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

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ABSTRACT
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. UO₂ 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 ↔ 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 are given.

**INTRODUCTION**

Pyrochemical reprocessing of spent nuclear fuels in molten salts is a promising and potential alternative to modern day extraction technology. The original, and successful, molten salt reactor developed and built at the Oak Ridge National Laboratory in Tennessee in the 1960s used LiF-BeF\(_2\) eutectic as coolant and heat transfer agent and, in a separate loop, the same eutectic containing uranium and thorium as fuel. The well-known corrosive nature of molten salts, particularly fluorides, was well controlled in the Oak Ridge reactor but alternative melts, based largely on chlorides, have long been considered. Around the same time, at Harwell in the UK, a reactor using LiCl-KCl eutectic was under consideration.

Today, the emphasis is upon using molten salts as efficient heat transfer liquids, and for reprocessing spent fuel rods. Inorganic melts have high radiation stability and so are excellent for this purpose, especially since such fuels would need only a relatively short cooling time. A key factor for developing a safe and effective process is to understand the behavior and basic chemistry of the components of irradiated fuels and their fission products. The identity and quantities of the radioactive fission elements can readily be established, but the nature of the entities in which they exist within molten salts is less well understood and is now needed. The nature, identity and structure of the complexes present need to be known in order to understand, amongst others, the corrosive nature of these systems, and how best to remove, selectively and as far as possible completely, the various fission product complexes from such systems. Not all the fission product elements have spectroscopic properties that depend upon the structure of, and ligands participating in, the corresponding complex ion in the melt. The structural analysis tool of X-ray diffraction, for the study of complex ions in liquids, is a fairly recent development, and has generally required almost saturated solutions. The synchrotron, with its supply of monochromatic radiation, has engendered variants of diffraction studies and made X-ray studies of the structure of complex ions in molten salts at high temperatures now possible.
In 1996 we commenced a study that was, essentially, an attempt to answer the question “Can molten carbonates be used for reprocessing spent fuel?” Initially we investigated the oxidation of uranium dioxide in molten carbonates and recently switched to the precipitation of the major fission product elements from molten chlorides and their speciation in these melts. We report here examples of our extensive results and the first set of inter-nuclear distances determined for complex ions in molten salts.

We can now review our work and here show that by a combined theoretical and practical approach the requirements of a reprocessing system using molten carbonate, and the stages involved can be achieved experimentally. Certain potential difficulties have been identified, and many overcome. All the necessary experimental work has not been completed but we are pursuing this.

EXPERIMENTAL

The stages of pyrochemical reprocessing spent fuel

Three basic stages are involved. First, all the spent fuel should be chemically dissolved in a suitable solvent, and the uranium and plutonium should be the first material to be separated out in a form that can be readily re-used. Second, the radioactive fission products should be all removed simply, simultaneously and completely; and third the reprocessing agent should be stable and immediately available for re-use, without further treatment. These criteria may seem over ambitious but there is a high probability they can be achieved.

We have essentially achieved the first stage; are having success with the second; and consequently the third is almost certain. Indeed, we have achieved both parts of stage one simultaneously: the fission products are taken into solution and the uranium dioxide oxidized into insoluble uranate salt. By analogy, the plutonium dioxide will behave the same, (but we have not been allowed to use plutonium). In practice, some fission products might form insoluble oxides in carbonate melts but this is not known: however they could probably be easily separated out from uranates since uranates are readily soluble in dilute acids.

The fission products would remain in the molten carbonate and can subsequently be removed by precipitation as phosphates, as most phosphates, except the alkali metal phosphates, are insoluble in molten salts. For the remainder, ion exchange methods could be employed. In order to achieve this we have concluded that it is necessary to know the speciation of the fission products in solution, their chemistry and the identity of the complex ions in solution.

Removing uranium and plutonium from spent fuel

A molten mixture or eutectic composition of alkali metal carbonates is a suitable solvent, and we have investigated several compositions, including with added chloride and sulfate. The oxidant is air or oxygen bubbled through the molten carbonate, and oxygen dissolves chemically in these melts, forming peroxide and superoxide ions, a super-efficient oxidizing agent at the reasonably high temperatures involved, 500 to
800°C. The insoluble black UO₂ powder is oxidized to insoluble yellow-orange alkali metal uranates, M₂UO₄ and/or M₂U₂O₇, which can be filtered off (1). The separation of these uranates is essentially complete since their solubility in molten carbonate is in the region of 200 ppm (2). These uranates are readily soluble in dilute mineral acids and thus ready for further treatment. The details of this conversion process for uranium, and its optimization, have been published (3-5).

The basic equations are:

\[ \text{M}_2\text{CO}_3(s) + \text{UO}_2(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{M}_2\text{UO}_4(s) + \text{CO}_2 \]

which form uranate and

\[ \text{M}_2\text{CO}_3(s) + 2\text{UO}_2(s) + \text{O}_2(g) \rightarrow \text{M}_2\text{U}_2\text{O}_7(s) + \text{CO}_2 \]

to form diuranate, and M is an alkali metal. A mixture of mono and diuranates is thus formed. The relative proportions of the mono- and di- forms depend upon the melt temperature, the monouranate being favored at higher temperature.

**Solving remaining problems**

The above experiments were largely performed on uranium dioxide powder. Conversion to uranate in molten carbonate would take several hours and was incomplete unless the concentration of peroxide and superoxide ions were increased by the addition of these ions or promoters such as nitrate and nitrite. The presence of chloride ions increases the solubility of oxygen. When uranium dioxide is used as fuel, the powder is compressed and heat-treated to convert it into a ceramic. As such, it was difficult to oxidize in molten carbonate. We did succeed in fully oxidizing ceramic UO₂ in around 2 h in molten carbonate but only at 600°C and when it was bubbled with oxygen and contained added KNO₃. Thus spent ceramic fuel can in principle be converted to uranates and its fission products concentrated in molten carbonate. The uranates can be periodically filtered off and the molten carbonate continually used until the fission products reach a predetermined level.

Using spent fuel, the oxygen off-gas would have to be treated as it would contain volatiles such as radioactive iodine and xenon, etc.

**Removing fission products from molten carbonate**

At this point we had to deviate from our plan. We had been conducting our experiments in molten carbonates using alumina-based crucibles: molten carbonates are too aggressive towards optical silica for us to use them for the absorption spectroscopy experiments needed for studies on the behavior of fission product elements in carbonate melts. We needed another melt. Chloride was the obvious choice since we had already used it to extend the solubility of oxygen in molten carbonate and if a UK molten salt nuclear reactor was to be build it would likely use a chloride rather than a fluoride melt. Most phosphates were insoluble in molten chlorides and other melts that had been investigated. Their insolubility in molten carbonates was thus anticipated. In any case, the principles to be learned for studies using chloride would be a good future basis, especially since the same cations would be used in our chloride melts, namely, lithium, sodium and potassium, and they have, as we shall see, an important role to play.

The quantities of fission product elements in spent fuel are relatively small. If spent fuel rods have been treated in molten carbonate, then only after several applications and filter cycles, will reasonable quantities of fission product elements be present in
solution. We anticipate that the addition of an alkali metal phosphate, e.g., Li$_3$PO$_4$, to the residual molten carbonate will precipitate the fission product elements as phosphates. These can be filtered off and encapsulated or vitrified and stored in a suitable and safe location. What is left in the melt will determine the next stage, but we anticipate that sufficient will be removed so that the molten carbonate can be immediately re-cycled several times. In due course, as necessary, the molten carbonate can be quenched, undergo aqueous treatment to remove the remaining fission products, and then dried and re-used.

That is the principle, and the completeness or otherwise of phosphate precipitation will not prevent stage three of this molten salt reprocessing technique, the re-use of the molten carbonate after removal of fission products. Since in practice the melt will contain all the fission product elements, studies of the phosphate precipitation of the individual species will not provide all the answers required: we have also commenced studies on mixtures of the most abundant fission products. Other pyrochemical techniques are available to separate out fission products, including high temperature ion exchange, for example using alumina, and our parallel studies using synchrotron sourced X-ray diffraction will potentially assist in identifying the best method for isolating complexes of known structure and dimensions.

**Precipitation of phosphate from molten chlorides**

Using molten chlorides as solvents, we have investigated the behavior 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. We also investigated the formation and precipitation of the phosphates of these elements. In addition, the efficiency of the precipitation process and the dependence on the melt composition of the solid phases formed have been measured (6).

**Re-use of solvent carbonate melt**

As is now clear, the molten carbonate can in principle be continuously re-cycled, after filtering off uranates and plutonates and then, later, fission product phosphates. In practice, the system will have to be optimized, and the allowable limits of excess phosphate in the carbonate, and the cation composition, determined. The carbonate melt will have to contain a certain amount of nitrate, to achieve complete ceramic UO$_2$ oxidation, and this will have to be monitored and replaced as necessary. Excess phosphate ions will probably be required to optimize the precipitation of fission product phosphates. This has not been fully established yet and it may be necessary to remove some or possibly most of the excess phosphate because otherwise fission product phosphates may be deposited at the same time as the uranates and plutonates are formed, and thus will continue to contaminate these compounds. However, once the limits have been determined, the measures required to adjust their concentrations in the melt to be recycled, though not known in detail at this time, will be conventional chemistry.

**Future research needs**

At some future time, if a decision is taken to implement pyrochemical reprocessing of spent nuclear fuels using molten carbonates some of our experiments in
molten chlorides will need repeating, to confirm that the same precipitation characteristics apply, and that they are within allowable parameters. These will have largely to be conducted in alumina crucibles and, on a larger scale, in ceramic-lined baths. It will also be necessary to determine suitable corrosion resistant materials for long-term large-scale containment and the associated pipework.

RESULTS AND DISCUSSION

Of the most abundant fission product elements, cesium heads the list at around 3000 mg per kilogram of uranium. Many kg of uranium will therefore have to be processed before the carbonate melt will contain significant quantities of even cesium to merit the addition of phosphate, but the limiting factor may be the radiation level. Examples of the relatively abundant fission product elements in the various groups in the Periodic Table are now given.

Group 1 – Cesium

When Li3PO4 was added to the LiCl-KCl melt containing CsCl (PO43−: Cs+ mole ratio 3.55), a complicated mixture of products and an insoluble white precipitate resulted. Since alkali metal phosphates are soluble in water (lithium only sparingly), the precipitate formed could not be separated from the melt by washing. From the X-ray powder diffraction (XRD) patterns of quenched melt samples four phases were identified, viz. LiCl, KCl, Li3PO4 and Cs3PO4. No remaining CsCl was found. Thus the formation of caesium phosphate was essentially complete, but the solubility of Cs3PO4 in this eutectic is not known, but probably low.

However, upon the addition of Na3PO4 to NaCl-KCl melt containing CsCl (PO43−: Cs+ mole ratio 3.07), a mixture of products was formed but the reaction did not proceed to completion and some CsCl was still present after 3 hours.

The identity of the cations present in the melt is thus important. Cesium therefore is likely to remain in the melt (at least partially) during the phosphate precipitation in both LiCl-KCl and NaCl-KCl systems. Caesium can be removed from chloride melts by ion exchange (7) on, for example, double alkali metal – lanthanide, or alkali metal – zirconium, phosphates.

Group 2 – Strontium and Barium

The concentrations of these two elements per kilogram of uranium are around 1000 and 2000 mg, respectively. In high temperature NaCl-KCl-based melts strontium and barium separated out as the corresponding crystalline double phosphates, NaMPO4 (M = Sr, Ba). Over 90% of barium and essentially all the strontium were converted into insoluble phosphates, but on using LiCl-KCl eutectic much less was precipitated out.

The Lanthanides

The early lanthanides are the most abundant of this group in spent fuel, with around 1500, 2800 and 1500 mg per kilogram of uranium for La, Ce and Pr, respectively.
Addition of lithium phosphate, $\text{PO}_4^{3-}$ : $\text{Cs}^+$ mole ratio around five, to LiCl-KCl-LnCl$_3$ melts (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy) gave essentially complete precipitation of LnPO$_4$. With NaCl-KCl based melts, and Na$_3$PO$_4$ as precipitant, double sodium-lanthanide phosphates were formed. Complete removal of lanthanide fission products from chloride melts, both LiCl-KCl and NaCl-KCl-based, is therefore potentially possible but with LiCl-KCl based melts, the bulk of phosphate waste precipitated is reduced due to precipitation of normal rather than double phosphates.

**Determining Speciation in Molten Salts**

Changing lithium ions for sodium ions can thus determine which phosphate will precipitate from a chloride melt. The factors involved include size differences, and a marked difference in the surface charge, in terms of charge density per unit area.

More detail is now needed to understand, and then use, chloride melts for designed complete or specific precipitations. Spectral studies can identify that there is a regular geometric arrangement of chloride (and other) ligands around a central metal ion, and when the complex is slightly or somewhat distorted away from regular symmetry but bond angles and bond lengths in a negatively charged complex ion in a molten salt, and the possible identity and siting of counter ions, require X-ray studies.

Monochromatic X-ray radiation from the synchrotron source at Daresbury in England, for both EXAFS and XANES spectroscopy measurements, has established, essentially the first time, the speciation of a range of chloro complexes in molten chlorides.

**X-ray absorption spectroscopy (XAS) measurements in molten chlorides**

These measurements could not be performed in molten carbonates. With our furnace, measurements could only be carried out in transmission mode, which necessitated the use of a weakly X-ray absorbing salt, LiCl.

EXAFS spectroscopy is largely model dependent, and to ensure the correct coordination number of chloro ligands in each complex data from absorption spectroscopy is needed. The fitting program determined a coordination number for the species in the melt, but it was also determined unambiguously by other techniques, as far as possible, and compared with that obtained by the program. EXAFS also provides the element–Cl distance in the melt, not previously available. At high concentrations, the presence of bridging chlorine atoms can now be established. For example, in the Figure, for U concentration 13.64 wt %, peaks beyond the first coordination sphere can be seen, but these are not well fitted by the model. At this high concentration the uranium atoms are statistically quite close: further studies are in progress. Results on uranium in oxidation states 3, 4 and 6, at lower concentrations, around 5 wt%, are given in Table 1.
Table 1. Comparison of bond lengths in molten and quenched states

| Complex ion | Uranium bond | Molten LiCl at 750 °C | Quenched Samples |
|-------------|--------------|-----------------------|------------------|
| UO$_2$Cl$_4^{2-}$ | Axial U–O | 1.75-1.77 Å | 1.76-1.77 Å |
|              | Equatorial U–Cl | 2.63-2.67 Å | 2.75-2.76 Å |
| UCl$_6^{2-}$  | U–Cl | 2.63 Å | 2.69 Å |
| UCl$_6^{3-}$  | U–Cl | 2.72 Å | 2.91 Å |

The short strong axial U–O double bond does not change upon quenching but the longer U–Cl bonds increase, due to distortion from $D_{4h}$ ("UO$_2$Cl$_4$") and $O_h$ ("UCl$_6$") symmetry. The small Li$^+$ ions can partially insert between the chloride ligands, creating distortion. This is the first direct observation of the prediction by Shannon (8) that distortion of $O_h$ sites produces an increase in interatomic distances.

CONCLUSIONS

Our results, of which the above is a selection and summary, show that the principle that the reprocessing of spent fuel using molten carbonate has been established, though further experiments are required. The important role of the next nearest neighbor cations present in the melt has not previously been fully appreciated and it is believed that a better understanding of the complexation and speciation occurring in molten salts, using EXAFS, will contribute to specific procedures for the controlled precipitation of most of the fission product elements as phosphates. The molten carbonate can then be recycled.
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