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Mineralogical and Chemical Characterization of Historical Mine Tailings from the Valenciana Mine, Guanajuato, Mexico: Environmental Implications

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Since the beginning of mankind, mining activities have played a key role in the social and economic development of human society. As a country, Mexico is not the exception, and it has a long and extensive mining history going back to pre-colonial time. Mining has also been a very profitable activity and represents around 5% of the gross national product in Mexico. Until the mid 1990's, silver represented 50% of the exported mineral products. In this context, Guanajuato mines, in central Mexico, have been exploited for over 450 years (since 1548), for their gold-silver epithermal veins. Currently, the Guanajuato Mining District is still a very important silver and gold producer, with nearly 13% of the gold and 8% of the silver production in Mexico. However, the exploitation of ore deposits, in general, generates high amounts of non-economic by-products or mineral waste material known as mine tailings. The average economic mineral grade within the ore deposit is below 1% for Au and Ag. For base metal (Pb, Zn, Cu), the average ore grade is approximately 3 to 5 %. Thus, it is estimated that between 95% and 99% of the material extracted from the mines is disposed as mine tailings (Allan 1995). The extraction of large quantities of ore with lower grades is producing more tailing material. It is estimated that 64% of industrial residues disposed in Mexico are from mining activities (García-Meza 1999). In the Guanajuato Mining District, tailing material has been accumulated since the late 1500's. Estimations indicate that, in 1945, 2.5 million tons of tailings were disposed in tailings piles and tailings impoundments in the zone. At the present, the rate of tailings disposal is approximately of 3,000 tons per day. Thus, the current amount of tailings is estimated to be more than 5 million tons scattered all around this Mining District (Morton 2000; Ramos 1991).

Controversially, the tailings have been catalogued as both, hazardous waste (metal-rich material potentially of generating acid mine drainage and metal-rich leachates), and as economically potential natural resources (easily extractable low grade ore). In both cases, it is assumed that mine tailings include heavy metals in relatively high concentrations. So far, no economic technique has been established for the use of tailing material, nor is a metallurgical processes capable of producing non-impurity material (Basulto 1984; Ramos 1991). Whatever the tailing materials are classified, one thing is true: they represent a source of heavy

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metal-rich material with a potential hazard for public health and for the surrounding ecosystem. The purpose of this paper is to present data on the mineralogy and major and trace element composition of one of the historic tailing piles of the Valenciana mine, Guanajuato. This represents a first approach for a further environmental assessment of these material and possible reclamation efforts.

MATERIALS AND METHODS

The samples of tailing material were collected from a mine tailing pile of the very productive mine of Valenciana, in November 1999. The Valenciana tailing piles are located 4 km northwest of the city of Guanajuato, at the lower elevation of the Guanajuato mountain range. The average elevation of the study site is 2,120 m above sea level in a semi-dry climate, with heavy rain during the summer months. There are three tailing piles in the area, two are continuous terraces and one is in different steps (different heights). The distribution of these tailing piles is controlled by the local topography. Each pile represents one depositional event. Thus, each time a pile filled up, the mining company takes a new site for waste disposal, next to the previous site. The newest site was chosen for the present study. This pile was abandoned in 1998 and contains waste material from processing silver-rich ore of the Guanajuato Mother-Lode (Veta Madre) and La Luz veins. The Valenciana Mine silver processing plant belongs to the Santa Fe de Guanajuato Corporation Society (SFG-CS). The SFG-CS processes nearly 750 tons/day of ore using the flotation method for silver and gold recovery.

The samples were collected from the central part of the pile. A circle 15 m diameter was marked in the field, and ten samples were taken from the surface material (less than 5 cm depth). The samples were thoroughly mixed to obtain a single composite and homogeneous sample. The final sample was collected in double sealed plastic bags. A sample from non-disturbed soil at a nearby hill next to the tailings impoundment was also collected as a control sample. The site selection and sampling method was based on a previous work from other authors (Ramos-Arroyo and Siebe, 1997).

For major elements (Si, Al, Fe, Ca, Mg, Na and K), the sample was digested at 1,000° C with boric acid and sodium metaborate and analyzed with a flame atomic absorption spectrophotometer (AAS, Perkin-Elmer 1100B). The sample was also analyzed with X-Ray diffraction (SIEMENS D500) and thermo-analysis (Universal V2.5H TA Instruments) for mineral identification. Based on the mineral and chemical information, the mineralogical reconstruction was done as described in Ramos (1991). The extraction of some selected metals (Cr, Ni, Cu, Zn, Cd and Pb) was carried out by sequential extraction and analyzed with ICP-MS. Each of the chemical fractions was defined as:

1) Oxides and other crystal structures (primary minerals): tailing sample extracted with 10 ml of concentrated HNO_3 and 3 ml of concentrated HCl with continuous agitation at 90°C for 2 hr.

2) Secondary mineral-phases: extracted with HNO_3 50% for 2 hr, with continuous agitation at room temperature.
3) Bioavailable: using EDTA 0.05 M, pH 7, for 2 hr, with continuous agitation at room temperature.
4) Water-soluble: with distilled water, for 2 hr, with continuous agitation at room temperature.
5) Potentially bioavailable or leachable: with 8 ml of 0.1 M acetic acid (pH 7) for 72 hr, with continuous agitation at room temperature.

The last three fractions represent mobile fractions: (i) potentially active, (ii) bioavailable, and (iii) leachable (Gupta et al. 1996). The total concentrations were represented as the sum of all the fractions.

Other analyses on the tailing material include: (a) texture based on the Bouyoucos method (Black 1965); (b) color, (c) density, (d) electric conductivity (EC) (Richards, 1974); (e) cation exchange capacity (CEC) (Bower 1952); (f) paste and rinse pH (Morin & Hutt 1997); (g) percent of organic matter by titration; and (h) percent of carbonates by titration (Walkey 1947; Richards 1974). The measurements were done per triplicates.

RESULTS AND DISCUSSION

The results of the physical and chemical characterization of Valenciana mine tailings material (Table 1) indicate that the tailings are sand-silt material with particle diameter between 0.025 and 0.25 mm, with varying proportion of clays. The clay content alters the plasticity, cohesion, infiltration rates, permeability, aeration and drainage capacity, key factors for the successful development of soil and a vegetation cover on top of the tailing impoundment. However, the low clay content of the material (Table 1) also indicates very low water absorption capacity, very low cation retention and, consequently, low fertility. In fact, the Valenciana tailing material has a relatively low cation exchange capacity (CEC = 2.7 meq/100g), and a substrate material with low CEC favors the quick leaching of nutrients (Tamhave 1978). Therefore, under the current conditions, these mine-tailing will continue being an infertile poor substratum, lacking the needed nutrients, and therefore without the bacterial activity needed for the nitrification and ammonification processes vital characteristic of a fertile substrate such as a soil.

The general results of Valenciana mine tailing material from this study (Table 1: texture, color, pH, organic matter percent, and carbonate content) are similar to those reported by Ramos (1991), Ramos-Arroyo and Siebe (1998) and García-Meza (1999), who worked with different tailing materials of the Guanajuato Mining District.

Table 2 shows the major elements composition of the tailing material and the control soil sample. The reconstruction of the mineralogy of the tailing material,a based on bulk chemistry and XRD data is reported in Table 3 (Ramos 1991). The main minerals of the Valenciana tailings are primary minerals from the vein

Table 1. Selected physical-chemical properties of the Valenciana tailing material and the sample of soil. ND= No detected.

		Tailings	Soil
Color	dry	Light gray	Reddish yellow
	wet	Light olive gray	Reddish yellow
Clay content (%)		6	8
Silt (%)		52	44
Sand (%)		42	48
Density (real; g/mL)		2.37	2.70
Porosity (%)		51.4	66.5
PH		8.1	7.1
EC (mS/cm)		1.7	0.1
CEC (meq/100g)		2.7	17.8
Total Phosphorous (%)		0.08	ND
Organic matter (%)		0.81	5.6
Carbonates (%)*		12.80	ND

* Sum of $CaCO_3$ + $MgCO_3$

(Jambor & Owens 1993): quartz, K-spar, calcite, magnetite, hematite and sulfides. Less than 4 percent of the materials correspond to secondary minerals (mostly gypsum, kaolin and other clays). Most of the detected minerals were already reported in mine tailings of the Guanajuato Mining District, such as quartz, orthoclase, plagioclase, calcite, chlorite, kaolin, and pyrite (Petruk and Owens 1974; Ramos 1991, Oelsner 2001). Parsons et al. (2001) found various silicate (as feldspar and quartz), oxide (magnetite, hematite), sulfides (pyrite) and glass phases in the Penn Mine slags (Calaveras County, California), while Berger et al. (2000) also reported quartz, calcite, gypsum, and hematite, and others Al-hydroxides and oxides (Pecos Mine Piles, New Mexico). Finally, the present mineralogical reconstruction shows consistency with the mineralogy of quartz-rich epithermal veins (Mother-Lode ores).

Table 2. Major elements components (oxides) of Valenciana tailing material and the control soil.

Component	Tailings (wt%)	Soil (wt%)
SiO_2	72.6	70.7
Al_2O_3	5.8	13.3
Fe_2O_3	1.9	6.4
CaO	7.2	0.2
MgO	2.5	0.7
Na_2O	0.3	0.4
K_2O	2.7	2.3

An important result related to the mineralogical phases is that the environmental risk for generation of acid rock drainage (ARD) associated with this tailing material is very low, due to the low concentration of sulfide (low acid generation capacity) and the abundance of carbonates and feldspar ($KAlSi_3O_8$) (Table 3), with high neutralization capacity (Morton et al. 2000; Oelsner 2001). Actually, the paste and rinse pH of the tailing samples is between 7.6 and 8.1

Table 3. General mineralogical reconstruction of the Valenciana tailing material and the control soil (based on bulk chemistry and XRD).

Valenciana tailing		Soil	
Quartz, SiO_2	57 %	Quartz	46 %
Orthoclase, $KAlSi_3O_8$	16 %	Kaolinite	30 %
Calcite, $CaCO_3$	8 %	Orthoclase	14 %
Kaolinite, $Al_2Si_2O_5(OH)_4$	6 %	Hematite	6 %
Gypsum, $CaSO_4$-$2H_2O$	3 %	Plagioclase	3 %
Magnesite, $MgCO_3$	3 %	Chlorite	1 %
Plagioclase, $NaAlSi_3O_8$	2 %	Gypsum	1 %
Chlorite, $Mg_5Al(Si_3Al)O_{10}OH_8$	2 %	Magnesite	<1 %
Hematite, Fe_2O_3	2 %		
Sulfides (ionic forms)	<1 %		

Previous analysis of tailing material from the Guanajuato Mine District reflected the presence of 29 trace elements in concentrations of ppm and ppb (Basulto 1984; Ramos 1991). Results of chemical analyses for some trace elements are shown in Table 4. Different authors report different trace elements in mine waste material (Grimalt et al. 1999; Wong et al. 1999), since the trace elements can greatly vary from place to place due to the local geology and geochemistry of the mineral ore deposits. But, Allan (1995) considers that Cr, Ni, Cu, Zn, As, Cd, and Pb, are the most common trace elements of mine tailings.

Table 4. Concentration in ppm (mg/kg) of some trace elements. Data: average $\pm$ standard deviation (Oelsner, 2001; García-Meza et al., 2003)

	Average	Min. Value	Max. Value
Be	3.6 $\pm$ 2.36	0.8	3.6
Cr	72.9 $\pm$ 36.6	23.5	130.4
Mn	202.2 $\pm$ 193.2	66.5	570.6
Co	7.6 $\pm$ 3.6	2.6	12.9
Ni	38.7 $\pm$ 28.6	11.5	110.0
Cu	87.2 $\pm$ 76.3	32.6	300.0
Zn	409.5 $\pm$ 462.6	148.1	1271.0
As	43.0 $\pm$ 22.0	5.1	63.1
Se	1.3 $\pm$ 0.8	0.4	3.4
Cd	10.2 $\pm$ 4.4	0.6	35.0
Sb	7.8 $\pm$ 8.4	0.5	19.0
Tl	1.1 $\pm$ 1.0	0.0	2.2
Pb	59.9 $\pm$ 24.5	22.1	93.8

The results of the sequential extraction on the tailing material show that Cr, Ni, Cu and Zn are primarily adsorbed onto the mineral phases, especially to oxides-sulfides crystal structure, but Cd and Pb seem to be bound to secondary minerals (Table 5). It is known that primary and secondary minerals are the ultimate and most important sinks of trace elements in the near surface of soils, and the trace elements absorbed onto this fraction are normally unavailable to plants (Ma & Rao 1997). However, the bioavailable Cu represents an important proportion of its total amount (30.91% Cu), while the sum of its last three fractions (bioavailable, water soluble and extracted with a weak acid, acetic acid) represents up to 46% of total Cu. Additionally, the 59% of Cd, and 42% of Pb are in the water-soluble fraction, and the 11.5% of total Zn is bioavailable. These results indicate that leaching to groundwater, mobility, and bioavailability are potential risk related with Cu, Cd, Pb and Zn. Finally, Cr, Cu, Zn and Cd totals are above the acceptable limits for soils (Kabata-Pendias & Pendias 1992). The total concentrations of these metals are similar to the results obtained by Morton et al (2000).

Table 5. Concentration of some trace elements extracted sequentially with different matrix for the determination of fractions adsorbed to (1) oxides and other crystal structures (sulfides); (2) secondary minerals; (3) bioavailable fraction; (4) water-soluble; and (5) potential bioavailable fraction. The total indicated is the sum of the 5 fractions.

Extracted with:	**Cr**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
(1) HNO_3+HCl	102.91	68.05	102.49	626.53	6.22	27.39
(2) HNO_3 50%	13.12	17.22	35.16	199.86	2.44	14.48
(3) EDTA	4.38	7.75	78.64	109.42	1.52	11.94
(4) Water	3.48	10.03	34.13	17.05	14.67	39.08
(5) CH_3COO	0.06	0.25	3.92	0.17	---	0.01
Total	**123.95**	**103.30**	**254.34**	**953.03**	**24.85**	**92.90**

Concentration in ppm (mg/kg).

Berger et al. (2000) described a geochemical process for drainage water, which implies that when the calcite is dissolved, the pH increases (consumes acid) and, at higher pH, metals may precipitate as Fe-Al hydroxides: The hydroxide precipitates may scavenge metals from the solution through sorption reactions. Thus, metal concentration decreases via these precipitation and adsorption reactions (Cu, Pb), or by simple dilution (Zn). The former may explain why the groundwater is richer in Zn, while Fe concentration decreases towards the groundwater (Morton et al. 2000).

The Sociedad Cooperativa Minero Metalúrgica Santa Fe de Guanajuato (SFG-CS) has considered rehabilitation of mine-tailing piles through vegetation, as a control of the dispersion of fine particles (eolian). As already mentioned, under the present conditions this mine tailing material does not posses suitable conditions for healthy plant development. First, the plants to be chosen for tailing piles reclamation must be able to grow and develop within the poor physical structure (coarse texture, poor water retention, erosion) and the unsuitable nutrient capital (less than 1%). Furthermore, artificial fertilization might be ineffective due to the low CEC (added nutrients might be easily leached). Additionally, the plants must be metal-tolerant, such as Cu, Cd and Pb since the sum of the water-soluble fraction and the bioavailable fraction of these metals results in high proportion

(40% Cu, 46% Cd, and 55% Pb), which could severely limit the plant development (Ma & Rao 1997). Finally, it is not well known what the effects of the vegetation will be in some mine-tailings characteristics, closely related with chemical speciation (pH, redox potential), which may enhance the leaching, mobility and bioavailability of trace metals. Experimental work on the tailing material, focusing on column leaching experiments and other sequential experiments (more trace elements such as As, Se and Hg) will be useful to complement the current data and to predict the environmental impact associated with mine-waste materials, as well as for a better environmental assessment of the effects of vegetation campaigns on the surface of the tailing piles.

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