

## Water Rock Interaction [WRI 14]

# Hydrogeochemical trends of the Valenciana tailings, Mexico

Ramos-Arroyo Yann\*, Martínez-Arredondo Julio

*Hydraulics and Geomatic Engineering Department, Av. Juárez 77, Centro, Guanajuato, 36000, México*

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### Abstract

This work describes water fluxes and chemistry of leachates draining from two tailings dams in Valenciana, Guanajuato, Mexico. From 2006 to 2010, water and suspended matter samples were collected regularly and analyzed. Sequential extraction was applied to solids in view of characterizing the As bearing phases. Valenciana tailings dams are a structure of 2.5 million cubic meters ( $Mm^3$ ) of wastes that annually receive a rain volume of  $0.121 Mm^3$ . Per year, drains account for  $0.0057 Mm^3$  of circum-neutral, calcic-sulphate leachates with significant concentrations of manganese, iron, and arsenic. Iron and manganese oxides seem to be the principal phases containing arsenic.

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### 1. Introduction

Nearly  $2,000 Mm^3$  of mine wastes are indexed on the Mexican territory ([www.sgm.mx](http://www.sgm.mx)) and  $8,000 Mm^3$  over the whole earth surface [1]. More than 70% of tailings in Mexico proceed from epithermal ores, with high calcite content. The main problem of this kind of tailings is arsenic liberation [2]. Tailing dams has a great spatial variability in depth and longitude. This variation controls formation's zones with different aeration and moisture retention. Main process that stimulates potentially toxic elements (PTE) liberation is pyrite oxidation. PTE liberation can be as soluble species or associated to mineral phases. Reductive environment allows arsenic mobility [2, 3]. Natural attenuation mechanisms consider adsorption on ferrihydrite or co-precipitation of jarosite, goethite and schwertmannite that form in situ [2, 4]. This work analyzes fluxes in Valenciana tailings and report trends of PTE concentrations dissolved and in solid phase.

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\* Corresponding author. Tel.: +52-473-734-1246; fax: +52-473-102-0100.

E-mail address: [yannramos@ugto.mx](mailto:yannramos@ugto.mx).

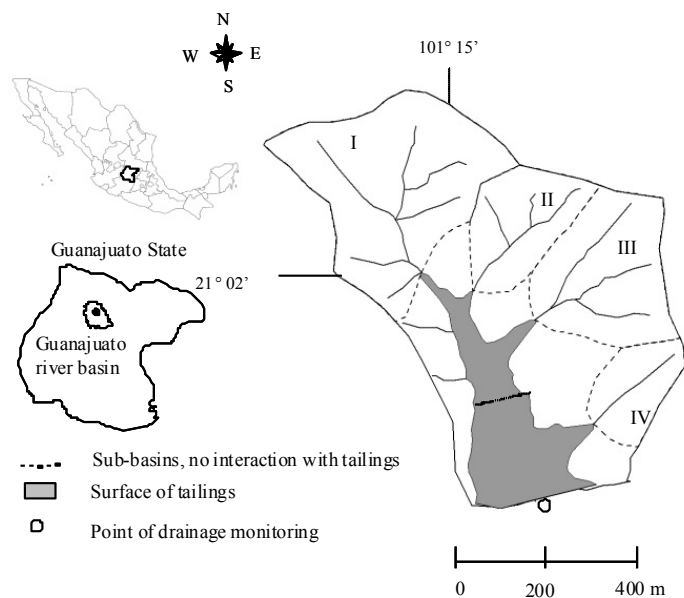


Fig. 1. Location of Valenciiana tailings dams in the Guanajuato river basin.

## 2. Site description

Guanajuato is a classical example of a low sulphidation epithermal district; there are nearly  $60 \text{ Mm}^3$  of tailings in dams. Valenciiana tailings are representative of an isolated hydrological system, consists of two dams with an area of 10 hectares (has) and nearly  $2.5 \text{ Mm}^3$  of materials (Fig. 1). Valenciiana basin covers an area of 56 has. Tailings receive water from direct precipitation and surface runoff. This dam is protected from hydric erosion effects with a deviation tunnel. Sub-basins I to IV, cover 39 ha. Water that interacting with tailings (Over Tailings, OT in Fig. 1) falls directly or can infiltrate from the slope. Main minerals are: quartz, calcite (15 to 10 %), kaolinite and smectite (10 % each one), pyrite and iron oxides at nearly 1%. Variation ranges of PTE concentrations [ $\text{mg kg}^{-1}$ ] are: As 13 to 67, Cu: 45 to 210, Pb: 50 to 190, Zn: 143 to 1129 [5]. PTE in solid phases are associated mainly to amorphous oxides [6].

## 3. Methodology

### 3.1 Hydrological analyses

During four years a hydrological monitoring was developed to measure the rain volume over tailings surface and to evaluate the drained rain. Precipitation's data were collected from a hydro-meteorological station net. Annual rain volume was evaluated by isohyetal method. To estimate the drained total water, a depletion curve was constructed with flow data collected every two months.

### 3.2 Water chemical analysis

32 water samples were collected during four years in three points: a natural source up-stream, deviation tunnel and tailings drainage. Samples were filtered by  $0.22 \mu\text{m}$ , acidified and refrigerated. At

field: pH, temperature, electric conductivity and redox potential (Ag-AgCl electrode and Zobell solution) were measured. Alkalinity was measured by titration with validated  $\text{H}_2\text{SO}_4$  0.1 N and chloride with validated  $\text{AgNO}_3$  0.01 N. Sulphates were analyzed by turbidimetry and nitrates by the cadmium reduction method. The following cations were quantified in waters and solids by absorption atomic spectrophotometry (AAS), by flame: Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Si and Zn; As with a graphite furnace. Standards and reference samples of water and sediments were analyzed by AAS. Saturation index of secondary minerals that might precipitate were calculated using the PHREEQC2 code [7], with WATEQ database. In drainage tailing point, six solid samples were collected and processed by a sequential extraction procedure focused to reactive phases accord to BCR methodology [8].

## 4. Results and discussion

### 4.1 Hydric balance

Figure 2 presents the hydrogram from 2006 to 2009. According to rains in 2008, over Valencià basin falls  $0.712 \text{ Mm}^3$  and OT surface  $0.121 \text{ Mm}^3$ . In that period drained  $0.0057 \text{ Mm}^3$  of circum-neutral calcic-sulphated leachates. Tailings have at least 20 years exposed to the atmosphere, thus, we can deduce that total rain OT in that period could be  $2.42 \text{ Mm}^3$ , that might evaporated or infiltrated. Volume of tailings is  $2.5 \text{ Mm}^3$  with a porosity of 20 % [5]. Considering the model of a depletion curve and adding all annual volumes estimated, it is possible to deduce from tailings that has drained  $1.305 \text{ Mm}^3$ .

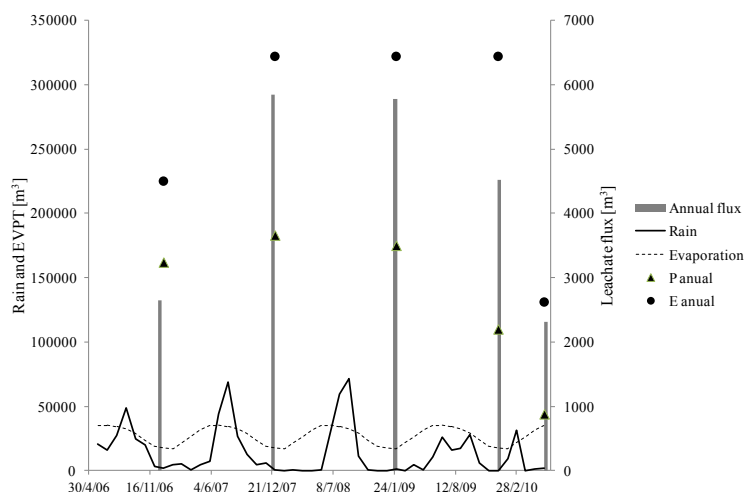


Fig. 2. Hydric balance at Valencià tailings.

### 4.2 Water chemistry

Samples from natural waters are bicarbonate-calcic. Leachates from tailings and deviation tunnel are sulphate-calcic, circum-neutrals and moderately reductive. Leachates have As concentrations between 4 and  $18 \mu\text{g/L}$ , dominant species is  $\text{As}^{5+}$  according to PHREEQC2. Fig. 3 shows saturation index with calcite, ferrihydrite and gypsum. Solutions were near to saturation with gypsum and ferrihydrite from 2006 to 2007. After this period, the SI decrease, probably by a change in the use of the tailings surfaces.

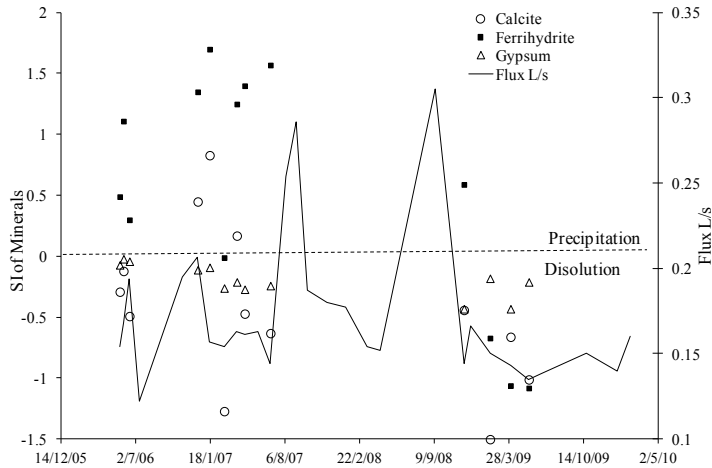


Fig. 3. Trends of Valencia tailings drainage and saturation indices of calcite, ferrihydrite and gypsum.

Suspended materials contain averages compositions of  $\text{Fe}_2\text{O}_3$  (40 %),  $\text{SiO}_2$ , (26 %), S (2%), CaO (6.4 %),  $\text{Al}_2\text{O}_3$ , (2.85 %) and  $\text{MnO}_2$  (2.2 %). Average content of As was determined at  $570 \text{ mg kg}^{-1}$ , which upper to 95 % associated to iron and manganese oxides (reducible fraction accord BCR extraction).

## 5. Conclusion

Valenciana basin receives per year a rain volume of  $0.78 \text{ Mm}^3$ , over tailings only  $0.12 \text{ Mm}^3$ . In 2008 tailings liberate  $5,392 \text{ m}^3$  of leachates; we reconstruct that drainage from tailings in the last 20 years are nearly  $1.3 \text{ Mm}^3$ . These leachates liberate 1.5 to 3 kg of arsenic associated to iron and manganese oxides. In 2008, only 4.5 % of rain volume was transformed in leachates.

## References

- [1] Lottermoser BG. *Mine Wastes: Characterization, treatment and environmental impacts*. Springer-Verlang; 2003.
- [2] Smedle PL, Kinniburgh DG. A review of the source, behaviour and distribution of arsenic in natural waters. *App Geochem* 2002; **17**: 517–568
- [3] Bowell RJ. Sorption of arsenic by iron oxides and oxyhydroxides in soils. *App Geochem* 1994; **9**: 279-286,
- [4] Asta MP, Ayora C, Acero P, Cama J. Field rates for natural attenuation of arsenic in Tinto Santa Rosa acid mine drainage (SW Spain). *J Hazard Mater* 2010; **177**: 1102–1111
- [5] Ramos-Arroyo YR, Siebe-Grabach C. 2006. Estrategia para identificar jales con potencial de riesgo ambiental, caso de estudio del distrito de Guanajuato. *Rev Mex C Geol* 2006; **23** (1): 54-74.
- [6] Ramos-Arroyo Y R, Siebe-Grabach C. Weathering of sulphide mineral sand trace element speciation in tailings of various ages in the Guanajuato mining district, Mexico. *CATENA* 2007; **71**: 497-506.
- [7] Parkhurst DL, Appelo CAJ. *User's guide to PHREEQC (version 2) a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. U.S. Department of the Interior, U.S.G.S. 1999; 326 p.
- [8] Quevauviller Ph. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *Trends Anal Chem* 1998, **17**: 289–298.