



	<b>Experiment title:</b> Towards a sustainable recovery of critical metal resources: a XAFS study of <u>W</u> and <u>Re</u> $L_1$ - and $L_3$ -edges in tailing materials from the Panasqueira tungsten mine	<b>Experiment number:</b> ES-128
<b>Beamline:</b> BM-25A	<b>Date of experiment:</b> from: 13 June 2014                      to: 17 June 2014	<b>Date of report:</b> 12/08/2014
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Eduardo Salas	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): T.P. Silva, *M.J. Batista, D. de Oliveira, LNEG - National Laboratory for Energy & Geology, Unit of Mineral Resources & Geophysics, 2721-866 Alfragide, Portugal *M.O. Figueiredo, LNEG (id.) & CENIMAT/I3N, Materials Science Dept., Faculty of Sciences & Technology, New Univ. Lisbon (UNL), 2829-516 Caparica, Portugal *J.P. Veiga, CENIMAT/I3N, Mat. Sci. Dept., Fac. Sci. Technol., UNL, 2829-516 Caparica, Portugal		

## Report:

The exploitation of Panasqueira mine has turned Portugal the major European tungsten producer. With a history overpassing a century, this mine has given rise to a large deposit of tailings estimated to contain over 200 tons of wolframite. Considering recent EU efforts to implement a sustainable recovery of critical mineral resources, it is essential to enhance tungsten recuperation from mining debris and simultaneously to point out mineral phases carrying scarce metals - namely rhenium, that according to recent analyses occurs in Panasqueira mine tailings at more than ten times its mean concentration in the earth's crust.

Tungsten displays unique and remarkable physical plus chemical properties that render impossible its replacement in certain relevant specialized industrial applications, being regarded as an essential commodity and a metal of high strategic importance. It has the highest melting point of all elements (except carbon) and the lowest expansion coefficient combined with the highest tensile strength of any pure metal above 1650C, associated to very high thermal and electrical conductivity plus high compression and elasticity modules.

Rhenium is a very scarce metal with a melting point above 3100C occurring in Nature carried by molybdenite ( $\text{MoS}_2$ ). When roasting the concentrates molybdenite, rhenium is lost as a gaseous molecular oxide ( $\text{Re}_2\text{O}_7$ ) in which structure the metal assumes both tetrahedral and octahedral coordinations. The formal valence of rhenium ranges from  $-1$  to  $+7$  and, due to the stability of such high oxidation state, it became technologically relevant for the production of catalysts, along with platinum. Nowadays, rhenium is extensively applied in distinct areas, like the biomedical and nuclear fields, plus the electrical and aero-spatial industries, particularly for the production of superalloys with high mechanical strength, ductile properties at high temperatures and resistance to corrosion.

A previous Re  $L_3$ -edge XANES experiment (CH-3421) has allowed to focus the binding state in molybdenite [1] and in wastes from the old pyrite mine of S. Domingos [2], thus enhancing the importance of addressing Panasqueira tungsten mine tailings. The present experiment focused both  $L_3$  and  $L_1$  absorption edges of W and Re in various model minerals and compounds and in these mining residues (which phase constitution was previously characterized by X-ray diffraction in the laboratory).

Rhenium metal was irradiated for energy calibration purposes. Rhenium oxides (commercial products checked by laboratorial XRD) configuring various formal cation valences and coordination geometries – tetrahedral  $\text{Re}^{7+}$  in  $\text{KReO}_4$ , octahedral  $\text{Re}^{6+}$  in  $\text{ReO}_3$  (perovskite-type arrangement) and octahedral  $\text{Re}^{4+}$  in  $\text{ReO}_2$  (rutile-type crystal structure) – were irradiated as model compounds, along with W-minerals (scheelite,  $\text{CaWO}_4$ , with tetrahedral  $\text{W}^{6+}$ , and wolframite  $(\text{Fe,Mn})\text{WO}_4$  in which crystal structure  $\text{W}^{6+}$  ions have a slightly distorted octahedral environment) and  $\text{W}^{6+}$ -O synthetic compounds ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , tetrahedral, and  $\text{WO}_3$ , octahedral).

The binding state of tungsten was efficiently addressed in the irradiated materials. Figure 1(a) compares the  $W L_1$ -edge XANES spectra obtained for tetrahedral  $W^{6+}$  model compounds with the spectrum collected from a sample of Panasqueira mine tailings [3] where vestigial scheelite was detected by laboratorial XRD (despite not efficiently checked by XAS), and Figure 1(b) compares the  $W L_3$ -edge XANES spectra collected from wolframite-containing tailings – well represented in 4-2 sample and vestigial in 6-1 materials [4].

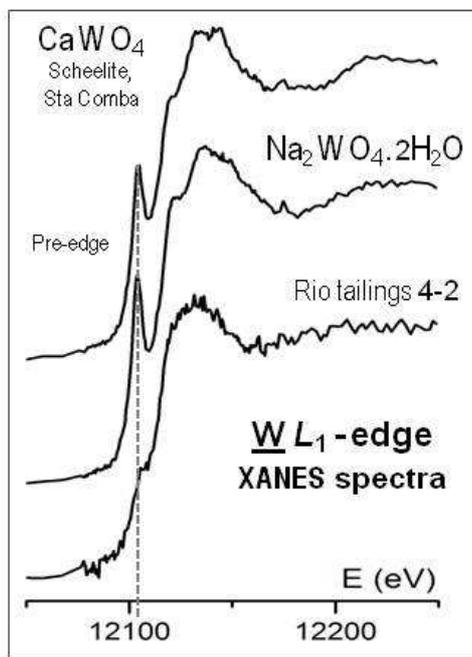


Figure 1(a)

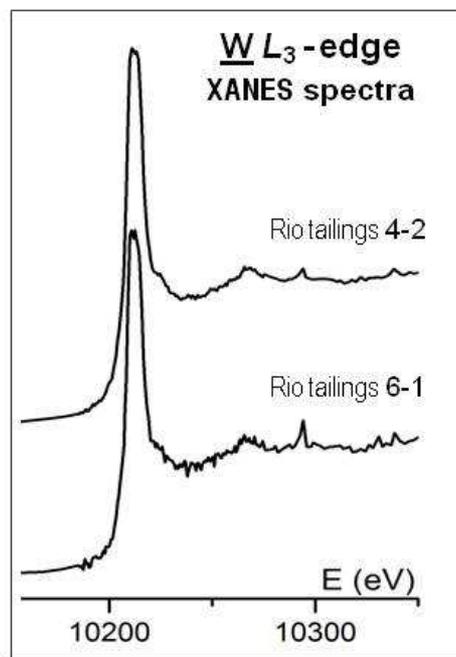


Figure 1(b)

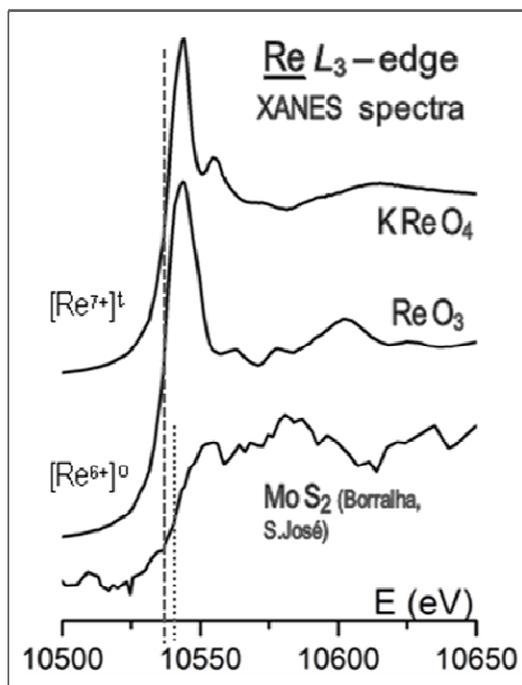


Figure 2

The very low concentration of rhenium in the studied natural materials (both minerals and mine tailings) hinders an efficient XAS study, as clearly illustrated by the  $Re L_3$ -edge XANES spectrum collected from a sample of molybdenite which Re-

content was tentatively tackled using ICP-MS [5]. Figure 2 compares the  $Re L_3$ -edge XANES spectra obtained for two model oxides with an identical but poorly defined spectrum obtained for a molybdenite sample containing vestigial rhenium.

- [1] T.P. SILVA *et al.* (2013) Molybdenite as a rhenium-carrier: first results of a spectroscopic approach using synchrotron radiation. *J. Minerals & Materials Characterization and Engineering* **1**, 207.
- [2] M.O. FIGUEIREDO *et al.* (2014) Towards the recovery of by-product metals from mine wastes: an X-ray absorption spectroscopy study on the binding state of rhenium in debris from a centennial Iberian Pyrite Belt mine. *J. Min. Mater. Charact. Engin.* **2**, 135.
- [3] P.F. ÁVILA *et al.* (2008) Geochemistry and mineralogy of mill tailings impoundments from the Panasqueira mine (Portugal): implications for the surrounding environment. *Mine Water Envir.* **27**, 210.
- [4] C. GRANGEIA *et al.* (2011) Mine tailings integrated investigations: the case of Rio tailings (Panasqueira mine, central Portugal). *Engineering Geology* **123**, 359.
- [5] T.P. SILVA *et al.* (2014) Valorisation of mineral resources: contributions of MinReMol project to a sustainable rhenium recovery from mining residues. In press, *Comunicações Geológicas*.