Tl	Pb
1	2.64	2.24	66.81	0.63	5.78	33.90	5.89	8.76	20.73	30.72	0.39	8.68	0.89	3.78
2	5.53	4.95	151.73	1.08	6.26	28.00	14.42	9.64	12.08	28.75	0.44	5.76	0.76	8.55
3	8.42	7.65	236.65	1.53	6.74	22.10	22.95	10.51	3.42	26.78	0.48	2.84	0.62	13.31
4	0.69	0.30	72.03	0.12	0.03	6.77	9.97	5.09	1.05	9.11	0.15	0.87	0.09	1.54
5	0.32	0.10	76.86	0.02	0.95	3.67	3.14	4.76	1.73	3.78	0.05	0.39	0.22	0.37
6	0.33	0.13	82.83	0.15	0.94	1.44	471.02	0.27	0.73	0.08	0.03	0.15	0.08	0.07
7	0.26	0.06	40.85	0.10	0.62	0.92	1.34	1.05	0.91	0.90	0.04	0.98	0.03	0.05
8	0.12	0.14	26.15	0.04	0.34	0.76	8.03	0.33	0.60	0.90	0.05	0.32	0.02	0.15
9	0.68	0.21	45.18	0.23	1.79	3.85	476.12	2.95	2.88	2.95	0.04	0.23	0.11	0.95
10	0.23	0.11	19.33	0.09	0.94	11.16	2.61	1.87	1.01	1.19	0.02	0.04	0.06	0.10
11	1.69	3.60	20.05	0.22	3.33	6.56	50.27	0.00	0.00	1.65	0.00	0.10	0.03	0.00
12	1.43	4.30	16.64	0.23	5.08	4.66	80.84	1.07	2.12	2.43	0.00	0.09	0.08	0.00
13	1.03	5.60	9.27	0.31	5.79	20.79	342.73	1.22	0.00	3.85	0.41	0.05	0.13	0.00
14	0.80	4.42	9.60	0.22	3.52	167.25	26.02	1.53	0.02	1.40	0.00	0.10	0.07	0.00
15	0.48	4.04	6.45	0.25	3.59	22.81	58.22	0.27	3.05	0.71	0.00	0.10	0.05	0.00
16	1.18	2.30	8.76	0.16	6.02	10.24	44.14	1.90	4.48	2.48	0.13	0.73	0.10	1.45
17	6.88	15.90	30.32	1.14	6.71	22.92	13729.00	2.92	2.32	4.15	0.16	1.69	0.11	1.29
18	0.17	0.74	2.83	0.10	0.83	1.22	7.94	1.98	3.11	2.49	0.09	0.62	0.08	0.08
19	0.60	1.14	14.07	0.22	1.46	3.20	7.10	2.88	3.36	2.98	0.09	0.60	0.07	0.66
20	0.69	1.87	34.68	0.16	2.33	22.10	146.21	1.51	1.00	1.91	0.06	0.25	0.08	0.17
Average	**1.71**	**2.99**	**48.55**	**0.35**	**3.15**	**19.72**	**775.40**	**3.03**	**3.23**	**6.46**	**0.13**	**1.23**	**0.18**	**1.63**
DWS	n.e.	50.00	50.00	n.e.	n.e.	1,000.00	5,000.00	50.00	10.00	n.e.	10.00	10.00	n.e.	50.00
ACFW	<1.0	n.a	n.a.	0.20	<1.00	1.00	1 -- 10	1 -- 10	0.02 - 1	n.a.	<1.0	0.3 - 5	<0.01	1 -- 10

n.e. : not evaluated; n.a.: not available

Table 1 indicates also the maximum concentrations from drinking water standards (DWS) based on the U.S. Environmental protection Agency (EPA, 1975) and World Health Organization (WHO, 1970). As noted from the data on the Table 1, only Mn, Zn and Se are above the DWS in some of the leachates. Manganese is higher than DWS in the leachates from week 1 to 6 with a highest concentration of 236.65 μg/l, but with a general average slightly lower than the DWS concentration (48.55 μg/l). Zinc concentration in the leachates is higher than the DWS only at week17, where a marked spike in concentration was measured (13.73 mg/), very likely corresponding to the dissolution of a carbonate bearing Zn phase (smithsonite?). But the general average concentration of Zn (775.40 μg/l) is much lower than the DWS (5,000 μg/l). Selenium concentration in the leachates is slightly higher (20.73 and 12.08) μg/l) than the DWS (10 μg/l) only in week 1 and 2, then the concentrations decrease noticeably. This indicate that Se is very likely to easily dissolved secondary mineral phases.

Despite the fact that the humid cell test experiment represents and accelerated weathering and dissolution rate of the natural environment, the average concentration for all the 14 trace elements is lower that the DWS.

This indicate the low-risk potential of the mine tailing to liberate trace elements to the natural environment. Also, shown for comparison in Table 1, is the average concentration in fresh waters of some of these trace elements (ACFW; Cox, 1995; Emsley, 1998).

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An noted in the table, the average concentrations in the leachates for all the trace elements is very close to the ACFW. Vanadium is slightly higher (1.71 μg/l)) than the ACFW (<1.0 μg/l) , Co and Ni averages are about the same than ACFW. Zinc average concentration in the leachates is much higher that the ACFW (775.40 μg/l compared with 1- 10 μg/l). Arsenic average in the leachates is slightly lower than the ACFW, and Se average in the leachates is slightly higher.
The Guanajuato mining district is a low sulfidation quartz-calcite-rich epithermal ore deposit. The carbonates (mostly calcite) – sulfides (mostly pyrite) ratio is 12:1 (Oelsner, 2001). So, any acidity generated by the oxidation of pyrite would be buffered by carbonate dissolution. The average pH of all the leachates is 7.3, thus, the dissolution and solubility of trace metals phases in inhibited. It has been reported that the concentrations of trace metals leaching from this kind of ore deposits are relatively low (Plumlee, 1999). The present study confirms the poor concentrations of trace elements draining from low-sulfidation epithermal ore deposits.

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