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# Weathering of primary minerals and mobility of major elements in soils affected by an accidental spill of pyrite tailing

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Available online 20 February 2007

## Abstract

In the present work, soil profiles were sampled 40 days and three years after an accidental pyrite tailing spill from the Aznalcóllar mine (S Spain) in order to figure out the effects of the acidic solution draining from the tailing. The composition of the acidic solution, the mineralogy, and the total and soluble content of the major elements were analysed at varying depths. The results show a weathering process of carbonates and of primary silicates. Calcium released is leached or reacts with the sulphate ions to form gypsum. Magnesium, aluminium and potassium tend to leach from the uppermost millimetres of the soil, accumulating where the  $\text{pH} \geq 5.0$ ; also the iron, probably forming more or less complex hydroxysulphates, precipitate in the upper 5 cm. The strong releasing of soluble salts increases the electrical conductivity, while the soluble potassium tends to decrease in the uppermost part of the soil due to the neoformation of jarosite. Iron is soluble only where the  $\text{pH} \leq 2.3$ , and aluminium where the  $\text{pH} \leq 5.5$ .

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**Keywords:** Pyrite tailings; Acidic solution; Major elements; Mineral neoformation

## 1. Introduction

The collapse of a tailing pond dam on the pyrite mine in Aznalcóllar (SW Spain), occurred in 1998, spilled to the Agrío and Guadiamar river basin some 4.5 hm<sup>3</sup> of acidic waters and tailings with high concentration in sulphur, iron, heavy metals and other potential pollutant elements, affecting some 45 km<sup>2</sup> of agricultural lands (Simón et al., 1999; López-Pamo et al., 1999). The subsequent drying and aeration of tailings produced a rapid and intense oxidation of the sulphides, strongly affecting the covered soils (Simón et al., 2001).

The sulphide oxidation is a complex biogeochemical process (Nordstrom, 1982), that released sulphate ions, increase acidity and solubilized different elements associated with sulphides (Stumm and Morgan, 1981). When the acidic solution infiltrates the soil by the rainfall, the H<sup>+</sup> reacts with the primary minerals of the soil (carbonates and silicates), producing their alteration and the subsequent reduction in the H<sup>+</sup> concentration (Cravotta and Trahan, 1999). With the increase in pH, the dissolved elements tend to reduce their solubility mainly by reactions of precipitation, co-precipitation or adsorbed in the exchange complex of the soil (Xu et al., 1997).

In this work, the alteration processes produced after the oxidation of the pyrite tailings in a carbonate

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soil was studied during a period of three years. We present the results involving the effect of the acidic solution on the dynamics of the major elements and the mineralogical transformations produced in the affected soil.

## 2. Materials and methods

The affected soil is a calcaric Regosol located in the Quema area (Sevilla, SW Spain), 25 km from the Aznalcollar's mine. The first sampling (Q0) was carried out at 40 days from the spill and the second one (Q1) 3 years later. In the first sampling, the soil was covered by a layer of tailing 4.5 cm thick, the profile was homogeneous in depth and had a brown colour (2,5Y 5/4). 3 years later (soil Q1) the profile showed a strong morphological differentiation in depth. Just beneath the tailing, a pale-greyish (2,5Y 7/2) layer appear, with a mean thickness of 5 mm,

followed by a reddish-brown layer (10YR 5/6) with a mean thickness of 70 mm; below this depth, the unaffected soil appear with the same brown colour (2,5Y 5/4) as in soil Q0. In the Q0 soil, a sample was taken every 5 mm to a depth of 20 mm, then a sample every 20 mm to a depth of 100 mm, and finally a sample every 50 mm to a depth of 550 mm. In Q1 soil, a sample was taken every 5 mm to a depth of 70 mm, then a sample every 10 mm to a depth of 120 mm, and finally a sample every 50 mm to a depth of 570 mm. In all soil samples, pH was determined potentiometrically in a 1:2.5 suspension, the content in calcium carbonate equivalent was measured by the method of Williams (1948) and the gypsum by precipitation with acetone (Bower and Huss, 1948). The total content in major elements was determined by X-ray fluorescence in a Philips PW-1404 apparatus. The mineralogical composition was determined by X-ray diffraction in a Philips PW-1710 apparatus with  $\text{CuK}\alpha$  radiation.

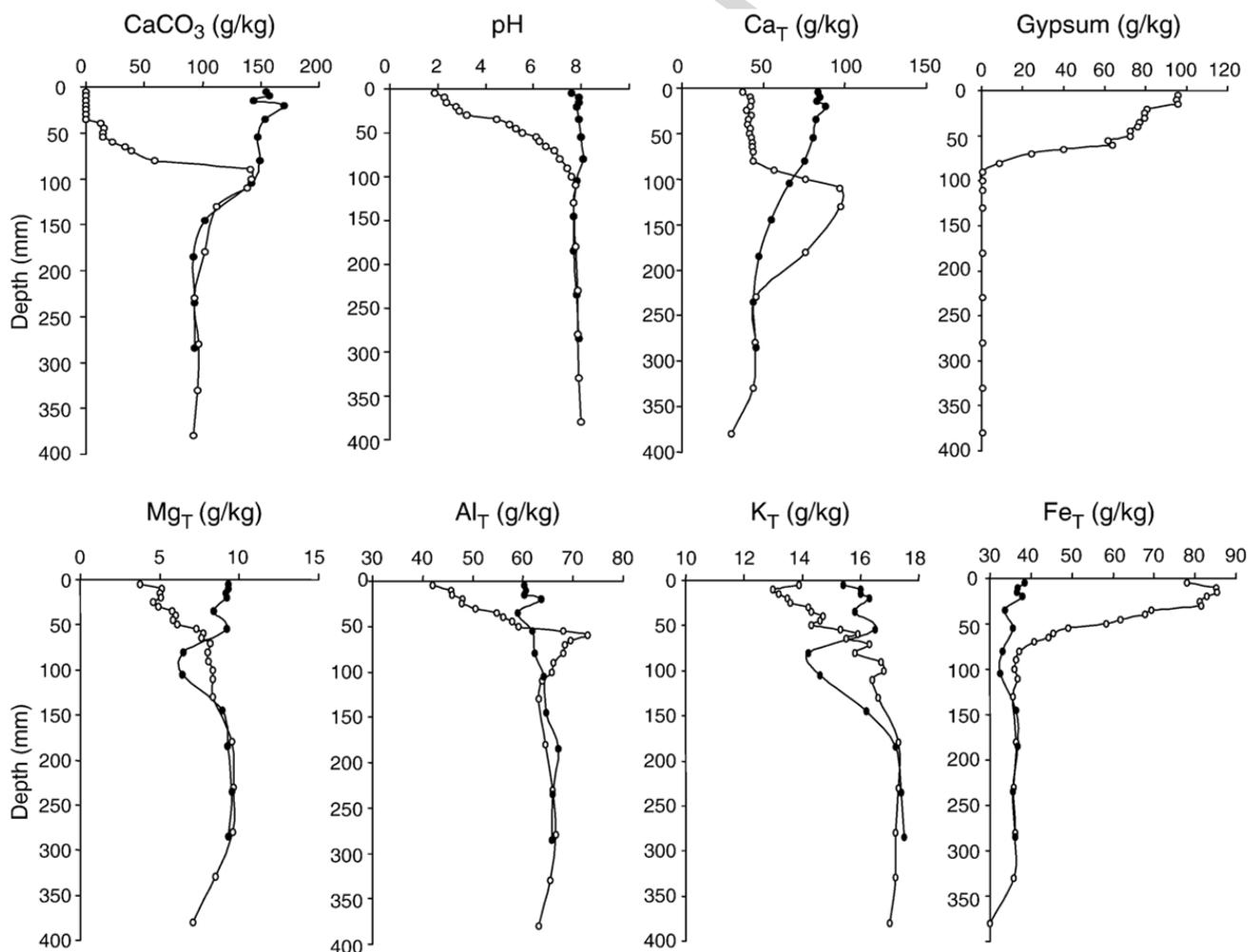


Fig. 1. Distribution in depth of  $\text{CaCO}_3$ , pH, gypsum, and total calcium ( $\text{Ca}_T$ ), magnesium ( $\text{Mg}_T$ ), potassium ( $\text{K}_T$ ), aluminium ( $\text{Al}_T$ ), and iron ( $\text{Fe}_T$ ) in soil Q0 (—●—) and soil Q1 (—○—).

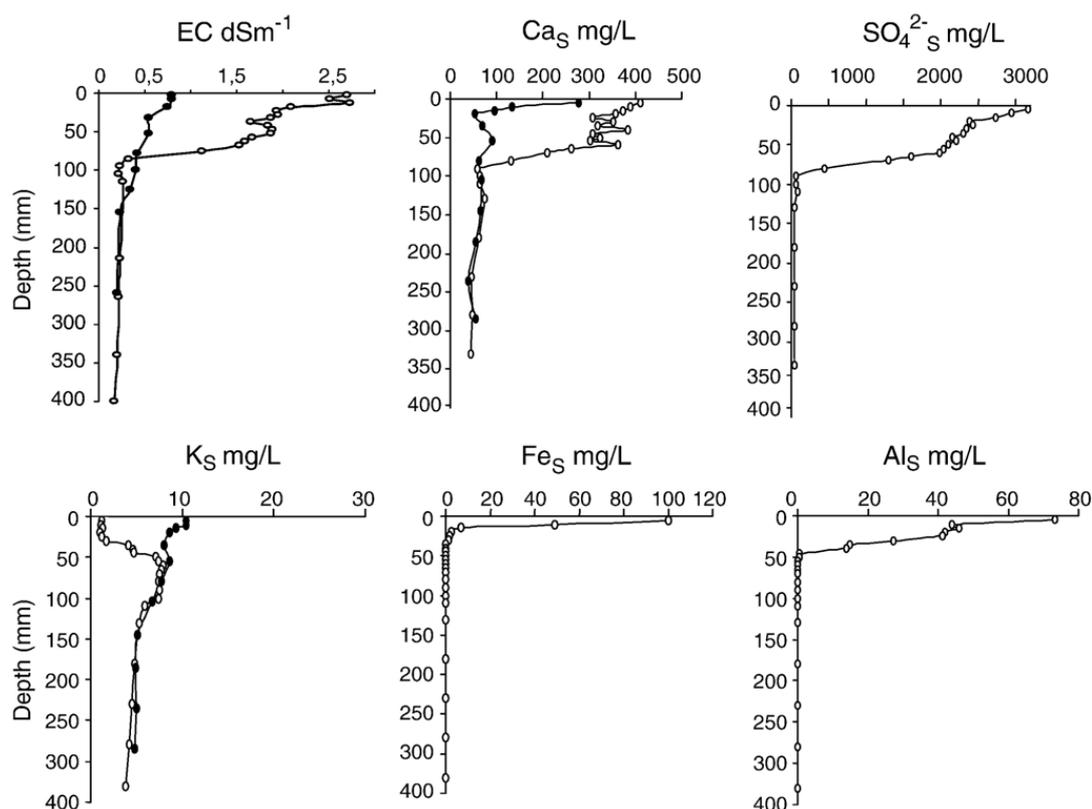


Fig. 2. Distribution in depth of electrical conductivity (EC) and soluble forms of calcium (Ca<sub>s</sub>), sulphate (SO<sub>4</sub><sup>2-</sup><sub>s</sub>), potassium (K<sub>s</sub>), aluminium (Al<sub>s</sub>) and iron (Fe<sub>s</sub>) in soil Q0 (—●—) and soil Q1 (—○—).

Finally, soil extracts were prepared at a ratio soil:water of 1:10 (Norma DIN 38 4 14-4, 1984); after 24 h the soil extracts were filtered to measure: pH; electrical conductivity; sodium and potassium contents (by flame photometry in a METEOR NAK-II device); calcium, magnesium, iron and aluminium contents (by atomic absorption spectrometry in a VARIAN SpectrAA 220FS machine); and sulphate content (by liquid chromatography in a DIONEX DX-120 apparatus).

### 3. Results

#### 3.1. Mineralogical transformations

Mineralogy of soil Q0 is dominated by quartz (58%), calcite (18%), phyllosilicates (13%) and feldspars (11%), and it is very homogeneous in depth. On the other hand, soil Q1 shows a clear mineralogical differentiation; in the uppermost 5 mm (pale-greyish layer) carbonates completely disappear, feldspars (8%) and phyllosilicates (7%) are reduced and a neoformation of gypsum (12%) and iron hidroxysulphates (jarosite group minerals; 6%) occurs. These mineralogical changes are less intense with increasing depth.

#### 3.2. Major element content

Total concentration of the major elements (Si<sub>t</sub>, Al<sub>t</sub>, Mg<sub>t</sub>, K<sub>t</sub>, Na<sub>t</sub> and Ca<sub>t</sub>) strongly decreases in the uppermost 70 mm of the soil Q1 (clear difference with soil Q0) and tend to accumulate with depth (Fig. 1). On the contrary, the dissolved iron in the acidic solution tend to precipitate in the uppermost 30 mm, where the total content of iron (Fe<sub>t</sub>) in the soil Q1 increases two fold compared with Q0.

In the soil solution, the electrical conductivity has an inverse behaviour of pH (Fig. 2), and the highest values appear in the uppermost millimetres of the soil Q1, indicating an accumulation of soluble forms in this layer of the soil, with the exception of soluble potassium (K<sub>s</sub>) which sharply decrease in the first 50 mm of the soil.

### 4. Discussion

The continuous infiltration in the soil of the acidic solution coming from the oxidation of the pyrite tailings, produced the complete weathering of carbonates in the first 35 mm of the soil and its partial weathering between 35 and 80 mm. The disappearance of carbonates

produced a strong acidification in the uppermost 35 mm (pH < 3.5); below this depth pH increases progressively to 100 mm, where it has similar values to the soil Q0 (pH 7.9). On the other hand, part of the  $\text{Ca}^{+2}$  ions released from the weathering of carbonates, are leached from the uppermost 80 mm and tend to accumulate between 100 and 200 mm, while another part of these ions react with the  $\text{SO}_4^{-2}$  of the acidic solution precipitating as gypsum. Simultaneously, a partial weathering of feldspars and phyllosilicates occurs, corroborated by the reduction of the total concentration of silicon, aluminium, magnesium and potassium (Fig. 1) in the first 50 mm of the soil, coinciding with the soil pH < 5.5. The dissolved iron in the soil solution tends to precipitate in the uppermost part of the soil Q1, mainly in the first 30 mm of the soil.

The acidification of the soil produced an increase of the soluble elements ( $\text{Ca}_s$ ,  $\text{Fe}_s$ ,  $\text{Al}_s$ ,  $\text{SO}_4^{-2}$ ) and, therefore an increase in the electrical conductivity in the first millimetres of the soil Q1; with the exception of soluble potassium ( $\text{K}_s$ ) which reduces its solubility in this layer of the soil, this reduction could be related to the neoformation of jarosite (Dorronsoro et al., 2002), clearly detected in the X-ray diffraction analysis. The soluble iron ( $\text{Fe}_s$ ) concentrates in the first millimetres of the soil, where pH < 2.3, while soluble aluminium ( $\text{Al}_s$ ) remains in the solution in a larger pH range (< 5.5), due to the differences in the solubility reactions of both elements.

### Acknowledgment

We express our gratitude to the Science and Technology Ministry of Spain for supporting this study (Project REN 2003–03615).

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