

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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Scientific Research Area: CHEMISTRY

Keywords: Re L_3 -edge; XANES; Re oxides; molybdenite; mine waste materials.

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.

References

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[#] Project ProMine (FP7-NMP-2008-LARGE-2, 228559, *Nanoparticle products from new mineral resources in Europe*)

* Experiment CH-3421 at beamline BM23, September 2011.