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Selenium Speciation in Waste Materials From an Exhausted Iberian Pyrite Belt Mine

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Abstract

Selenium is an essential nutrient for humans, animals and microorganisms, but it becomes toxic at concentrations slightly above the nutritional levels. This naturally occurring trace element can be released to the environment from various anthropogenic sources such as mining, agricultural, petrochemical and industrial processes and its toxicity is developed along a complex cycle involving adsorption by soil components and subsequent accumulation by plants. In the environment, selenium can occur in several oxidation states ranging from selenide ($Se^{=}$) to elemental selenium (Se^0), selenite (Se^{4+}) and selenate (Se^{6+}). Selenium contents above 900 ppm were recently assigned in mine wastes from the sulphur factory at the São Domingos exhausted pyrite mine exploited in the Iberian Pyrite Belt (south Portugal) since Roman times until 1966. Aiming at a sustainable remediation of this mining site, an X-ray absorption spectroscopy study using synchrotron radiation, combined with X-ray diffraction, was undertaken to clarify the speciation state of selenium and the nature of Se-carrier phase(s). The results show that selenium does not significantly replace sulphur under the form of selenate in the dominant sulphate phases and occasionally remains as a substituting selenide anion in debris of the original sulphides present in the mine waste materials.

Keywords: Selenium, mining wastes, Iberian Pyrite Belt, X-ray absorption spectroscopy, XANES

1. Introduction

Mine wastes configure nowadays two quite opposite interests since they represent simultaneously an environ-mental concern due to the presence of hazardous metals and other toxic elements, plus a potential mineral resource when they are the object of a sustainable recovery of economically valuable metals.

The increased demand of some scarce metals observed in the last decade has intensified the search for their recuperation from mine wastes and residual exploitation materials, thus enhancing the need for a full comprehension of the way these metals are incorporated. A successful accomplishment of this task requires the use of advanced X-ray absorption methodologies, as exemplified by a recent study on mining debris of the exhausted centennial Iberian Pyrite Belt (IPB) mine of São Domingos in southeast Portugal (Alvarez-Valero et al., 2008) to assess the binding state of a very scarce metal, rhenium (Figueiredo et al., 2014). The actual interest in exploring mining residues plus industrial wastes derived from former ore deposits processing plants was clearly highlighted in the context of the recently concluded EU research project, *ProMine* (Nano-particle products from new mineral resources in Europe, FP7-NMP-2008-LARGE-2, 228559).

Selenium is known for its toxicity (Lenz & Lens, 2009), developed along a complex cycle involving adsorption by soil components clays and iron-rich particulate minerals (Hayes et al., 1987; Peak & Sparks, 2002; Scheinost & Charlet, 2003) and subsequent accumulation by plants (Ellis & Salt, 2003); as a component of radioactive wastes, it also configures a concern through the isotope ^{79}Se (Ashworth & Shaw, 2006). Aside these apprehensions,