THE RECOVERY OF SCARCE CRITICAL METALS IN ENVIRONMENTAL TREATMENTS OF MINING RESIDUES: THE CASE OF RHENIUM IN PANASQUEIRA TUNGSTEN MINE TAILINGS

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CRITICAL METALS for EU industries: rhenium

"ProMine has created an excellent network of expertise that should deliver results long after the project's completion."

Research and development

ProMine

research and industry partnerships yield lasting results

Products with commercial potential have already been demonstrated by this EU project for nano-particle products from new mineral resources.

PROMINE
- Nanotechnology project part funded under the EU's Seventh Framework Programme
- Duration: 2009–2013
- Budget: approx. €18 million
- Participants: 31 partner organizations from eleven countries
- Coordinator: Geological Survey of Finland (GTK)

More information: http://promine.gtk.fi

Re

Innovation in a sustainable recovery of by-product metals from wastes of old mines

What has ProMine achieved so far?

The EU wanted to see tangible results i… ing EU resources and sustainability, as… of new products. The products had to … products, not simply proposals on paper… to truly benefit European industry. In th… got what it paid for. ProMine successfully… products from European minerals. It id… for handling mine wastes and byproduc… ing the nano-materials from them. Life… performed on the developed products.

SCHWERTMANNITE FOR WASTEWATER TREATMENT

A team working with Schwertmannite, an iron-rich orange precipitation sometimes associated with acid mine drainage, devised a way to convert the mineral into high-quality pigments for the paint and ceramic industries. Schwertman…

RHENIUM FOR AEROSPACE

The rhenium group developed processes for spherical rhenium and several new rhenium compounds. The work has attracted the interest of jet turbine makers, who see the possibility of using rhenium compounds on turbine blades and engines to increase their high-temperature durability.

NANOSILICA FOR CONCRETE AND INDUSTRY

Nanosilica from the olivine byproduct generated at magnesite mines was demonstrated to be a good substitute for cement in concrete. The new concrete is not only more durable but also lighter, which translates into transportation savings in the case of concrete building elements. Nanosilica's utility as a paper coating for binding abrasives to sandpaper and as a replacement for organic binders in ink-jet printing was shown.

3D/4D MODELING FOR THE MINING INDUSTRY

3D and 4D models were developed for four major European ore belts located in Scandinavia, Germany, Poland, Greece and the Iberian Peninsula. Ore deposits were modeled to depths as great as five kilometers. 4D, which adds the time dimension to the model, was shown to help in understanding how ore deposits evolved at a specific site. Such modeling should help our understanding of geological processes and suggest new areas with ore potential for study.

2/2013 Geofoorumi 23 ← 2013

ProMine — **Critical raw materials in Europe**

Project ProMine (FP7-NMP-NMP-2008-LARGE-2, 228559, *Nanoparticle products from new mineral resources*

Portugal & **Austria** are the two european **producers of** *tungsten*

The list of commodities is based on the report published by the EC, DG Enterprise and Industry: The raw materials initiative - Critical raw materials for the EU. Report of the Ad-hoc Working Group on defining critical raw materials.

Commodity	Very large (> X)	Large (> X)	Medium (> X)	Small (> X)
Antimony	100,000	25,000	2,000	1,000
Beryllium	20,000	2,000	200	50
Cobalt	500,000	50,000	2,000	200
Fluorspar	5,000,000	1,000,000	200,000	50,000
Gallium	100	50	10	1
Germanium	500	100	20	5
Graphite	10,000,000	1,000,000	100,000	10,000
Indium	500	100	25	5
Magnesium	100,000,000	10,000,000	1,000,000	100,000
Niobium	1,000,000	100,000	10,000	2,000
PGM	1,000	100	10	1
Rare Earth	1,000,000	100,000	10,000	1,000
Tantalum	25,000	2,000	1,000	200
Tungsten	200,000	50,000	5,000	500

Deposit classes according to the tonnage expressed in metric tons (1,000 kg)

Commodity: Antimony, Beryllium, Cobalt, Fluorspar, Gallium, Germanium, Graphite, Indium, Magnesium, Niobium, PGM (Platinu…, Rare Earth, Tantalum, Tungsten

Pattern: Old deposits and prospects; Deposits under exploitation

Deposit size: Very large deposit, Large deposit, Medium deposit, Small deposit

[Data from **2010**]

SEVENTH FRAMEWORK PROGRAMME — NMP — Nanosciences, Nanotechnologies, Materials and New Production Technologies

Draft 2010/09 v. 1.1

Fig. 1

Fig. 3

R. HALIGOWSKI, Technology Management, EU Project Coordinator

Polish Aerospace Technology Platform Transport in FP7 (Brussels, April 7, & Warsaw, June 6-7, **2006**)

www.kpk.gov.pl

CFM 56 jet engine: **blades** made with 3% Re

F-15 engine uses Re-containing second generation **superalloys** [From: ***Wikipedia*** (rhenium)]

2014 International Year of Crystallography

United Nations Educational, Scientific and Cultural Organization — International Union of Crystallography — 2014 international year of crystallography

Crystallography matters!

International Year of Crystallography 2014

Rhenium in aerospace industry

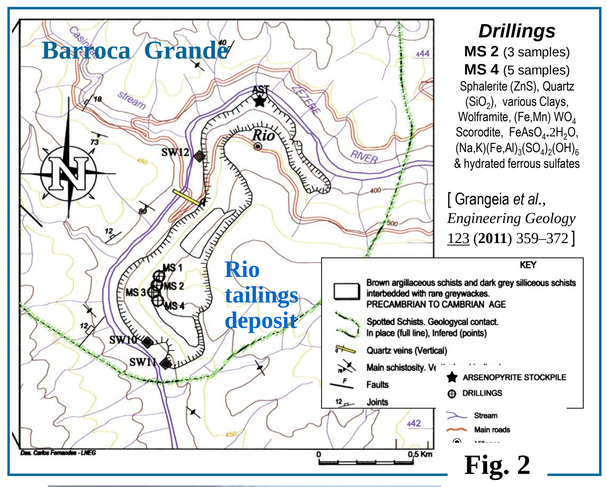
Problematic

Tungsten displays ***unique physical-plus-chemical properties*** that hinder its replacement in relevant specialized industrial applications and render it a critical commodity for the EU (Fig.1). For long been mined at ***Panasqueira (Beira-Baixa district), making Portugal the main European producer***, this mine has given rise to a huge tonnage of debris (attaining 0.3% WO_3 [1] at Barroca Grande slimes, Fig.2). Considering ***Horizon 2020*** objectives and recent ***efforts to implement a sustainable retrieval of critical mineral resources,*** it became mandatory to improve the recovery of tungsten from mine tailings and, simultaneously, to ***identify mineral phases carrying valuable scarce metals*** – namely ***rhenium***, a singular metallic element with high melting point, high density, high modulus of elasticity and resistance to creep, high electrical resistivity, low friction and no ductile-to-brittle transition, and ***a critical commodity for the aero-space industry*** (Fig. 3).

W-Re associations were focused in studies on synthetic $(1\text{-}x)WO_{3\text{-}y}.xReO_2$ [2] and "WO_3" [3] for electro-chromic and catalytic applications, being therefore adequate to look for the eventual presence of similar phases in Panasqueira tailings.

Spectroscopic study: fundamentals

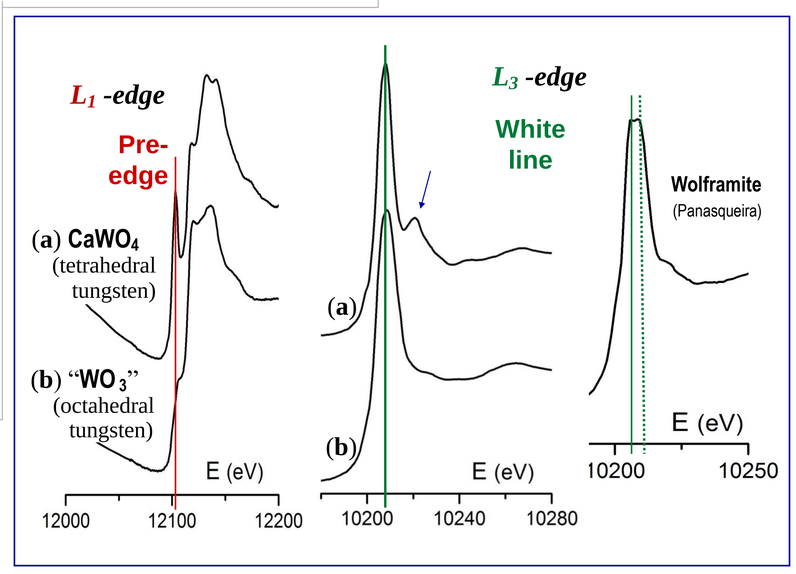
X-ray absorption energies quoted for W ***L_1- and L_3-edges*** are **12099.8** and **10206.8** eV respectively. The energy of the ***white-line in the L_3-edge XANES spectrum*** is clearly indicative of the ***metal ion valence*** in oxide compounds (W^{6+} in the present case) and the occurrence of a ***pre-edge feature in the L_1-edge XANES spectrum*** denotes a non centro-symmetric coordination geometry [3,4], namely for ***tetrahedral ions*** – as in scheelite (Fig.4). Conversely, a ***perceptible splitting of the white-line in the L_3-edge spectrum*** obtained for ***wolframite*** is indicative [5] of a distorted environment of W^{6+} ***octahedral ions*** by oxygen anions (Fig. 5). Therefore, the ***analysis of XANES data*** decisively contributes to elucidate both the ***valence*** and the ***coordination*** of ***W ions*** when irradiating ***samples of mining residues*** (Fig.2), particularly if the X-ray absorption spectroscopy assay is combined with an ***X-ray diffraction characterization*** (Fig.6).

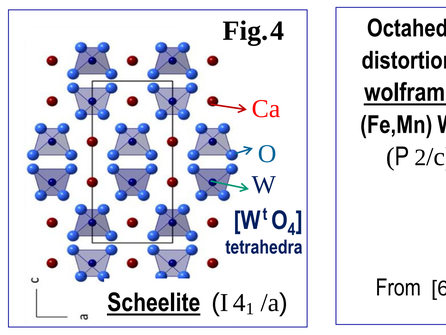


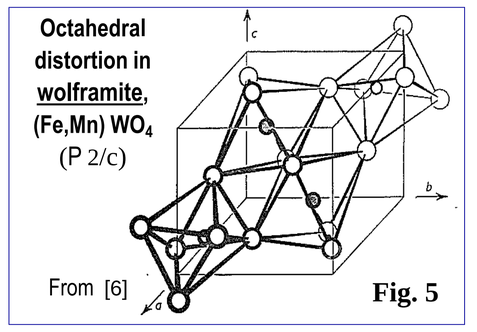
[Grangeia *et al.*, *Engineering Geology* 123 (**2011**) 359–372]

Fig. 2

Fig. 8 – XANES spectra at W L_1– **and** L_3 **– edges** obtained for an ***oxide*** with W^{6+} ***in octahedral coordination*** and for selected ***model minerals*** (scheelite, with a *pre-edge feature* due to tetrahedral W^{6+}, and wolframite, showing the *splitting of the white line* due distortion of the octahedra).



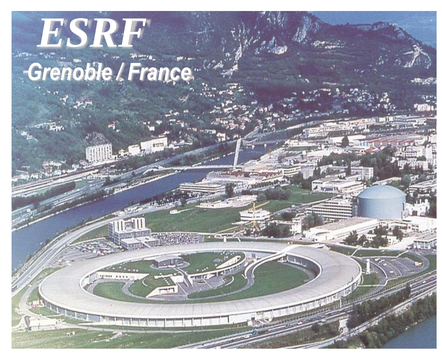


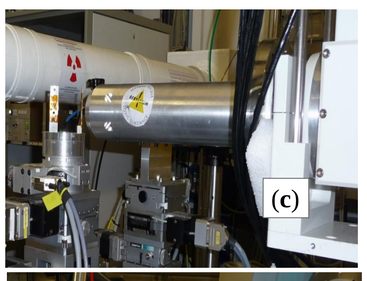


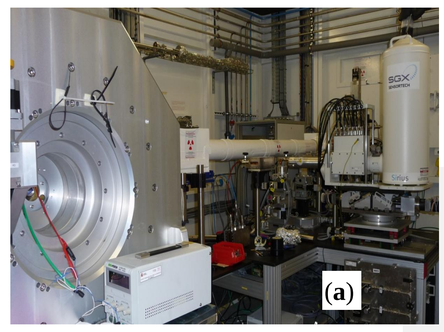
(a) Partial view of **tailings deposit** (dust in the air due to the wind).

(b) Vehicles ready to unload coarse materials in the deposit.

From: **Heavy metal pollution in mine-soil-plant system in São Francisco de Assis, Panasqueira mine (Portugal),** by C. Candeias *et al.*, *Appl. Geochem.* 44 (**2014**) 12–26







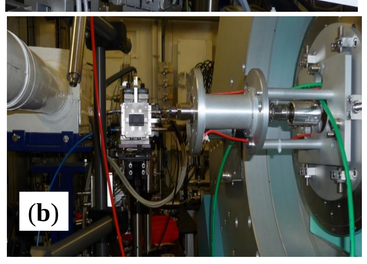


Fig. 7 – Instrumental set-up of beamline **BM-25A, SpLine: (a) g**eneral view; (**b**) details of sample mounting to collect XRD patterns and (**c**) for XANES assay.

Table 1 - Analyses of Panasqueira mine materials

Report: A12-14159-UT6
Report Date: 2/15/2013
Activation Laboratories

Analyte Symbol		Cu	W	Re	Pb	Mo	Zn
Unit Symbol		ppm	0.001	ppm	ppm	ppm	ppm
Detection Limit		0.2	FUS-MS - Na_2O_2	0.001	0.5	0.1	0.2
Analysis Method	[TD-MS]						
CONCENTRADO GROSSEIRO = 70% (W+Sn)	PAN - 12	5050	1,08	0,011	507	2,7	3510
CONCENTRADO FINO = 68% 70% (WOLFRAMITE)	PAN - 13	17,2	15,3	0,013	145	0,8	300
CONCENTRADO FINO = 68% 70% (CASSITERITE)	PAN - 14	216	5,81	0,013	567	1,1	103
CONCENTRADO CALCOPIRITE (Lav.	PAN - 15	> 10000	0,561	0,013	> 5000	28,7	> 10000
CONCENTRADO CALCOPIRITE	PAN - 16	> 10000	0,11	0,012	> 5000	51,9	> 10000
CONCENTRADO SULFURETOS + W +	PAN - 18	7550	6,2	0,015	417	3,1	> 10000

Not related

Experimental

A preliminary XANES approach to the *L*-edges of tungsten was attempted through an approved X-ray absorption experiment (***ESRF, EV-13****) focused on selenium binding states in mine waste materials. The spectra were collected in fluorescence yield mode at ***beam-line BM-25A*** (Fig.7) using a 13-elements Si(Li) solid-state detector and a Si(111) double-crystal monochromator with detuning for harmonic rejection, in this way assuring an energy resolution of $\Delta E/E=1.5x10^{-4}$. Energy calibration was assured by irradiating a rhenium metal foil.

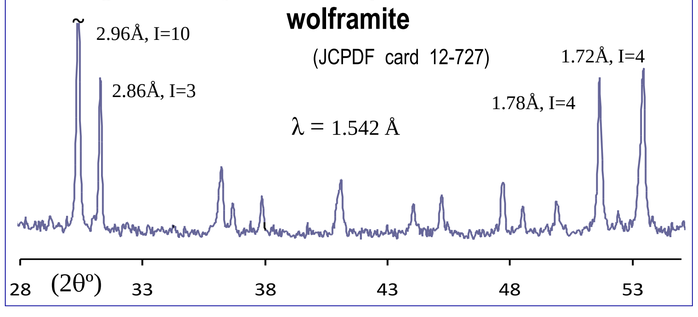
Obtained W ***L_1– and L_3–absorption edges*** spectra display energies and details in good agreement with theoretical values (Fig.8).

Samples of grinded debris collected at Panasqueira mine tailings (Fig. 2) were irradiated and, profiting from the instrumental facilities available at the beam-line [7], the phase constitution of irradiated materials was characterized by high-resolution powder diffraction (HRPD) at a fixed wave-length of 0.825Å. Pellets of slightly grinded model compounds mixed with boron nitride were prepared in a proportion adequate to optimize the absorption jump and minimize total absorption, thus improving the display of edge features in the XANES spectra.

Experiment of June 13-17, 2014

Experiment **ES-128 (**approved by the ESRF for beam-time) is focused on a ***future sustainable recovery of critical metal resources from Panasqueira mine tailings*** with two main objectives: the design of a methodology for ***recovering tungsten*** and to ***identify phases hosting scarce metals*** (not addressed in already published studies about Rio tailings [8]), namely ***rhenium***, that occurs in those mine debris at a level more than ten times its mean concentration in the Earth's crust (according to recent chemical analyses#, Table 1).

Fig. 6 – X-ray diffraction pattern obtained for a wolframite



References

[1] A. M. Botelho de Sousa, 1994. *Est., Notas e Trabalhos, IGM*, 36, 77-90.
[2] A. Kuzmin *et al.*, 1998. *J. Appl. Phys. 84, 5515-5524.*
[3] S. Yamazoe *et al.*, 2008. *J. Chem. Phys. 112, 6869-6879.*
[4] A. Kuzmin & J. Purans, 2001. *Radiat. Measuremt.* 33, 583-586.
[5] L. Garcia *et al.*, 2011. *J. Appl. Phys. 110, 04350-1-8.*
[6] R.O. Killing, 1957. *Acta Cryst. 10, 209-213.*
[7] J. Rubio-Zuarzo & G.R. Castro, 2009. *Sem. Soc. Esp. Min.* 6, 89-108. http://www.ehu.es/sem/seminario_pdf/SEMINARIO_SEM_6_089.pdf
[8] C. Grangeia *et al.*, 2011, *Engineering Geology* 123 , 359–372.89.pdf

The authors thank Dr. P. Ávila (LNEG) for providing the studied Rio samples. Research carried out under the exploratory project ***MinReMol*** financed by FCT-MEC ((EXPL/AAG-REC/0978/2012) .

FCT Fundação para a Ciência e a Tecnologia — MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA

Thanks are also due to FCT-MEC for the grant PEst- C/CTM/LA0025/2013-14.

* EU financial support to perform the experiment EV-13 at the *ESRF* is acknowledged**.**

\# EU project **ProMine**, *Nanoparticle products from new mineral resources in Europe* (FP7- NMP-2008 - LARGE-2, 228559).