

Study of Soil Contaminated with Arsenic, Cadmium and Lead in Ancient Tailings in Zacatecas, México

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Abstract—Due to the growth of the urban area towards lands contaminated with ancient tails, in this work we evaluated if the leaching with calcium thiosulfate (CaS_2O_3) for the recovery of silver, gold and mercury from this soil, also dissolves arsenic, cadmium and lead; for this, we determined their quantity per each fraction of size of particle of the soil before and after the dissolution. Half of the soil samples were leached in the plant Beneficiadora de Jales del Centro, S. A. de C.V. and the rest of them remained in the laboratory. The ICP-OES technique was used to determine the amounts of arsenic, cadmium and lead, in the samples of both lots. The soil samples were collected in a neighboring area at El Lampotal, Vetagrande, Zacatecas, México, with an extension of 600 m^2 at $22^\circ 52' 37.69'' \text{ N}$, $102^\circ 25' 11.73'' \text{ W}$. The amount of arsenic, cadmium and lead found in nonleached soil and for a particle size of $47 \mu\text{m}$ was 203.72 ± 3.73 , 33.63 ± 1.31 and $3480.99 \pm 20.4 \text{ mg/kg}$ respectively.

Keywords—Arsenic, Cadmium, Lead, Soil, Tails.

I. INTRODUCTION

ZACATECAS, México is located in a semi-arid plateau at 2,492 m above mean sea level (msl), at the heart of the Sierra Madre mountain chain. The mines, with an elevation of 2500 - 2600 m, are located around the edge of the Plateau which extends to the valley. The discovery of the silver deposits by the Spaniards, in areas that today are the settlement of the city of Zacatecas, originated the exploitation of these deposits using the direct fusion method. But to make this method affordable, it was required that these minerals were high in silver contents. The "new" silver extraction process called "Patio Process" discovered by Bartolomé de Medina in 1555 extracted the silver via the formation of an amalgam of silver/mercury in cold and was used in Zacatecas throughout the colonial period and until the end of 1800 [1,2]. The tailings produced were placed next to the extraction site. These tailings, mostly coming from the mines in Vetagrande and Zacatecas, were dragged by the rains into streams; mainly to "la Plata" stream, which flowed into the reservoir of "El Pedernalillo" dam. There, and at the lower part of this dam,

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the tailings were deposited, and reached the communities of Zóquite, Tacoaleche, El Lampotal, and El Bordo, scattering in an area of approximately 18-30 km x 2-3 km. Some mining companies [3], Ogura *et al.* [4] and Santos-Santos *et al.* [5] have carried out a quantitative analysis of the soil from the zone and have reported that there are large amounts of arsenic, lead and mercury there.

The quantity of silver found in the soil contaminated with tailings from this valley prompted the establishment of some recovery plants to recover silver, gold and mercury. Nowadays, there is only one plant. The recovery process is a variation of the Russell process [6], and involves the excavation of the tailings-rich soil and the transfer to large concrete pools where it is leached with an aqueous solution of CaS_2O_3 . This soil remains in the pool for a period of 10-14 days, time during which the mercury, silver and gold in the tailings dissolve as thiosulfate complexes. The cementation/precipitation is carried out in a pool containing scrap copper where elemental mercury containing silver and gold amalgamated, precipitates. Then mercury is volatilized in an oven, leaving a residue of silver and gold. On the other hand, the soil already leached is deposited as heap in the vicinity of the reprocessing plant.

Due to the growth of the urban area to lands contaminated with ancient tailings, and knowing in advance that the $\text{S}_2\text{O}_3^{2-}$ complexes of cadmium and lead show a low solubility in water, but dissolve in solutions of ion $\text{S}_2\text{O}_3^{2-}$. The aim of this paper is to assessment if the recovery of precious metals from soil contaminated with ancient tailings releases arsenic, cadmium and lead to the environment when they are transformed into soluble chemical species and to know which fraction of soil size contains the biggest quantity of these metals before and after the leaching process.

II. METHODOLOGY

A. Instrumentation

The elemental concentrations in fractions of soil samples were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) Optima 2000 DV, for the determination of cadmium and lead. An atomic absorption spectrometer with a graphite oven and an AS-60 (GFAAS) 3110 self-sampler was used in the aqueous samples; for arsenic, an AANALYST 100 with FIAS 100 and an AS-60 self-sampler was used. All the equipment comes from Perkin

Elmer, USA. An Advanced Microwave Digestion System Ethos Plus (Milestone, Italy) was used for sample digestion.

B. Sampling and sample preparation

The soil samples were collected from an area neighboring the community of El Lampotal, Vetagrande, Zacatecas, México, at 22°52'37.69"N, 102°25'11.73"W (Fig. 1). The sampling area covered an extension of 600 m² (30 m x 20 m) and a method previously reported was used [7]. The field was divided into forty equal parts. Using a plastic shovel, 20 samples of 3 kg each were taken from the center of a square measuring 15 m² and 15 cm deep. A systematic sampling was used and the samples were stored in plastic bags.

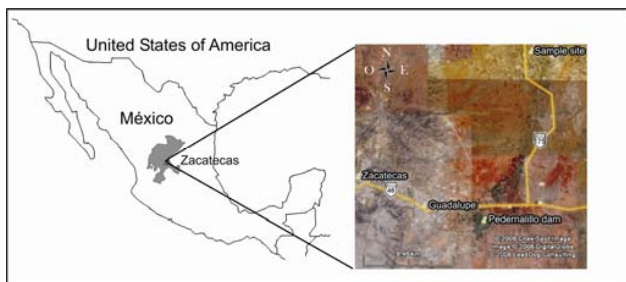


Fig. 1 Sampling site location. Latitude 22°52'37.69"N, longitude 102°25'11.73"W [8]

The final sample was obtained by the quartering method, and immediately divided into two parts, one of which was stored in a polyethylene bag in a dry place in the laboratory and without direct sunlight contact. This was named nonleached soil. The other part of the sample was taken to the reprocessing plant and put in a mosquito net bag. Then a 50 cm-deep hole was made in the center of the leaching pool. The mosquito net bag sample was put into this hole and covered with soil to be leached at the same time as the total soil. This was what was called leached soil. Once the leaching time concluded, the bag was taken to the laboratory to dry and to be kept in a polyethylene bag for later analysis. Aqueous samples were collected from the leach solution and posterior to the concrete pool stage, they were put in 1 L PET bottles rinsed three times with the leach solution and preserved at 4° C prior to analysis.

The analysis for the sample particle size of leached and nonleached soil was made taking 1 kg of open-air-dried soil, screening until the weight of the different sieves did not vary. The used sieves were 500, 300, 125, 75 and 47 (µm) sizes and every determination was made in triplicate.

C. Arsenic, cadmium and lead determination

Using the analytical method EPA 3051A [9], an acid digestion was made for each soil fraction. 0.25 g of each fraction of soil and 10 ml of HNO₃ were taken and put in a PTFE container, then digested in a microwave system. A two-stage program was used with maximum temperature of 175° C

and the maximum power of a microwave, 1000 W (5 min: 20-175° C; 10 min: 175° C). The digested samples were centrifuged at 3000 rpm for 15 min and the supernatant was diluted to 50 ml with a solution of HNO₃ to 1 % in deionized water; an aliquot of 5 ml was taken and gauged to 100 ml. The digestion of the samples was made in triplicate and for each size of particle, although only the average values are shown. The hydrides method (Perkin-Elmer USA) was used for the quantification of arsenic.

The aqueous samples were mineralized using a microwave oven according to the EPA 3015A [10] method taking 45 ml of deionized water and 5 ml of HNO₃. The determination of cadmium and lead was carried out by atomic absorption spectroscopy with a graphite oven as atomizer (GFAAS), the cadmium was determined without a matrix modifier and for lead, a blend of (NH₄)₂HPO₄ at 0.5 %, HNO₃ at 0.2 % and Triton X-100 at 0.5 % [11] was used as a matrix modifier

The arsenic was determined using the hydrides (Perkin Elmer, USA) technique. To ensure a greater response, the sample was pre-reduced as follows: 5 ml sample + 2 ml of KI at 10 % + 1 ml HCl + 2 H₂O. The mixture was heated 5 min at 75° C, using a carrier solution of HCl 10 % (v/v) and NaBH₄ 0.2 % in NaOH at 0.05 % HNO₃ as a reducing agent.

III. RESULTS AND DISCUSSION

In Zacatecas, México, as well as in other mining areas of the world, the environmental problem associated with the tailings is linked to wind dispersion which scatters them to housing zones and to lands where foodstuffs are grown and to acid drainage resulting from sulfides oxidation (mainly pyrite) and their dispersion due to surface runoff.

We separated the two parts of the soil in 5 fractions of particle size to sieve the soil through a series of sieves. The recovery for non-lixivated soil was 9.51±7.73 % in the fraction of 47 µm, 6.6±5.2 % in the fraction of 75 µm, 36.03±10.47 % in 125 µm, 11.19 ±0.77 % in 300 µm, 36.69±2.63 % in 500 µm. The data for leached soil were very similar.

A. Arsenic

The comparison of the amount of arsenic found per each fraction of non-leached and leached soil can be seen from Fig. 2 part A. For sizes 500 µm and 300 µm the amount found is greater in leached soil, not for size fractions 125, 75 and 47 µm respectively, where As concentration is greater in non-leached soil. The maximum value found for all fractions of non-leached and leached soil was 203.72±3.73 mg/kg corresponding to the size of particle of 47 µm of nonleached soil, which is consistent with that reported, in the sense that the largest amount of heavy metals is in the smaller fraction of soil, since in this fraction there is a greater surface area formed by, among other species, the particles of iron oxyhydroxides which have a great capacity of adsorption of As and other heavy metals, by controlling their mobility [12].

Delfini *et al.* [13] reported that in the presence of ion S^{2-} the arsenic in its species, orpiment (As_2S_3) and realgar (As_2S_3) dissolve with formation of soluble thioarsenite complexes. However, depending on the oxidizing power in the atmosphere of the reaction, the formation of oxothioarsenites, sulfates and thiosulfates might also occur, and, the undissolved complex ($Fe_2O_3 \cdot As_2O_3 \cdot 5H_2O$) which retains As even at the highest concentrations of ion S^{2-} may also be formed.

The amount of As corresponding to the size $47 \mu m$ of non-leached soil 203.72 ± 3.73 mg/kg in this work, is greater than 182.41 ± 7.87 mg/kg reported as the maximum concentration of As in a sample of soil in a site of the zone [5]. This shows that the As is expanded in heterogeneous form in the old tailings accumulation area. The As found represents 9 times the criterions of the Mexican standards of such element for agricultural, residential and commercial use which is 22 mg/kg and is below the value for industrial use of 260 mg/kg [14]. According to the mineralogical analysis of a typical ore in the municipality of Veta Grande, Zacatecas, Mexico, the As is found as Arsenopyrite ($FeAsS$), being this species the source of As in the tailings, demonstrating an anthropogenic source.

The value 0.903 of the relation of the amount of As found in leached and non-leached soil suggests that the precious metals recovery process dissolves a small amount of As which is in accordance with that reported [4].

B. Cadmium

From Fig. 2 part B corresponding to Cd we can see that for all particle sizes the values are very similar among each other except for sizes $500 \mu m$ 24.63 ± 3.65 mg/kg for leached soil and 14.92 ± 0.38 mg/kg for nonleached soil and $47 \mu m$ of 33.63 ± 1.31 and 24.37 ± 0.72 mg/kg respectively. As it can be seen, the maximum concentration value found for Cd was 33.63 ± 1.31 mg/kg corresponding to the size $47 \mu m$ of the non-leached soil, amount which is below the criterions of the Mexican standards for agriculture, residential and commercial use which is 37 mg/kg and for industrial use, 450 mg/kg [14]. In this case again the fact of the largest concentration of the element found in the fraction of smaller soil is repeated pointing out the same considerations as for As.

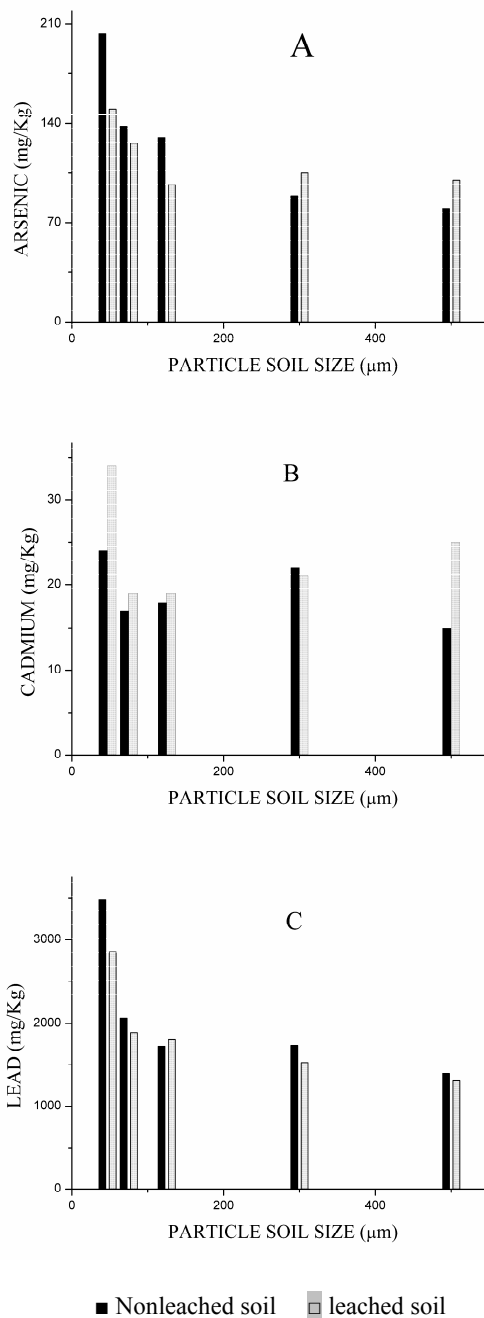


Fig. 2 Amount of Arsenic (A), Cadmium (B) y Lead (C) versus particle soil size

The value 1.22 of the relation of the amount of Cd found in leached soil to nonleached soil suggests that the precious metals recovery process provokes an enrichment in the amount of Cd, this probably caused by the formation of the $[CdS_2O_3]$ complex which is probably conveyed by the leach solution and that once it has left the cementation/precipitation

process without suffering any modification goes back to another leaching pool different from the one it came from originally, thus creating a closed process.

Since we did not find any report on the determination of cadmium on the soil of this area for our data comparison, we took as a reference a farming soil in the municipality of Valparaiso, Fresnillo, Zacatecas, Mexico where we knew in advance that there has not been a mine near or in the workplace, the amount of cadmium found was 11.81 ± 1.2 mg/kg which is lower than the values found in the soil contaminated with tailings, this comes to verify the amount found in contaminated soil originates in the mining operations.

C. Lead

From Fig. 2 part C, the analysis of lead data on leached and non-leached soil shows that for all size fractions, except $125 \mu\text{m}$, all values are higher for nonleached soil. The value 0.90 of the relation of the amount of lead found in leached to nonleached soil suggests that the precious metals recovery process dissolves the lead contained in the soil by forming the $[\text{PbS}_2\text{O}_3]$ complex. The difference which is statistically significant could be that some amount of lead complex coprecipitates in the Ag-Au-Hg amalgam at the stage of cementation, considering that from the oxidation potential data, metallic copper cannot reduce lead; however, there is not any other option for metals than cementation and sedimentation because the process is a closed system.

Ogura *et al.* [4] reported that a sample of soil contaminated with tailings before the leaching process contained 1,770 mg/kg and then declined to 1,060 mg/kg, concluding that the lead was released by the process used in Zacatecas, Mexico, in an amount of 624.26 mg/kg which represents the difference of the values of lead found, contrasting with a difference of 710 mg/kg obtained in this work for the fraction of $47 \mu\text{m}$. The amount of lead found was $3,480.99 \pm 20.4$ mg/kg for non-leached soil which compared with $8,968.13 \pm 22.17$ mg/kg found by Santos-Santos *et al.* [5] in a sample of the contaminated site confirms in the same way as for arsenic, the heterogeneous distribution of lead at the site of the tailings deposit.

The amount of lead found in the tailings of this area represents 8.7 times the value of the Mexican standard for agricultural, residential, commercial use of 400 mg/kg and for industrial use of 800 mg/kg [14]. It is accepted by the scientific community that data on the total concentration of a metal by itself is insufficient to assess the pollution of a site. It is necessary to know the speciation of it in order to assess the risk to the health of the population. The lead is considered an element of low mobility in the tailings since it can be absorbed in iron and manganese oxides.

D. Arsenic, cadmium and lead in leach solution

In the process of cementation (or metal displacement), the

effluent of leach solution conveying the values of the precious metals coming from the leaching vat, download onto the cement sink, there, the precious metals ions are reduced to the metallic state by copper wires, the metallic Hg dissolves these metals forming an Ag-Au-Hg amalgam. Since the copper oxidation potential ($\text{Cu} = \text{Cu}^{2+} + 2\text{e}^-$: -0.345 V in Hg) is very low, the copper reduces only few metal ions which have a lower potential, as they are: Ag (-0.80 V), Au (-1.7 V) and Hg (-0.85 V). This is very good for the purpose of recovery of these metals, but the copper cannot reduce Cd (0.35 V), Pb (0.12 V) and the respective species of arsenic [15], since they have potential values above it and therefore remain in the leach solution without precipitating.

From the data in Table I you can see that for arsenic the difference between values $14.32 \pm 0.32 \mu\text{g/L}$ and $26.03 \pm 0.10 \mu\text{g/L}$ before and after the cementation have a statistically significant difference with ($p = 0.013$), these values are very low compared to an average of As of $42 \mu\text{g/L}^{-1}$ as quantified in aqueous samples of an ancient tailings runoff in an abandoned mine in the State of Guanajuato, Mexico [16].

TABLE I
CONCENTRATION OF ARSENIC, CADMIUM AND LEAD IN
LEACH SOLUTION

Element	Cementation	
	Before	After
$\mu\text{g As /L}$	14.32 ± 0.33	26.03 ± 0.10
$\mu\text{g Cd/L}$	384.9 ± 0.49	334.0 ± 1.16
$\mu\text{g Pb/L}$	54.46 ± 0.92	48.82 ± 0.43

The cadmium and the lead decrease their values before and after the cementation; this means that the Ag-Au-Hg amalgam formed in the process of cementation also carries an amount of cadmium and lead traces, but not of arsenic, since as shown in Table I the latter suffers an enrichment.

From the analysis of the previous data we can say that the cadmium remains in the soil in a stable form, because it does not present a statistically significant difference (with $p = 0.055$), but in the case of lead the difference in values does show a statistically significant difference (with $p = 0.045$).

Finally, we conclude that, although the process dissolves a small amount of the elements considered here, the remarkable quantity of soil used for the recovery of the precious metals makes the amounts of arsenic, cadmium, and lead magnify to a point that they become potentially dangerous for human health.

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