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Environmental assessment of the potential for arsenic leaching into groundwater from mine wastes in Baja California Sur, Mexico

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RESUMEN

La arsenolita (As_2O_3) ha sido un sub-producto de la extracción de oro y plata en Baja California Sur. En el área de San Antonio-El Triunfo hay más de 800,000 toneladas de desechos mineros con un contenido promedio de 4% de óxido de arsénico. La reacción química que produce el trióxido de arsénico (arsenolita) es la oxidación de la arsenopirita (AsFeS) con oro (mena) formando óxido de hierro (Fe_2O_3) con oro y desprendiendo vapores de SO_2 y As_2O_3 . Los vapores de arsénico se subliman en las paredes interiores de las cámaras de las antiguas plantas de procesamiento. Una vez llenas, las cámaras eran vaciadas periódicamente formando grandes pilas de jales oxidados. Las cámaras abandonadas quedaron parcialmente llenas con aproximadamente 600 toneladas de arsenolita pura. Estudios por difracción de rayos-X y microscopía electrónica-espectrometría de energía dispersa (EDS) muestran que la fluctuaciones en los elementos traza y la estructura bandeada de la arsenolita se deben al uso de diferentes minerales de mena para la extracción del oro y de la plata. Un cálculo aproximado del potencial de lixiviación, basado en resultados de la prueba de celda húmeda del material de desecho (arsenolita y otros jales oxidados con arsenolita), indica que por lo menos 0.5 a 2.0 mg/l de arsénico pueden contaminar anualmente el sistema de agua subterránea de la región. Los datos obtenidos del acuífero local concuerdan con los resultados calculados, indicando una relación directa entre el contenido de arsénico en los jales y en el agua subterránea.

Palabras clave: Arsenolita, contaminación de arsénico, minería en Baja California.

ABSTRACT

Arsenolite (As_2O_3) was historically produced as a byproduct of gold and silver extraction in southernmost Baja California Peninsula. There are in the San Antonio-El Triunfo area more than 800,000 tonnes of mine waste material with an average content of 4% arsenic oxide. The chemical reaction to produce arsenic trioxide (arsenolite) was the oxidation of arsenopyrite (AsFeS) with gold (ore) to produce iron oxides (Fe_2O_3) with gold and releasing SO_2 and As_2O_3 fumes. During the process the arsenic fumes sublimated onto the inner walls of old, mineral processing plants. When the chambers filled up, they were periodically emptied out on big piles of oxidized tailings. But once the plants were abandoned, the chambers remain half filled with approximately 600 tonnes of pure arsenolite. X-ray diffraction and scanning electron microscopy/energy dispersive X-ray spectrometry (EDS) indicate that the trace element content in the arsenolite and its banded structure may be due to the use of different ore for gold and silver extraction. A rough but conservative analysis of the potential leaching, based on results of the humidity cell test on mine waste material (arsenolite and arsenolite-bearing oxidized tailings) indicates that from 0.5 to 2.0 mg/l arsenic could be released into the groundwater system of the region. Real world data from the local aquifer show a close match with the calculations, indicating the close relation between arsenic content in tailings and groundwater.

Key words: Arsenic contamination, arsenolite, Baja California mining.

INTRODUCTION

The San Antonio-El Triunfo (SA-ET) mining area, in southernmost Baja California peninsula, has been exploited for gold and silver since the late 1700's. Between 1784 and 1983 approximately 3,600 kg of Au, 700 tonnes of Ag and 2,500 tonnes of Pb were produced in the mining area (Altamirano, 1971; Amado-Manríquez, 1984; Escandon, 1983). Estimates are that more than 800,000 tonnes of mine waste material are scattered in the ~400 km² of the SA-ET area. These materials were classified by Carrillo (1996) as: (a) oxidized tailings, (b) low-grade mineral ore, (c) cyanide heap-leached material, and (d) byproducts of old, mineral processing plants, mostly arsenic trioxide ("arsenolite", As_2O_3). The ruins of, at least, three old mineral processing plants whose chambers are partially filled with arsenolite remain in the area containing about 600 tonnes of arsenolite (El Triunfo, San Juanes and Rosario-Valle Perdido).

Samples from different arsenic-bearing oxidized tailings and samples of arsenolite from San Juanes and El Triunfo processing plants were collected in sealed plastic bags for further analysis. Once in the laboratory, the samples were first analyzed for major and minor elements using scanning electron microscope/energy dispersive spectrometry (EDS; semi-quantitative analysis) and for mineralogy by X-ray diffraction. Samples were digested at 100°C with concentrated HCl and HNO_3 for detailed quantitative analysis using inductively coupled plasma emission spectrometry (ICP). The samples were also tested by the humidity cell test (HCT).

The HCT is a kinetic method that tries to simulate the weathering conditions of the tailings in the field, especially acid-producing–acid-consuming processes, and the potential leaching of contaminants (heavy metals) to the natural environment (Sobek *et al.*, 1978). The HCT was run for 10 weeks for 18 different samples of arsenolite and arsenic bearing tailings, with sampling of the leachate every week. The HCT leachates were stored overnight at 40°C before analysis. All the glassware and plasticware were cleaned with detergent, 0.12M HCl, and rinsed with deionized water.

The purpose of the present paper is to make an environmental geochemical assessment of mine tailings and arsenolite, its trace element content, and to model the yearly potential leaching of contaminants (As and heavy metals) into the groundwater system of the SA-ET mining area. The model calculations are based on the following:

- (1) amount of water input to the humidity cell,
- (2) amount of mine waste material used in the humidity cell,
- (3) an estimate of the average rainfall in the catchment area,
- (4) estimates of the total tonnage of the mine waste material in the SA-ET area.

GENESIS AND GEOCHEMISTRY OF ARSENOLITE

Of all the old mineral processing plants in the SA0ET mining area, the best preserved is the San Juanes plant. This plant is composed of a bottom chamber, where the ore was burned in order to oxidize the sulfides. Next there is a series of sublimation chambers, where the ash and sublimated volatiles are collected. Finally, the high smokestack released fumes to the atmosphere (Figure 1). The sublimation chambers of the San Juanes plant and the other plants are partially filled with material of high As content (arsenolite, As_2O_3). Although only approximately 600 tonnes of this material are present, its high arsenic content and high solubility poses a risk to the environment. Samples for X-ray diffraction analysis were taken from 18 different piles of arsenic-bearing tailings, and from two old mineral processing plants. At these plants (EL Triunfo and San Juanes), the samples were taken directly from the inner walls of the partially destroyed sublimation chambers. The arsenolite from El Triunfo plant shows a very well preserved "banded" structure. This could represent different ore processed in the plant (Figure 2).

X-ray diffraction patterns of the material from the processing plants show only arsenolite peaks. EDS shows,

Fig. 1. Schematic diagram of the San Juans abandoned mineral processing plant and the generation of arsenolite inside the sublimation chambers.

Fig. 2. Banded arsenolite from El Triunfo plant. The different bands are caused by processing different ore minerals and contain different contents of Fe, Zn and SO₄. See text for details.

besides As, traces of Fe, Zn, Cu, Pb and S. The chemical analyses of the arsenolite show that these elements are present in very small amounts (Fe < 0.2 wt%, Zn ~ 0.06 wt%, Cu ~ 0.003 wt% and Pb ~ 0.09 wt%). The different bands in the El Triunfo arsenolite show differences in Fe and Zn content. This confirms the idea that the banding is due to different ore minerals used during the time the plant was in operation (i.e., material from different mines). In the HCT of the arsenolite the main element leached was As (up to 800 mg/l with an average of 440 mg/l). The average Zn content in the leachate was 25 mg/l and the average SO₄ concentration in the leachate was 280 mg/l.

The rest of the samples from the different arsenic bearing tailings present a complex mineralogy dominated by quartz, feldspars, ± calcite, ± chlorite, ± illite, iron oxides. EDS indicates that significant amount of As is present in all samples. Chemical analysis of these tailings show that the As content varies from 0.03 to ~30 weight percent (wt%), with an average content of ~ 4 wt%. The average As content in the HCT leachate from these tailings is ~1.5 mg/l.

The geochemical and mineralogical analyses of the arsenolite and other tailings, along with results of the HCT, indicate that there is a potential for release of arsenic and zinc to the environment. The main mechanism for releasing As is the dissolution and oxidation of arsenolite (arsenolite → arsenate; As(III) → As(V)). The dissolution-oxidation of arsenolite and speciation reactions of arsenate (As(V)) are:

* Based on thermodynamic data in Dzombak and Morel, 1990.

Even though acidity is generated through these speciation reactions (H⁺), as is indicated by the average pH value of the leachate of the arsenolite (pH = 3.73), the natural waters from the SA-ET mining area present near neutral pH values. This could be explained by the abundant feldspars and calcite in the rock/soil material; dissolution reactions consume any acidity generated by dissolution of arsenolite, pyrite or hydrolysis of Fe oxides (Smith *et al.*, 1994). Moreover, the average pH value of leachate from the other tailings is near neutral.

POTENTIAL LEACHING OF As AND Zn TO GROUNDWATER

Far more important than the acidity generation and consuming processes is the amount of As and Zn that is being released to the environment. A rough but conservative calculation of the total amount of As leached yearly into the environment from the mine waste material is shown in Table 1. This calculation was done by normalizing the cumulative leachate of the HCT (total mg/l after ten weeks of the experiment) to the amount of mine waste material used in each HCT (200 g) and the amount of water poured every week during the

ten weeks of the experiments (200 ml x 10 weeks = 2000 ml; considering that the surface area of each cell used in the experiments is 50 cm², and the equivalent precipitation is 40 cm of rainfall). To normalize the calculation to the real world, the following assumptions were made:

- total rainfall in the area = 15 cm/year
- catchment area = 400 km²
- 100% infiltration
- three different scenarios considering different amounts of tailings.

The logic behind the calculation is quite simple. We had 200 mg of mine waste material in the HCT and we added 2000 ml of water (equal to 40 cm of rainfall); then we extracted (leached) ~5 mg/l As (average of all the samples). How much As and Zn would be leached in the field if there are different amounts of mine waste material (three scenarios), and if the yearly average rain precipitation of the SA-ET area is of 15 cm.? Table 1 shows that in the

Table 1

Model for the potential As, Zn, Fe and SO₄ leaching from mine waste material to groundwater in the SA-ET mining area. The three different scenarios correspond to different estimates of the total amount of mine waste material

best-case scenario (scenario 1, low tonnage), the As released to the groundwater is equivalent to ~0.5 mg/l. In the worst-case scenario (scenario 3, high tonnage) the As released to the groundwater is equivalent to ~2.1 mg/l. It is interesting to note in the table that most of the As and Zn released to the environment comes from the arsenic-bearing tailings ("rest of tailings" in Table 1), because these material represent the main mine waste material in the area. However, as previously shown, the arsenolite could leach up to 800 mg/l. Very locally, it could pose a real danger to the environment.

Concentration due to evapo-transpiration was not considered in this calculation. This model of potential leaching is an over-simplification because less infiltration would mean less dilution but also less leaching. Still the model gives a good approximation of the potential As and Zn leaching into the groundwater system of the mine region. In any case, this calculation yields values of As concentration in groundwater above the World Health Organization (WHO) and US Environmental Protection Agency (EPA) standard for maximum As concentrations in drinking water (0.05 mg/l). The WHO and EPA standard for Zn in drinking water is 5 mg/l, so Zn is not of environmental concern.

Finally, real world data for As, Zn, Fe and SO₄ analysis from groundwater in the SA-ET mining area show a close match with our potential leaching model. The chemical analysis gives As values in a range between 0.4 to 1.5 ppm. The variation in results is due to different location of wells sampled, different sampling seasons and different assay laboratories. The average Zn content in the groundwater is ~0.20 mg/l and the average for SO₄ is ~ 192 mg/l. The model predicts slightly higher values for Zn; however adsorption and other chemical controls could be acting on the Zn. The model predicts slightly lower values for SO₄ but the chemical controls over SO₄ also are complex (i.e. dissolution-precipitation of gypsum).

This calculation clearly shows the relation between the As detected in the groundwater of the region and the leachates from the mine waste material. Current research of the environmental problems of the SA-ET area is focusing on the monitoring of the As plume in groundwater from the mine area, and the geochemical controls for As in the environment.

CONCLUSIONS

- The average As content in the mine waste material of the SA-ET mining area is ~0.4% wt.
- The mineral inside the chambers of the abandoned mineral-processing plants is almost pure arsenolite (As₂O₃).
- The banding and different trace element content in the arsenolite is due to the use of different ore for extracting gold and silver.
- Rough but conservative calculations suggest that resulting average concentrations in groundwater could be between 0.5 - 2.0 mg/l As, which is above the WHO and EPA standard for drinking water (0.05 mg/l As).
- A comparison of the results from the model predicting As concentrations in water with real world data groundwater samples from the mining area indicates a close match. This shows the direct relation between the As bearing tailings of the area with the As content in the groundwater.

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