

# EFFECTS ON ELEMENT MOBILITY BY THE CONSTRUCTION OF A WETLAND ON THE MARINE SHORE PORPHYRY COPPER TAILINGS DEPOSIT, BAHÍA DE ITE, PERU<sup>1</sup>.

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**Abstract.** The marine shore tailings deposit at the Bahía de Ite, Atacama desert, Southern Peru was studied in order to understand the biogeochemical processes resulting from the construction of a wetland on the oxidizing tailings. For this purpose, un-remediated and remediated parts of the tailings were studied by solid and aqueous geochemistry, mineralogy, and microbiology methods. Preliminary results show that the oxidizing tailings have a low-pH oxidation zone (pH 1 – 4) with a strong accumulation of efflorescent salts (10 – 20 cm thick) at the surface due to the upward capillary transport of metal cations in the arid climate (up to 800 mg/L Fe, 160 mg/L Cu, 15 mg/L Zn, 70 mg/L Mn, 0.2 mg/L Cd, 1.3 mg/L Co and 2.5 mg/L Ni). In contrast, these bivalent metals occur in very low concentrations (mainly under the detection limit) below the wetland due to the established near neutral pH and reducing conditions (~150 mV). The alkaline waters (pH 8) that infiltrated into the Bahía de Ite tailings deposit contained high natural background arsenic concentrations (~500 µg/L As). The preliminary data suggest that the infiltration of the wetland induced retention of the metal cations and the formation of a Fe(II) plume. The Fe(II) plume was pushed toward the sea due to the increased hydraulic pressure of the wetland, where, in contact with the more oxidizing (400 mV) and alkaline sea water, the precipitation of Fe(III) hydroxides was triggered in the area of the shore line. In the shoreline samples, the As concentrations in the pore water are below the detection limit, suggesting that the As is retained by the Fe(III) hydroxide. This conclusion was confirmed by sequential extraction data.

**Additional Key Words:** acid mine drainage (AMD), efflorescent salts, wetlands remediation, pyrite oxidation, marine deposit.

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## Introduction

The Bahía de Ite tailings contain approximately 785 million metric tons of material deposited from 1960 to 1997. The tailings were generated from the Cuajone and Toquepala porphyry copper deposits in Moquegua, Peru and operated by the Southern Peru Copper Corporation (SPCC). The tailings were directly sent via the Locumba River for final shore deposition in the Bahía de Ite, located in the Atacama desert, about 50 km south of Ilo, Moquegua, Southern Peru (Fig. 1). The shore tailings deposit occupied a surface of about 16 km<sup>2</sup> and had a maximum depth of 16 m at the current shore line, which was located approximately 1.8 km seawards from the original shore line.

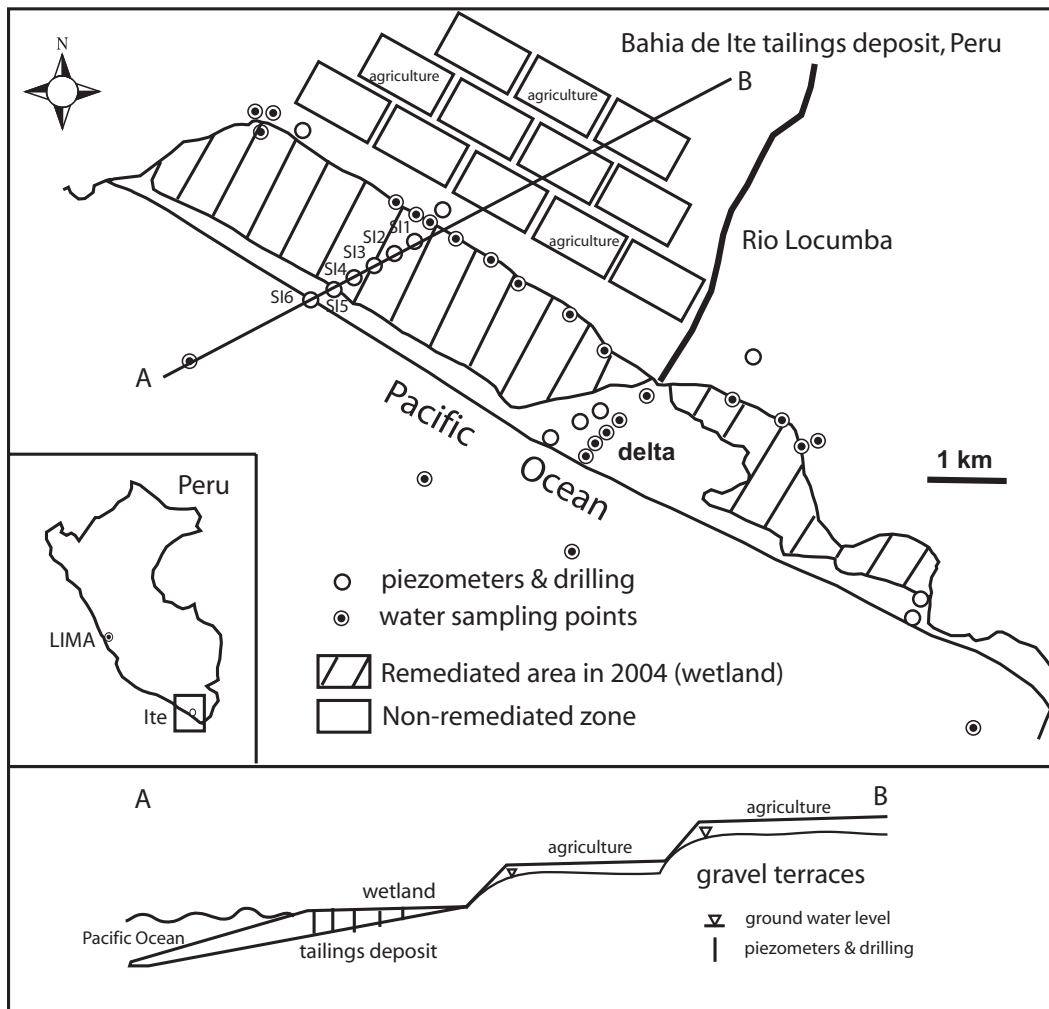


Figure 1. Overview of the Bahía de Ite marine shore tailings deposit, Peru with the location of the sampling point from the 2004 campaign. The vertical scale in the lower profile is strongly exaggerated for better visibility.

The Bahía de Ite area is characterized by gravel terraces on which extensive agriculture was practiced starting in the early 1940's (Fig. 1). The water for irrigation was taken from the Locumba River, which contains high natural As concentration (400 – 700 µg/L As). Due to this

strong irrigation the ground water level is shallow in the gravel terraces (~ 5 m), which results in a high hydraulic gradient towards the Bahía de Ite. The groundwater level is visible in the outcrop as a series of sweet water fountains at the original coastline that have an alkaline pH of 8.

After deposition ceased in 1997, remediation was initiated by SPCC. They installed a wetland cover on the oxidizing tailings using alkaline water from the Locumba River and transplanted locally-developed flora, where the alkaline water infiltrated into the oxidizing tailings. Since then, about 80% of the tailings deposit surface has been covered with wetlands, except for the central delta area and some areas close to the shoreline (Figs. 1 - 3). Currently, the Bahía de Ite represents the largest wetland along the Peruvian Coast, with the highest biodiversity in flora and fauna in the area.



Figure 2. Oxidation zone with efflorescent salts in the delta area, Bahia de Ite, Peru.



Figure 3. Bahia de Ite marine shore tailings deposit with constructed wetland.

The goal of this study is to investigate the biogeochemical processes induced by the installation of the wetland cover and the effects on element liberation and retention processes in the tailings stratigraphy in order to assess the long-term stability of the remediation. Un-remediated and oxidizing parts of the tailings, such as the delta area and the beach area in the North and South of Ite (Fig. 2) and the remediated area (Fig. 3) in the northern part, were investigated to meet these goals.

### **Methodology**

In October 2004, nine piezometer nests were installed in three profiles (North, Delta, and South) to a maximal depth of 10 m in order to sample the water from the saturated zone (Fig. 1). To sample the pore water from the unsaturated zone, 3" Al tubes were used for coring to a depth of 2 m and instantly frozen (-20°C) until the pore water was extracted. The pore water was obtained by replacement with epoxidized soybean oil in the laboratory. Pore water pH, Eh, Fe<sup>+2</sup>, and alkalinity were measured immediately during sampling of the piezometers or directly after pore-water extraction using a flow-cell with a peristaltic pump. Alkalinity was measured with a digital titrator and Fe<sup>+2</sup> was measured by Merck Spektrouquant® with pH electrodes that were

calibrated by pH 4 and pH 7 standard solutions. The performance of the Eh electrodes was controlled by Light and Zobell's solutions and the values were corrected with respect to the standard hydrogen electrode (SHE). Two hundred and twenty water samples were taken from the piezometers and surrounding water flows and seeps. All water samples were filtered (0.2 µm; regenerated cellulose) and stored at +4°C in darkness prior to analysis. Samples for cation analyses were acidified to pH < 2 with suprapure HNO<sub>3</sub>. Water samples were analyzed for 20 elements (Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, SiO<sub>2</sub>, Zn) by ICP-AES. Arsenic and Se were measured by atomic absorption spectroscopy (AAS) with a hydride system. Phosphate, nitrate, and nitrite were analyzed colorimetrically at the Environmental Laboratory, Southern Peru Copper Corporation, Ilo, Peru. Sulfate and Cl<sup>-</sup> were measured by ion chromatography at the Centre d'Analyse Minérale, University of Lausanne, Switzerland.

For the isotopic study, dissolved SO<sub>4</sub><sup>-2</sup> was precipitated from the water samples by addition of a saturated BaCl<sub>2</sub> solution. The BaSO<sub>4</sub> was separated from the solution by filtering through a 0.45 µm NH<sub>4</sub>OAc filter and then air-dried. These BaSO<sub>4</sub> samples were analyzed for S and O<sub>2</sub> isotopes. Minerals from the mines (gypsum, copper sulfates, Fe(III) hydroxides, sulfides minerals) that are potential sources of SO<sub>4</sub><sup>-2</sup>, as well as SO<sub>4</sub><sup>-2</sup> precipitated from the seawater, were also analyzed. Sulfur isotopes were analyzed by Dr. Jorge Spangenberg as described by (Dold and Spangenberg, 2005), using an on-line elemental analyzer (Carlo Erba 1108) coupled through a continuous helium flow interface to a Thermo Finnigan (Bremen, Germany) DELTA S isotope ratio mass spectrometer (EA/IRMS) system. Oxygen isotopic composition of the BaSO<sub>4</sub> was measured with a Thermo Finnigan high temperature conversion elemental analyzer (TC/EA) coupled to a Delta Plus XL isotope ratio mass spectrometer at the Stable Isotopes Laboratory, Institute of Mineralogy and Geochemistry, University of Lausanne, Switzerland.

Solid samples were obtained by flush drilling at each piezometer nest down to a maximum depth of 16 m. At point SI6, which is located on the "beach", a 3.5 meter core was taken. The pH was measured with a WTW pH-meter (WTW pH 323) with a special pH-electrode (WTW-Sentix RP) inserted directly into the tailings. Three hundred and fifteen solid samples were taken and 60 selected samples were subjected to sequential extractions using the method described by Dold (2003) at the SGS laboratory, Toronto, Canada. Mineralogy was determined using polished thin sections and by powder X-ray diffraction (XRD; Philips 3020) at the University of Lausanne. Samples were also taken for a microbiological study, for which we present preliminary results here.

## **Results and Discussion**

### **Stratigraphy and Mineralogy**

Data from the northern profile A – B (Fig. 1) is presented in order to illustrate the change from the oxidizing tailings towards the wetland covered tailings that occurred after remediation. In this profile (Fig. 4 and 5), SI5 represents the un-remediated oxidizing tailings which behave in a manner very similar to the tailings in the delta and in the southern profile (data not shown). SI2 to SI4 were located in the remediated area.

Un-remediated oxidizing tailings. The stratigraphy of the oxidizing tailings was generally characterized by a 10 – 20 cm thick cover of efflorescent salts on the surface (Fig. 2) containing mainly water-soluble sulfates and chlorites (tamarugite, hexahydrate, pentahydrate, aubertite, melanterite, siderotil blodite, thenardite, dansite, halite, eriochalcite, atacamite) in shades of

white, blue, yellow-greenish, and reddish colors. This enrichment of the mobile elements from the oxidation zone towards the surface was controlled by the high evaporation in the Atacama desert, which induced a strong capillary transport to the tailings surface as frequently observed in arid climates (Dold, 2005; Dold and Fontboté, 2001).

The underlying low-pH oxidation zone (pH 1 – 4) shows straw-yellowish color (jarosite), with orange-ochre-brown Fe(III) hydroxides (possibly goethite and schwertmannite), which are mainly related to dehydration cracks and grain size limits where the Fe(III)-rich solutions percolated. The gangue mineralogy of the oxidation zone was dominated by quartz, muscovite, biotite, plagioclase (albite-sanidine-anorthoclase), anhydrite, gypsum, a vermiculite-type mixed layer mineral resulting from the alteration of biotite (Dold and Fontboté, 2001), and relics of pyrite. The underlying neutral primary zone was characterized by the primary mineral assemblage from the ore (quartz, muscovite, biotite, plagioclase, anhydrite, gypsum,) with about 4% pyrite and traces of chalcopyrite, molybdenite, and chalcocite-covellite. The sulfide concentrations vary strongly with a trend toward higher concentrations in the delta area due to the deposition of the heavier sulfide minerals and coarser grain size close to the deposition point. The beach area also shows a coarser grain size (sandy – fine sandy) due to grain size separation by the wave action of the sea. It is important to mention that in the northern profile the primary zone is an orange-reddish colour, resulting from fine Fe(III) hydroxide coatings of the silicates which appear in the drill cores close to the shore line (SI4 and SI5) for the entire depth of the stratigraphy.

Remediated tailings. The stratigraphy of the remediated area shows patterns similar to the oxidized tailings (yellow oxidation zone with underlying gray primary zone). On top of the oxidation zone, a horizon up to 30 cm thick of black organic matter covered with water from several cm up to 1.5 m is present.

#### Aquatic chemistry

Un-remediated oxidizing tailings . At SI5 (Fig. 4), the pH ranged from 1 to 2.5 in the oxidation zone (Eh = 620 mV) with high metal concentrations in solution (220 mg/L Fe, 74 mg/L Al, 8.19 mg/L Mn, 19.6 mg/L Cu, 2.4 mg/L Ni, 2.08 mg/L Zn). Arsenic concentration was below the detection limit in the oxidation zone, probably because this element is frequently associated with the secondary Fe(III) hydroxides in the low-pH oxidation zone. This was confirmed by sequential extraction data, which showed that As is mainly associated with the fraction of secondary Fe(III) hydroxides (7 mg/kg) and with the primary sulfides (5 mg/kg). Below the oxidation front, the pH increases to values of 4.5 to 5.5 and the Eh decreases to 170 mV at 3 m depth. At 3 m depth a plume of Fe<sup>2+</sup> (650 mg/L Fe) was observed, as is typically found in porphyry copper tailings below the oxidation zone as a result of microbial mediated iron reduction (Dold et al., 2005). Arsenic reached maximum concentrations of 100 µg/L at 100 cm depth (Fig. 5), but was generally very low (close or below detection limit of 2 µg/L in SI5 and SI4). At SI5 and SI4, the scavenging of arsenic by the Fe(III) hydroxide coating was confirmed by sequential extraction data.

Chlorine, SO<sub>4</sub><sup>-2</sup> and Na showed a very similar distribution in all profiles (Fig. 5). The concentrations for these three parameters are about 1500-2000 mg/L in the tailings stratigraphy with slightly higher concentrations of about 3000 mg/l in the lowest part of the stratigraphy. These data suggest that nearly the entire tailings body is saturated with the infiltrating sweet water and that the seawater has very low influence on the hydrological system of the tailings

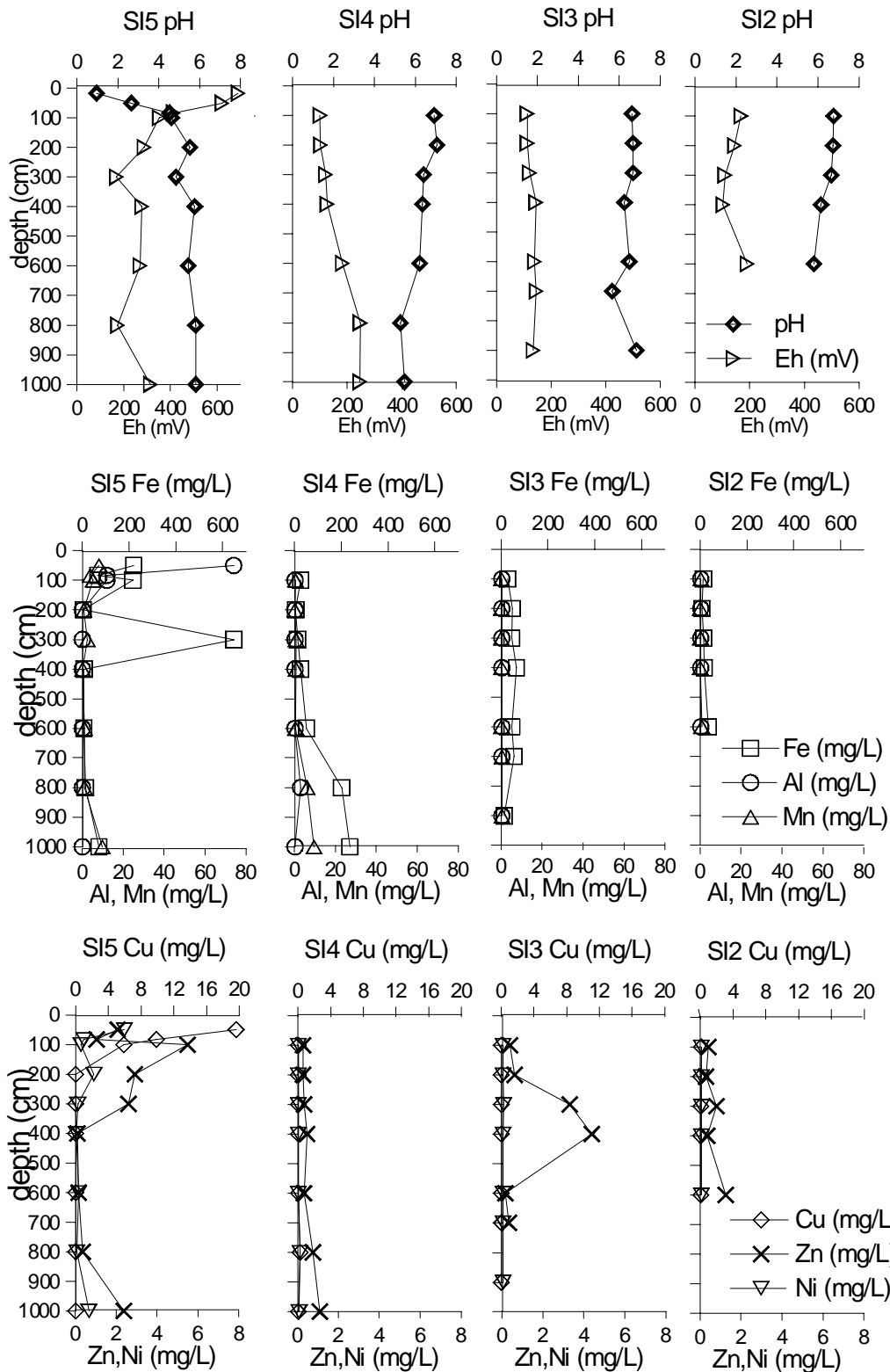


Figure 4. Hydrogeochemical data (pH, Eh, Fe, Al, Mn, Cu, Zn, Ni) from the northern piezometer profile SI2 to SI5. SI2 to SI4 were located in the remediated area, whereas SI5 was still oxidizing.

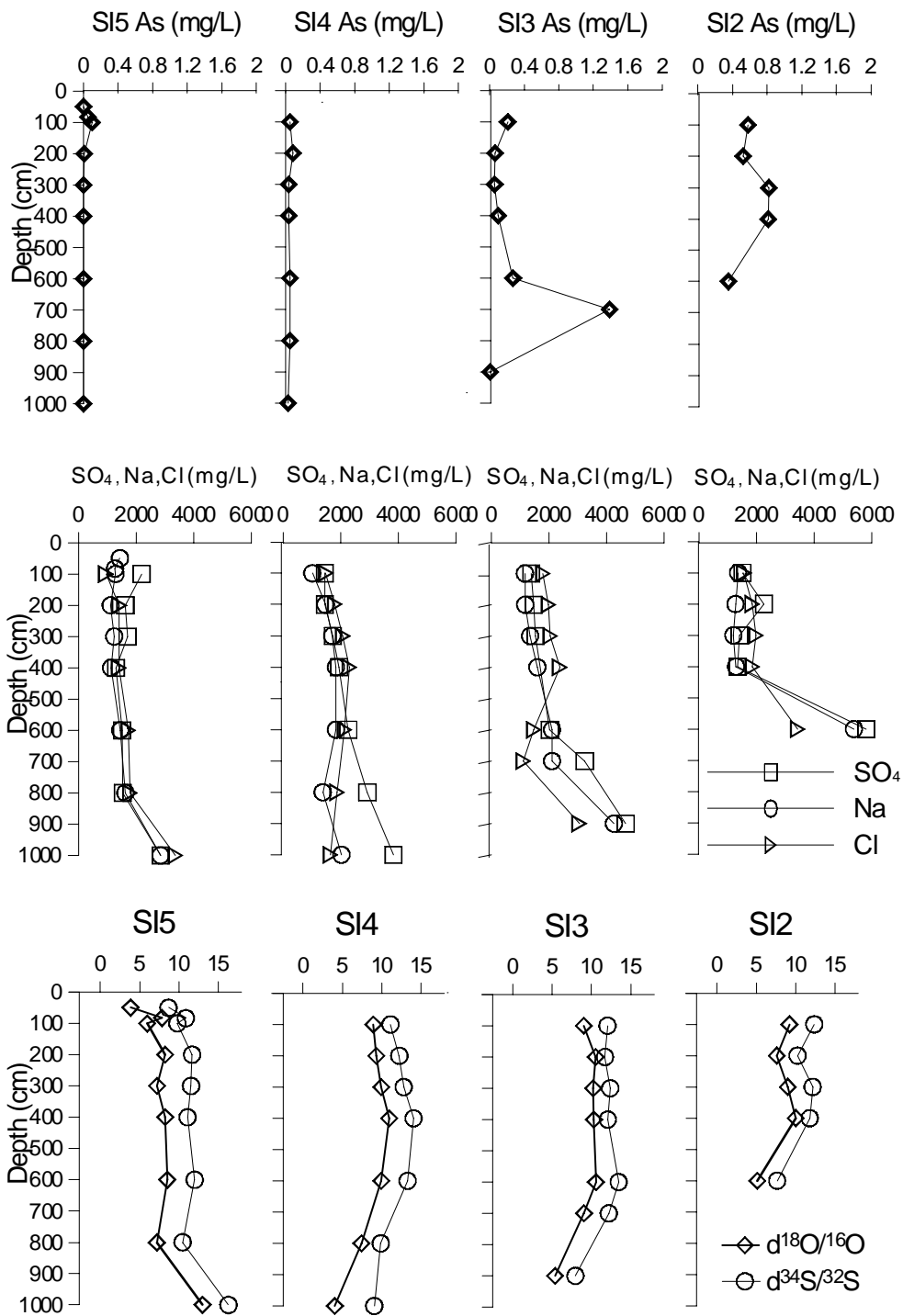


Figure 5. Hydrogeochemical data (As, SO<sub>4</sub>, Na, Cl) and isotopic data ( $d^{18}O/^{16}O$  and  $d^{34}S/^{32}S$ ) from precipitated SO<sub>4</sub><sup>-2</sup> from the northern piezometer profile SI2 to SI5. SI2 to SI4 were located in the remediated area, whereas SI5 was still oxidizing.

deposit. The increase of these parameters in the deepest piezometers at SI2 and SI3 could be explained by the fact that these piezometers were installed down to the sediment basement and could reflect the influence of some marine sequences on the pore water. At SI4 and SI5 the deepest piezometers did not reach the basement. Therefore, the increase of  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  in the lowest piezometer of SI5 (10 m depth) could suggest mixing with marine water. This interpretation is supported by the isotopic data of the precipitated  $\text{SO}_4^{2-}$ , which shows a clear shift towards heavier values of  $\delta^{18}\text{O}_{\text{sulfate}} = 13\text{‰}$  V-SMOW and  $\delta^{34}\text{S}_{\text{sulfate}} = 16.2\text{‰}$  V-CDT only in this sample. These values are close to the values of seawater ( $\delta^{18}\text{O}_{\text{sulfate}} = 10.4\text{‰}$  V-SMOW and  $\delta^{34}\text{S}_{\text{sulfate}} = 20.4\text{‰}$  V-CDT). These data suggest a minimal presence of seawater in the tailings deposit and also explain the dominance of sulfates over chlorites as efflorescent salts at the tailings surface as expected in a marine setting (Dold, 2005).

Remediated tailings. Below the wetland, in SI2 – SI4 (Figs. 4 and 5), the pH are close to neutral values and the Eh shows more reducing conditions (100 – 150 mV). Due to this strong geochemical change, the heavy metal concentrations in solution are generally low (7.4 – 236 mg/L Fe, up to 4.3 mg/L Zn; Al, Cu, and Ni were generally close or below detection limit). However, As maintains high concentrations under these conditions (up to 1.4 mg/L) with highest concentrations at SI2 (Fig. 5), especially close to the infiltration of the sweet water with its natural As concentrations of around 500  $\mu\text{g/L}$  of As.

### **Preliminary Conclusions**

The preliminary data of the mineralogical and geochemical study of the marine shore tailings deposit at the Bahía de Ite, Peru indicates the following preliminary conclusions:

1. The hydrology of the tailings deposit is controlled by the inflowing sweet water from the Locumba River and the infiltrations of the irrigation water applied on the gravel terraces, with very low infiltrations of marine water into the tailings deposit. These sweet waters are most likely the source of the arsenic in the system (natural background of around 500  $\mu\text{g/L}$  As), as the tailings themselves contain very low As concentrations (5-10 mg/kg As).
2. The oxidizing tailings in combination with the arid climate formed a low-pH oxidation zone at the top. The liberation of acidity and Fe, Al, Mn, Cu, Zn, Ni, and  $\text{SO}_4^{2-}$  resulted in the precipitation of efflorescent salts at the surface of the tailings.
3. The construction of the wetland on the oxidizing tailings resulted in an increase of pH to neutral values and a decrease of redox to more reducing conditions. This geochemical change reduced the mobility and the further liberation of the bivalent cations Cu, Ni, and to a lesser extent Zn. The installation of the wetland also promoted the reduction of Fe(III) rich water in the oxidation zone, forming a plume of Fe(II), which was pushed towards the sea by the increasing hydraulic pressure of the wetland. In contact with the more oxidizing seawater (Eh = 400 mV), the Fe(II) oxidized to Fe(III) and hydrolyzed, forming a thin coating of Fe(III) hydroxides on the sandy material in the area of the shore line. This Fe(III) hydroxide coating seems to act currently as a filter for the As, which migrates from the seeps along the former shore line into the tailings deposit.



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