

Supplementary Information

Oxidative transformation of Tungsten (W) nanoparticles potentially released in aqueous and biological media *in case of Tokamak (nuclear fusion) Lost of Vacuum Accident (LOVA)*

Transformation oxydative de nanoparticules de tungstène (W) potentiellement libérées dans les milieux aqueux et biologiques en cas d'accident de perte de vide dans un réacteur de fusion (*Tokamak*).

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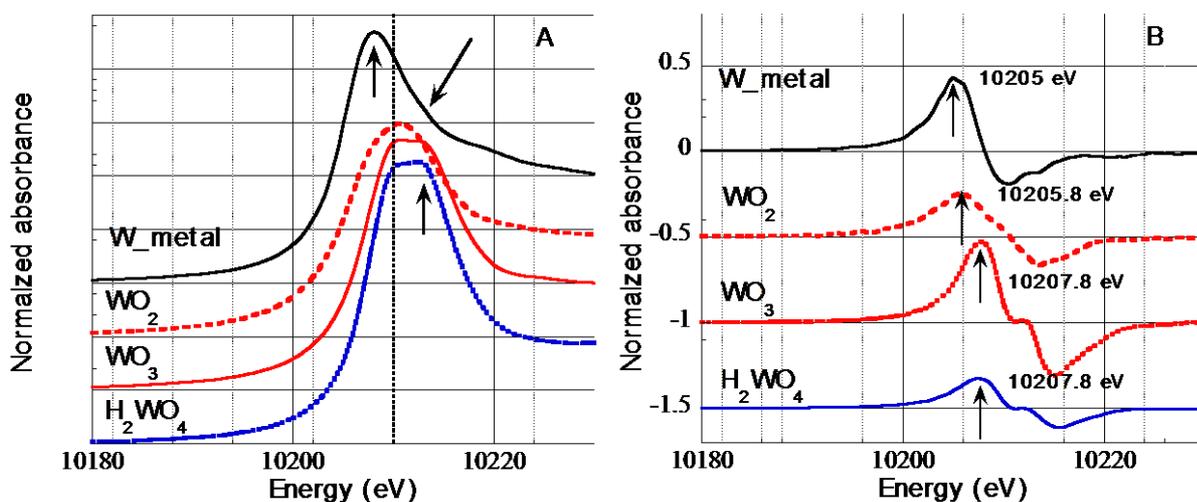
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1-Redox state of the tungsten particles in suspension: XANES results

X-ray absorption spectroscopy (XAS) is sensitive to the W redox state and atomic structure for crystalline as well as for amorphous materials. XANES spectra of W reference compounds allow discriminating W with different redox states. Indeed, a shift in energy can be seen when W redox state increases from W^0 to W^{+4} (WO_2) and W^{+6} (WO_3 and H_2WO_4) (Fig.SI-1A). The shift at the first inflection point of the XANES spectra (first maximum on the derivative curve (fig. SI-1B)) reaches 0.8

eV and 2.8 eV for W^0 - W^{+4} and W^0 - W^{+6} respectively. The XANES spectra are not only shifted as function of the redox state, the shape of the curve is also modified. For instance a shoulder can be seen at 10210-10214 eV for metallic W^0 , while two non-well isolated peaks can be seen for W^{+6} spectra at 10210 and 10213.5 eV (Fig. SI-1A). The energy shift between the three redox forms does not follow a linear law. Therefore, even if the sensitivity of XANES can easily discriminate W^0 from W^{+6} forms, the presence of W^{+4} in the case of mixture and low amount of W^{4+} , is more difficult to prove.

The XANES spectra (and their derivative) of the 4 solid samples from the W_Milling dissolution kinetic experiment in TRIS can be seen on figure SI-1C&D. From $t=0$ to 24 h, it is difficult to accurately quantify the energy shift while for the $t=48$ h sample, the shift reached (0,8 eV). For $t=0$, 2h and 24h the first inflection point of the XANES spectra occurred at 10205.6 eV, while for $t=48$ h the value is 10206.4 eV. In the case of W_Plasma in TRIS after 24h, the first inflection point occurred at 10206.9 eV and at 10207.8 eV for W_Milling in LHC9 medium at 10mg/l. XANES spectra of the kinetic experiments were fitted using LCF of the spectra of the reference compounds (one example is seen in fig. SI-1E&F). Quantitative results are detailed in figure SI-2. It is first worth noting that the quality of the adjustment was not perfect as seen in fig. SI-1E&F and that the sensitivity between the different fractions is known to vary between 15 to 20% (e.g. O'Day et al., 2004). From $t=0$ to 48h the variation of the proportion of metallic W are limited and remained smaller than the sensitivity of the technique. Indeed, the proportion of metallic W varied between 90 ± 15 to 82 ± 15 % in the solid part of the suspension. From XANES results, only metallic W and W^{6+} were detected in the particles whatever the sampling time, except at $t=2$ h with a low contribution of W^{4+} at the limit of the uncertainty.



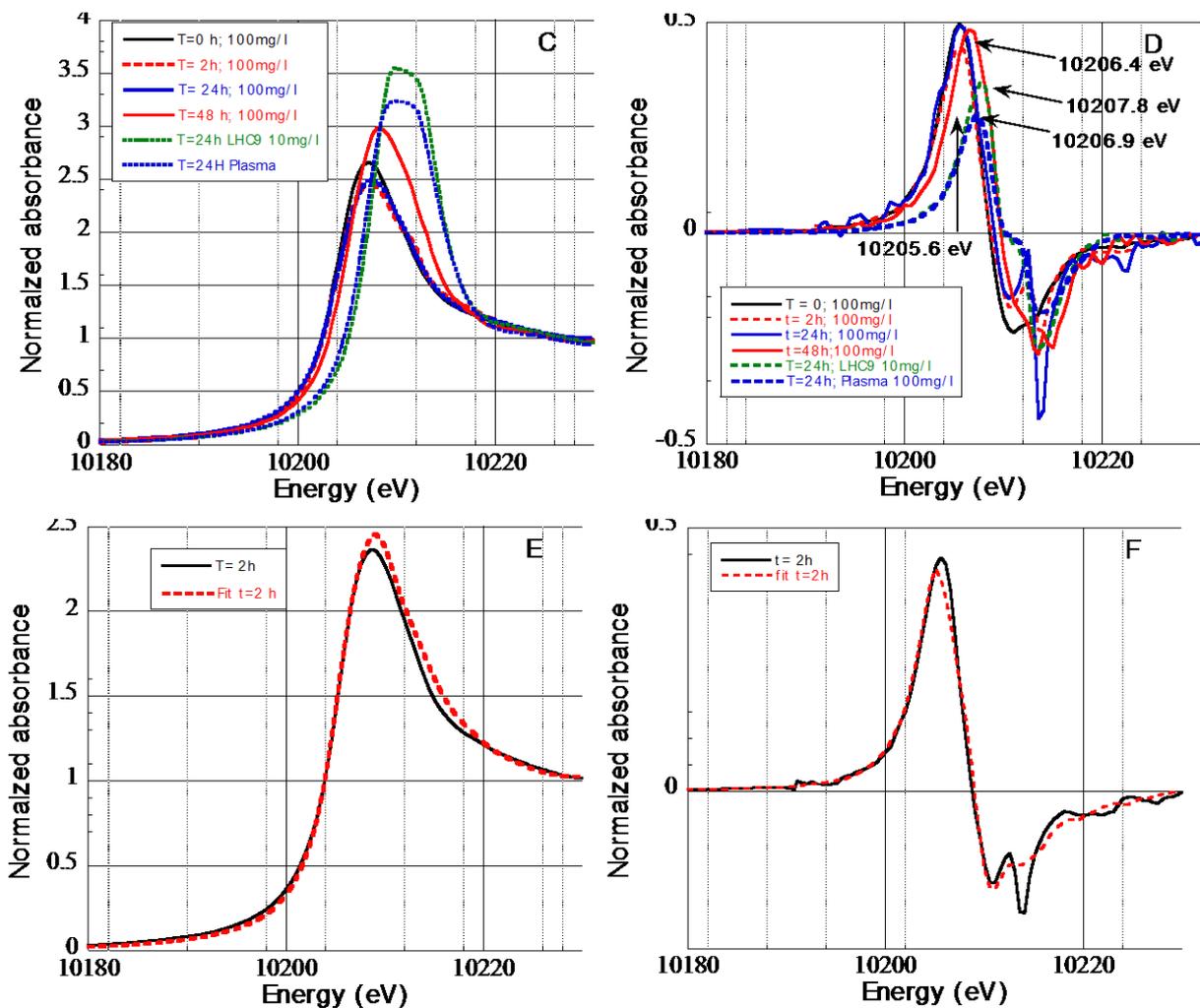


Figure SI-1: XANES spectra and first derivative at the W L_{III}-edge of A-B) reference compounds, C-D) Solid samples from the dissolution experiment (W_milling in TRIS and LHC9 media, Plasma in TRIS) E-F) example of XANES Fit (W_Milling in TRIS after 2h) using LCF.

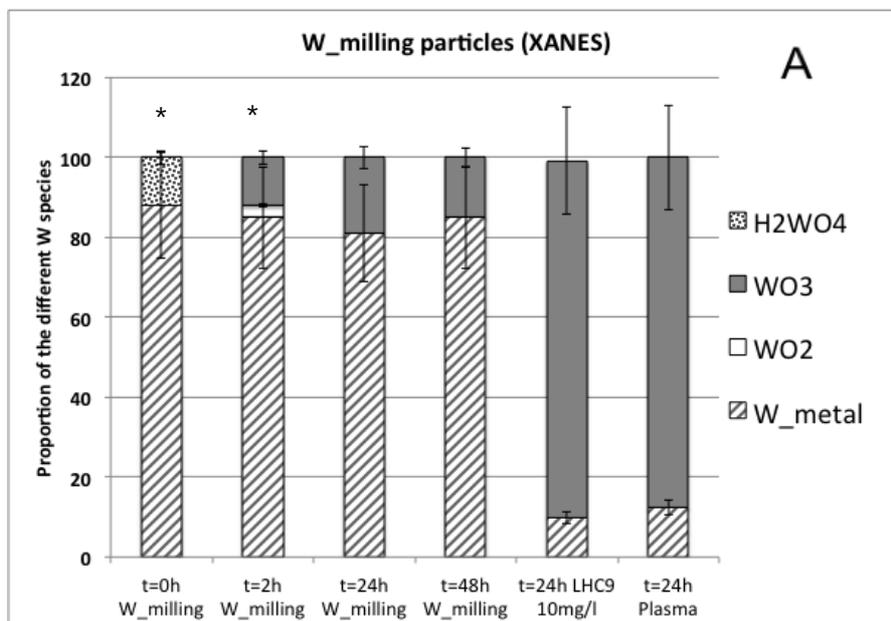


Figure SI-2: quantitative results of the LCF of XANES spectra of the W_milling particles samples using the reference compounds as database. * Poor quality of the fit (high residue).

Determination of the oxidation state of W in the particles

As mentioned earlier, XAS is sensitive to the redox state and atomic local structure of W and can be used to quantify the atomic proportion of the different forms of tungsten. XAS is based on the X-ray photoelectric effect, i.e. an incident X-ray photon is absorbed by the target atom (W) and liberates an electron from an inner atomic orbital. XANES which occurs in the region from the edge to approximately 40eV above the edge, is sensitive to the interactions between the photoelectron and the core hole. EXAFS extends from ~40 eV to 1000 eV above the edge and is due to the "photoelectron" wave scattering from the atoms around the X-ray target atom.

EXAFS is sensitive to the local order around the absorbing W atom, i.e. mainly the interatomic distances, the chemical nature of the bounding atoms and their numbers. The backscattered photoelectron interactions with the forward scattering photoelectrons can be described mathematically as follow (e.g.²⁸):

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2R_j + \delta_j(k)]$$

With $f_j(k)$ and $\delta_j(k)$ Scattering amplitude and phase shift functions (theoretical functions that depend on the absorbing atom (W) and neighbour atom type), $\lambda(k)$ the electron mean-free path, σ_j the Debye-Waller factor (structural disorder and thermal motion), R_j the distance from the central atom to the neighbour of the j^{st} atomic shell, N_j the number of neighbour atoms in the j^{st} shell around the central atom (coordination number). Each atomic pair (central/absorbing atom – neighbouring atom) will create a sinusoidal function, and the EXAFS curve corresponds to the sum of all atomic pairs i.e. the sum of all sine waves. The distance and chemical nature of neighbouring atoms will strongly affect the wave frequency, while the coordination number as well as the distance will strongly influence the amplitude of the signal. Even if the EXAFS is not directly sensitive to the redox state, the redox state will influence the atomic structure of the various W compounds.

XANES and EXAFS did not provide similar quantitative results (Fig. 6). XANES of the different redox states can mainly be distinguished thanks to the energy shift of the spectra. However, the energy shift does not follow a linear law as function of redox state and the difference between W^{+4} and W^0 are much lower than between W^{+6} and W^0 . Therefore, XANES does not provide a good sensitivity to W^{+4} . EXAFS spectra of the different W reference compounds exhibit a better sensitivity to W redox states as shown by the distinct features shown in figure 5A. EXAFS quantification results were selected for the discussion.

Figures Caption

Figure SI-1: XANES spectra and first derivative at the W L_{III}-edge of A-B) reference compounds, C-D) Solid samples from the dissolution experiment (W_milling in TRIS and LHC9 media, Plasma in TRIS) E-F) example of XANES Fit (W_Milling in TRIS after 2h) using LCF.

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