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Abstract

The operation of an ADT system with the associated nuclear reactions has a profound effect upon the chemistry of the fuel -especially with regards to container compatibility and the chemical separations that may be required. The container can be protected by maintaining the **redox** chemistry within a relatively narrow, non-corrosive window. Neutron economy as well as other factors require a sophisticated regime of fission product separations. Neither of these control requirements has been demonstrated on the scale or degree of sophistication necessary to support an ADT device. We review the present situation with respect to fluoride salts, and focus on the critical issues in these areas which must be addressed. One requirement for advancement in this area - a supply of suitable materials - will soon be fulfilled by the remediation of **ORNL's** Molten Salt Reactor Experiment, and the removal of a total of 11,000 kg of enriched (Li-7 > 99.9%) coolant, flush, and fuel salts.

Introduction

Papers at previous ADDTA conferences provided an excellent overview and general assessment of the requirements for a circulating molten salt in an ADT device [1, 2]. Three basic themes were developed: (a) constituent solubility, (b) **redox** control, and (c) separations. In this paper we seek to explore a few of the more critical elements in greater detail and in a coordinated fashion. Implicit in previous discussions was the interaction of these three basic *themes* in the overall system design. Here we explicitly consider the importance of the combined system in meeting the requirements. Of particular importance are the requirements (or lower limits) for salt additives needed for solubility and **redox** control; because these agents inevitably complicate downstream separations. This issue is explored in the Container and Loop Chemistry section, and special emphasis is given to assessing the need for sacrificial precipitating agents (e.g., **ZrF₄**).

Most of the important separations issues have been identified and are, or have been, pursued on some level. In the Separations section we seek to organize the discussion in a useful manner and identify a strategy for making progress in this area. Finally, we describe the condition of the MSRE salts that have, or will be, removed from the reactor. We will show that these salts serve as an excellent resource for ADT development activities. In all of these discussions the **2LiF•BeF₂** system is used as the example case because it is a well-characterized and proven system. Very similar arguments will apply to other molten fluoride systems.

Container and Loop Chemistry

The primary requirements for maintaining the integrity of the salt loop and container are to keep the salt constituents and fission/activation products in solution, and to control the **redox** state of the salt in a non-corrosive window. The requirement for good solubility of constituents is critical (especially for fissile components) and the failure to meet this demand was the downfall of fluid-fueled reactors prior to the **MSRE**. Because of this history, proponents at ORNL were (and continue to be) **especially** concerned about solubility control. However, there are important differences between the MSRE system and an ADT device that may offer some important simplifications. In order to explain this point it is necessary to review the primary path for precipitation — oxide/moisture contamination .

The driving force for oxide formation in molten fluorides is proportional to the (ionic **charge**)²/(ionic radius), and thus the precipitation order follows the electrochemical series: tetravalent actinides (least soluble) – trivalent actinides – trivalent rare earths – **divalent** – monovalent (most soluble) [3]. In addition to the basic free energy effects, the potential for forming solid solutions with other oxide species, and the competition between precipitating species can influence the outcome. This competition effect is typically explained in terms of the stability of the saturating oxide phase with respect to the candidate precipitant. For **2LiF•BeF₂** the saturating oxide species is **BeO**. For tetravalent actinides moderate oxide levels can lead to significant precipitation if no other sacrificial **precipitants** are present (other than the saturating BeO phase).

This fact led to the addition of at **least** a 5 moles of zirconium for every mole of uranium in the MSRE fuel salt [4]. The presence of this level of zirconium scavenged oxide from the system (otherwise present as **BeO**), and thus precluded uranium precipitation in the event of oxide contamination. The transuranic elements and rare earths are much less susceptible to oxide precipitation in the presence of a BeO saturating phase. It has been shown that plutonium precipitation will not occur in **2LiF•BeF₂** salts except in the presence of large amounts of **ThO₂** and extremely oxidizing conditions [5]. The behavior of Np is intermediate to that of uranium and plutonium, and the oxide sensitivity of the heavier actinides are bounded by the behavior of plutonium. We can summarize these results as follows:

- A **Zr/U** mole ratio of 5 is required to prevent uranium precipitation by oxygen in **2LiF-BeF₂** based salts.
- Pu and the higher actinides do not require a protective agent (e.g., **ZrF₄**) to prevent oxide precipitation in **2LiF-BeF₂** based salts.

- The oxide sensitivity of Np has not been fully explored in experiments, but can be estimated [6], and is intermediate between that of U and Pu.

By careful operation and system design the MSRE demonstrated a record of minimal oxide contamination in the fuel salt [7]. This increases our confidence in being able to operate without ZrF_4 under normal conditions, but does not remove the uranium precipitation concerns that must be addressed in an accident or worst-case scenario. In the near term it is expected that the requirement for a sacrificial precipitating agent (e.g, ZrF_4) will remain for uranium, and that for applications involving trivalent actinides they will not be needed. For minor levels of neptunium, a sacrificial precipitating agent is probably not necessary.

Because the fission process does not automatically balance the actinide and fission product valences, it inevitably produces a chemical effect [3, 8]. For the tetravalent actinides an oxidizing effect is produced (as during the MSRE), and for the trivalent actinides a smaller reducing effect is realized. It is important to understand and control the effects of this process because significant corrosion or unwanted reduction can occur in the salt loop. During operation of the MSRE the redox state of the salt was adjusted to avoid: (a) oxidizing reactions with either the container wall or moderator graphite, or (b) reducing reactions with moderator graphite and the container wall. For an ADT device the container will impose similar redox constraints, but the constraints imposed by graphite will be replaced by those of a metallic target. It is likely that graphite imposes more significant chemistry limitations than that of the metallic target, and the safe operating window for salt will be wider. The issue of target compatibility with the salt under a range of redox conditions needs to be considered in greater detail. The disposition of the “noble metal fission products” (Nb, Mo, Tc, Ru, Rh) in the salt loop is not well defined and may have a significant influence on the target performance [9].

Redox control of the salt loop is achieved by a combination of redox adjustment and redox buffering. A redox buffer, such as the U(III)/U(IV) couple used during MSRE, is a sink for absorbing the chemical effects of fission in safe manner. For ADT systems that do not contain uranium it is proposed that the Ce(III)/Ce(IV) couple be used as a buffer. The level of buffer need not be any greater than that of the uranium used during the last phase of MSRE operation (0.13 mole %), and can probably be much less. If in-line, side stream, or semi-batch adjustment of redox state of the salt is accomplished (either electrochemically or by hydrofluorination) then it may not be necessary to add a redox buffering agent at all. Hydrofluorination of the salt to set the redox state of the salt is well established and the only barrier to its implementation is the natural desire to exclude HF from the primary off-

gas systems. Because of this bias, it is probably more practical to consider a side stream or semi-batch hydrofluorination operation.

Separations

Separations for an **ADT** device can be ordered by both immediate importance and degree of maturity: (a) in-line removal of neutron poisons (noble gases, rare earths), (b) clean-up of solvent salt for reuse, and (c) fission product separations for waste disposition. Noble gas removal is readily demonstrated, so the present focus is on removal of rare earths from molten fluorides. A number of rare earth separations schemes have been **proposed [10, 11]**, but none of them possess the ideal characteristics of simple and selective removal of a minority constituent (i.e., rare earths) in the presence of a majority component (i.e., actinides). At present, proposed separations remove the entire trivalent inventory (actinides and rare earths) and then fractionate these groups. Discovery of a way to selectively remove traces of rare earth directly from an ADT molten fluoride is, as yet, an unrealized goal – but it should remain high on our list of research targets.

In order to achieve highly selective and difficult separations it is usually necessary to exploit specific chemical interactions (“non-ideal behavior”); either in the “salt solvent” or “metallic extractant” **phase**. Much more emphasis has been placed on metallic interactions, with the salt phase often considered a relatively structureless solvent. The importance of acid-base effects in the solvent salt (due to changes in the uncomplexed fluoride concentration) is relatively under appreciated. As an example we cite the dramatic influence of uncomplexed fluoride on the extraction of rare earths in liquid bismuth in the “metal transfer” process developed at **ORNL**. In Figure 1 it is clear that the selectivity for rare earth removal rapidly increases as the uncomplexed fluoride concentration increases.

The metal transfer process can also serve as a link to mature pyroprocessing technology, as shown in Figure 2. From the chloride salt solvent it is possible to progress along the lines developed by Argonne National Laboratory **[12]** and/or integrate the desirable elements of aqueous processing **[13]**. Fluoride salts are so insoluble in water that direct use of aqueous processes are typically not considered, thus the chloride salt can serve as a bridge to both chloride-based pyroprocessing and some aspects of aqueous chemistry.

MSRE Salts

Recent **remediation** efforts at ORNL should provide a significant inventory of MSRE salts suitable for use in various scientific projects. At present there have been a number of expressions of interest in these salts, but the final disposition of these salts is still in question. All of these salts are highly enriched in Li-7 (>99.999%), have $2\text{LiF}\cdot\text{BeF}_2$ as their base, and are premier neutron-transparent high-temperature solvents.

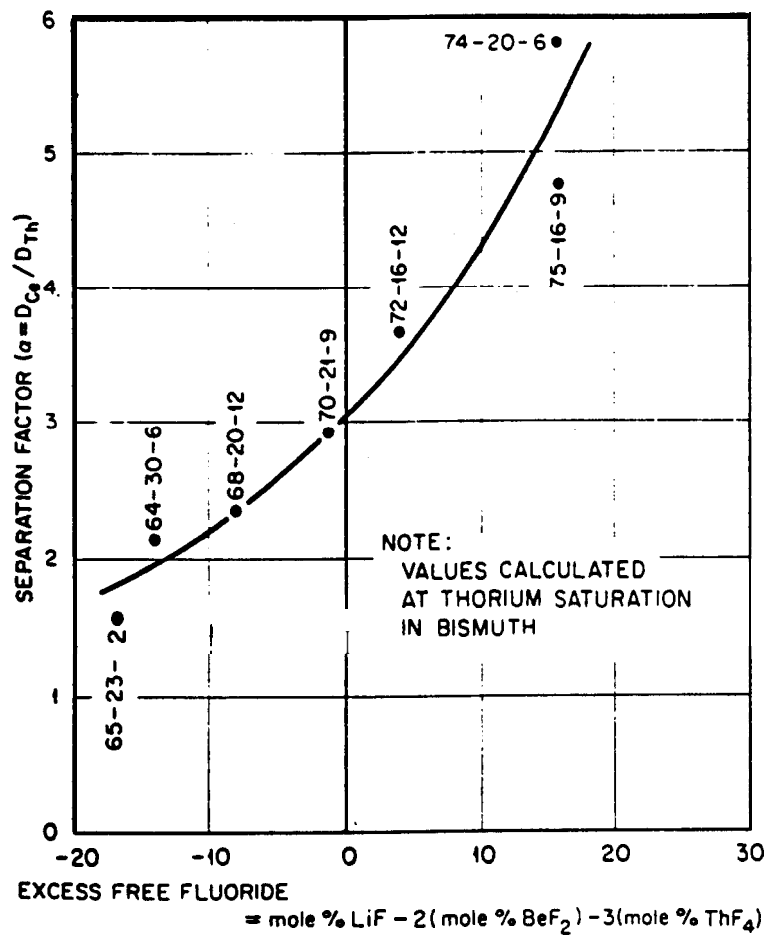


Figure 1. Effect of salt composition on the separation of cerium from thorium during reductive extraction of cerium from $\text{LiF}\text{-BeF}_2\text{-ThF}_4$ mixtures into bismuth at 600°C (from Nucl. Appl. Tech. 8, p.153, 1970).

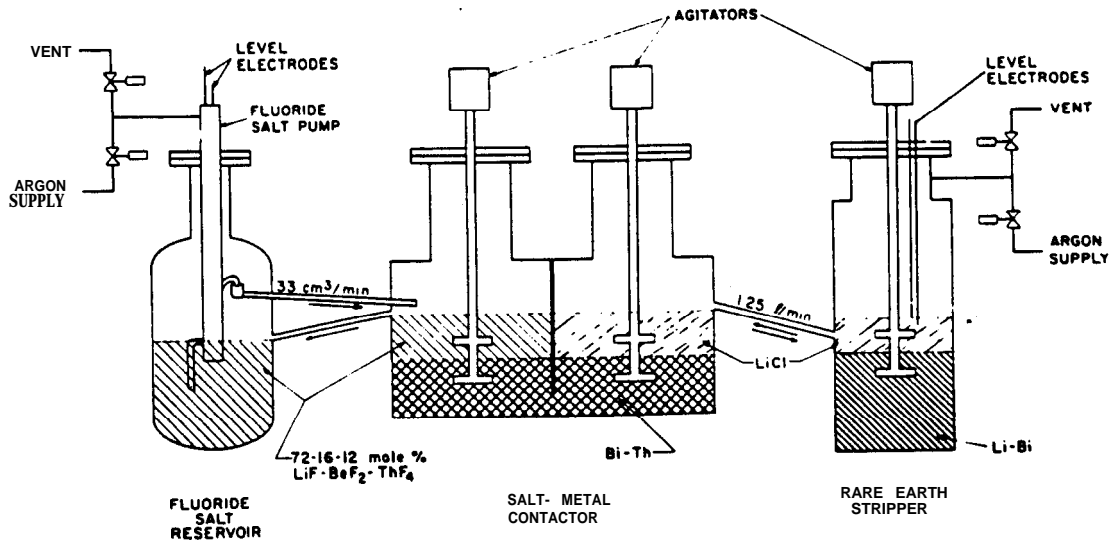


Figure 2. Schematic of apparatus for a "metal transfer process" experiment (from Radiochimica Acta 25, p. 213, 1978).

The characteristics of the three categories of salt – fuel, flush, and coolant – are documented in Table 1. The coolant salt is pure $2\text{LiF}\cdot\text{BeF}_2$ except for the minor tritium contamination ($\sim 1\text{-}10\mu\text{Ci/g}$) that diffused across the heat exchanger during reactor operation. It is now believed to be tied up in a relatively non-volatile “hydrous” form associated with the minor oxide contamination in the salt. There is no penetrating radiation associated with this salt, and the traces of tritium and oxide contamination can be removed by hydrofluorination. The entire coolant salt inventory (2610 kg) was recently removed from its original storage tank and now resides in five 60-cm ID tanks. A photograph of the coolant salt in the original storage tank, just prior to its removal, is displayed in Figure 3.

Table 1. Characteristics of MSRE Salts after Removal [14]

	Coolant salt	Flush salt	Fuel salt
Inventory (kg)	2610	4200	4650
Composition (mol%) ($\text{LiF}\text{-}\text{BeF}_2\text{-}\text{ZrF}_4$)	66- 34	65.9–33.9–0.18	64. 5- 30. 5- 5. 0
Density at 25°C (g/mL)	2. 22	2. 22	2. 48
Fission products (Ci)	0	415	24, 400
TRU level (Ci)	0	5. 3	293
U-level (ppm)	0	< 50	< 50
Pu content (kg)	0	0.013	0. 72
Tritium estimate	1-10 $\mu\text{Ci/g}$	—	—

The 4200 kg of flush salt is identical to the coolant salt except that it has a minor fraction ($< 2\%$) of the actinides, fission products, and ZrF_4 from fuel salt. Small amounts of flush salt can be contact-handled, and light shielding should be adequate for tanks. This salt will be stripped of its uranium content prior to removal. Removal is expected within the next two years. The 4650 kg of fuel salt contains almost all of the actinides and fission products **from** the MSRE operation, and will also be stripped of its uranium content before removal. It will remain highly radioactive unless extensive separations are performed. Removal of this **salt** is **also** expected within the next two years.

Summary

Molten fluoride loop **requirements** for solubility (especially **fissile** precipitation), **redox** control, and separations are not independent and often compete with one another in the overall system design. Salt constituents added as sacrificial precipitating agents (e.g.,

*See
attachment*

Figure 3. Recent photograph of MSRE coolant salt in the original drain tank before its removal (ORNL 2053-99).

ZrF₄) or **redox** buffers (e.g., **CeF_x**) inevitably complicate downstream separations and can limit the solubility of other critical components (e.g., **PuF₃**). Substantial reduction in the levels of the agents used in the MSRE is possible and should be pursued. Systems restricted to trivalent actinides do not require a sacrificial precipitant such as **ZrF₄**. A combination of in-line **redox** adjustment of the salt and scrupulous off-gas isolation and treatment may substantially reduce the need for these additives.

The complete separations picture for an ADT device encompasses a vast set of requirements; therefore, a staged approach to tackling this issue is absolutely necessary. The initial focus is on in-line removal of neutron poisons. It is clear that the primary unresolved question for the successful nuclear operation of the salt loop is the removal of the rare-earth neutron poisons, and it is appropriate that it is receiving the major attention. For in-line separations technology that has not been demonstrated to the level of reliability necessary, it is expected that truly continuous devices will only evolve from experience with semi-batch operations. The next level of separations addresses the clean-up of the loop salt **from** the balance of the fission products so that it can be reused. The final focus is on the waste disposition processing of the fission products. In these last two stages a considerable amount of integration with previous pyrochemical developments and aqueous technologies is needed, and therefore this must be considered a much longer term activity.

One requirement for advancement in this area – a supply of suitable materials – will soon be fulfilled by the remediation of **ORNL's** Molten Salt Reactor Experiment, and the removal of a total of 11,000 kg of enriched (Li-7 > 99.999%) coolant, flush, and fuel salts. The 2610 kg of coolant salt (**2LiF•BeF₂**) is basically non-radioactive and has been removed from the coolant loop storage vessel. The 4200 kg of flush salt (**2LiF•BeF₂**) is only slightly contaminated and is contact-handleable in small quantities. The 4650 kg of fuel salt will remain highly radioactive due to its actinide and fission product loading. The flush and fuel salts are scheduled to be removed in the next two years.

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