Arsenic phase distribution in Zimapán mine tailings, Mexico

M. Méndez[1] and M. A. Armienta[2]

[1] *Posgrado en Ciencias de la Tierra, UNAM*

[2] *Instituto de Geofísica, UNAM, México, D.F.*

RESUMEN

En Zimapán, México, se ha contaminado el agua subterránea con arsénico debido a fuentes naturales y antropogénicas. La lixiviación de los jales mineros ha sido una de las fuentes debidas a la actividad humana. Se presenta una investigación sobre la movilidad del arsénico en cuatro depósitos de jales mediante métodos químicos. Se consideraron los valores de conductividad, pH y concentraciones de sulfatos en lixiviados acuosos de los jales, como indicadores de las condiciones físico-químicas capaces de influir en la movilidad del arsénico. Además, se utilizó la extracción secuencial selectiva de los jales, para determinar la distribución del arsénico en las fracciones asociadas con diferente disponibilidad. Se encontraron altos contenidos de arsénico (desde 2550 mg/kg hasta 21 400 mg/kg) en todos los jales. La mayor parte del contaminante se asoció a las fracciones residual, considerada más estable, y a la fracción de oxihidróxidos de Fe y Al. El arsénico en las fracciones soluble e intercambiable (hasta 1560 mg/kg) puede movilizarse y contaminar al ambiente. Por otro lado, la calcita presente en los depósitos de jales puede disminuir la lixiviación del arsénico. Las concentraciones de arsénico y sulfatos, la especiación y el pH, indican que los jales más nuevos son una fuente importante de contaminación. Se encontró que aun formas estables del arsénico pueden movilizarse y representar un riesgo ambiental. Sería recomendable mezclar los jales con óxido de calcio o calcita para incrementar el pH y prevenir la disolución del arsénico ligado a carbonatos.

PALABRAS CLAVE: Arsénico, jales, minería, Zimapán, México, fraccionamiento geoquímico.

ABSTRACT

Arsenic contamination of groundwater has been linked to natural and anthropogenic sources in Zimapán, Mexico. Leaching of mine tailings was identified as one of the man-made causes of environmental arsenic pollution. Arsenic mobility from four tailing piles was studied by chemical procedures. Conductivity, concentration of sulfates, and pH in aqueous leachates were used as indicators of the physico-chemical conditions influencing arsenic mobility. Arsenic geochemical fractionation was determined through sequential extraction from the tailings. High arsenic contents from 2550 mg/kg to 21 400 mg/kg were found in all the tailings. Most arsenic was contained in the residual considered more stable, and in iron and aluminium oxyhydroxides fractions. Arsenic found in the soluble and exchangeable fractions (up to 1560 mg/kg) may mobilize easily and pollute the environment. On the other hand, presence of calcite in the tailings may decrease arsenic leaching. Arsenic and sulfate contents, speciation, and pH, indicate that the recent pile is a major source of pollution. This shows that even stable forms of arsenic may mobilize and may represent an environmental risk. Higher pH is observed to prevent the dissolution of arsenic bound to carbonates. Hence, addition of calcium oxide or calcite to the tailings is recommended.

KEYWORDS: Arsenic, solid speciation, mine tailings, Zimapán, México.

INTRODUCTION

Water contamination by arsenic is a worldwide environmental concern. Groundwater arsenic levels above the permissible limits prescribed for drinking water have been found in several areas of Mexico including Comarca Lagunera (Durango-Coahuila states), Los Azufres (Michoacán), San Antonio (Baja California Sur), Durango (Durango), Hermosillo (Sonora), Zacatecas (Zacatecas), Acámbaro (Guanajuato); Puebla, (Puebla), Cuautla (Morelos), Delicias (Chihuahua) and Zimapán (Hidalgo) (Cebrián *et al.,* 1983; Quinto *et al.,* 1995; Gutiérrez *et al.,* 1996; Armienta *et al.,* 1997; Birkle *et al.,* 1998; Carrillo and

Drever, 1998; Wyatt *et al.,* 1998; Simeonova, 1999; Rosas *et al.,* 1999; Alarcón *et al.,* 2001) (Figure 1). At Zimapán, in Hidalgo state, water-rock interactions polluted the deep wells and arsenic concentrations of up to 1.1 mg/L have been found. The extraction and processing of silver, lead and zinc ores has been identified as one of the man-made causes of environmental arsenic pollution in shallow dug wells (Armienta *et al.,* 1993; Armienta *et al.,* 2001; García *et al.,* 2001). Arsenic minerals occur in association with deposits of Pb-Ag-Zn. Arsenopyrite (FeAsS) is the main arsenic mineral, but also scorodite ($FeAsO_4.2H_2O$), lolingite ($FeAs_2$), tennantite (($Cu,Fe)_{12}As_4S_{13}$), adamite ($Zn_2(AsO_4)(OH)$, mimetite ($PbS(AsO_4)3Cl$) and hidalgoite ($PbAl_3(AsO_4)(SO_4)(OH)_6$) are
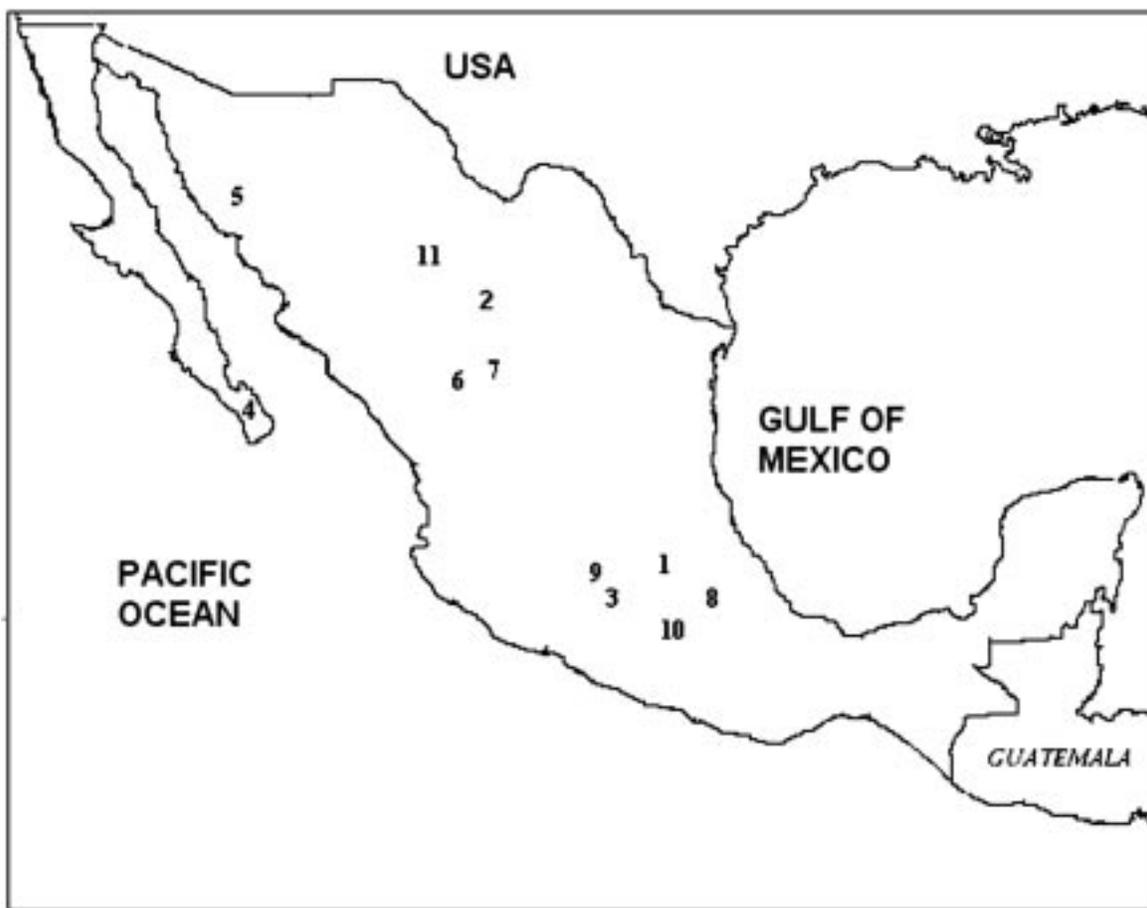
Fig. 1. Map of Mexico showing sites where groundwater arsenic levels above the drinking water standard have been reported. (1) Zimapán (study area), (2) Comarca Lagunera, (3) Los Azufres, (4) San Antonio, (5) Hermosillo, (6) Durango, (7) Zacatecas, (8) Puebla, (9) Acámbaro, (10) Cuautla, (11) Delicias.

present in the Zimapán area (Simons and Mapes-Vázquez, 1956; García and Querol, 1991). The ore processed at Zimapán may be thus enriched in arsenic. One ore sample had an arsenic concentration of 16 % wt. (Ongley *et al.,* 2001); thus, wastes may include a high concentration of arsenic (Armienta and Rodríguez, 1996). Tailing piles from the flotation process have accumulated in Zimapán for more than 60 years. Most of the current exploitation occurs outside the Zimapán basin, but old tailings near the edge of the town are still an arsenic pollution source. Arsenic concentrations up to 0.437 mg/L were measured in shallow wells located near such tailings (Armienta *et al.,* 1993).

Arsenic in the environment occurs as arsenous acid and products of its dissociation (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$), arsenic acids (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$), arsenites, arsenates, methylarsenic acid $H_3AsO_3CH_3$, dimethylarsinic acid $(CH_3)_2AsO_2H$, arsine AsH_3, dimethylarsine $HAs(CH_3)_2$ and trimethylarsine $As(CH_3)_3$ (Bodek *et al.,* 1988). Environmental arsenic mobility may be limited by sorption on soils and sediments. This process takes place mainly on Fe and Al

hydrous oxides, clays, and carbonate surfaces. Arsenic may also co-precipitate with Fe oxides (Bodek *et al.,* 1988; Dzombak and Morell, 1990; Romero, 2000).

The mobility of arsenic in sediments depends mainly on three conditions of the sediments: their physical form, their chemical speciation and their environmental conditions (Mok and Wai, 1994). Tailings are sediments resulting from settling of wastes from flotation processing of ore. Arsenic may be retained in different sediment fractions on a temporary or permanent basis. The capability of various sediment constituents to accumulate contaminants, and their mobility, may be evaluated by sequential extraction procedures (Tessier *et al.,* 1979; Salomons, 1993). Sequential extraction of metal fractions has been used to determine environmental mobility and toxic potential of metals in soils and sediments (Abdel-Saheb *et al.,* 1994; Li and Shuman, 1996; McLaren *et al.,* 1998; Land *et al.,* 2002; Cai *et al.,* 2002). It has also been used to study the geochemical processes of metals in tailings (Dold and Fontoboté, 2001). In the sequential fractionation scheme, the metal in solution from a weak salt or water ex-

traction is referred to as potentially mobile. Other fractions are considered immobile unless specific environmental conditions are induced in the soil or sediment environment (McGowen and Basta, 2001).

We evaluated the geochemical mobility of arsenic in Zimapán tailings as part of an assessment of environmental hazard. Mobility was studied in four tailing piles by adopting a sequential extraction procedure. The mineralogy and some physical and chemical parameters including pH, conductivity and sulfate concentration were also considered. Differences were expected both in concentration and in As distribution depending on the mineralogy and age of the deposits.

METHODOLOGY

Samples were obtained from four different tailing piles (Figure 2). Location was measured with a hand-held Garmin GPS II Plus. For each pile, one sample was collected near the top (below the cover) and another near the bottom, digging with a shovel into less altered material. The samples were air-dried, quartered and sieved through a 1.70 mm mesh. The physical and chemical determinations were performed on sieved samples.

Twenty grams of sample were added to 100 ml of deionized water, agitated for one hour and filtered through 0.45 μm. The filtrate was used for conductivity and sulfate determinations. One gram of sample was added to 10 ml of deionized water for pH measurement by potentiometry. Conductivity and pH were determined with a Conductronic PC18 instrument. The equipment was calibrated with pH=4, pH=7, and pH=10 buffers, and with a solution of 1000 mg/L of NaCl corresponding to a conductivity value of 1990 μS/cm. Sulfate was analized by turbidimetry (Armienta *et al.,* 1994) with a UV-visible diode array spectrophotometer Hewlett Packard 8452a.

Arsenic in different geochemical fractions of the tailings was determined with a modified method based on the sequential extraction scheme developed by Tessier *et al.* for transition metals (1979), modified by McLaren *et al.* (1998)
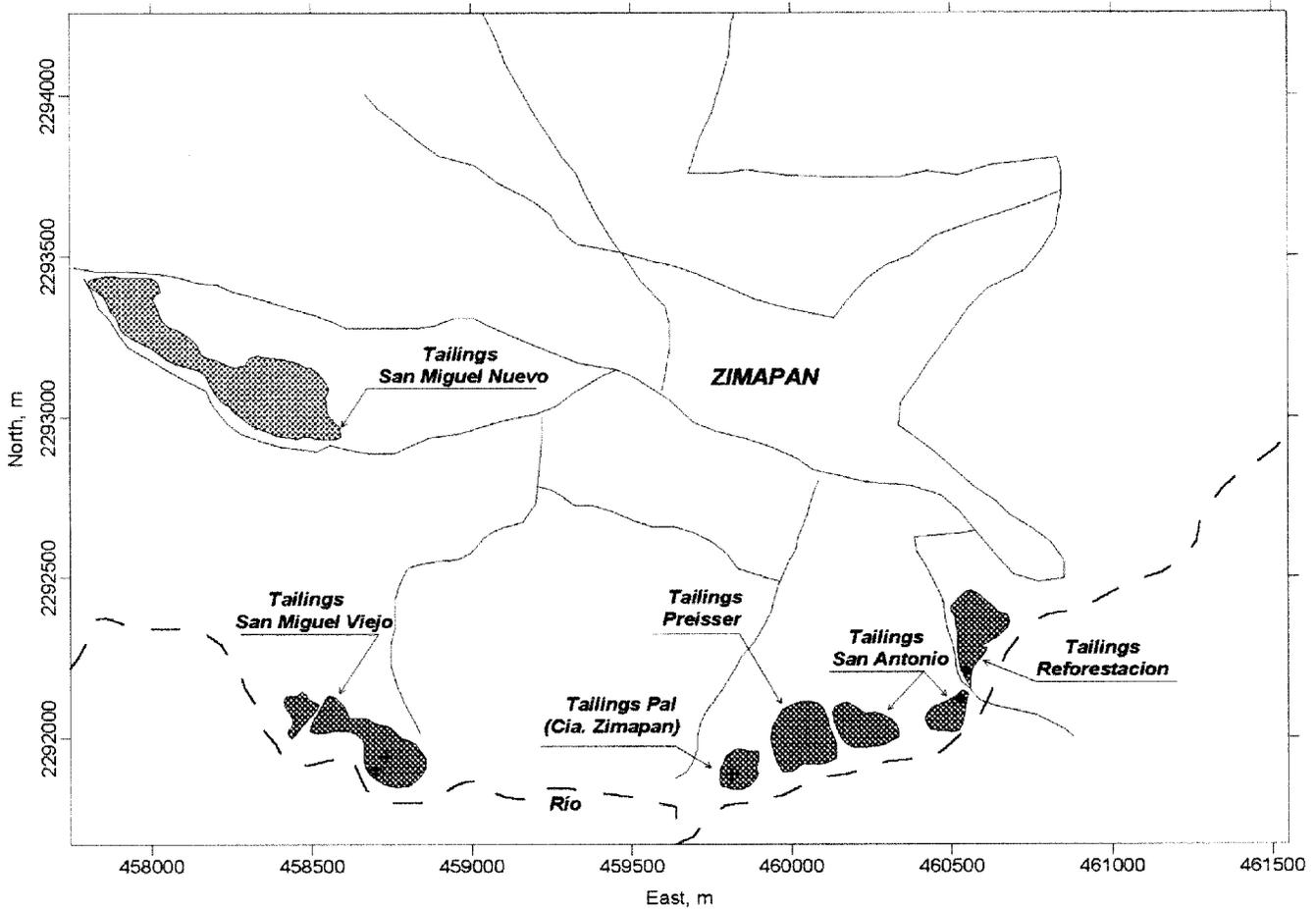
Fig. 2. Sampling locations, UTM coordinates. SMV =San Miguel Viejo, CMZ= Cía. Zimapán, SA=San Antonio, R= Reforestación. The crosses correspond to the sampled points.

for arsenic. In the first extraction step to obtain soluble arsenic, 2 g of the sample was leached with deionized water, agitated for 24 h and centrifuged at 3500 rpm, arsenic concentration was measured in the supernatant. In the next step, the residue was treated with 25 ml of $NaHCO_3$ (0.5M), agitated for 16 h and centrifuged; exchangeable arsenic was determined in the supernatant. The residue was added to 25 ml of NaOH (0.1M), shaken for 16 h and centrifuged. Arsenic bound to Fe and Al hydroxides was determined in the supernatant. The residue was treated with 25 ml of 1M HCl and shaken for 16 h. After centrifugation, the liquid was analyzed for arsenic bound to carbonates. The residue was treated with a mixture of 10 ml HF (conc.) and 10 ml $HClO_4$ (conc.) and heated to near dryness. It was then treated with 1 ml $HClO_4$ + 10 ml HF and heated again to near dryness; 1 ml $HClO_4$ was added, heated until the appearance of white fumes, dissolved with 12 M HCl and diluted to 25 ml with deionized water. The concentration of residual arsenic was determined in this solution.

Arsenic concentration in solutions from sequential extractions was analyzed by flameless atomic absorption spectrometry with a GBC 903 GF 2000 graphite furnace atomic absorption spectrophotometer (GFAAS). Graphite furnace atomic absorption spectrometry is a common analytical technique used in the routine determination of arsenic (Iverson *et al.,* 1979; Burguera and Burguera, 1997; Dakuzaku *et al.,* 2001; Matera and Le Hécho, 2001). The lowest detection level was 0.01 mg/L of arsenic. Differences lower than 10 % were found in duplicates subjected to the overall procedure. Lack of standard samples reporting sequential extraction concentrations prevented the use of reference materials. Nevertheless, to control the accuracy, bulk analysis of a total acid digestion (Armienta and Juárez, 1986) of every sample was done. The sums of the sequential extraction and the bulk analysis showed a fairly good agreement within 15 % difference.

X-ray diffraction determinations were performed with a JEOL DX-GERP12 powder diffractometer with CuKα radiation.

RESULTS

Visible physical characteristics, mineralogy, pH, sulfates and total arsenic concentrations, and conductivity of tailings samples are shown in Table 1. "Reforestación", "San Antonio", and "Compañía Minera Zimapán" are old deposits showing chemical reaction crusts and oxidation processes on their surface. "San Miguel Viejo" is a recent tailing pile. Samples with number 1 correspond to those collected from the top and samples identified with number 2 correspond to those collected from the bottom of the tailing piles.

Oxidation-reduction reactions in the tailings may result in sulfate production, low pH and iron hydroxide pre-

cipitation. These processes may be occurring through the following main reactions for a tailing pile containing Fe, and As sulfides (Blowes *et al.,* 1991; Rimstidt *et al.,* 1994):

$$FeS_2+7/2O_2+H_2O \rightarrow Fe^{2+}+2SO_4^{2-}+2H^+ \tag{1}$$
$$Fe^{2+}+1/4O_2+H^+ \rightarrow Fe^{3+}+1/2H_2O \tag{2}$$
$$FeS_2+14Fe^{3+}+8H_2O \rightarrow 15Fe^{2+}+2SO_4^{2-}+16H^+ \tag{3}$$
$$Fe^{2+}+1/4O_2+5/2\,H_2O \rightarrow Fe(OH)_3+2H^+ \tag{4}$$
$$4FeAsS+13O_2+6H_2O \rightarrow 4Fe^{2+}+4SO_4^{2-}+4H_2AsO_4^-+4H^+ \tag{5}$$
$$FeAsS+13Fe^{3+}+8H_2O \rightarrow 14Fe^{2+}+SO_4^{2-}+14H^++H_2AsO_4(aq) \tag{6}$$
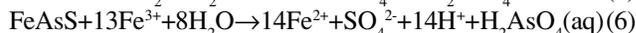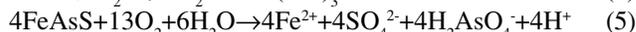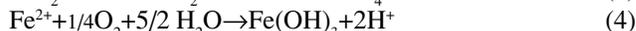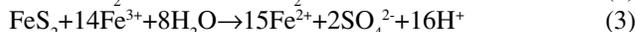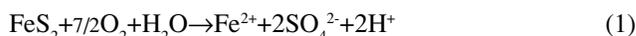
Mineralization at Zimapán is localized in massive limestone layers, as skarn and chimney/manto (Villaseñor *et al.,* 1987; García and Querol, 1991). The wastes produced in the extraction process may thus include limestone, and may give rise to the following neutralization reaction of the acid produced by sulfide oxidation:

$$CaCO_3 + H^+ \Leftrightarrow Ca^{2+} + HCO_3^- \;. \tag{7}$$
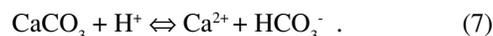
Arsenic geochemical fractionation (solid speciation), mineralogy and main physico-chemical characteristics for each of the tailings are discussed below.

Site "San Antonio"

The two samples obtained from these tailings showed different mineralogy (Table 1) and total arsenic contents (14 600 mg/kg in SA1 and 4000 mg/kg in SA2). Calcite and gypsum were the main phases in SA1, while gypsum and arsenopyrite were identified in SA2. Higher SO_4^{2-} contents and a lower pH value were measured in SA2 compared to SA1. Arsenic was mostly bounded to Fe and Al hydroxides and in the residual fraction in SA1 (Table 2). A low As proportion was present in the most labile fractions (soluble, exchangeable and bound to carbonates), as shown in Figure 3. The high concentration of sulfates and conductivity of this sample are evidence for the occurrence of oxidation reactions as reported above (reactions 1 through 6). The slightly basic pH of 7.6, resulting from the neutralization reaction of limestone (reaction 7), may be responsible for the observed patterns of As fractionation: at this pH value, iron and Al hydroxides form a precipitate. Sorption on these minerals is an important control of As in natural systems (Dzombak and Morel, 1990; Bowell, 1994; McLaren *et al.,* 1998), and may significantly retain the As released by the oxidation process.

Higher sulfate concentration was found in SA2. XRD showed gypsum as the main mineral, arsenopyrite was identified as a possible phase in this sample. The majority of the arsenic was in the residual phase (52 %); arsenic in this phase may thus exist mainly as arsenopyrite. On the other hand, the exchangeable, soluble and carbonate fractions accounted for more than one third of the total arsenic (Figure 4). Oxidation of sulfides is reflected in the acidic pH of 6.4, and in high sulfate concentration resulting from reactions (1), (3),

Table 1

Physical and chemical characteristics of tailings. (p) predominant, (a) abundant, (s) very low, (?) uncertain

Tailings	Location		Physical features	Mineralogy	pH	Sulfates ppm	Conductivity μS/cm	As (total) ppm
	East m	North m						
San Antonio (SA1)	460528	2292119	Reddish-brown, Limestone clasts with caliche, vegetation	calcite (p) gypsum (a)	7.6	1639	2320	14600
San Antonio (SA2)			Reddish-brown, Limestone clasts with caliche, vegetation	gypsum (p) arsenopyrite (?)	6.4	2207	2750	4000
Reforestación (R1)	460546	2292207	Lime covered, limestone clasts with caliche, vegetation	gypsum (p) arsenopyrite (s)	7.5	1572	2290	6140
Reforestación (R2)			Lime-covered, limestone clasts with caliche, vegetation	gypsum (p) calcite(?), jarosite (s) quartz (?)	6.5	1671	2380	2550
Compañía Minera Zimapán (CMZ)	459813	2291888	Reddish-brown without vegetation	gypsum(p), quartz (?) jarosite (?)	3.3	1736	25800	8300
San Miguel Viejo (SMV1)	458731	2291943	Gray, silt-clay, without vegetation	calcite(p), quartz (a) gypsum (s), arsenopyrite (s)	7.6	512	2280	21400
San Miguel Viejo (SMV2)	458698	2291904	Gray, silt-clay, without vegetation	Calcite(p), quartz (a), Gypsum (s) arsenopyrite (s)	7.6	1463	2230	18310
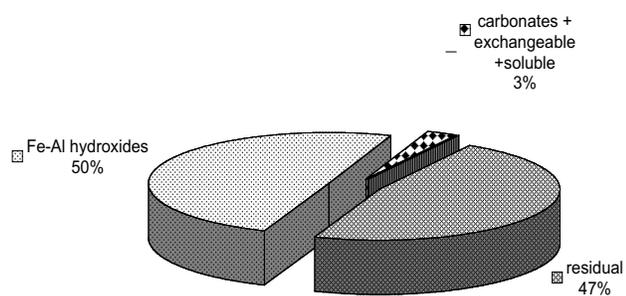
Fig.3. Arsenic fractionation (percentages) in sample SA1.

(5) and (6). Arsenic may thus be mobilized through arsenopyrite oxidation which in turns lowers the pH. Arsenic fractionation also indicates that it may be released from the deeper layers of these tailing deposits.

Site "Reforestación"

These tailings are about 10 m from "San Antonio". Different mineralogical characteristics were observed in these two deposits. Calcite, gypsum, and arsenopyrite; gangue minerals like quartz; and secondary minerals like jarosite were identified in this pile (Table 1). Mixing with lime near the top of this tailing pile was taking place during the sampling campaign. Added lime favors gypsum formation by the reaction of sulfide oxidation products like SO_4^{2-} (Blowes *et al.,* 1991) with $Ca(OH)_2$ through:

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^- \qquad (8)$$

$$SO_4^{2-} + Ca^{2+} \Leftrightarrow CaSO4\downarrow . \qquad (9)$$

Calcium hydroxide addition also increases the pH to 7.5 in sample R1. Most of the arsenic (59%) was bound to

Table 2

Arsenic distribution in geochemical phases of Zimapán tailings

Sample	Soluble ppm	Exchangeable ppm	Bound to Fe and Al Hydroxides ppm	Bound to Carbonates ppm	Residual ppm
San Antonio (SA1)	2	380	7275	22	6925
San Antonio (SA2)	4	1345	440	120	2090
Reforestación (R1)	2	120	3650	51	2325
Reforestación (R2)	3	160	670	68	1650
Compañía Minera Zimapán	17	418	3460	595	3810
San Miguel Viejo (SMV1)	20	1370	5920	2840	11250
San Miguel Viejo (SMV2)	14	1560	5055	2070	9610
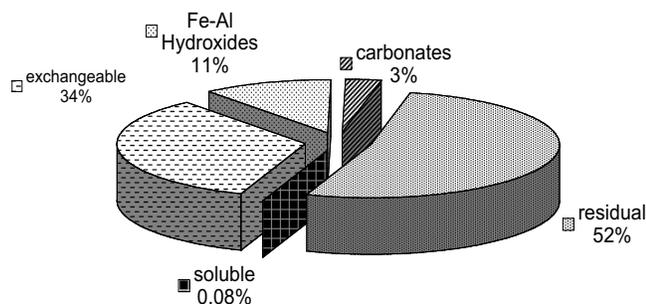
Fig. 4. Arsenic fractionation (percentages) in sample SA2.
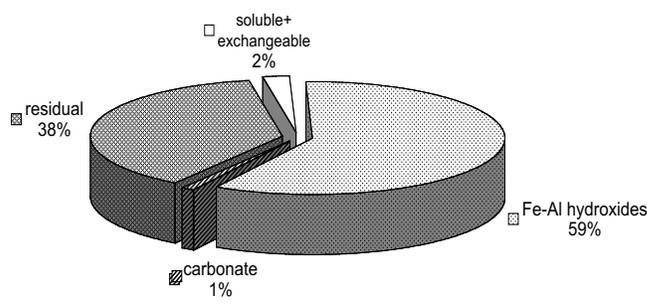
Fig. 5. Arsenic fractionation (percentages) in sample R1.

Fe and Al hydroxides (Figure 5). The residual fraction accounts for almost all the remaining arsenic (38%). A higher proportion of arsenic was obtained in the residual fraction of sample R2 (65%), followed by arsenic bound to Fe and Al hydroxides (Figure 6). Exchangeable and soluble fractions accounted for only 6% of the total As but had high arsenic content (163 mg/kg). The As concentration in a sample close to the bottom of the pile may pollute the shallow aquifer by leaching and infiltration through the unsaturated zone. A leachate pool has been observed at the base of this tailing. A contaminated well (0.25 mg/L of As in 1997) is located about 30 m southeast of this pile.

Site "Compañía Minera Zimapán"

This is one of the oldest tailing piles at Zimapán (older than 50 years). It has an uncovered surface, without any vegetation or particulate material. This lack of surface protection favors weathering, transformation of sulfides to sulfates and arsenic solubilization. Low pH (3.3) and high conductivity (25 800 µS/cm) (Table 1) of this tailing (CMZ) suggest the active oxidation process. Oxidation reactions release arsenic to the soluble and exchangeable phases, secondary minerals like jarosite may also be formed by the oxidation products. The percentage of As in the hydroxides (41.6 %)

Fig. 6. Arsenic fractionation (percentages) in sample R2.

Fig. 7. Arsenic fractionation (percentages) in sample SMV1.
Available corresponds to the soluble plus exchangeable fractions.
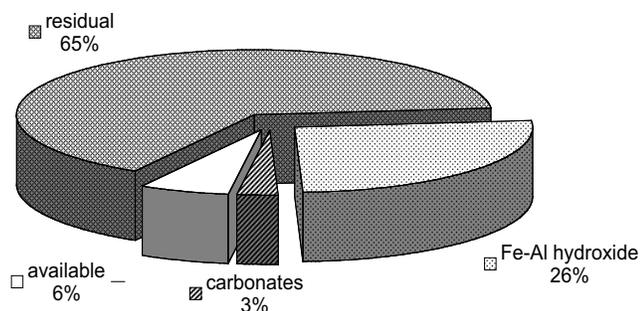
and carbonate (7.2 %) phases indicate that part of the As released has been sorbed onto the Fe and Al hydroxides and on the carbonates. Besides retention by sorption, arsenic as arsenate could also be substituted for sulfates in the structure of jarosite (Foster *et al.,* 1998). The low pH measured in the tailings indicates that rain may produce an acid solution capable of dissolving the carbonate phase and mobilizing the As contained in this phase. Low pH results in less stability of As bound to carbonates than the As associated to this phase in other tailings. With its high content in the more labile phases (435 ppm of As soluble and exchangeable), this pile is a potential pollution source to the aquifer. A leachate stream with 16 g As/L was observed near CMZ pile (Ongley *et al.,* 2001). The settling of this pile over permeable alluvial material composed mainly of gravel, sand, silt and clay (Carrillo-Martínez and Suter, 1982; Armienta and Rodríguez, 1996) increases its hazard, since it favors As infiltration to the groundwater. Release of As from this tailings has polluted nearby dug wells with up to 0.44 mg/L of As (Rodríguez and Armienta, 1997).

Site "San Miguel Viejo"

This is one of the youngest tailing piles at Zimapán town. It consists of very fine gray material currently deposited in the northwest part, without any mineral or vegetal cover. Similar pH and conductivity values and sulfate concentrations were found at the two sampled points (Table 1). Most of the arsenic is in the residual phase both, in the top and the bottom samples. Arsenic distribution shows a higher arsenic sorption on Fe and Al hydroxide surfaces than on calcite (Figure 7). The observed conductivity and sulfate concentration indicate that sulfide oxidation is taking place. Oxidation of arsenopyrite, identified in this sample, appears to release arsenic mainly to the Fe and Al hydroxide fractions, but also to the soluble and exchangeable fractions resulting on high labile As contents (1390 mg/kg).

Lower total arsenic concentration was found in the SMV2 sample as compared to SMV1 (Table 1). Most of the arsenic is in the residual phase (Table 2). Carbonates play an important role in As distribution in both samples. Abundance
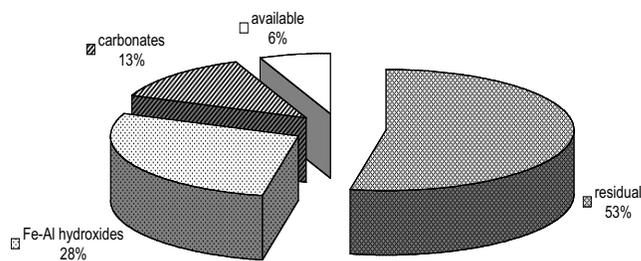
of calcite increases the pH and favors As sorption on carbonate and hydroxide fractions. The percentage of As in the exchangeable and soluble fractions is not very high (9 %), but their concentrations (1560 mg/kg exchangeable plus 14 mg/kg soluble) are important.

DISCUSSION

A negative correlation (r = -0.92) was found between sulfate and total As concentrations in the tailings (Figure 8). This negative correlation seems contradictory since both anions may result from arsenopyrite oxidation, that releases sulfate and arsenic (Rimstidt *et al.,* 1994). It might be due to the particular chemistry and mobility of each anion. Sulfate may react with Ca^{2+} from limestone or lime dissolution, precipitating as gypsum or anhydrite that remain in the tailings (Table 1). On the other hand, part of the arsenic may be sorbed on the different tailings fractions but a significant proportion may be transported by water away from the tailings. No correlation was found between As and pH, or As and conductivity, showing the complexity of the geochemical processes occurring in the tailings, including neutralization reactions with limestone and lime, and the formation of secondary minerals like jarosite and gypsum.

Higher As concentrations were found in the more recent tailings, compared to the older ones. Besides different mineralogy of the processed ore, many years of arsenic mobilization from the old piles may have decreased As contents in the older tailings, thus giving rise to this difference. The residual and Fe and Al oxide fractions contained most of the As in both; the recent and older piles. This fractionation emphasizes the importance of Fe and Al hydroxides in As retention. Tailings should be added to sites in which this process has previously been reported (Dzombak and Morel, 1990; Bowell, 1994; Carrillo and Drever, 1998). Arsenic pollution of a dug well (0.29 mg/L in October 2001) near "San Miguel Viejo" site shows that mobilization of arsenic is currently taking place also in the more recent deposits. Furthermore, high arsenic contents (up to 6575 mg/kg) from weathered tailings have also been found in Tolimán river sediments (García *et al.,* 2001).
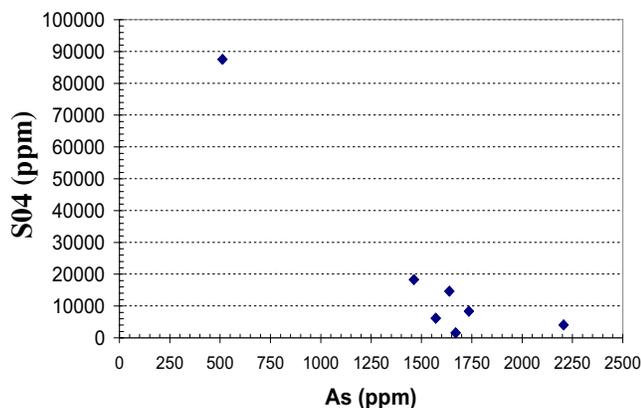
Fig. 8. Total arsenic versus sulfate concentrations (mg/kg) in the tailings.

CONCLUSIONS

The occurrence of arsenic minerals in Zimapán tailings results in high As concentrations. The arsenic contents of the soluble and exchangeable phases make tailings a potential pollution source at Zimapán. Arsenic in these fractions is mobile and may be leached to the groundwater.

Fe and Al hydroxides are important phases in all samples and limit arsenic mobility by sorption on this less mobile fraction. Calcite may control arsenic leaching by increasing the pH, thus favoring precipitation and As sorption.

All of the sampled tailings constitute an environmental hazard. Total arsenic contents, arsenic speciation, and the fine and little cemented characteristics, suggest that the recent pile "San Miguel Viejo" represents a higher environmental hazard than the other piles at Zimapán.

Use of calcite or lime and ground protection measures should be adopted to prevent arsenic dispersion to the environment.

ACKNOWLEDGEMENTS

BIBLIOGRAPHY

ABDEL-SAHEB, I., A. P. SCHWAB, M. K. BANKS and B. A. HETRICK, 1994. Chemical characterization of heavy-metal contaminated soil in southeast Kansas. *Water Air Soil Poll. 78,* 73-82.

ALARCÓN, H.M.T., F. I. MONTENEGRO, N. P. ROMERO, D. I. R. MARTÍN and V. R. TREJO, 2001. Contenido de arsénico en el agua potable del valle del Guadiana, México. *Ing. Hidr. en México XVI(4),* 63-70.

ARMIENTA, M. A. and F. JUÁREZ, 1986. Métodos Cuantitativos Vía Húmeda para el Análisis de Rocas, Comunicaciones Técnicas IGF, Serie Investigación No.23, 31 pp.

ARMIENTA, M. A., R. RODRÍGUEZ, G. VILLASEÑOR, A. AGUAYO, N. CENICEROS, F. JUÁREZ and T. MÉNDEZ, 1993. Estudio de Reconocimiento de la Contaminación por Arsénico en la Zona de Zimapán, Hidalgo, Informe Técnico il., Informe del IGF al Municipio de Zimapán, Hgo., noviembre 1993, 60 pp.

ARMIENTA, M. A., V. ZAMORA and F. JUÁREZ, 1994. Manual para el Análisis Químico de Aguas Naturales en el Campo y en el Laboratorio, Comunicaciones Técnicas IGF, Serie Docencia y Divulgación No.4, 86pp.

ARMIENTA, M. A. and R. RODRÍGUEZ, 1996. Arsénico en el Valle de Zimapán, México: Problemática Ambiental. *Rev. MAPFRE Seguridad 63,* 33-43.

ARMIENTA, M. A., R. RODRÍGUEZ, A. AGUAYO, N. CENICEROS and G. VILLASEÑOR, 1997. Arsenic Contamination of Groundwater at Zimapán, México. *Hydrogeology J. 5,* 39-46.

ARMIENTA, M. A., G. VILLASEÑOR, R. RODRÍGUEZ, L. K. ONGLEY and H. MANGO, 2001. The role of arsenic-bearing rocks in groundwater pollution at Zimapán Valley, México. *Environ. Geol. 40,* 571-581.

BIRKLE, P., B. MERKEL, V. TORRES-RODRÍGUEZ and E. GONZÁLEZ-PARTIDA, 1998. Efectos ambientales por la descarga de salmueras en el campo geotérmico de Los Azufres, México, Resúmenes, 1ª. Reunión Nacional de Ciencias de la Tierra, México. D.F., 21-25 septiembre 1998, p. 127.

BLOWES, D. W., E. J. REARDON, J. L. JAMBOR and J. A. CHERRY, 1991. The formation and potential im-

portance of cemented layers in inactive sulfide mine tailings. *Geochim. Cosmochim. Acta 55,* 965-978.

BODEK, I., W. J. LYMAN, W. F. REEHL and D. H. ROSENBLATT, 1988. Environmental Inorganic Geochemistry, Pergamon Press N.Y.

BOWELL, R. J., 1994. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem. 9,* 279-286.

BURGUERA, M. and J. L. BURGUERA, 1997. Analytical methodology for speciation of arsenic in environmental and biological samples. *Talanta 44,* 1581-1604.

CAI, Y., J. C. CABRERA, M. GEORGIADIS and K. JAYACHANDRAN, 2002. Assessment of arsenic mobility in the soils of some golf courses in South Florida. *Sci. Total Environ. 291,* 123-134.

CARRILLO, A. and J. I. DREVER, 1998. Adsorption of arsenic by natural aquifer material in the San Antonio – El Triunfo mining area, Baja California, México. *Environ. Geol. 35,* 251 – 257.

CARRILLO-MARTÍNEZ, M. and M. SUTER, 1982. Tectónica de los alrededores de Zimapán, Hidalgo y Querétaro. *En:* Alcayde M. and De Cserna Z (eds) Libro guía de la excursión geológica a la región de Zimapán y áreas circundantes, estados de Hidalgo y Querétaro. 6 Conv. Nal. Soc. Geol. Mex.

CEBRIÁN, M., A. ALBORES, M. AGUILAR and E. BLAKELY, 1983. Chronic arsenic poisoning in the North of Mexico. *Human Toxicol. 2,* 121-133.

DAKUZAKU, C. S., G. P. G. FRECHI, M. MORAES, J. A. NÓBREGA and N. J. A. GOMES, 2001. Direct determination of arsenic in sugar by GFAAS with transversely heated graphite atomizer and longitudinal Zeeman-effect background correction. *Atomic Spectroscopy 22,* 271-275.

DOLD, B. and L. FONTBOTÉ, 2002. Element cycling and secondary mineralogy in porphyri copper tailings as a function of climate, primary mineralogy, and mineral processing. *J. Geochem. Explor. 74,* 3-55.

DZOMBAK, D. A. and F. M. MORELL, 1990. Surface complexation modeling (hydrous ferric oxide), Wiley Interscience Publication, N.Y.

FOSTER, A. L., G. E. BROWN JR., T. N. TINGLE and G. A. PARKS, 1998. Quantitative arsenic speciation in

mine tailings using X-ray absorption spectroscopy. *Am. Min. 83,* 553-568.

GARCÍA, A., M. A. ARMIENTA and O. CRUZ, 2001. Sources, distribution and fate of arsenic along the Tolimán river, Zimapán, México, *In:* M. C. Acreman (editor) Hydro-Ecology: Linking hydrology and aquatic ecology. IAHS publ. 266, 57-64.

GARCÍA, G. G. and S. QUEROL, 1991. Description of some deposits in the Zimapán District, Hidalgo. *In:* Salas G. P. (editor) Economic Geology, Mexico: Boulder, Colorado, Geological Society of America, The Geology of North America, P-3, 295-313.

GUTIÉRREZ, P. A., R. E. RODRÍGUEZ, G. J. ROMERO and A. G. VELÁZQUEZ, 1996. Eliminación del arsénico en agua potable de pozos. Actas INAGEQ 2, 319-322.

IVERSON, D. G., M. A. ANDERSON, T. R. HOLM and R. R. STANFORTH, 1979. An evaluation of column chromatography and flameless atomic absorption spectrophotometry for arsenic speciation as applied to aquatic systems. *Environ. Sci. Technol. 13,* 1491-1494.

LAND, M., J. THUNBERG and B. ÖHLANDER, 2002. Trace metal occurrence in a mineralised and a non-mineralised spodosol in northern Sweden. *J. Geochem. Explor. 75,* 71-91.

LI, Z. and L. M. SHUMAN, 1996. Heavy metal movement in metal-contaminated soil profiles. *Soil. Sci. 161,* 656-666.

MATERA, V. and I. LE HÉCHO, 2001. Arsenic Behavior in Contaminated Soils: Mobility and Speciation. *In:* M. Selim, D.L. Sparks (editors) Heavy Metals Release in Soils. Lewis Publ., Boca Raton, pp 207-235.

MCGOWEN, S. L. and N. T. BASTA, 2001. Heavy Metal Solubility and Transport in Soil Contaminated by Mining and Smelting. *In:* M. Selim, D.L. Sparks (editors) Heavy Metals Release in Soils. Lewis Publ., Boca Raton, pp 89-107.

MCLAREN, R. C., R. NAIDU R and J. SMITH, 1998. Fractionation and Distribution of Arsenic in soils contaminated by cattle dip. *J. Environ. Qual. 27,* 348-354.

MOK, W. M. and C. M. WAI, 1994. Mobilization of arsenic in contaminated river waters. *In:* J.O. Nriagu (Ed.) Arsenic in the Environment, Part I: Cycling and Characterization, John Wiley & Sons, Inc., N.Y., 99-118.

ONGLEY, L. K., M. A. ARMIENTA, K. HEGGEMAN, A. LATHROP, H. MANGO, W. MILLER and S. PICKELNER, 2001. Arsenic Removal from contaminated water by the Soyatal Formation, Zimapán Mining District, Mexico-a potential low-cost low-tech remediation system. Geochemistry, Exploration, Environment, Analysis 1, 23-31.

QUINTO, A., E. SANTOYO, V. TORRES, E. GONZÁLEZ and D. CASTILLO, 1995. Estudio geoquímico-ambiental de los efluentes naturales producidos en la zona geotérmica de Acoculco, Puebla. *Ing. Hidr. en México X(3),* 21-27.

RIMSTIDT, J. D., J. A. CHERMAK and P. M. GAGEN, 1994. Rates of reaction of galena, sphalerite, chalcopyrite, and arsenopyrite with Fe(III) in acidic solutions. *In:* Alpers Ch. and Blowes D.W. (eds.) Environmental geochemistry of sulfide soxidation. Symposium series 550. Washington D.C., American Chemical Society, pp 2-13.

RODRÍGUEZ, R. and A. ARMIENTA H., 1997. The Role of Mine Waste Disposal in the Arsenic Pollution of Groundwater in Zimapán, México. Groundwater in the Urban Environment: Problems, Processes and Management, Chilton *et al.* (eds.), Balkema, Rotterdam, 527-533.

ROMERO, F. M, 2000. Interacción del agua contaminada con arsénico con las rocas calizas de Zimapán, Hidalgo. Maestría en Geología Ambiental, Posgrado en Ciencias de la Tierra, UNAM, agosto, 2000, 125 pp.

ROSAS, I., R. BELMONT, A. ARMIENTA and A. BÁEZ, 1999. Distribution of Arsenic Levels in Dairy Farms at Comarca Lagunera, Mexico. *Water, Air, Soil Poll. 112,* 133-149.

SALOMONS, W., 1993. Adoption of common schemes for single and sequential extractions of trace metals in soils and sediments. *Intern. J. Environ. Anal. Chem. 51,* 3-4.

SIMONS, F. S. and E. MAPES-VAZQUEZ, 1956. Geology and ore deposits of the Zimapán mining district, State of Hidalgo, Mexico. USGS Prof. Pap. 284.

TESSIER, A., P. G. C. CAMPBELL and M. BISSON, 1979. Sequential extraction procedure for the speciation of particulate metals. *Anal. Chem. 51,* 844-851.

VILLASEÑOR, C. M. G., J. A. GÓMEZ-CABALLERO, J. L. MEDINA DE LA PAZ and R. LOZANO, 1987. Boulangerita de chimenea Las Ánimas, Zimapán, Hidalgo: mineralogía y metalogenia. *Bol Min. 3,* 1-30.

WYATT, J. C., C. FIMBRES, L. ROMO, R. O. MÉNDEZ and M. GRIJALVA, 1998. Incidence of Heavy metal contamination in water supplies in Northern Mexico. *Environ. Res. 76,* 114-119.

_____

M. Méndez[1] and M. A. Armienta[2]
[1] Posgrado en Ciencias de la Tierra, UNAM
[2] Instituto de Geofísica, UNAM
Circuito exterior, Cd. Universitaria,
04510 México, D.F., México
Email: victoria@tonatiuh.igeofcu.unam.mx