



Weathering and neoformation of minerals in carbonate soils affected by pyrite tailings

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The pollution

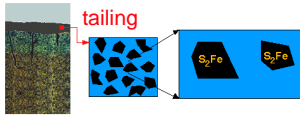
We have studied the oxidation of the tailings spilled when the retention walls of a pond containing the residues from a pyrite mine in Aznalcóllar (southern Spain) broke open, as well as the effects on the weathering and neoformation of minerals in carbonated soils ($\text{CaCO}_3 = 7.1\%$; $\text{pH} = 7.9$). The climate of this area is typically Mediterranean.

	g/kg		g/kg		g/kg		g/kg		g/kg
S	397.0	Pb	11.0	Mg	6.4	Sb	0.8	Tl	0.06
Fe	364.0	Zn	9.6	Ca	4.1	Bi	0.08	Co	0.05
Al	16.2	As	7.2	Cu	2.6	Cr	0.06	Cd	0.03

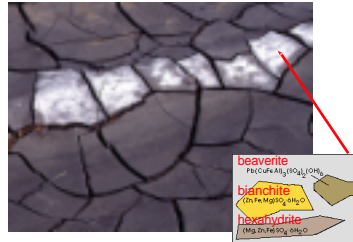
Elemental composition of the tailings

The pollution evolution

Initial contamination

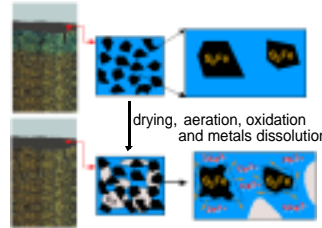


On spreading over the soil surface the tailings were saturated in water and therefore reducing conditions predominated and the sulphide particles remained stable.



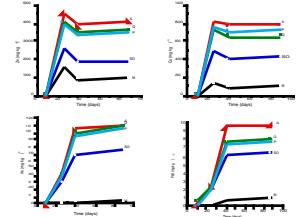
In the first step, when drying took place (10 days after the spill), the soluble elements from the tailings rose by capillary action to the surface, precipitating and forming a white salty layer.

Formation of the acidic pollutant solution in the tailings



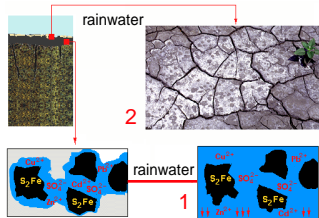
As a result of drying and consequently aeration of the tailings, sulphides oxidized to sulphates, the pH markedly fell, due to the formation of sulphuric acid, while the pollutants solubilized.

Soluble metals in the tailings over time. A, Q, P, SO, M = sampling points.

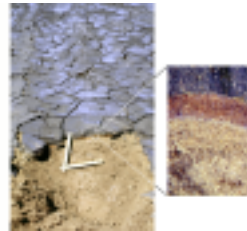


The concentration of metals in the soluble phase greatly increased with time. The oxidation of the sulphides bonded to Zn and Cu (such as sphalerite or chalcopyrite) was very rapid and intense. Other sulphures present in the tailings, such as arsenopyrite and galene, oxidized more slowly and less intensely (As and Pb).

Infiltration of the acidic pollutant solution : soil alteration



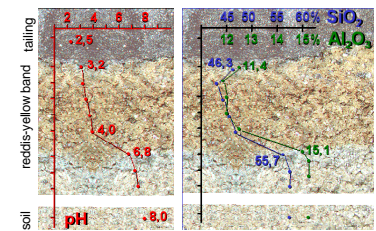
With the rainwater, the acidic pollutant solution (1) and the salts that had previously formed on the surface of the tailings (2) infiltrated the soil.



As a result, in the first 12 mm of the soil, a reddish-yellow band formed, in which the weathering of the carbonates, the hydrolysis of the finest particles (silt and clay) and the precipitation of part of the pollutants took place.

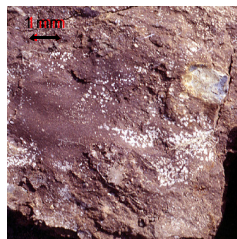
	Soil not contamin.	2 months after	15 months after
pH	7.9	6.0	3.5
CaCO_3	7.8	3.3	0.0
Clay	18.4	5.9	3.8
Fine silt	12.8	n.d.	4.7
Coarse silt	12.1	n.d.	9.1

n.d. = not determined

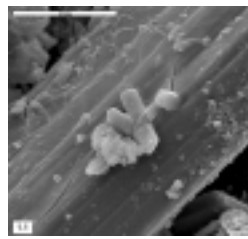


The intense acidity produced in the reddish-yellow band originated the mineral hydrolysis, revealed by significant losses of SiO_2 and Al_2O_3 .

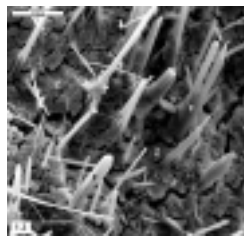
Infiltration of the acidic pollutant solution : mineral neoformation



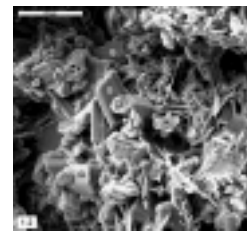
The acidic solutions, when penetrating the soils, produced the precipitation of salts and the neoformation of minerals.



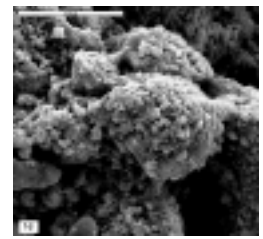
The SO_4^{2-} ions in the acidic pollutant solution precipitated in the reddish-yellow band, primarily as gypsum (G) ...



... also, as needle-like crystals of iron sulphate (F) (melanterite?) ...

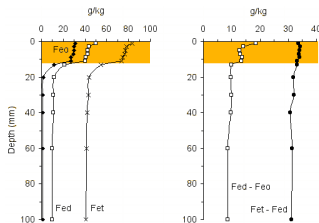


... projecting from a mass of sulphate complexes with Zn, Fe and Mn (Z), as well as raised scaly formations of aluminium sulphate (probably alunite = A) ...

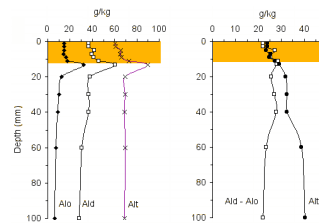
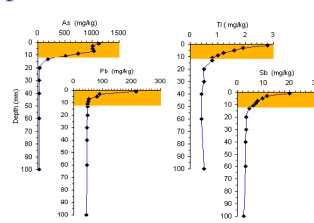


... and aggregated microcrystals of iron and potassium sulphates (jarosite = J).

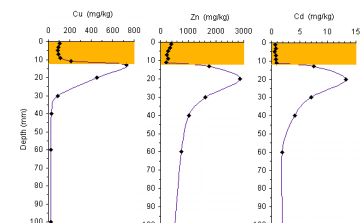
Infiltration of the acidic pollutant solution : soil contamination



Amorphous hydrous Fe-oxides also precipitated in the reddish-yellow band (orange colour in picture), adsorbing As, Pb, Tl and Sb dissolved in the acid solution.



The Al which had dissolved in the acidic solution, although precipitated partially in the form of aluminium sulphate in the first 12 mm, almost precipitated as amorphous hydrous Al-oxides between 12 and 14 mm ...



... in depth ($\text{pH} = 6.0$) adsorbing the Cu dissolved in the acidic solution. The Zn and Cd also accumulated mainly at $\text{pH} = 6.8$ (12-20 mm in depth).