Bechtel Bettis, Incorporated
Bettis Atomic Power Laboratory
West Mifflin, Pennsylvania

MATERIALS TECHNOLOGY
ADVANCED MATERIALS TECHNOLOGY

Fact Sheet

TITLE: Fuel System Compatibility Issues for Prometheus-1 (U)

AUTHORS: D.C. Noe
K.B. Gibbard
M.H. Krohn

DATE: JAN 20 2006

ABSTRACT: Compatibility issues for the Prometheus-1 fuel system have been reviewed based upon the selection of UO_2 as the reference fuel material. In particular, the potential for limiting effects due to fuel- or fission product-component (cladding, liner, spring, etc) chemical interactions and clad-liner interactions have been evaluated. For UO_2 -based fuels, fuel-component interactions are not expected to significantly limit performance. However, based upon the selection of component materials, there is a potential for degradation due to fission products. In particular, a chemical liner may be necessary for niobium, tantalum, zirconium, or silicon carbide-based systems. Multiple choices exist for the configuration of a chemical liner within the cladding; there is no clear solution that eliminates all concerns over the mechanical performance of a clad/liner system. A series of tests to evaluate the performance of candidate materials in contact with real and simulated fission products is outlined.

SIGNIFICANCE TO THE NR PROGRAM: Designing a fuel system that met the requirements for Prometheus-1 was expected to be one of the most challenging aspects of this program. The unique demands of this project – operation at extremely high temperatures for extended periods and without the option of maintenance or replacement – required a fuel system that operated outside the range of performance of any previously tested fuel elements. This report represents an initial assessment of chemical and mechanical compatibility issues for Prometheus-1 fuel elements.

SUMMARY OF RESULTS:

1. For UO_2 -based fuels (the reference fuel for Prometheus-1), fuel-component chemical interactions are not expected to fundamentally limit the performance of the proposed cladding materials.
2. Based upon thermodynamic considerations, oxidation due to fission product-component interactions is a potential problem for several candidate materials, including those choices containing tantalum, niobium, zirconium, and silicon carbide.

3. The potential for embrittlement or reaction with fission products is more difficult to assess, however, the commercial experience with more common alloys and materials (Zircaloy, stainless steel, superalloys, SiC, etc) suggest there is adequate cause for concern. Embrittlement issues and other time dependent/kinetic attributes are unlikely to be resolved without a suite of tests, including those on both irradiated and non-irradiated specimens.

A testing program was under development to evaluate compatibility-related issues. This program included a series of phases that became increasingly complex and more prototypical. Early phases of this program were designed to weed out materials with basic incompatibility or embrittlement issues, and later phases were designed to demonstrate the performance of fuel pins under semi-prototypical conditions.

1.0 Introduction

The performance demands on Prometheus-1 fuel elements were unique. Conventional nuclear reactor fuel elements generally operate for relatively short lifetimes (~3-6 years in commercial reactors) at relatively low temperatures and are utilized in an environment where periodic inspection and replacement of defective fuel elements are possible. For Prometheus-1, fuel elements would have needed to operate at extremely high temperatures (up to 1450K in some concepts) for periods of 15 or more years. Inspection and replacement would not be possible, so an extremely high degree of reliability also was necessary.

Fulfilling these requirements necessitated a detailed understanding of how the various components of a fuel element interact. In particular, studies of the interaction of fuel and fission products with other components (claddings, liners, springs, etc) and between components (e.g. the clad and liner materials) were underway at the point NRPCT involvement in Project Prometheus was discontinued.

At the point of NRPCT closeout, the fuel for Prometheus-1 was chosen to be UO_2 . Several factors influenced this decision, but one of the primary considerations was that UO_2 offers fewer compatibility issues than UN. Table 1 lists several systems that were under consideration as cladding and fuel element materials. This document will summarize the key issues to be addressed in order to select a fuel element system capable of a 15 year, maintenance-free lifetime as was suggested for a Prometheus-1 reactor, focusing on the compatibility of fission products and fuel with candidate core materials.

Table 1: Candidate Core Materials	
Refractory Metal Systems	Mo-41.5Re
	Mo-47.5Re
	Ta-10W
	ASTAR 811C (Ta-8W-1Re- 0.7Hf-0.025C)
	FS-85 (Nb-27Ta-10W- 1Zr)
Silicon Carbide Systems	SiC (with Re liner)
	SiC (with C liner)

The fissioning of ^{235}U atoms produces a large number of daughter atoms, including approximately 22 long-lived elements with yields exceeding one percent (Table 2). A detailed study of fission product yield studies is currently under preparation¹. These daughter products are chemically heterogeneous, including such diverse species as noble gases, halogens, alkaline metals, transition metals, and rare earth elements. The interaction of these species with core materials has been a problem since the early days of nuclear power when stress corrosion cracking of Zircaloy cladding tubes due to fission products was first reported.

Table 2. Fission Product Yields²

Element	Fractional Yield
Ba	0.0809
Ce	0.1930
Cs	0.1505
I	0.0111
Kr	0.0397
La	0.0665
Mo	0.1937
Nb	0.0145
Nd	0.1511
Pd	0.0130
Pm	0.0180
Pr	0.0450
Rb	0.0363
Rh	0.0145
Ru	0.1351
Sm	0.0203
Sr	0.1291
Tc	0.0620
Te	0.0234
Xe	0.2698
Y	0.0597
Zr	0.3079

Fission product attack has been reported for virtually every material that has been selected for core applications, including zirconium alloys, stainless steels, superalloys, refractory metals, and silicon carbide. In many cases, the mode of embrittlement is poorly understood, although several key chemical elements have been identified. These include I, Cs, and Cd for zirconium alloys and Te for stainless steels and superalloys. The mechanisms of embrittlement are believed to include stress corrosion cracking and liquid metal embrittlement.

The core materials for the Prometheus-1 reactor had not yet been selected when NRPCT involvement in the project was terminated. To guide material development and selection, a multi-phase program had been developed based upon theoretical and experimental programs to screen potential interactions between fission products and core materials.

The theoretical program was based upon equilibrium thermodynamic calculations and literature reviews. The thermodynamic calculations were completed with a variety of tools, including the computer programs HSC and FactSage. The planned experimental program, which was not initiated, consisted of several phases that are detailed in Section 4 of this report.

Although this report is restricted to compatibility concerns within fuel elements, similar concerns over fission product attack may exist elsewhere throughout the reactor system. Concerns over fission product attack in the direct Brayton system selected for Prometheus will be discussed elsewhere.³

2.0 Theoretical Assessment of Compatibility

Three main areas are addressed in this report: reactions between components and the fuel material, reactions between components and fission products, and interactions between components. Due to the extremely limited information available for reaction rates, reaction kinetics had not yet been addressed at the time of closeout.

2.1 Reaction with UO_2

In general, few incompatibilities are expected between UO_2 and the candidate structural materials. As shown in the Ellingham diagram in Figure 1, the only incompatibilities are with hafnium, which is predicted to chemically reduce UO_2 , and, possibly, with zirconium. Figure 1 plots the free energy of various compounds per mole of oxygen in those compounds. Formation of compounds with the lowest free energy per mole will minimize the free energy of the system and will be the most thermodynamically stable. As can be seen, the potential for reaction with zirconium is marginal and these materials are successfully used in direct contact in the vast majority of nuclear reactors currently in service. ZrO_2 is observed on the internal surfaces of PWR fuel rods⁴ with the amount of the reaction limited by corrosion kinetics and engineering solutions. However, it is not clear whether this oxidation results from the reduction of UO_2 or from reactions with fission product oxides.

Figure 1. Compatibility with UO_2

2.2 Fission Product Oxidation Mechanisms

A much more serious threat arises from incompatibilities due to fission products. Most of the oxygen released from the fissioning of uranium atoms combines with fission products to form stable binary oxides or multicomponent compounds. There are two benefits to this arrangement. First, a large number of potentially problematic fission products are tied up as stable oxides, including the rare earth elements, strontium, barium, and zirconium. Second, the vast majority of liberated oxygen also is effectively immobilized. If only binary oxides formed, a portion of the fission-produced molybdenum would oxidize before the system exhausted the supply of free oxygen (Table 3). However, based upon thermodynamic models, most of the oxygen and molybdenum that would otherwise form molybdenum oxide is believed to combine with cesium to form cesium molybdate. The question of whether core materials will be oxidized by liberated oxygen depends on the relative thermodynamic stability of these oxides compared to cesium molybdate.

Table 3. Binary Fission Product Oxides

Fission Product	Fission Yield	Oxide Formed	ΔG_f° moles Oxygen at 1400K	Moles Oxygen Consumed
Y	0.0597	Y ₂ O ₃	-119.7	0.08955
Ba	0.0809	Ba ₂ O	-115.6	0.04045
Sm	0.0203	Sm ₂ O ₃	-112.9	0.03045
Pm	0.018	Pm ₂ O ₃	?	0.027
Nd	0.1511	Nd ₂ O ₃	-112.6	0.22665
Pr	0.045	Pr ₂ O ₃	-112.1	0.0675
Ce	0.193	Ce ₂ O ₃	-111.7	0.2895
La	0.0665	La ₂ O ₃	-111	0.09975
Zr	0.3079	ZrO ₂	-99.6	0.6158
Nb	0.0145	NbO	-70.2	0.0145
Sr	0.1291	SrO	-44.1	0.1291
Mo	0.184	MoO ₂	-40.29	0.368
Mo	0.0097	Mo		0
Te	0.0234	TeO	-35.6	0
Rb	0.0363	Rb ₂ O	-25.4	0
Cs	0.1505	Cs ₂ O	-23.6	0
Tc	0.062	TcO ₂	-22.2	0
Ru	0.1351	RuO ₂	-9.4	0
Rh	0.0145	Rh ₂ O(g)	-8	0
Pd	0.013	PdO	7.1	0
I	0.0111	IOO(g)	16.22	0
Kr	0.0397			
Xe	0.2698			

Oxygen is Depleted Here

As shown in Figure 2, several materials that would not be oxidized by uranium dioxide are predicted to be oxidized by cesium molybdate. These materials include tantalum, zirconium, silicon carbide, graphite, and niobium. The three materials most commonly proposed for Prometheus-1 that should not be oxidized are molybdenum, tungsten, and rhenium. These three materials therefore make attractive candidates for fuel pin liners. Conversely, alloys and ceramics containing substantial quantities of tantalum, zirconium, silicon carbide, graphite, or niobium may require a liner to ensure adequate mechanical performance after long-term exposure to irradiated fuel.

Figure 2. Compatibility with Cesium Molybdate

2.2 Fission Product Embrittlement Mechanisms

In addition to oxidation, materials in contact with nuclear fuels can become embrittled after exposure to fission products. This problem is also present for terrestrial reactors. For example, Zircalloys can become embrittled from $\text{I}^{5,6,7,8,9}$, $\text{Cd}^{10,6,5}$, and possibly $\text{Cs}^{10,6,5}$; stainless steels and superalloys are embrittled by tellurium^{11,12,13}.

The potential for embrittlement of candidate Prometheus-1 materials is difficult to assess. For reference, there is still debate even for the well-studied cases of Zircaloy, stainless steels, and superalloys. This assessment is further complicated by the fact that some fission products are far more potent embrittlors when acting in tandem with other fission products. For example, cadmium and tellurium have both been shown to have a greater potential for embrittlement when dissolved in cesium^{13,12,11,10}.

To some degree, this enhanced embrittlement is apparently related to the enhanced mobility of fission products when combined with cesium rather than the stability of the cesium telluride phases. As shown in Figure 3, several cesium telluride phases have a lower melting point than pure tellurium. However, as seen in Figure 4, cesium telluride is far more stable than pure tellurium over the temperature range of interest. In fact, cesium telluride is more stable than zirconium below about 1373 K. This finding may explain the general lack of reported reactions between cesium telluride and Zircaloy at normal PWR operating temperatures. The observed dependence of embrittlement upon interactions not just between fission products and cladding materials but between the fission products themselves emphasizes the need for screening tests that contain a wide spectrum of simulated fission products.

Figure 3. Cesium Telluride Phase Diagram¹⁴

Figure 4. Stability of Cesium Telluride

With respect to candidate Prometheus-1 materials, there is a small potential for the reaction of iodine with Nb, Ta, Mo, or SiC below roughly 1173-1473K (Figure 5). There is a greater potential for reaction with zirconium, although this assessment is complicated by the relative stability of cesium

iodide compared to zirconium iodide below 1573K. Despite the stability of cesium iodide, iodine has been shown definitively to embrittle Zircaloy^{7,9,5}. Different theories have been proposed for the mechanism by which free iodine becomes available to cause this embrittlement, including radiolysis of CsI molecules and ionic diffusion of iodine through a corrosion layer⁸. The presumed mode of attack is intergranular stress corrosion cracking rather than bulk corrosion of the cladding. As such, relatively small quantities of iodine have the potential to embrittle cladding materials. Thermodynamic assessments have been used as an initial evaluation of the driving force for iodide formation along grain boundaries. It is possible that a similar mechanism could result in the iodine embrittlement of Nb, Ta, Mo, or SiC, although these reactions are much less energetically favorable than that of Zircaloy. It should be noted that no thermodynamic data were readily available for the formation of tungsten or rhenium iodides.

Figure 5. Stability of Cesium Iodide

Tellurium is predicted to act in relatively analogous fashion to iodine. Cesium telluride is an extremely stable compound. Tungsten, molybdenum, rhenium, and silicon carbide should only react with tellurium if some other mechanism liberates tellurium from cesium telluride. Above ~1473K, zirconium telluride should become more stable than cesium telluride resulting in the strong embrittlement of zirconium-based alloys, but may also be significant for zirconium-bearing materials (e.g. Nb-1Zr or FS-85). No thermodynamic data were readily available for niobium or tantalum tellurides.

Despite the demonstrated effect on Zircaloy^{10,6,5}, there are few data available for the effect of cadmium on candidate Prometheus-1 materials. However, it should be emphasized that the available data for Zircaloy are based upon cadmium concentrations that greatly exceed those that would be generated in Prometheus-1 elements. The small cadmium concentrations expected under Prometheus-1 conditions reflect both the very small fission yield of the element (approximately two tenths of a percent) and the low burnup for this fuel. Therefore, even if cadmium preferentially

reacted with cladding materials, it is not clear that it would form or migrate in sufficient quantities to pose a substantial threat.

Palladium represents an additional threat for silicon carbide-based systems, in which it acts as a reactant^{15,16,17,18}. In high-temperature gas reactor (HTGR) fuel particles, the SiC coatings are separated from the fuel/fission product mixture by graphite-based layers. Although the carbon layers present an extra barrier in the migration of Pd from the kernel to the SiC coatings, the diffusion coefficient for Pd in carbon is high so the effect of these carbon layers is small. As a result, Pd-attack of SiC layers has been cited in several studies. The severity of this attack depends on several factors, including temperature, the rate at which Pd is released from the UO₂ fuel (which is thought to be the primary rate-limiting step) and the rate at which Pd is generated (which is a function of the fission rate, neutron energy spectrum, and enrichment of the fuel).

Additional complications exist in that Pd attack is not uniformly distributed across the SiC coating. There is a pronounced temperature dependence in which preferential attack occurs on the cold side of HTGR particles. Even in the colder regions, the attack forms nodules rather than a uniform corrosion layer¹⁶.

Given the highly localized attack and general uncertainties surrounding Pd attack of SiC, the potential for this mechanism to significantly degrade SiC clad fuel elements under Prometheus conditions was unclear. Potential mitigation strategies include the incorporation of sacrificial SiC layers within the SiC fuel elements. At the time of program redirection, the need for and effectiveness of potential mitigation strategies had not been fully addressed.

3.0 Liners

The use of liners within fuel pins has been recommended to chemically and physically separate the cladding from the fuel/fission product mixture. The need for chemical separation arises from the potential interactions with fission products and/or oxygen described in the previous section. A possible need for physical separation arises from the effect of recoiled fission products on the cladding material.

Different types of liners have been suggested. The SP-100 program investigated free-standing tubes within the cladding (which were open at the ends), liners that were both free-standing and hermetically sealed, and liner tubes that were bonded to the cladding (but open at the ends)¹⁹. The optimal liner configuration was not definitively identified. Figure 6 illustrates the different liner configurations suggested.

Free-standing liner tubes may be most appropriate when they serve the limited function of preventing recoil damage of the liner material. In terms of chemical performance, they will not protect the cladding from fuel or fission products components that are gaseous or have a high vapor pressure. This type of liner would therefore not be protective against the nitrogen overpressure associated with the use of uranium nitride²⁰, but may be with volatile fission products such as iodine, cesium, or cesium molybdate if the access point is in a colder location. This would be the case for a fuel pin with a long plenum area protruding out of the core or one that is intentionally cooled.

Free-standing but hermetically sealed liners offer both chemical and physical protection of the cladding. However, the need to hermetically seal in fission product gases essentially makes the liner take on the role of cladding. In essence, this system would reflect a duplex clad geometry with an outer cladding optimized for both contact with the reactor coolant and providing additional strength for the inner cladding. The inner cladding would be optimized to withstand the chemical and physical challenges associated with irradiated fuel. This arrangement poses mechanical design issues. Because the inner cladding is subjected to the full gas pressure inside the fuel pin, it needs to either be strong and thick enough to withstand the gas pressure without significant deformation, which would cause it to interfere with the outer cladding, or it must rely upon the outer cladding for structural support to prevent excess deformation. Failure of the inner cladding would also result in the distribution of fission products between the inner and outer cladding which would reduce the chemical benefit of having the inner cladding.

The use of a bonded liner (in which the liner is physically bonded to the cladding) eliminates the gap between these components and prevents the possible accumulation of fission products in this region. It also alleviates concerns related to the cracking of an unsupported, thin liner and offers advantages in the thermal transfer between the fuel and coolant. However, there are three potential problems with this arrangement: crack propagation, intermetallic phase formation, and Kirkendall void formation. As noted previously, direct recoil and/or fission product attack from the fuel may embrittle liner materials. In a bonded system, any cracks that form in the liner as a result of these or other processes have the potential to propagate through the cladding.

Rhenium forms intermetallic phases with most of the materials of interest for Prometheus-1, including Nb, Mo, Ta, and Si (Figures 7 and 8). The situation is reversed for tungsten and molybdenum, which exhibit complete solid solution with each other and with tantalum and niobium (Figure 9). Because intermetallic compounds tend to be brittle, their formation may affect the cladding performance. On the other hand, intermetallics also have the possibility of limiting diffusion between the cladding and liner, which may minimize the potential for Kirkendall void formation.

Figure 7. Intermetallic Formation With Rhenium¹⁴

Figure 8. Intermetallic Layer Formation²¹

The Tantalum-CVD Rhenium X-Phase Interdiffusion Zone
After Ageing at 1800°C for 2000 hours (4CA-6) at 200X

Figure 9. Intermetallic Formation With Molybdenum and Tungsten¹⁴

Molybdenum and Niobium

Tungsten and Niobium

Molybdenum and Tantalum

Tungsten and Tantalum

Molybdenum and Tungsten

Finally, at high temperatures, bonded materials have a tendency to interdiffuse. At the notional operating temperatures and lifetimes cited for Prometheus-1, a substantial amount of interdiffusion is anticipated (Figure 10).

Figure 10. Interdiffusion

Equations and constants used for these calculations are from Interdiffusion Behavior of Tungsten or Rhenium and Group V and VI Elements and Alloys of the Periodic Table²¹

As can be seen, the predicted interdiffusion distances for selected material couples range from 75 μm to 300 μm . Because diffusion occurs more rapidly from the material with a lower melting point into the material with a higher melting point, void formation can occur in the lower melting point material (Figure 11). In addition to the mechanical effect upon the materials, the formation of these voids has the possibility to affect thermal transfer between the fuel and coolant.

Figure 11. Kirkendall Void Formation²¹

(a) W(arc cast)/Ta Junction After 1800°C/1000 hours Ageing
(Control) (200X)

4.0 Planned Experimental Programs

The general test plan developed by the NRPCT was focused on evaluating compatibility in a series of phased experiments (Table 4). The earliest phases were the least complex and had the shortest lead times. Later phases reduced the number of material candidates as the testing proceeded to more sophisticated experiments. Although anticipated to yield more detailed data, the advanced phases also had the downside of being more complicated, more expensive, and possessing inherently longer lead times. These tests also could be used to validate some of the screening selections based on thermodynamic properties and may have provided insight on the corrosion kinetics of the materials selected.

Table 4. Experimental Compatibility Test Plan

Phase	Description
1A	Basic compatibility testing to screen material interactions between fission products and core materials. Non-irradiated.
1B	Similar to 1A, except that the specimens would be mechanically stressed to enhance stress corrosion cracking. Non-irradiated.
2	Similar to 1B, except that non-enriched UO_2 fuel would be added to the simulated fission products for a more prototypical chemical environment. Non-irradiated.
3	Construction of a semi-prototypical fuel element with internal heating to simulate the thermal and chemical profiles within an actual element. The primary intent of this phase was to assess the mobility and distribution of fission products within an actual fuel element. Non-irradiated.
4	Accelerated screening for fission product interactions during irradiation. This test was conceived to contain simulated fission products in contact with mechanical test specimens. The use of simulated fission products avoids the relatively long time period associated with their production and accumulation via irradiated fuel. In addition, the lack of fuel in this test affords the opportunity to examine the specimens in beta-gamma facilities, rather than the alpha facilities required for irradiated fuel. This is an irradiation test.
5	Semi-prototypical fuel element tests. These tests were intended to use fuel elements closely approximating those to be used in Prometheus-1, although accelerated fission rates may have been necessary. This is an irradiation test.

Phase-1A (General Compatibility)

Phase-1A was intended to assess whether certain fission products with either a relatively high yield or known to be of special concern could react with or embrittle candidate materials in an out-of-pile setting. This test, which was the simplest and quickest of the planned phases, was to be the initial screening tool to determine whether concerns existed for longer term applications; a failure in this test did not necessarily rule out a candidate material, but indicated that engineering solutions would be necessary for successful application. Similarly, a successful result in this experiment did not guarantee the suitability of a particular material for use in a fission product environment.

The simulated fission products chosen for this initial test included elements that are volatile at the Prometheus-1 operating conditions or those displaying a substantial vapor pressure. This list included cesium, rubidium, tellurium, palladium, and iodine. These elements represent some of the primary fission product elements associated with the corrosion and SCC of alloys and ceramics. Although cadmium has been implicated in the liquid metal embrittlement of Zircaloy, the fission yield of this element is very low (0.2%). This makes it impractical to uniformly mix cadmium into the simulated product mixture. In addition, this low fission yield suggests that previous tests, which used high concentrations of cadmium in contact with Zircaloy, may not have been appropriate for fuel elements with a low burnup. The cladding and liner materials identified for this testing were Haynes 230, IN-617, PE-16, ASTAR-811C, MoRe, FS-85, TZM, W, Re, SiC, ZrC, and graphite. Specimens of various cladding and liner materials were to be exposed to a representative mixture of the candidate fission product elements in a controlled environment at high temperature. After heating, the specimens would have been removed and examined to determine the extent of interaction or degradation.

Bend specimens were to be used for testing of the metallic cladding and liner materials. Ten bend bars needed to be machined from each sample material before testing could begin. The bend bars would have been pickled after machining to standardize the surface finish to 16 RA and remove surface defects when applicable. Miniature tensile specimens of SiC, ZrC, and graphite would have been used for mechanical testing of the ceramic materials.

Given the high temperature associated with this testing and the uncertain effect of these chemicals on the mechanical properties of the testing hardware, the specimens were to be double encapsulated to prevent release within the annealing furnace. The primary barrier was a welded MoRe capsule into which the specimens and simulated fission products were to be placed. The secondary barrier was to be an outer 316 stainless steel capsule. The fission product mixture was to be made by combining small amounts of the selected fission product elements proportional to their fission yields and mixing to homogenize the blend. The MoRe capsules were to be loaded with 100 mg of the fission product mixture and five test samples of the same material. The MoRe capsule would then be vacuum sealed by welding on the end cap. The MoRe capsules would then be placed inside a single 316 stainless steel capsule and vacuum sealed by welding on the end cap. A schematic of the experimental setup can be seen in Figure 12.

Figure 12. Schematic of the experimental set-up for initial screen experiments

316ss Outer Capsule

The capsule apparatus would then be placed in a furnace and heated to 1300 K for 1000 hours to allow for interactions between the materials to take place. After cooling, the samples would be removed from the capsules and the alkali metals on the surface would be removed by heating in a gas flow. This would allow the elemental cesium and rubidium vapors (which pose a chemical hazard) to be collected in a cold trap for disposal without affecting the surface of the specimens. The samples would then be examined for indications of corrosion using optical and SEM techniques. Following these examinations, metallic specimens would have their ductile-to-brittle transition temperature (DBTT) measured to screen whether any reduction in the mechanical properties had occurred. DBTT testing was chosen due to the sensitivity of this property to slight changes in the microstructure of the material. After DBTT testing, selected specimens would be mounted for metallographic examination. Testing was also to be performed on control specimens that had been thermally aged for 1000 hours at 1300 K in an inert environment. The DBTT of these samples would provide baseline performance data for the cladding and liner materials. Ceramic samples were to be bend tested to determine the fracture strength which would be compared to the fracture strength of the thermally aged samples. This would give a measure of the degradation of the specimen mechanical properties.

Phase-1B (Stress Corrosion Cracking)

Phase-1B of this program would have exposed stressed test specimens to a simulated fission product environment to evaluate the potential for stress-corrosion cracking (SCC). SCC can be defined as an enhancement of the crack initiation and growth in a material when subjected to a particular chemical environment under stress. The selection of materials included in this phase of testing would depend on the results of the Phase-1A testing. An encapsulation scheme similar to what is shown in Figure 12 would have been used to for these SCC tests. This would require the use of statically loaded test specimens with relatively simple geometries in order to create a well-defined stress state before encapsulating the test specimens. The specimens would be stressed so as to remain below the yield strength of the material throughout the duration of the test in order to avoid plastic deformation. Additionally, corrections for stress relaxation during the test would need to be considered. All of the

above mentioned criteria would be used to develop a testing procedure which would need to be applicable to all of the materials involved, including both metals and ceramics.

Figure 13 shows an example of how stresses will relax for FS-85 and ASTAR 811C samples which were initially subjected to 90% of their respective yield stresses. These curves were created using equations for elastic modulus, yield stress, and creep taken from the preliminary draft of the design basis²².

Figure 13. Calculated Stress Relaxation at Different Test Temperatures as a Function of Time

During the initial planning three possible test geometries were considered (Figure 14). Variations of these test geometries or different test geometries could also be considered. The type of testing being planned required that the test specimen geometry result in a well defined stress state in addition to being statically loaded and relatively simple to allow for encapsulation.

Figure 14. Three Possible Test Specimen Geometries That Could Be Used For Stress Corrosion Cracking Experiments: (a) Bend Bar, (b) C-Ring, and (c) Double Cantilever Beam.

In a bend bar test (Figure 14a), stress is generated by bending a specimen to a particular radius. This results in the tensile stress on the outer surface and a compressive stress on the inner surface. The specimen is held in this configuration by a fixture which holds the ends of the specimen in place. If possible, this fixture would be machined from the same material as the specimen. Assuming the material is isotropic, this would eliminate differential thermal expansion effects on the stress state of the sample. Using similar materials for both fixtures and specimens would also prevent the preferential "gettering" of simulated fission products by the fixtures. The bending test methodology could be extended to include a three-point or four-point test geometry. The bending test method has the advantage of using a test specimen with a simple shape, which requires a relatively small amount

of material. A disadvantage of this test is that only a small volume of the material is subjected to the maximum load. A large volume was desired for this test in case there were inhomogeneities in the microstructure of the specimens or variation in the chemical atmosphere within the test capsule.

The C-ring test (Figure 14b) involves taking a C shaped specimen and increasing the inner radius, which results in a tensile stress on the inner surface and a compressive stress on the outer surface. The specimen would be stressed using either a brace that would be positioned in the center of the ring or a wedge that would be positioned between the ends of the ring. Advantages of this test are the relatively simplistic application of stress and similarity between test specimen geometry and the final component geometry. Similar to the stress state in the bend bar specimens, the stress state in a C-ring specimen is highly localized and not representative of the whole component stress state.

A wedge loaded double cantilever beam (DCB) specimen was also considered. The test specimens would require significantly more machining, but the pre-cracked specimen would bypass the crack initiation stage of failure. This would allow for more detailed information to be gained from the test relating to how the chemical environment affects crack growth.

Other specimen geometries such as pressurized tubes were also discussed. For the initial test, the bend test geometry seemed to be the most promising candidate because of the relatively simple specimen geometry and its similarities with the initial test specimen design. Depending on the results, more complicated specimen geometries such as a DCB or pressurized capsules could be considered if further testing was deemed necessary.

Once the specimens had been exposed to the fission product environment under stress for the duration of the test, the test specimens would be removed from the capsules and further testing and characterization would be performed. Mechanical testing of the exposed specimens would be done to characterize how the exposure affected the mechanical performance of the materials. In addition, optical and electron microscopy would be performed on the exposed and fracture surfaces to identify the characteristics of these surfaces and see if crack initiation or growth mechanisms could be determined.

Phase-2 Expanded Preliminary Testing

Phase-2 of this program was anticipated to include a larger variety of fission product elements along with uranium dioxide in an out-of-pile setting. The inclusion of uranium dioxide is important, despite the difficulties inherent upon the introduction of a radiological material, because the presence of oxygen has the potential to alter the chemical form in which fission products are present. In a simplistic analysis, oxygen liberated by the fissioning of uranium in UO_2 molecules forms a series of binary oxides with fission products (Table 3). In reality, the formation of ternary phases, some of which have poorly defined thermodynamic properties, complicates matters. In general, cesium is predicted to form ternary phases with molybdenum and oxygen, resulting in the formation of cesium molybdate. This compound has a different vapor pressure and chemical properties than pure cesium.

In addition to uranium dioxide and previous fission products of concern (cesium, rubidium, tellurium, palladium, and iodine), this test would have included simulated binary fission product oxides that could have led to the formation of ternary compounds, primarily molybdenum dioxide. The general testing strategy would have been similar to Phase-1 and included the use of stressed specimens to evaluate the potential for stress corrosion cracking and liquid metal grain boundary embrittlement.

Phase-3 Semi-Prototypical Fuel Element Testing

Phase-3 of this program proposed the use of a simulated fuel element that was resistively heated in an out-of-pile setting to assess the migration of chemical species and reaction of components in an actual fuel element. This testing would help to address the need for compatibility between fission products and the components outside the fueled region of the fuel pin, including the plenum spring and spacer. These cooler regions of the fuel element may have been subject to fission product deposition and liquid metal embrittlement that could have affected the design needs for the fuel pin.

The main design criteria for Phase-3 testing would be the replication of the radial and longitudinal thermal gradients that exist in fuel pins. Additional criteria would include the replication of the geometry and chemical environment inside the fuel pin as closely as possible. A modular design would allow the testing of multiple semi-prototypical fuel pins under different conditions. A schematic of the preliminary design for a semi-prototypical fuel element test is shown in Figure 12. The test fixture includes the semi-prototypical fuel element, an internal resistive heating element, and sealed external chamber. The internal heating element and external chamber would be designed to be reusable and more than one test element could be tested simultaneously in the external chamber. This design is preliminary in nature and the main factors that would influence the design would be the generation of the correct temperature gradients. Much more work is required on the design of all three of the components to generate a semi-prototypical system. The external chamber would most likely need to have a temperature control system provided by a coolant flow inside a furnace. Methods for temperature sensing and control would need to be investigated and designed to ensure proper test conditions are maintained throughout the tests. Additionally, the fabrication procedures used for producing the test specimens would need to be determined.

Phases 4 and 5 of the compatibility testing plan were expected to consist of in-pile irradiation tests including testing on prototypical fuel elements.

Figure 12. Schematic of a Semi-Prototypical Fuel Element Test Apparatus for Out-of-Pile Use

Phase-4 Accelerated Compatibility Testing in an Irradiation Environment

Radiation has the potential to affect compatibility issues. As an example, in the embrittlement of Zircaloy by iodine, radiolysis has been implicated in the disassociation of CsI molecules which frees up iodine to participate in stress corrosion cracking of grain boundaries. Unfortunately, the accumulation of fission products due to fissioning in a real fuel element is a rather slow process, limited by the rate at which fuel is fissioned and diffusion rates before the fission products are released.

To accelerate this process, a test in which mechanical specimens were exposed to a simulated fission product mixture in-pile was envisioned. In theory, this test could resemble the Phase-1B or Phase-2 tests along with necessary modifications for use in an irradiation test capsule. Based upon the previous test results, this test could have been performed either without UO_2 (as in Phase-1B), which would have facilitated fabrication and post-irradiation examinations, or with UO_2 to more accurately mimic a prototypical chemical environment (as in Phase-2).

Phase-5 Prototypical Fuel Element Testing

The final phase of irradiation testing was planned for near-prototypical fuel elements. The intention of this test was for the test elements to resemble as closely as possible the actual Prometheus-1 fuel elements in terms of size, construction, materials, and internal components. Based upon schedule requirements and possible limitations in test reactor facilities, some deviations in fuel loading, burnup rates, thermal profiles, neutron flux, and neutron spectrum were considered likely.

FUTURE ACTIONS: None Planned

TECHNICAL REVIEW: This report has been reviewed and agreed to by cognizant Materials Technology management and personnel at KAPL and Bettis.

ACKNOWLEDGEMENTS: A large community of individuals was active in the Prometheus program. This document was improved through extensive discussions with a wide range of personnel, including technical personnel and reviewers at Bettis and KAPL. Specifically, Dave Kramer and Lynne Kolaya are thanked for the final technical reviews of this document.

AUTHOR:

1/20/06
D.C. Noe, Senior Scientist
Advanced High Temperature Materials
Materials Technology

AUTHOR:

12/20/05
M.K. Krohn, Senior Scientist
Advanced High Temperature Materials
Materials Technology

AUTHOR:

12/20/05
K.B. Gibbard, Engineer
NRF East Engineering
NRF

APPROVED BY:

1/20/06
R. Baranwal, Manager
Space Reactor Materials Engineering
Materials Technology

References:

- ¹ MDO-723-0040, in progress.
- ² Gary Carpenter, personal communication (2005). Fission product concentration estimates were made using a point depletion calculation with the ORIGEN-S code simulating operation over a 15 year core life. The calculation used ORIGEN-S library fast spectrum averaged cross sections and thermal fission product yields with constant power operation to 6% Fissions per Initial Fissile Atom (FIFA). (No fast fission product yields were included in the available ORIGEN-S library). The ORIGEN-S calculations account for the transmutation and decay of fission products after they are produced.
- ³ B-MT(SPME)-30, in progress
- ⁴ Bailly, Menessier, Prunier, ed. The Nuclear Fuel of Pressurized Water Reactors and Fast Reactors design and behaviour, Intercept Ltd., 1999, ISBN INTERCEPT 1-898298-57-2.
- ⁵ Haddad R and Cox B (1986) On the Initiation of Cracks in Zircaloy Tubes by I₂ and Cs/Cd Vapours. *Journal of Nuclear Materials*. V138, pp 81-88
- ⁶ Cox B, Surette BA, and Wood JC (undated) Pellet-Clad Interaction Failures: Stress Corrosion Cracking by Iodine or Metal Vapour Embrittlement by Cesium/Cadmium Vapours.
- ⁷ Cox B (1990) Pellet-Clad Interaction (PCI) Failures of Zirconium Alloy Fuel Cladding – A Review. *Journal of Nuclear Materials*. V172, pp. 249-292
- ⁸ Cox B, Surette BA, and Wood JC (1986) Stress Corrosion Cracking of Zircaloys in Unirradiated and Irradiated Csl. *Journal of Nuclear Materials*, V138, pp. 89-98
- ⁹ Une K (1979) Deformation and Fracture Behavior of Zircaloy-2 Deformed at Constant Strain Rate in Iodine Environment. *Journal of Nuclear Science and Technology*, V16, pp. 577-587.
- ¹⁰ Grubb WT (undated) Cadmium Embrittlement of Zircaloy-2 and Certain Other Metals and Alloys. General Electric Company, Corporate Research and Development Center
- ¹¹ Adamson MG and Aitken EA (1985) On the Cs, Te Fission Product-Induced Attack and Embrittlement of Stainless Steel Cladding in Oxide Fuel Pins. *Journal of Nuclear Materials*, V132, pp. 160-166
- ¹² Adamson MG and Aitken EA (1985) Chemical Thermodynamics of Cs and Te Fission Product Interactions in Irradiated LMFBR Mixed-Oxide Fuel Pins. *Journal of Nuclear Materials*, V130, pp. 375-392
- ¹³ Pulham RJ and Richards MW (1990) Chemical Reactions of Cesium, Tellurium and Oxygen with Fast Breeder Reactor Cladding Alloys. Part IV – The corrosion of ferritic steels. *Journal of Nuclear Materials*, V172, pp. 304-313
- ¹⁴ Binary Alloy Phase Diagrams, Second Edition. ASM International, 1990.
- ¹⁵ Schweitzer DG (1995) Status Of Fission Product Diffusion and Transport in HTR Fuels. Brookhaven National Laboratory BNL-DGS-GFDIF-3.
- ¹⁶ Minato K, Ogawa T, Kashimura S, Fukuda K, Shimizu M, Tayama Y, and Takahashi I (1990) Fission Product Palladium-Silicon Carbide Interaction in HTGR Fuel Particles. *Journal of Nuclear Materials*, V172, pp. 184-196.
- ¹⁷ Ogawa T and Ikawa K (1986) Reaction of Palladium with SiC and ZrC. *High Temperature Science*, V22, pp. 179-193
- ¹⁸ Tiegs TN (1982) Fission Product Pd-SiC Interaction in Irradiated Coated-Particle Fuels. *Nuclear Technology*, V57, pp. 389-397
- ¹⁹ Makenas BJ (1994) Road Map for SP-100 Fuel Pin Irradiation Testing. Westinghouse Hanford Company. WHC-SP-1083
- ²⁰ M.A. DeCrescente, M.S. Freed, and S.D. Caplow. "Uranium Nitride Fuel Development SNAP-50." Pratt & Whitney Aircraft, PWAC-488. October 1965.
- ²¹ Arcella FG (1974) Interdiffusion Behavior of Tungsten or Rhenium and Group V and VI Elements and Alloys of the Periodic Table, Part I. Westinghouse Electric Corporation, Astronuclear Laboratory. NASA-CR-134490.
- ²² B-MT(SRME)-36, dated October 25, 2005

(This Page Intentionally Blank)

• DOCUMENT NUMBER: B-MT(SRME)-55

- CONCURRENCE SIGNATURES (Activity must be included) - RESOLVE COMMENTS BEFORE SIGNING

DETAILS OF REVIEW REQUESTED (if necessary)

Per email, 1/20/05
Lynne Kolaya / KAPL

Lynne Kolaya / KAPL

TYPE OF REVIEWS (to be determined by author) [See table at end of instructions for definitions.]

1-Peer:Summary 2-Peer:Intermediate 3-Peer:Detail 4-Independent 5-Informal Committee 6-Formal Committee 7-Specialist 8-Interface

NAME TYPED AND SIGNATURE OF NEXT HIGHER MANAGER NOT SIGNING ON LETTER

DATE _____

J.E. Hack

John E. Hack

1120106

- CONTRIBUTORS AND IMPACTED PARTIES NOT REQUESTED TO CONCUR AND WHY:

DISTRIBUTION**NR**

DI Curtis (3)	08S (INFO)
JD Yoxtheimer	08S/8034
S. Bell	08I/8024
DE Dei	08A/8011
WE Evers	08E/8019
JP Mosquera	08C/8017
TJ Mueller	08R/8033
MD Natale	08I/8024
CH Oosterman	08C/8017
TN Rodeheaver	08I/8024
SJ Rodgers	08E/8019
SJ Trautman	08V/8037

PNR

J. Andes
H. A. Cardinali
J. F. Koury

SNR

DR Clapper
G. M. Millis

BETTIS

M. N. Smith	02B/GM
S. D. Harkness	01Q/MT
J. E. Hack	05R/MT
M. Zika	01C/SE
C.D. Eshelman	36E/SE
R. Baranwal	05P/MT
R.W. Smith	05R/MT
W.L. Ohlinger	05P/MT
D. Hagerty	38D/SE
R.C. Jewart	01C/SE
D. C. Noe	05R/MT
M.K. Krohn	05R/MT
K.B. Gibbard	05P/NRF

KAPL

MJ Wollman	MS 111
SA Simonson	MS 081
DF McCoy	MS 111
JM Ashcroft	MS 132
PF Baldasaro	MS 111
CF Dempsey	MS 111
D.A. Kramer	MS 154
L. E. Kolaya	MS 092
R. J. Grossman	MS 154
S. Harrison	MS 154
J. Beale	MS 092