X-ray absorption spectroscopy at Re L_3-edge applied to mine waste materials: a possible input to the sustainable recovery of rhenium

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Rhenium belongs to 7th column of the Periodic Table along with a widespread element (manganese) and a non-naturally occurring one (technetium). It is a valuable but very scarce metal with very high melting point appearing in Nature mainly carried by molybdenite (MoS_2) through a diadochic replacement of molybdenum and it was for long assumed to be related with the volatile transport and deposition of the refractory metals Mo and W in high temperature magmatic fluids [1]. However, while molybdenum and rhenium are typical chalcophile elements, tungsten oxidizes quite easily and very seldom occurs as a sulphide (WS_2, tungstenite). The formal valence of Re ranges from -1 to +7 and the prevalence of this exceptionally high oxidation state has rendered rhenium technologically relevant for the production of catalysts [2].

Due to these unique properties, actual applications of rhenium cover distinctive areas ranging from the nuclear field to the electrical and aero-spatial industries, particularly for the production of superalloys applied in jet engines. Because of its very low availability (1 ppb average concentration in the Earth´s crust) comparative to the actual industrial demand, rhenium is nowadays one of the most expensive industrial commodities. It is mainly recovered as a by-product in the refinement of molybdenum concentrates from porphyry copper deposits because the flue dusts obtained from these metal concentrates are enriched in Re as a result of the high volatility of the molecular oxide Re_2O_7 [3]. Notably rare as a distinct mineral species, the first Re-mineral (rheniite, ReS_2) was identified twenty years ago [4] as a condensate in the fumaroles of Kudriavy volcano, Kurila Islands, and more recently assigned in the Pagoni Rachi Mo-Cu prospect in northern Greece [5].

In view of the actual interest in exploring exhausted mine residues from the exploitation of sulphide ore deposits in Europe[#], it is clear that finding about 3 ppm of Re in waste materials sampled close to the old sulphur factory from São Domingos abandoned mine [6] deserves a particular attention, specially because no reference is known to a significant occurrence of molybdenite in association with the volcanic-hosted massive sulphide deposits from the Iberian Pyrite Belt, SW Iberian peninsula. ~~Taking profit~~Profiting from an experiment focused on studying the binding state of rhenium in molybdenite*****, a first X-ray absorption near-edge spectroscopy (XANES) study at Re L_3-edge was carried out at the ESRF; along with a sample of São Domingos mine wastes, model compounds displaying various Re formal valences and coordinations - ReO_3, Re_2O_7, $KReO_4$ - were studied [7]. These preliminary results clearly showed that rhenium is bound to oxygen in the mine waste sample - a relevant conclusion within the frame of a future prospect on a sustainable Re-recovery; however, further work is needed with the aim of ascertaining the original Re-carrier mineral phase.

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