



ROBL-CRG

Experiment title: **Application of EXAFS to technetium speciation in pyrometallurgy reprocessing of spent nuclear fuel and in sulfur-rich environmental samples. Part 1. Technetium in chloride system.**

Experiment number:
20_01_23

Beamline: BM 20	Date of experiment: from: 21/06/2000 to: 23/06/2000	Date of report: 19/03/2001
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Report:

EXAFS is one of most promising methods to enable us with speciation of radioactive nuclides. It is important to use it for Tc speciation in pyrometallurgy which is now considered the alternative approach to reprocessing of nuclear fuel. The associated study of long-lived fission products forms the basis for its non-hazardous treatment in radioactive wastes. During pyrometallurgical reprocessing, technetium can remain in the molten salt or enter either the sedimented phase contaminating Pu enriched phase, either electrodeposited U phase. Our preliminary results show that under some conditions Tc can also form several oxydes, oxychlorides and chlorides of different but rather high volatility, turning on an important polluting risk for gas-off treatment. As the data on EXAF spectra of technetium is now very fragmentary and do not present the whole of the species possible in the pyrometallurgy conditions, it is of high importance to carry synthetic work to supply a large set of technetium compounds in the closed containers which will meet the ESRF/ROBL security and quality demands, radioactivity level, special requirements on sample size, thickness, sample

homogeneity. The chemical part of the work is planned to be carried out in Laboratory of radioanalytical and bioenvironmental chemistry, UMR5084, Gradignan. It includes the construction of pyrometallurgical reactors for the treatment of radioactive technetium samples in molten salts permitting to separate the truly dissolved, as well as sediments and sublimates.

The first part of the program deals with the pyrochemical behavior of technetium under reducing conditions. It comprises a set of samples with 13 reference technetium compounds (2 chlorides, 2 bromides, 2 pertechnetates, 2 sulfides, 5 Tc alloys) and some samples of simulated pyrometallurgically reprocessed nuclear fuel including technetium hexachlorides in fused salts, and Tc precipitated fraction from sulfur-rich environmental fresh water lake sediments with the only Tc as a radionuclide. These samples were studied by means of EXAFS spectroscopy at the Radiochemistry Hutch of ROBL providing with beamsizes of 3 x 20 mm², integrated flux at sample 6 x 10¹¹ /s, 200mA, 20 keV, spectral range 5-35 keV, 2/3 filling mode, beam line control carried out with VME, SUN workstation. A glove box was used for radioactive sample positioning.

During this series of shifts, we analysed 7 reference technetium compounds and 2 samples of simulated pyrometallurgically reprocessed nuclear fuel.

We are now involved in the treatment of spectra to obtain quantitative results.

Preliminary results have been presented by posters:

- K. GUERMAN, T. REICH, C. SERGEANT, R. ORTEGA, V. TASAROV, M. SIMONOFF
Technetium metal and pyrometallurgically formed sediments study and speciation by Tc-NMR and EXAFS/XANES
OECD/NEA Workshop on pyrochemical separations, march 14-15, 2000, Villeneuve les Avignon, France
- M. SIMONOFF, K.E. GUERMAN, T. REICH, C. HENNIG, R. ORTEGA, C. SERGEANT, G. DEVES, M.H. VESVRES
Technetium speciation in radioactive wastes generated in pyrochemical reprocessing
2nd Euroconference and NEA workshop on speciation, techniques, and facilities for radioactive materials at Synchrotron light sources, september 10-12, 2000, Grenoble, France
- K.E. GUERMAN, T. REICH, C. SERGEANT, R. ORTEGA, V.P. TARASOV, M. SIMONOFF, G. SIMONOFF
Etude et speciation par RMN et EXAFS du Technétium métallique et de sels formés par voie pyrométallurgique
7^e Rencontres Nationales de Radiochimie, september 27-29, 2000, Saint Rémy les Chevreuse, France