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MOLTEN FLUORIDE FUEL SALT CHEMISTRY*

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Abstract

The chemistry of molten fluorides is traced from their development as fuels in the Molten Salt Reactor Experiment with important factors in their selection being discussed. Key chemical characteristics such as solubility, redox behavior, and chemical activity are explained as they relate to the behavior of molten fluoride fuel systems. Development requirements for fitting the current state of the chemistry to modern nuclear fuel system are described. It is concluded that while much is known about molten fluoride behavior which can be used effectively to reduce the amount of development required for future systems, some significant molten salt chemical questions must still be addressed.

INTRODUCTION

Molten fluoride fuel salts were developed and utilized more than twenty five years ago originally for use in the Aircraft Nuclear Project and finally, in the Molten Salt Reactor Experiment, MSRE. A considerable R&D effort was devoted to these systems during the 1950's and 1960's which culminated in the construction and operation of the MSRE during the late 1960's. After shutdown of the MSRE in late 1969, research on fluoride systems was drastically curtailed, even in fundamental studies. However, after a 25 year hiatus, there has been renewed interest in utilizing molten fluoride solutions in nuclear applications because of the same unique advantages that were recognized decades ago.

This report will summarize the key features in molten fluoride chemistry that makes it desirable for application to such nuclear systems. The significant chemical characteristics of molten salts will be described along with their impact on the design of a molten salt reactor system. The presentation will be integrated with fundamental chemical principles related to these characteristics. In addition, the final post-mortem experience will be discussed in view of the fundamental inorganic chemistry which has evolved since 1970. Finally, the current needs in further molten fluoride R&D will be addressed in order to fulfill the goals in utilizing molten fluorides for Accelerator Driven Transmutation Technology, ADTT, requirements.

MOLTEN SALT REACTOR EXPERIMENT

The MSRE consisted of a primary loop containing approximately 4 tons (4650 kg or approximately 2 m³) of molten salt, LiF-BeF₂-ZrF₄-UF₄(64.5-30.3-5.0-0.13 mole%) which was pumped through the core by the fuel pump and on to the heat exchanger. At this point, 2610 kg of coolant salt was pumped by the coolant pump from the heat exchanger to the radiator where fans blew the 7.5 MWt generated power up the stack. The molten fuel mixture varied from 823-923K as it was moved through the fuel circuit by an impeller pump which also provided the most convenient access point for salt sampling and salt additions through the pump bowl cavity. This access point was farthest from the high radiation levels in the reactor vessel and, thus, could be routinely used on a weekly/monthly basis. Finally, inert gas sparging of the pump bowl contents through the bubbler enabled the removal of the noble gases, Kr and Xe into the offgas line.

GENERAL REQUIREMENTS FOR MOLTEN SALTS

A molten salt reactor makes the following stringent minimum demands upon its fluid fuel. The fuel must consist of elements of low (and preferably very low) capture cross section for neutrons typical of the energy spectrum of the chosen design. The fuel must dissolve more than the critical concentration of fissionable material at temperatures safely below the temperature at which the fuel leaves the heat exchanger. The mixture must be thermally stable and its vapor pressure must be low over the operating temperature range. The fuel mixture must possess heat transfer and

hydrodynamic properties adequate for its service as a heat-exchange fluid. It must be relatively non-aggressive toward some otherwise suitable material --- presumably a metal --- of construction and toward some suitable moderator material. The fuel must be stable toward reactor radiation, must be able to survive fission of the uranium --- or other fissionable materials --- and must tolerate fission product accumulation without serious deterioration of its useful properties. In order to be economical, there must be a low fuel cycle cost which presupposes a cheap fuel and an effective turn-around of the unburned fissionable material or (more reasonably) an effective and economical decontamination and reprocessing scheme for the fuel.

CHOICE OF THE FUEL COMPOSITION

Of all the compounds that could be used as high temperature fluids in reactor systems, fluorides best encompass the properties of stability, low vapor pressure, reasonable melting points, and low neutron cross section. These characteristics are summarized in Table 2, Grimes 1967, for several candidate fluorides from which the LiF , BeF_2 , and ZrF_4 components were found to be optimal. (The inclusion of ZrF_4 will be discussed later in more detail.)

CHEMICAL CONSIDERATIONS

Three important chemical concepts play a major role in controlling the behavior of the MSRE fuel. These are solubility, redox chemistry, and chemical activity.

Solubility Solubility takes on a broad meaning in molten salt considerations since the major concern is to keep the components, especially the fuel entity, in a homogeneous molten solution during reactor operation. For pure, unreacting halide salts, solubility is determined by the melting point of the mixture. Therefore, the determination of melting points as a function of salt composition (in a broader sense, phase diagrams) played a major role in the early stages of reactor chemistry development.

For criticality control and safety, *it is highly desirable that the primary phase (the first solid phase that precipitates out on cooling) not contain the fuel component*. While this was achieved with the MSRE for the UF_4 component, it is less certain for PuF_3 fuel mixtures which have apparent solubilities of approximately 1 mole % in most molten fluoride solvents at typical operating temperatures. Of equal importance in the overall performance of the molten salts, it is necessary that the fuel component should not segregate on cooling when the reacting salt mixture is removed and cooled. It is clear that additional phase diagram studies are necessary for future applications involving PuF_3 fuels. Phase segregation studies on cooling would be an important element of such work, as well.

In addition to the pure fluoride component solubility concerns, chemical reaction of the fluoride salts with impurities (for example, moisture) or system components (for example, graphite) can form metal oxides or carbides which have a much higher melting points and therefore appear as insoluble components at operating temperatures. Reactions of the uranium fuel component with water vapor:



are of particular concern because they result in the formation of the insoluble oxide. Because this occurrence would have disastrous consequences on the operation of a circulation fuel solution, a means on insuring against it was essential. The most direct method of preventing the fuel oxide formation is through the addition of ZrF_4 which reacts in a similar fashion with water vapor:



The net reaction, by subtracting the two above, would be:



The concentrations at equilibrium for Eq. 3 are shifted far to the right with the consequence that ZrO_2 is formed, preferentially, to UO_2 , providing there is enough ZrF_4 in the solution. The molten fluoride solution for the MSRE contained 5.0 mole % of ZrF_4 and was more than adequate to handle any oxide impurity problems. No significant oxide was ever formed during the operating experience of the MSRE; and, consequently, it is practical to consider reducing the ZrF_4 concentration if the oxide control system is as reliable as that for the MSRE. Similar considerations for reactions such as those above, but now involving plutonium, must be carefully considered if plutonium based fuels are used in future fuel compositions.

Reactions of the fuel or solvent with the other system components such as the metal container or the moderator graphite can also produce insoluble components. These reactions are largely governed by the second major chemical factor, redox behavior, and will be discussed in the context of how it is used to control both insolubility and corrosion mechanisms.

Redox Control Corrosion of the metal container for molten fluoride reactor systems was also a major concern during the development of the MSRE. As a result, much effort was given to the development of a suitable metal alloy, namely, Hastelloy N, which contains, in addition to the nickel base composition, the following percentages of: Mo, 15-18; Cr, 6-8; Fe, 5; C, 0.04-0.08; Mn, 1.0; Si, 1.0; W, 0.5; Al+Ti, 0.5; Cu, 0.35; Co, 0.2; P, 0.015; S, 0.02; B, 0.01; Others, 0.5. Since the most reactive of the metal alloy components is Cr, the following corrosion reaction could be expected in a uranium fueled system:



Realizing that this is an equilibrium reaction, the corrosion can be controlled by adding a substantial quantity of UF_4 to the solution. The addition was, however, accomplished by the beryllium reduction of the UF_4 already in solution according to:



For plutonium fueled reactors, similar redox control will be necessary but will be more difficult because the $Pu(III)/Pu(IV)$ redox couple is outside the range of stability in contact with the other reactor components. It is anticipated that redox control in plutonium fueled systems could be accomplished with $Ce(III)/Ce(IV)$, $U(III)/U(IV)$ additions or, preferably, by sparging with a redox gas mixture such as HF/H_2 .

Chemical reaction of the fuel components with the moderator graphite were also of concern in the MSRE. They included:



From thermodynamic values, the reaction in equation 6 is expected to produce $<10^{-8}$ atm of CF_4 and none was ever seen --- giving assurance that graphite oxidation was unimportant in MSRE. The formation of uranium carbides, as indicated in equation 7, could occur if the UF_3/UF_4 ratio became too large. Careful control of this ratio between 0.007 and 0.02 prevented the formation of carbides, if too reducing, and corrosion products via equation 4, if too oxidizing. Similar considerations should be documented for plutonium-fueled systems.

Redox control would be a relatively simple matter were it not that the fissioning actinides produce changes in the redox potential of the melt. For example, in the case of UF_4 fission, the net oxidation state of the fission products is less than four and yet four fluorine atoms are released, leaving a slightly oxidizing event for each fission. In the case of PuF_3 fission, it is expected that the net oxidation state of the fission products will be slightly greater than three while only three fluorine atoms are released to produce a slightly reducing event for each fission. Taken alone, $^{239}PuF_3$ fission would produce opposite effects from those found in the $^{235,233}UF_4$ fission. This is clearly a matter that requires further

investigation if plutonium fuels are to be used in future designs.

In addition to changes in the redox potential due to fission, transmutation of LiF and BeF₂ in high neutron fluxes is expected to produce redox changes and oxide impurities which will require further consideration in future systems as described by Cantor 1974.

Chemical Activity. Chemical activity, per se, in the molten salt system was not of prime concern during the MSRE development. Rather, such changes were represented as shifts in the equilibrium quotients for the various metal ions in equilibrium with each other, realizing all the while that these equilibrium shifts were actually the result of changes in the chemical activity. Since that time, ligand coordination changes have been related by Toth 1971 to changes in the activity coefficients to give a better understanding of those factors which alter the chemical activity.

Changes in the chemical activity are defined by:

$$a = \gamma \cdot [] \quad (8)$$

where γ is the activity coefficient and [] is the concentration of the ion in solution. Coordination equilibria occurring for U(IV) and U(III) over the composition range of the phase diagram can account for activity coefficient variations of several orders of magnitude. The net impact is that the equilibrium chemistry of ions in solution can change dramatically as the solvent system is varied. Typically, the experience with molten salt systems is with the very basic (ie., F⁻ rich) to neutral solutions.

Solvent changes with accompanying changes in component activity coefficients are expected to bring on great changes in the chemistry of the system and would require much additional R&D development if vastly different salt compositions were to be used as reactor fuels. One of the most noticeable changes on going to F⁻ deficient systems is a great increase in volatility of those species which are normally volatile in pure form (eg., ZrF₄ and BeF₂) because there are not enough F⁻ present to adequately solvate them in solution.

Summary

The experience with the MSRE demonstrates that most of the molten fluoride chemistry is well known and controllable. The chemical stabilities and volatilities were easily controlled due to a well designed fuel/solvent system. The use of plutonium fuels will lead to several uncertainties including solubility and redox control and these, along with the effects of high neutron fluxes on the molten fluoride behavior, will require further study. While several thousand man-years of effort have already been invested in the development of the MSRE and these results are largely applicable to future ADTT requirements, additional work is necessary prior to formal system design so that a credible machine can be offered.

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