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Fission Product Release as a Function of Chemistry and Fuel Morphology[1]

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INTRODUCTION

Analysis of the consequences of severe reactor accidents requires knowledge of the location and chemical form of fission products throughout the accident sequence. Two factors that strongly influence the location and chemical form of fission products are the chemistry within the core and the morphology of the fuel or fuel-bearing debris. This paper reviews the current understanding of the these factors garnered from integral and separate effect experiments and the TMI-2 accident, and provides perspective on the significance of contributing phenomena for the analysis of severe accidents, particularly during the in-vessel phase.

Information has been obtained recently on phenomena affecting the release of fission products from fuel and the reactor vessel during the in-vessel melt progression phase of a severe accident. The influence of a number of these phenomena will be reviewed, including fuel chemistry, H_2/H_2O ratio, fuel liquefaction, molten pools, and debris beds.

FUEL CHEMISTRY

The chemistry of uranium dioxide fuel changes as a function of burnup due to the production of fission products and the concomitant increase in the oxygen-to-metal (O/M) ratio. However, the O/M ratio is only a weak function of burnup indicating that burnup has a relatively small influence on the oxidation state of fission products under accident conditions. The main effect of burnup is on the concentration of fission products, the distribution of fission products within the fuel, and the fuel structure itself. The uranium dioxide undergoes restructuring as a function of burnup resulting in the formation of fission gas bubbles on grain boundaries that tend to interlink to form tunnels along grain edges at burnups above _ 5,000 MWd/MtU. This restructuring is enhanced by irradiation at higher powers and elevated fuel temperatures. During irradiation, fission gases and vapors migrate to the grain boundaries and, if tunnels have developed, the gas bubbles can be released fairly easily to the gap outside the fuel pellets. Grain boundary tunnels also provide a pathway for volatile fission product release during fuel heatup under

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accident conditions. The GRASS family of computer codes[1] explicitly models these changes in fuel morphology as a function of burnup. However, it has been found that simple Booth diffusion modeling gives results that are in good agreement with in- and out-of-pile experimental data[2,3] by varying the effective diffusion distance. Burnup can enhance release by a factor of as much as thirty at a burnup of 47,000 MWd/MtU[4].

The increase in fission product inventory with higher burnup affects the chemical form of fission products in the gas phase in the reactor vessel following release from the fuel rod. Calculations have shown a strong dependence of the chemical form of iodine on the concentrations of iodine and cesium in the gas phase relative to hydrogen and steam[5]. With trace-irradiated fuel, the H_2/I ratio is large and hydrogen iodide tends to be favored as the preferred iodine chemical form for gas phase transport at high temperatures, whereas with highly irradiated fuel, the H_2/I ratio is reduced and cesium iodide is favored. Such differences in chemical form can lead to differences in the transport of fission products within the reactor coolant system after release from the fuel.

HYDROGEN TO STEAM RATIO

After fuel rod failure, the oxygen potential of the fuel is determined by the H_2/H_2O ratio in the gas space of the damaged reactor core. Chemical equilibrium is a reasonable assumption at the high temperatures experienced by core materials during severe accidents. Free energies of formation of oxides of various core materials are displayed in Figure 1. Also shown in the figure is the oxygen potential corresponding to H_2/H_2O ratios from ten to one-tenth. This range brackets many of the conditions anticipated in the reactor vessel during core melt progression in a severe accident. Toward the high oxygen potential end of this range, oxides can be formed by the fission products molybdenum and antimony. Tin from the zircaloy cladding, indium from silver-indium-cadmium control rods, and iron from structural stainless steel can also be oxidized. At oxygen potentials lower in the range, representative of steam-starved conditions, these materials would be expected to exist as metals. The volatility of these oxides is very different than the volatility of the corresponding metals. Fission product cesium is stable as an oxide at low temperatures (<800 K) but should exist as elemental vapor at the fuel temperatures expected under accident conditions (>2000 K).

In the example of the TMI-2 accident, there is evidence from the temperature of control rod drive lead screw material in the upper plenum and the nature and thickness of the oxide on the surface of this material that the H_2/H_2O ratio was unity or less over most of the time that high temperature effluent was exiting the core[6]. Reference to Figure 1 indicates that gas with H_2/H_2O ratio in the range 1.0 to 0.1 is capable of oxidizing UO_2 to $UO_{2.05}$. As indicated in a previous review[4], such oxidation is capable of increasing volatile fission product release rates by factors of four or more and is the basis for models of enhanced volatile fission product release in solid UO_2. Some evidence of localized fuel oxidation has been observed in the examination of materials from the TMI-2 core[6] and from the steam-rich test Severe Fuel Damage-Scoping Test (SFD-ST)[7] in the Power Burst Facility (PBF), but evidence of widespread fuel oxidation in TMI-2 or in the integral in-pile tests conducted to date (most of which have been steam limited) has not been found.

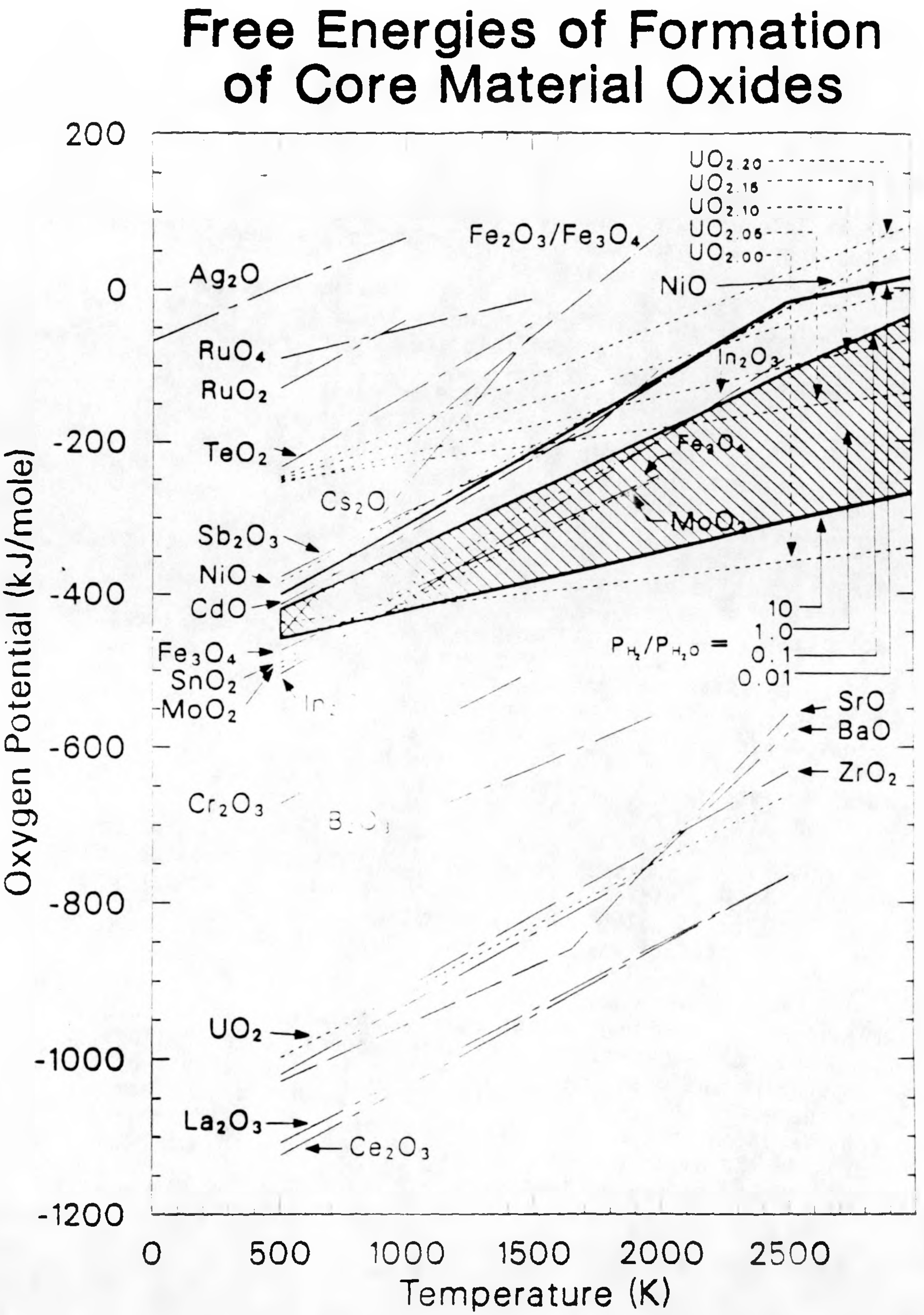

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FIGURE 1. Free energies of formation of core material oxides.

A strong effect of the oxidation of zircaloy cladding on the release of tellurium has been observed in small scale laboratory tests at Oak Ridge National Laboratory[8] and confirmed in larger scale in-pile SFD tests in the PBF[9]. The tellurium released from the fuel apparently reacts with zirconium and tin in the fuel rod cladding and is released when the cladding is oxidized enough to concentrate the tin in a thin unoxidized layer. The release data from TMI-2 are consistent with this theory[6]. In both SFD-ST and in the TMI-2 accident, the tellurium that exited the core transported far downstream suggesting an unreactive chemical form such as SnTe or CsTe. SnTe has been found to be evolved from zircaloy containing small amounts of tellurium which was then oxidized [10].

Very small releases of barium and strontium are expected when steam is present because these materials are expected to be in the form of low volatility oxides in the fuel. Indeed, the releases of barium measured in the SFD tests in PBF are one percent or less[9] and the release of strontium from the fuel in the TMI-2 accident is also small[6]. Recent in-pile measurements of fission product release from highly irradiated fuel in a reducing atmosphere (hydrogen/inert gas mixture) in the ST-1 and ST-2 experiments in the Annular Core Research Reactor (ACRR) at Sandia National Laboratories indicate barium and strontium releases of several percent[11]. These results are consistent with those of the out-of-pile SASCHA experiments[12] and can be explained as the reduction of the oxides to more volatile elemental barium and strontium.

According to Figure 1, ruthenium should exist in its elemental form under severe accident conditions and very small releases are expected based on the low volatility of the metal. It is interesting to note that large releases from the fuel, but negligible releases from the core, have been reported for ruthenium in the TMI-2 accident[6]. Examination of debris removed from the TMI-2 core indicates that ruthenium is retained in molten metallic materials in agreement with earlier observations from out-of-pile meltdown studies[6].

The foregoing discussion of the effects of steam oxidation demonstrates that the H_2/H_2O ratio in the gas surrounding the degrading fuel and the extent of zircaloy and UO_2 oxidation are important factors in determining the release of fission products from fuel, their volatility and their chemical forms in the gas and condensed phases. Results of equilibrium thermodynamic calculations of chemical species for vapor transport of fission products under postulated severe accident conditions are found to be dependent on fission product concentrations, system temperature and pressure, H_2/H_2O ratio, and the variety of species considered in the calculations[13]. This realization leads to the consideration of the chemical effects of a variety of materials in LWR cores on the distribution of fission products within a reactor vessel undergoing a severe accident.

CONTROL MATERIAL CHEMISTRY

Boric acid in the reactor coolant and in the emergency coolant is used as a reactivity control material in PWRs, and boron carbide encased in stainless steel control blades is used in BWRs. Boric acid vapor reacts with cesium iodide in either the vapor or condensed states to form cesium borate and hydrogen iodide [14]. Boric acid vapor also reacts with cesium hydroxide in either the vapor or condensed phases to form cesium borate [14]. Separate effects tests have demonstrated that hydrogen iodide can be formed by reaction of boron carbide in steam with cesium iodide [15].

The ability of boron compounds to interact with fission product cesium and iodine depends on the reactor type and the accident sequence. The in-pile integral-effects Test DF-4 has shown that boron carbide in a BWR control blade may be prevented from interaction with steam and cesium iodide by preferential interactions with the stainless steel cladding of the blade [16]. This in-pile result confirms earlier results from small-scale out-of-pile laboratory experiments that showed boron carbide undergoes interaction with steel to form boron and carbon eutectics with iron and nickel [17].

In a PWR, the availability of boric acid vapor to interact with cesium iodide and cesium hydroxide depends on the accident scenario. Large break loss-of-coolant accidents without emergency core cooling tend to result in nearly complete loss of water and thus boric acid before core heatup and fission product release, whereas small break loss-of-coolant accidents and station blackout entail slow boiloff of the coolant such that considerable steaming and boric acid vaporization could be present during fission product release from the fuel. Accumulator injection in a small-break loss-of-coolant accident would provide an additional source of boric acid.

Thermodynamic studies indicate that silver vapor from silver-indium-cadmium control rods can form silver iodide under severe accident conditions in PWRs. The formation of silver iodide is favored by high silver-to-iodine ratios in the vapor[18]. High pressure accident scenarios result in control rod failure by melting of the stainless steel cladding and runoff of much of the control alloy with relatively little vaporization of silver[19]. In this case, the formation of silver iodide is not favored. In accident scenarios at low system pressure (such as a large break loss-of-coolant accident) the control rods fail by bursting and silver is sprayed throughout the core, tending to enhance vaporization[19]. These conditions tend to maximize the vaporization of silver and the formation of silver iodide.

FUEL LIQUEFACTION

Fuel liquefaction, the creation of liquids containing UO_2 below the melting point of UO_2 (3100 K), can occur at 2200 K by dissolution with molten zircaloy, or, perhaps, at even lower temperatures by dissolution in eutectic mixtures of zircaloy with transition metals and/or silver[20]. The dissolution rate of UO_2 in liquid zircaloy has been measured[21] but dissolution in eutectic mixtures at temperatures below 2200 K has not yet been studied. The dissolution process is complicated and involves the diffusion of oxygen out of the fuel and into the metallic melt. Oxygen diffusion takes place most rapidly along grain boundaries and the formation of molten uranium metal in the grain boundaries occurs just ahead of the broad moving boundary between the UO_2 and the molten metal. However, to model this process it is important to realize that the rate of dissolution is associated with the broad moving boundary and that the grain boundaries are not filled with liquid metal at great distances beyond the uniform moving boundary.

Fuel liquefaction destroys the crystal structure of the UO_2 so that the release of fission products is now governed by the migration of atoms and bubbles in a liquid. This is a much faster process than diffusion in a solid and fission product release rates should be enhanced. This effect has been measured in out-of-pile tests[22] using small chunks of irradiated fuel, but has not been measurable in in-pile integral effects tests such as the PBF-SFD test series, possibly because of the smearing in time and space of the liquefaction process inherent in an intrgral experiment.

MOLTEN POOLS

Molten pools of primarily $(U,Zr)O_2$ ceramic formed in the TMI-2 accident[23] and in severe fuel damage tests, both in-pile[3,7,24,25,26] and out-of-pile[20]. Analysis of fission product release from the molten ceramic pool in the TMI-2 accident indicates that fission product chemical form and concentration dominate the release of medium and low volatile fission products and that bubble dynamics dominates the release of fission gases and volatile fission products[2]. Fission product chemical forms are influenced by the oxygen potential of the large molten pool. The presence of iron oxides in the melt in TMI-2 establishes a lower limit on the oxygen potential of about -150 kJ/mole at 2800 K. At this oxygen potential, rare earth elements such as europium and cerium would exist as oxides (Eu_2O_3 and Ce_2O_3 or CeO_2), strontium would exist as SrO, and ruthenium and antimony would be present as metals immisible in the ceramic melt. Low releases are calculated for these materials primarily because of the low concentration and volatility of these species in the melt and the low surface-to-volume ratio of the molten region. Virtually all of the fission gases and volatile fission products should be released from the melt due to bubble coalesence and buoyancy. However, cesium has been found in the molten debris transported to the lower plenum of the TMI-2 reactor vessel[6]. The retention of cesium in a previously molten ceramic is unexpected and has implications for fission product chemical forms and for accident analyses that are discussed later. Evidence for cesium retention in previously molten ceramics has also been found in the SFD experiments, but the results are ambiguous[3,7,26]. The retention of the less volatile fission products in the melt that relocated to the lower plenum is discussed below.

DEBRIS BEDS

Two debris beds were formed in the TMI-2 accident, one on top of the molten pool, and one in the lower plenum. In the TMI-2 accident[23], the PBF SFD-ST[7], and the LOFT FP2 test[24], the upper debris bed is thought to have been produced when coolant was introduced into the hot core/bundle causing thermal shock and fragmentation of the oxidized fuel rods in these steam-rich transients. In less steam-rich transients, such as Test SFD 1-4[3], an upper debris bed was formed by the melting (probably aided somewhat by eutectic reactions with structural and control materials) and relocation of the zircaloy fuel rod cladding leaving the fuel pellets without mechanical restraint.

The upper debris bed is found to consist principally of fuel fragments with little zircaloy cladding or control materials. The mass mean diameter of the particles in the upper debris bed in the TMI-2 core is about 1 mm. This is two orders of magnitude larger than fuel grain size. As a consequence, fragmentation into a debris bed should have no significant affect on fission product release from solid fuel.

The molten debris in the pool in the TMI-2 accident failed the upper crust between the pool and the upper debris bed along one side near an upper corner by thermal ablation causing _20 metric tons of molten material to relocate into the lower plenum in a period of one to two minutes[23]. This liquid stream interacted with the coolant in the lower plenum to produce the debris in the lower plenum. This debris has been observed via video probe to vary from small particles about 1 mm in diameter to large chunks several centimeters in size to regions of consolidated debris forming walls in the debris bed.

Samples of large chunks of lower plenum debris contain primarily previously molten ceramic $(U,Zr)O_2$ with transition metal oxides in the grain boundaries. Fission product retention in the debris in the lower plenum and also in the upper debris bed is presented in Table 1 where it can be seen that the retentions of cesium and iodine in the upper debris bed are both about 20 percent, but the retentions in the lower head debris are quite different, about 3 percent for iodine and 13 percent for cesium.

The similar retentions of iodine and cesium in the upper debris are in agreement with the vast number of observations of similar release rates of these fission products from solid fuel. The high retention of cesium in the previously molten ceramic debris in the lower plenum is unexpected, based on analyses of the release of volatile fission products from melts discussed earlier in this paper, and suggests that some of the cesium is in an involatile chemical form stable at very high temperatures.

Some indication of possible chemical associations of cesium in the lower plenum debris has been obtained through elemental analysis of cores removed from debris particles and micro gamma scanning across surfaces sectioned from particles[27]. Results of this work suggest that cesium may be combined with transition metal oxides in the grain boundaries of the solidified ceramic in forms such as chromates.

Other fission product retention data of interest in Table 1 are the small retentions of antimony and ruthenium in both debris beds. Antimony is generally thought to be in the mid-volatility group and ruthenium to be of low volatility. Neither of these fission products were released from the reactor vessel in large amounts but they have been found to be associated with previously molten transition metals in the debris. These materials have migrated out of the ceramic phases to be sequestered in molten metallic phases where they would have low volatilities due to solution or alloying. The fission products strontium and cerium remain with the ceramic phase, cerium as an oxide (Ce_2O_3 or CeO_2) and strontium as an oxide (SrO) or uranate ($SrUO_4$). Only about 6 percent of the fission product tellurium was released from the core and much of the tellurium remaining in the core appears to be associated with metallic debris in the crusts surrounding the ceramic pool.

SUMMARY AND CONCLUSIONS

The locations of fission products and their chemical forms at the time containment integrity is lost are important in the analysis of the consequences of an unmitigated reactor accident. Fission products that are released from the core during the heatup and the in-vessel core melt progression phases of an accident likely will be deposited on upper plenum and reactor coolant system piping surfaces from which they may slowly revaporize depending on the accident scenario. Revaporization is likely to be an important contributor to the source term from containment only in the case of a relatively late containment failure (well after reactor pressure vessel failure). It is important to consider physical and chemical interactions between fission product vapors and aerosols when analyzing the behavior of fission products in the reactor coolant system.

TABLE 1. Fission Product Retention in TMI-2 Debris

	Percent of inventory retained			
	Lower Plenum		Upper Debris	
Radionuclide	Average	Range	Average	Range
I-129	3	0-25	23	10-29
Cs-137	13	0-34	19	5-39
Sb-125	6	0-35	47	37-78
Ru-106	6	0-17	49	31-77
Sr-90	107	68-178	87	74-96
Ce-144	96	78-142	99	78-113

If containment integrity is lost before reactor pressure vessel failure, deposition of fission products released from the core during heatup and core melt progression is an important retention mechanism. However, in this case as well as the case in which containment integrity is lost shortly after reactor pressure vessel failure, fission product releases due to ex-vessel processes (such as high pressure melt ejection and core-concrete interaction) will probably dominate the source term. For such cases, the fission product inventory and the chemical forms of the fission products in the molten debris that exits the reactor pressure vessel are controlling parameters for the source term. Analyses of ex-vessel fission product releases need to account for the small fraction of the core inventory of iodine and a larger fraction of the core inventory of cesium that may still be present in ceramic debris. It is also important to recognize that large fractions of the core inventory of tellurium, antimony, and ruthenium can be retained in metallic debris.

The results of the experimental work to date on core melt progression indicate that core melt progression phenomena influence the nature, timing, amounts, and chemical forms of fission product released during the in-vessel phase of severe accidents. This brief survey of results indicates the importance of careful modeling of core melt progression phenomena in severe accident source term analyses.

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