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SUBJECT: Thermodynamics in the Fused Salt Dissolution Process for Zirconium Fuel

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ABSTRACT

A limited discussion is given of the role of thermodynamics in the fused salt volatility process, particularly as it applies to oxidation-reduction reactions affecting zirconium, uranium, nickel, chromium, ruthenium, and other elements present in the hydrofluorination head-end step.

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INTRODUCTION

Comment on the role of thermodynamics in the fused salt dissolution process is appropriate in view of the present state of chemical development. Sufficient process knowledge has been accumulated to perhaps avoid the common error of placing too much emphasis and reliance on conclusions derived through thermodynamic reasoning. However, it appears equally unwise to proceed further in chemical development of the process without some consideration of thermodynamics. This is indicated by recent findings of crud and scale formation, and of the difference between conducting corrosion tests in the presence and absence of dissolving zirconium metal. Thermodynamics, used properly, is of value in the interpretation of results and as a guide to problems where experimental data is needed or at least to recognition of their existence.

Attention is given here only to the fused salt dissolution step for zirconium matrix fuel where hydrogen fluoride is the reacting gas. The thermodynamics in this case is quite different from that in the fluorination step where elemental fluorine gas is employed, i.e., where there is little uncertainty that the highest valence states are attained. The situation in the dissolution step on the other hand appears quite complex, involving as it does several structural and fuel alloy elements, fission products, and hydrogen in addition to the principal reactants; zirconium, uranium, and hydrogen fluoride. Although thermodynamic free energy values can be of assistance in unraveling the complex equilibria relations present, it must be emphasized that these occur in fused salt solution and deviate widely from standard state conditions.

BASIS OF DISCUSSION

Free energies of formation obtained from Glassner¹ were used to compute values relative to hydrogen fluoride gas over the temperature range of 300-1000°K (Fig. 1). Since the values are all expressed per gram-atom fluorine, the curves represent relative position in an electromotive force series appropriate for the chemistry being examined.

Some arbitrariness was necessary in the values selected for the sake of simplicity. The Sn^{+2} state has a higher negative free energy than Sn^{+4} and was therefore used in preference although it is quite possible that Sn^{+4} is formed as the result of complexing or of forcing through removal of product hydrogen. The difference is only 12-13 kcal. The same consideration holds true in the case of Cr^{+2} and Fe^{+2} . The Mo^{+4} state was used in the absence of MoF_3 data and in consideration that fluorine is required for MoF_6 formation. The Ru^{+3} and Ru^{+5} states were both plotted for reasons discussed later. The Nb^{+5} state is the only one known for that element.

SIGNIFICANCE OF Zr AND U FREE ENERGIES

The electropositive nature of Zr and U, relative to hydrogen, the structural metals and some fission products, is reflected in the high

Fig. 1. Relative free energies of formation of elements present in fused salt dissolution process.

negative energies. Elements having a more electropositive nature (higher negative free energies of formation) include those in the solvent salt (Na and Li), plutonium and fission products such as Cs, Sr, and the rare earths, and therefore these need not be considered further.¹ The free energies of Cr, Fe, Ni, Sn, Nb, Ru, Mo, and Cu indicate that these should be readily reduced by metallic Zr or U, as per example in the following reaction for Ni:

Recent laboratory findings have indicated that Ni particularly, and probably Fe, Cr, Mo, and Sn, make up a great part of black crud and scale present in the fused salt dissolution step. Such material is usually observed before zirconium dissolution is complete. The presence of Ni, Fe, and Mo as metal on the surface of zirconium metal has been shown in laboratory work. All of this appears consistent with the thermodynamic data.

The presence of plated-out metal on the surface of the zirconium fuel is possibly of great significance in hindering or changing the nature of the dissolution process. This is so because of the possible cycling of, for example, Ni between the reduced and oxidized states (Fig. 2). That is, Zr dissolution proceeds only after dissolution of some of the protective Ni plate, but any dissolved Ni is quickly replated at the same or another area. There exists also the possibility that the reduced Ni metal does not adhere firmly to the surface where it is formed, but is dispersed throughout the salt.

The above suggests that contamination of the salt with Ni or other reducible elements is highly undesirable. In fact, it might be possible to have sufficient NiF_2 contamination in salt to greatly affect Zr dissolution. In recent tests of the process the deliberate reduction of NiF_2 with H_2 before use of HF has helped the dissolution rate.

A further consequence of the plating out effect is that the tail-end of the dissolution step is essentially that of dissolving precipitated or plated metal with a high specific surface. In laboratory tests this tailing-out process is usually slow because of resistance of the material to dissolution. Reaction of HF with Ni occurs only due to the continuous and forced removal of hydrogen, since Ni is less electropositive than hydrogen (above 490°C).

EFFECT OF H_2/HF RATIO

H_2 gas is a product of the HF dissolution process and the ratio of H_2/HF varies with HF efficiency. It has been demonstrated that hydrogen sparging is an effective purification method for reducing NiF_2 and FeF_2 content in fused salts for nuclear reactors.² Examination of Fig. 1 shows, moreover, that Nb, Mo, Ru, and Cu could be expected to be reduced more readily even than Ni or Fe. Sn might also be expected to behave

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Fig. 2. The nickel cycle in the fused salt dissolution process.

similarly to Ni. The fact that the H_2/HF ratio changes so widely, however, during the process means that the oxidizing-reducing potential of the gas also varies. This is possibly of no importance when compared to the over-riding chemical potential of Zr metal, but in local areas the gas effect could be of some importance, dependent on dissolver geometry.

Essentially no data exist on the chemistry of the H_2 effect except in respect to NiF_2 . The writer, however, was keeping this as well as the Zr effect in mind when proposing that corrosion tests be made under operating conditions, i.e., with Zr being dissolved and in the presence of product H_2 . Confirmation of less corrosion under these conditions has been supported in corrosion as well as in other experimental work.^{3,4}

The use of H_2 sparging to reduce NiF_2 content in salt has been mentioned as having been used to improve dissolution rates. The use of H_2 simultaneously with HF input presumably serves to keep all Ni (and Sn) preferentially in the reduced state. It has also been frequently suggested that this would serve to reduce corrosion.⁵ Negative results on this point may have been due to use of too low a H_2 content.³

BEHAVIOR OF Nb, Mo, AND Ru FISSION PRODUCTS

The relative nobility of Ru, Mo, and Nb compared to H_2 is also illustrated in Fig. 1. All should be relatively difficult to dissolve with HF. However, an appreciable dissolution of 7 mils/hr was reported in one scouting test with Nb.⁶ This could be a case of forcing a reaction by removal of products, in this case NbF_5 and H_2 , as per the following reaction:

Here both products, NbF_5 and H_2 , are nominally gases at e.g. $600^\circ C$, and both would volatilize. Positive evidence of Nb activity volatilization has been reported, but the percentage so involved is apparently low and suggests that some solubilization of NbF_5 in molten salt occurs.

Ru volatilization as RuF_5 has never been observed in the dissolution step (some entrainment of course always occurs). This could signify that the Ru^{+3} state is trapped as a soluble complex in the salt with a lower net free energy than in the case of the Ru^{+5} state. Dissolution of powdered Ru metal did not proceed, but this is not important in the dissolution of uranium with a low burnup and no difficulty has ever been encountered in finding some Ru activity in salt after dissolution (possibly only dispersed). However, the Ru activity so measured has always indicated definite disappearance relative to the behavior of other fission products. A Ru plate-out effect has also been reported in nuclear fused salt fuel, and this does not appear inconsistent with thermodynamics.⁷

In the case of Mo, the Mo^{+4} nonvolatile state is the only one expected in dissolution, and Mo has been reported to have a low dissolution rate.⁶

It appears hence to be a relatively good element in construction metal, e.g., Hastelloy B or Inor-8.³ In conclusion one might expect Mo to be perhaps one of the most likely fission products to plate out, although no data are available on this point.

A POSSIBLE MULTIPLE VALENCE STATE EFFECT

Some elements exist exhibiting more than one valence state attainable with HF. Sn, Cr, and Fe are examples. This is unimportant, however, except in that case where there is an appreciable concentration possible in either or both states. Sn is perhaps such a case, being a minor element (1.5%) in Zircaloy-2. Attainment of quasi-equilibrium with a contacting mixture of H₂-HF gas represents an interesting redox salt which has no present significance.

GENERAL AREAS OF SUGGESTED EXPERIMENTAL WORK

It is perhaps obvious from the foregoing that the chemistry of the dissolution step is complex and interesting from the thermodynamic point of view. It is also obvious that experimental knowledge of some of the equilibria involved might lead to a better understanding of some of the difficulties involved in the dissolution step, as well as to improved operation of the entire process.

The most needed work is in the area of the plate-out effect and its importance in dissolution. Related to this is the permissible level of NiF₂ contamination in feed salt. The use of H₂ to obtain faster dissolution also deserves more attention.

The second area of needed effort lies in the suppression of fission product solubility in the fused salt, or removal of after complete dissolution. The partial disappearance of Ru suggests this effect might be magnified or enhanced not only for Ru but also for elements such as Mo, Nb, and possibly Cr. For example, passage of the dissolved salt after dissolution through a bed of Zr metal would lead to reduction of most of the contaminants discussed. This would be feasible only in the absence of any effect on UF₄.

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