

**THE REPROCESSING OF NUCLEAR WASTE
USING MOLTEN SALTS: SELECTIVE
PRECIPITATION USING PHOSPHATE AND
SOLVING PROBLEMS OF SPECIATION**

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Pyrochemical reprocessing of spent nuclear fuels in molten salts is a promising and potential alternative to modern day extraction technology. A key factor for developing a safe and effective process is the understanding of the behaviour and basic chemistry of the components of irradiated fuels, including fission products. Inorganic melts have high radiation stability and this allows reprocessing of fuels after a relatively short cooling time.

Uranium (and plutonium) can be separated from spent fuel by treatment in molten carbonates and air sparging. UO_2 is converted into insoluble uranate species that can be filtered off. Fission product elements in solution can be later precipitated using phosphates as precipitants. Using molten chlorides as solvents, we have investigated the behaviour of the following individual elements: Cs, Mg, Sr, Ba, lanthanides (La to Dy), Zr, Cr, Mo, Mn, Re (to simulate Tc), Fe, Ru, Ni, Cd, Bi and Te. The efficiency of the process and the composition of the solid phases formed depend on the melt composition. The distribution coefficients of these elements between chloride melts and precipitates were determined. Some volatile chlorides were produced and rhenium metal was formed by disproportionation. Lithium-free melts favour formation of double phosphates. Melts containing several added fission product elements were explored for possible co-precipitation reactions. Rare earth elements and zirconium can be removed from chloride melts but Sr, Ba and Mg are melt specific. Some metals form oxide rather than phosphate precipitates and caesium cannot be removed completely from chloride melts as a phosphate precipitate.

Changing the cations constituting the chloride melts can change the speciation of the complexes present. For example, the presence of lithium ions drives an octahedral \leftrightarrow tetrahedral equilibrium from the tetrachloro to the hexachloro complex. The speciation of transition metal complexes in molten salts has been established from the visible spectra of their $d-d$ electron transitions. When this is not possible, some information can be obtained from Raman spectra. We have now extended such studies by employing monochromatic X-ray radiation from the synchrotron source at Daresbury in England, for both EXAFS and XANES measurements. This is essentially the first time this approach in establishing the speciation of a range of both transition and non-transition elements in molten chlorides has been investigated. EXAFS is largely model dependent, and to ensure the correct coordination number of chloro ligands

in each complex it has been necessary to rely on absorption spectroscopy, and then EXAFS provides the element-Cl distance in the melt, not previously available. At high concentrations, the presence of bridging chlorine atoms can be established by EXAFS. Diffuse reflectance spectra of condensed melts have also shown that there can be a lowering of site symmetry from that in the molten state to that in quenched samples. The results on uranium in oxidation states from 3 to 6 and on yttrium and zirconium complexes in chloride melts will be included in the examples given.