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“Enhanced Thermal Conductivity Oxide Fuels”

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Executive Summary

The purpose of this project was to investigate the feasibility of increasing the thermal conductivity of oxide fuels by adding small fractions of a high conductivity solid phase. After examining a number of both metals and compounds, we proposed using a new technique to form β -SiC by the Polymer Impregnation and Pyrolysis or PIP process. This technique has been widely used to produce ceramic matrix composites, CMCs, but never heretofore applied to nuclear fuels. The PIP process is highly flexible, and can also be applied to the consolidation of particulates for Gas-cooled Reactors and Inert Matrix Fuels, and can be used for joining of ceramics.

The goal of the matrix phase for CMCs is simply to provide load transfer between the strong reinforcements, whereas for nuclear fuels, the density, defect structure, and purity all affect the goal of high thermal conductivity. For application in current LWR's, we selected a commercially available (Starfire Systems) polymeric precursor for SiC that yields almost stoichiometric high purity β -SiC. This polytype is cubic and thus unlikely to undergo anisotropic growth and cracking under irradiation. SiC has been widely used in nuclear applications because of its radiation stability, neutronic properties and high conductivity. The most notable application for fuels is the CVD coating of β -SiC used as a diffusion barrier on TRISO fuels. However, SiC like most compounds including UO_2 , suffers from radiation-induced loss in conductivity.

Ishimoto *et al.* [1] showed that significant improvements in thermal conductivity could be achieved with only 3.2 vol% of BeO as a *continuous* second phase at the grain boundaries of UO_2 . However, to achieve this microstructure, it was necessary to process above 2160°C, the UO_2/BeO eutectic temperature, which is difficult to transfer to a commercial setting, both because of the very high temperatures and volatilization, and the cost and difficulties with such high temperatures. We performed finite element analyses of such two phase structures and obtained the same enhancements in conductivity, indicating that a lower temperature processing method if it were feasible, would be promising.

After considering many compounds, we reduced the choices to SiC and BeO. Thermodynamic analyses of SiC showed that at high very high temperatures in the presence of oxygen-bearing compounds like UO_2 , reactions occur above 1370C CO and SiO are the likely vapor species that will form. We verified the solid reaction products by equilibration experiments. On the other hand, the Ellingham Diagram for BeO and UO_2 shows that BeO is the more stable species that has essentially zero solubility in UO_2 , and only forms a eutectic at 2160C. Also, the specific heat was evaluated based on the rule of mixing.

Throughout the investigation, the experimental work on processing was supported by extensive finite element modeling using the ANSYS code. Steady state heat transfer was modeled for continuous high conductivity phases and dispersed phases. Heat generation was also modeled. Special techniques were developed to handle the modeling of dispersed whiskers. The modeling revealed that there was no effect on heat transfer for the range of experimentally accessible microstructures, from coarse to fine structures. The thermal conductivity for the BeO/UO_2 system was reasonably well modeled, but sensitive to the structures and porosity produced from green or pre-sintered granules. IMF fuels were also modeled. The measured thermal conductivity for the SiC/ UO_2 specimens were also well modeled when using the measured rather low conductivity of the SiC matrix phase produced at 1300°C. The assumed microstructure consisted of isolated cells of UO_2 surrounded by the high conductivity phase. However, the complete dissolution of the UO_2 showed that it was not isolated but interconnected.

Our work on PIP using the organic precursor, allyhydridocarbosilane or SMP-10 (Starfire

Systems, Inc) required that we first produce a UO_2 body with high density and an easily impregnated open pore structure. We succeeded in doing this using a reverse preslugging process in which a high pressure pressing was followed by granulation, sizing by sieving, and presintering or “bisquing” to stabilize the granules prior to a final pelletizing and sintering. This resulted in a UO_2 phase of ~98%TD with an open porosity that could be varied between 5 to 15 vol%. We primarily focused on 10 vol% of the second phase as a compromise which did not reduce the UO_2 volume excessively.

We developed a vacuum impregnation system and procedure that focused on the important issue of degassing the precursor and impregnation at somewhat elevated temperatures to aid both processes. We measured the viscosity of the precursor as a function of temperature, and modeled the penetration of fluids in porous media to allow complete penetration of our specimens under the applied pressures utilized. We found that pressures up to 4 MPa were required to obtain the maximum in penetration, but that above 3 MPa, He as pressurizing gas showed high solubility in the precursor so we had to use argon above that pressure.

Studies to examine the lower temperature (~400C) “curing” of the polymer that involves the competitive processes of gas evolution by decomposition of the lighter molecules releasing H_2 and polymerization, showed that this stage was critical in filling the porosity; slow heating favored the latter process. Nevertheless, there was a 70% volume reduction of the precursor during pyrolysis and crystallization which meant that PIP was necessarily a cyclic process to obtain the maximum density of SiC in the pores.

We examined the compatibility between UO_2 and SiC at elevated temperatures by doing diffusion-couple type tests with the two materials in pressure contact at temperatures from 1300 to 1600°C. We found that the reaction above 1370°C to form CO and SiO that had previously been reported, could not be prevented or minimized by processing conditions that restricted the release of these gases, even though we showed that their equilibrium pressures were below 1 atm. Therefore, we restricted all processing to $\leq 1300^\circ\text{C}$ which was just above the reported crystallization temperature of 1200°C, but no thermal conductivity measurements were previously available for such low temperatures. In fact, only one previous thermal conductivity datum point of 50 W/m-K was available from the vendor for SMP-10 crystallized at 1600°C/4hrs and measured at room temperature

Our PIP processing under these conditions yielded a density of the SiC phase that was ~ 75% TD after 6 to 9 impregnations. This *bulk* density was defined as the weight of SiC divided by the original UO_2 open porosity. From microstructural examination it appeared that this low density arose primarily from pockets of porosity that had become sealed off during the impregnation process. Otherwise, the SiC phase had excellent contact with the UO_2 phase.

When we measured the thermal diffusivity of these “ UO_2 /SiC-PIP” specimens, we found essentially no improvement in thermal conductivity over published values and measured values for our own specimens and published values for UO_2 . To understand this null effect, we developed two methods of producing the SiC matrix phase using SiC powders as a “filler particle”. The first involved a casting process in which the precursor was used to impregnate a bed of particles in a stainless steel mold. The second was a pelletizing method using the precursor as binder. For casting, we used available β -SiC powders of only 98% purity, which would not be of high conductivity, but at only ~30% tap density (low volume fraction). Since after the first or second impregnation and pyrolysis, the specimens were free-standing, they could be PIP-processed to 1300 and 1500°C without the mold. The thermal diffusivity measurements made at INL showed a striking difference in conductivity for the different crystallization temperatures of 1300C and 1500C. The low conductivity for 1300°C revealed why

the UO_2/SiC -PIP specimens did not exhibit enhanced conductivity. When we further analyzed the SiC phase crystallized at 1300°C , we found a grain size of only 30 nm by x-ray line broadening and SEM. The latter method also revealed a very fine porosity. These nano defects are responsible for phonon scattering and reduced thermal conductivity in these primarily covalently-bonded materials. It should be pointed out that if processing were carried out in a closed pressure vessel, the reaction during processing could be prevented to much higher temperatures, but it would not prevent reactions if such temperatures were reached during service.

However, the experiment did show that PIP-SiC processing was successful in fully impregnating a porous specimen. We had earlier shown (Cadache) that the SiC-PIP process could be used to consolidate TRISO simulant spheres with a β -SiC outer layer that is completely compatible with the SiC precursor. We showed that the same process could be used to consolidate UO_2 spheres as well as long as the temperatures remained below 1300°C , but to obtain higher conductivity SiC required compatible materials. We therefore developed a process to produce UC microspheres by carbothermic reduction of our UO_2 granules mixed with graphite powders to show applicability to *High Temperature Gas-cooled Reactors*, and in particular, the *Gas-cooled Fast Reactor*. We successfully consolidated these spheres with SiC-PIP processing.

Finally, we also examined the use of dispersed *high density* SiC phases in UO_2 . We were able to perform oxidative sintering at low temperatures to avoid the UO_2/SiC reactions to achieve reasonably high density using our relatively low purity β -SiC powder. As a more promising alternative, we also tried pure SiC whiskers. Our finite element modeling showed the possibility of significant enhancements if we produced high density UO_2 . However, these whiskers were much more effective in restraining sintering than they were in our earlier work on SiC_w - reinforced alumina, and densities on the order of 75%TD were obtained for the UO_2 with 5 vol% whiskers.

With our lack of ultimate success with SiC as the high conductivity phase in UO_2 , we turned to another high conductivity compound, BeO, to produce enhanced conductivity fuels. We had initially had the usual “knee jerk” reaction that BeO was too toxic to consider, but when we began to look at the handling requirements, we found that they were not much different than those for UO_2 . With Purdue industrial hygienists we set up procedures which were identical to those for UO_2 except for the added protection (not required) to use a respirator when handling the material.

We tried various methods of producing a dense BeO matrix including mixing BeO and Be powders, but eventually found that the excellent sintering and chemical compatibility between UO_2 and BeO powders allowed the simple process of “co-sintering” UO_2 granules that were uniformly coated with BeO powder and pelletized. High densities were obtained no matter what the UO_2/BeO volumetric ratio. For ECO fuels we produced 5 and 10 vol% BeO, and for IMF fuels there was up to 80 vol% BeO. We examined both green and slug-bisqued UO_2 granules. The green granules were much more friable, and when mixing with BeO powders by our self-milling method we found that there was “contamination” of the BeO phase with UO_2 particles. On the other hand, with the SB granules, there was some evidence of interphase porosity. In addition, the grain sizes of the “contaminated” BeO was much smaller ($\sim 2\mu\text{m}$) than for the “uncontaminated” BeO (20 μm). Small grain size is highly desirable for BeO to prevent or delay irradiation induced microcracking as discussed below.

The thermal diffusivity of the UO_2 with 10 vol%BeO led to a thermal conductivity 50% higher than that of typical 95%TD UO_2 at all measured temperatures. Optical microscopy showed that the BeO phase ($\text{BeO} + \text{UO}_2$) was of high density without cracks, in good thermal

contact with the UO_2 , and apparently continuous on a 2D polished surface. But to verify that it really was continuous, we dissolved away the UO_2 phase in boiling nitric acid, leaving a BeO “skeleton” that was surprisingly robust and could easily be photographed.

The ability to dissolve away the UO_2 phase in the case of thermal reactors, or the U,PuO_2 phase for fast reactors, gives the potential for easy reprocessing. Moreover, the remaining BeO could be recycled into new fuel.

One open question in the use of BeO in ECO fuels is its radiation stability. Although it suffers *less* loss in thermal conductivity than other compounds, it can eventually crack from anisotropic radiation growth and high fast neutron doses. However, for ECO fuels there are a number of mitigating factors that strongly suggest in-pile testing and methods were developed for producing such specimens. These factors include small grain size, swelling constraint by the majority UO_2 phase, fission fragment annealing, and temperatures of irradiation.

The second question concerns the effects of BeO and reduced temperatures on fuel performance and reactivity. The COPENIC code was modified to examine UO_2/SiC fuel performance. Comparisons were made between the currently-used UO_2 fuel and ECO fuel in a particular 15x15 pin subassembly Babcock and Wilcox reactor.

Assuming the core was either all standard or all ECO fuel of *equal* enrichment, the ECO fuel with less uranium must go to 4% higher burnup to obtain the same total energy extraction per fuel assembly. For the calculations, it was assumed that the fuel temperatures are reduced by 0, 5 and 10%. (This is reasonable for 5 vol% BeO, but conservative for the 10vol% BeO fuel where the thermal conductivities are 50% higher at all temperatures, which reduces average temperatures by $\sim 200^\circ\text{C}$.) Comparing UO_2 and fuel 10% cooler, at end-of-life, EOL, the fission gas release is reduced from 17 to 11%, and the pin plenum pressure is reduced from 160 to 128 bar.

A LOCA initialization transient analysis was also performed. When compared to standard UO_2 fuel, the ECO fuel provides an increase in the maximum linear heat generation rate by 4.9 kW/m at BOL, and 3.2 kW/m at EOL (62 GWd/MTU).

Neutronics calculations were also done by comparing results with a previous B&W reactor analyses. In this case, the enrichments of the ECO fuels were increased to give the same core-averaged k_{inf} , and the fuel temperatures were again reduced 100°C . Both SiC and BeO type ECO fuels were considered, but while CASMO-3 was suitable for SiC, the $(n,2n)$ reactions in Be necessitated using the TRITON control module of SCALE 5.0 with the 238-energy group cross-section library. The TRITON calculations are performed with an appropriate cross-section library for beryllium, and to establish the amount of depletion of the beryllium isotope for three cycles of operation. Both the finer energy-group structure and the use of ORIGEN-S mean that TRITON is better able to treat $(n, 2n)$ reactions of beryllium.

Comparison of the results for the two ECO fuel types revealed a striking difference in their neutronic performance. Substitution of $\text{UO}_2\text{-SiC}$ fuel for UO_2 fuel required an increase in enrichment by 0.16 wt % to maintain the end-of-cycle value of k_{inf} . In contrast, substitution of $\text{UO}_2\text{-BeO}$ fuel for UO_2 fuel required an increase in enrichment by only 0.0073 wt % to maintain the end-of-cycle value of k_{inf} . The consumption of ^9Be through $(n, 2n)$ reactions is only 0.15% over three cycles of irradiation.

A third question was the difficulties and costs of incorporating BeO in a commercial fuel fabrication plant. (Fortunately, the largest world supplier of BeO, Brush Beryllium, is located in the U.S.) The operation considered the most problematic was pellet grinding. In comparing the

allowed air concentrations for BeO and UO_2 assuming they are airborne in proportion to their volume ratio, it appears that even the dry grinding procedures presently used for UO_2 should be adequate for BeO. But additional precautions of wet grinding, hoods and respirators can be readily added if necessary. Beryllium addition could also affect other aspects of pellet production, such as scrap recycling, waste disposal, and environmental releases. These areas require evaluation.

An estimate of the relative costs of ECO vs. standard fuel were also made assuming 60 and 56 subassemblies, and the additional enrichments necessary to maintain the same end-of-cycle k_{inf} . A significant factor is that there is less uranium in the ECO fuels so, despite the higher enrichments, the net result for the 60 subassembly core is a predicted decrease in uranium cost of about \$139,000 per batch for UO_2 -SiC fuel and \$501,000 per batch for UO_2 -BeO fuel.

A reduction in the reload batch size from 60 to 56 is expected to impose penalties in terms of increased power peaking, but these may be acceptable with ECO fuel because of its improved thermal conductivity. It was also assumed that an increase in the ^{235}U enrichment by 0.25 wt % would be required to maintain cycle length. The same increase in enrichment was assumed to apply for all three fuel types. The increase in enrichment was strictly an engineering judgment and was not supported by a specific neutronic analysis or core design. Therefore, it is not appropriate to compare costs between batches with 56 assemblies and those with 60. The decrease in uranium cost per batch is \$236,000 for UO_2 -SiC fuel and \$506,000 for UO_2 -BeO fuel. Brush Wellman [39] gives the following cost for their standard grade of BeO in quantities >12.5 Tons: \$115/lb or \$253/Kg. Assuming 5 vol% BeO gives an additional cost of \$350,000 for the BeO of 95%TD.

In addition, the net savings from reducing the batch size is estimated to be between \$100,000 and \$200,000. The reduction in uranium cost for UO_2 -BeO fuel is sufficient to offset an increase in manufacturing cost of nearly \$20/kg U, whereas the reduction in uranium cost for UO_2 -SiC fuel would offset an increase in manufacturing cost in the range of about \$5/kg U to \$10/kg U. However, the economic impact of using ECO fuel extends beyond the fuel cost. The improved thermal performance of the fuel could support less restrictive peaking, operating, and maneuvering limits, and less restrictive limits can contribute to the economic performance of a power plant.

Finally, the irradiation and PIE of the UO_2 /BeO ECO fuel was considered, and procedures for producing the pellets for irradiation were developed.

Task 1: Support pellet production with analysis

Sub task 1.1: Evaluate thermodynamic and thermophysical data

The purpose of this task is to collect and evaluate thermodynamic and thermophysical data that may be useful in predicting the stability and performance of ECO fuel. Compounds of interest are those related to uranium dioxide plus silicon carbide (UO_2 -SiC) fuel and to uranium dioxide plus beryllia (UO_2 -BeO) fuel.

Various reference works on thermochemistry have been collected. These include works of broad scope [1,2] as well as more specialized volumes on the chemistry of uranium or nuclear materials [3-5]. Collectively, these works provide good coverage of the compounds of uranium, oxygen, silicon, carbon, and beryllium. Thermodynamic data for the chemical species listed in Table 1.1 have been coded in Mathcad for use in calculations.

Table 1.1 Species included in thermochemical modeling

Be	SiO ₂	U ₂ C ₃
BeO	SiC	UC ₂
C	U	U ₃ Si
CO	UO ₂	U ₃ Si ₂
CO ₂	U ₄ O ₉	USi
O ₂	U ₃ O ₈	USi ₂
Si	UO ₃	USi ₃
SiO	UC	

Preliminary comparisons of the data from the various sources indicate that the sources are in good agreement. For example, Knacke et al. [1], Barin [2], and Cordfunke and Konings [3] all report the Gibbs free energy for UO₂, and their values agree to within 1.8 kJ/mol throughout the reported range of temperature. Similarly, Knacke et al. [1] and Barin [2] report values for the Gibbs free energy of SiC that agree to within 1.4 kJ/mol throughout the reported range of temperature. For comparison, note that Figure 4 below spans a range in oxygen potential of 1000 kJ/mol. Variations in thermochemical data from one source to another are therefore not expected to have significant effects on predictions of thermodynamic equilibria.

Some of the sources are not suitable for use on this project. A good example is the compilation of Grenthe *et al.* [4]. The data were compiled by an international team and are considered to be of very high quality. However, many compounds are not included, and for many others, the only data provided are for 298 K (25 °C). Temperature-dependent thermodynamic data are provided for the oxides and carbides of uranium. Data for the carbides are only given for the temperature range 298 to 600 K (25 to 327 °C), which is too low for significant chemical reactions between UO₂ and SiC.

The well-known and authoritative JANAF tables [6], do not include uranium compounds.

Some qualitative differences and inconsistencies have been found among the various thermodynamic data compilations. For example, Knacke et al. [1], Barin [2], and Grenthe et al. [4] all report data for UC and U₂C₃. However, Barin and Grenthe et al. [4] discuss “UC_{1.94}”, whereas Knacke et al. [1] discuss “UC₂” and note that its nonstoichiometry was not considered. Knacke et al. [1], report the melting point of “UC₂” as 2858 K (2585 °C), which agrees with the maximum melting temperature for the δ phase as given in the U-C phase diagram, Figure 1. Curiously, the maximum temperature for which they tabulate thermodynamic properties is 2041 K (1768 °C), which is not the melting point but the temperature of the eutectoid reaction $\epsilon + \text{graphite} \rightarrow \delta$.

Some inconsistencies have also been found in the data for uranium silicides. Allen et al. [7] state that “USi₂ does not exist”, but a more recent U-Si phase diagram (Figure 2) indicates that such a compound is stable up to 723 K (450 °C), and Barin [1] tabulates thermodynamic data for USi₂ up to 1800 K (1527 °C). In light of these inconsistencies, the results of thermodynamic calculations for uranium silicides should be used with some caution. A comparison of calculated results with the uranium-silicon phase diagram is included in the discussion of subtask 1.4.

Fig. 1.1. Uranium-carbon phase diagram [8].

Fig.1. 2. Uranium-silicon phase diagram [9].

References for subtask 1.1

- [1] O. Knacke, O. Kubaschewski, and K. Hesselmann, *Thermochemical Properties of Inorganic Substances*, second edition (Berlin: Springer-Verlag, 1991)
- [2] Ihsan Barin, *Thermochemical Data of Pure Substances*, third edition (VCH Verlagsgesellschaft: Weinheim, Germany, 1995)
- [3] E. H. P. Cordfunke and R. J. M. Konings, eds., *Thermochemical Data for Reactor Materials and Fission Products* (Amsterdam: North Holland, 1990)
- [4] Ingmar Grenthe, Jean Fuger, Rudy J. M. Konings, Robert J. Lemire, Anthony B. Muller, Chinh Nguyen Trung, and Hans Wanner, *Chemical Thermodynamics, Volume 1: Chemical Thermodynamics of Uranium*, Hans Wanner and Isabelle Forest, eds. (Amsterdam: North Holland, 1992)
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- [6] Malcolm W. Chase, Jr., *Journal of Physical and Chemical Reference Data Monograph No. 9: NIST-JANAF Thermochemical Tables*, fourth edition (American Institute of Physics: Woodbury, NY, 1998)
- [7] G. C. Allen, J. A. Crofts, and T. Swan, *The High Temperature Reactions Between Uranium Dioxide and Silicon Carbide* (Central Electricity Generating Board, Berkley Nuclear Laboratories, Berkley, Gloucestershire, UK, 1970)
- [8] T. B. Massalski, ed., *Binary Alloy Phase Diagrams*, Metals Park, Ohio: American Society for Metals, 1986.
- [9] Hugh Baker, ed. *ASM Handbook, Volume 3: Alloy Phase Diagrams*, (Materials Park, OH: ASM International, 1992)

Subtask 1.2: Calculate heat capacity

The purpose of this task is to calculate the heat capacity of a mixture of UO_2 and SiC . The heat capacity is used in determinations of thermal conductivity from thermal diffusivity.

The available compilations of thermodynamic data provide heat capacities for UO_2 , SiC , uranium carbides, and BeO , which are the dominant materials. The heat capacity of ECO fuels can be calculated by the rule of mixing. Inputs to the rule of mixing are the heat capacities and mass fractions of the individual phases. Excel workbooks have been developed to calculate heat capacity as a function of temperature for a UO_2 - SiC mixture and for BeO .

Some compilations of thermodynamic properties, such as Barin [1] and Knacke et al. [2], show a discontinuity in the heat capacity of UO_2 at 2000 K. This temperature is somewhat beyond the upper limit of what is of interest for this project, but it should be understood if higher temperatures are used. The high-temperature heat capacity of UO_2 has been heavily studied (see, for example, Chevalier et al. [3], Hiernaut [4], and Hyland and Ohse [5], and it appears that UO_2 undergoes a higher-order phase transition at a temperature of about 2600 to 2700 K. Knacke et al. [2] use a standard functional form that is generally useful but is ill-suited to describing higher-order phase transitions. The discontinuity appears to be an artifact of applying that functional form.

References for subtask 1.2

- [1] Ihsan Barin, *Thermochemical Data of Pure Substances*, third edition (VCH Verlagsgesellschaft: Weinheim, Germany, 1995)
- [2] O. Knacke, O. Kubaschewski, and K. Hesselmann, *Thermochemical Properties of Inorganic Substances*, second edition (Berlin: Springer-Verlag, 1991)
- [3] P.-Y. Chevalier, E. Fischer, and B. Cheynet, "Progress in the Thermodynamic Modelling of the O-U Binary System", *Journal of Nuclear Materials*, vol. 303 pp.1-28 (2002)
- [4] J. P. Hiernaut, G. J. Hyland, and C. Ronchi, "Premelting Transition in Uranium Dioxide", *International Journal of Thermophysics*, vol. 14, pp. 259-283 (1993)
- [5] G. J. Hyland and R. W. Ohse, "The Heat Capacity and Enthalpy of Condensed UO_2 : Critical Review and Assessment", *Journal of Nuclear Materials*, vol. 140, pp. 149-170 (1986)

Subtask 1.3: Phase stability

The purpose of this task is to determine what reactions might occur between the UO_2 fuel and SiC conductive phase. Such reactions have been observed during processing at temperatures of about 1400 °C and above, and are apt to reduce the thermal conductivity of the composite fuel. Understanding of the reactions is used in choosing processing conditions that will not cause degradation of the fuel. The work considered the thermodynamics of hyperstoichiometric UO_2 , UO_2 -SiC stability, and UO_2 -BeO stability. Most of the effort was directed to UO_2 -SiC stability because that was the most complex of the three subjects.

Oxidation stability of uranium

Figure 3 is an oxidation stability (Ellingham) diagram for uranium oxides. The boundaries between different phase fields were calculated from data provided by Barin (1995). Since nuclear reactor fuel is typically slightly hyperstoichiometric (e.g., $\text{UO}_{2.002}$ at beginning of life), the UO_{2+x} phase field is of particular interest. The conditions for stoichiometric UO_2 are shown by a dotted green line; similarly, the conditions for hyperstoichiometric UO_2 with various U/O ratios are shown by dashed green lines. The stoichiometries were calculated on the basis of data published by Lindemer and Besmann (1985). It will be noted that the lines for UO_{2+x} and UO_2 intersect, which is an apparent inconsistency. In a strictly calculated Ellingham diagram, the lines would not intersect, but the curves for UO_{2+x} would asymptotically approach the line for UO_2 at high temperatures. The lines for UO_{2+x} in Figure 3 are approximations that apply except in the vicinity of the line for UO_2 . Figure 3 makes it clear that if the fuel is even slightly hyperstoichiometric (e.g., $\text{UO}_{2.001}$), the oxygen potential will be fairly high in the UO_{2+x} phase field.

Also shown in Figure 3 are lines of constant oxygen partial pressure, $P(\text{O}_2)$. These are black, dot-dash lines and are for information only.

Reactions of UO_2 and SiC

Possible reactions between UO_2 and SiC have been studied in detail. This section discusses the thermochemistry of silicon carbide, uranium carbides, and uranium silicides.

Examination of the oxidation stability diagrams for UO_2 -SiC has shown that the oxidation reactions for several compounds are different at high temperatures than at low temperatures. Compounds that undergo a change in oxidation reactions include silicon carbide, uranium carbides, and uranium silicides. The oxidation stability diagrams have been revised to

reflect the high-temperature reactions. As in work reported previously, tabulated values of free energy from the literature were used to calculate the diagrams.

Fig. 1.3. Oxidation stability diagram for uranium oxides

The stability of silicon carbide against oxidation is controlled by four reactions. Figures 4 and 5 reflect three of these. At low temperatures, the oxidation reaction is

Since oxygen is the only gaseous species involved, the reaction is shown by a single line on the oxidation stability diagrams. The line is marked in light violet as the SiC – SiO₂ stability boundary.

At sufficiently high temperatures (greater than about 1200 K in the figures), the SiC – SiO₂ stability boundary intersects the C – CO stability boundary. Elemental carbon is not stable above the boundary, so reaction 1, which has carbon as a product, is replaced by the following reaction:

Reaction 2 includes CO as a gaseous product, so the stability boundary depends on the pressure of carbon monoxide, $P(\text{CO})$. As is indicated in Figure 4, the light violet lines marked (A) and (B) are for $P(\text{CO}) = 10^{-4}$ bar and $P(\text{CO}) = 1$ bar, respectively. The lines between (A) and (B) are for $P(\text{CO}) = 10^{-3}$, 10^{-2} , and 10^{-1} bar.

Information on the oxidation of carbon is also shown in Figure 1. 4. Graphite (C) is stable under conditions of sufficiently low temperature and pressure. The solid orange lines show the conditions for constant total $P(\text{CO}) + P(\text{CO}_2)$ from 10^{-4} bar to 1 bar. The orange dotted line shows the conditions for $P(\text{CO}) = P(\text{CO}_2)$. CO predominates below the dotted line, and CO_2 predominates above it.

At even higher temperatures than those for reaction 2, the SiC – SiO_2 stability boundary intersects the Si – SiO_2 stability boundary, as shown in Figure 5. SiO_2 is unstable at temperatures above the intersection, so the oxidation reaction is either

or

Reaction 3 will be considered first. The reaction has CO as a gaseous product, so the stability boundary again depends on the pressure of carbon monoxide. The five light violet lines starting with (C) and ending with (D) are for $P(\text{CO}) = 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}$, and 1 bar, respectively.

It will be noted from Figure 5 that lines (A), (B), (C), and (D) all pass through a region where SiO, rather than SiO_2 or Si, is the stable silicon species. Reaction 4 applies in that region.

Reaction 4 differs from reactions 2 and 3 in that it has two gaseous products. Therefore, the stability boundary for silicon carbide in this region depends on the pressures of both silicon monoxide and carbon monoxide. Figure 6 shows five dashed, light violet lines starting with (E) and ending with (F). These are for $[P(\text{SiO}) \cdot P(\text{CO})]^{1/2} = 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}$, and 1 bar, respectively. Although reaction 4 produces SiO and CO in equal quantities, there may be other sources of these gases. Therefore, it cannot be generally assumed that $P(\text{SiO}) = P(\text{CO})$.

The stability boundaries derived from reaction 4 cannot be directly connected to those derived from reactions 2 and 3 because the thermodynamics of reaction 4 depend on $P(\text{SiO})$, whereas those for reactions 2 and 3 do not. This distinction is emphasized in Figure 6 by using dashed and solid lines and by extending the dashed lines beyond their apparent intersections with the solid lines.

Similar changes in reaction occur for UC. At low temperatures, UC oxidizes by the reaction

The stability boundary for reaction 5 is shown in Figure 7 as a magenta line. At sufficiently high temperatures, the UC – UO_2 stability boundary intersects the C – CO stability boundary, and elemental carbon becomes unstable as a product. As a result, the oxidation reaction becomes

At even higher temperatures, the UC – UO_2 stability boundary intersects the U – UO_2 stability boundary, and UO_2 becomes unstable as a product, so the oxidation reaction becomes

Fig. 1.4. Oxidation stability diagram for SiC, showing relationship to oxidation of carbon.

Fig. 1.5. Oxidation stability diagram for SiC, showing relationship to oxidation of Si.

Fig. 1.6. Complete oxidation stability diagram for SiC.

Fig. 1.7. Oxidation stability diagram for UC, showing relationship to oxidation of carbon.

As with other reactions that yield CO as a product, reactions 6 and 7 yield different stability boundaries for different values of $P(\text{CO})$.

Decarburization of U_2C_3 and $UC_{1.94}$ has been considered, but the results are not plotted. The results at low temperatures are very similar to those calculated from equation 5, that is, there is little difference between the maximum oxygen potentials for stability of UC, U_2C_3 , and $UC_{1.94}$. At higher temperatures, $UC_{1.94}$ decarburizes successively to U_2C_3 and then to UC, with the excess carbon forming CO. The stability boundaries are very close to the corresponding C – CO stability boundaries. In a thermochemical sense, U_2C_3 and $UC_{1.94}$ act approximately like mixtures of UC and C rather than distinct compounds.

The uranium silicides also undergo a change in reactions at high temperatures. At temperatures up to about 1500 K, increases in the oxygen potential cause oxidation of uranium and conversion of uranium-rich silicides to more silicon-rich phases. The regions of stability for the various uranium silicides are shown with gray lines in Figure 8.

The final stage in removing uranium from uranium silicides is the conversion from USi_3 to Si:

At sufficiently high temperatures, however, the USi_3 – Si stability boundary intersects the Si – SiO stability boundary, and Si becomes unstable as a product. As a result, reaction 8 is replaced by

Since there are several uranium silicides, the oxidation equilibria are too complex to be shown clearly in Figure 8. Figure 9 shows the equilibria in more detail. Note that Figure 9 also shows the Si – SiO stability boundaries at smaller values of $P(SiO)$.

The uppermost gray line in Figure 1.9 is the stability boundary for reaction 8. This boundary applies if $P(SiO)$ is sufficiently large that reaction 9 is suppressed. The direction of the stability boundary changes slightly at the point marked “(m)” (1685 K), which corresponds to the melting point of Si.

of $P(SiO)$ from 10^{-6} bar to 10^{-3} bar. The lines marked “(B)” through “(E)” are, respectively, the stability boundaries for the reactions

Fig. 1.8. Oxidation stability diagram for uranium silicides, showing relationship to oxidation of silicon.

Fig. 1.9.. Detail of oxidation stability diagram for uranium silicides

The lines marked "(A)" in Figure 9 are the stability boundaries for reaction 9 with various values for the indicated values of $P(\text{SiO})$.

Reference for sub task 1.3

- [1] Terrence B. Lindemer and Theodore M. Besmann, "Chemical Thermodynamic Representation of $\langle \text{UO}_{2\pm x} \rangle$ ", *Journal of Nuclear Materials*, vol. 130, pp. 473-488 (1985).

Sub task 1.4: Oxidation stability of beryllium

An Ellingham diagram for beryllium is shown in Figure 10, superimposed on the diagram for uranium [1, 2]. It can be seen that Be oxidizes to BeO at an oxygen potential below that for oxidation of U to UO_2 , and that BeO does not undergo any further oxidation. This is an excellent situation because it means that BeO will be stable whenever UO_2 is stable. The low oxygen potential for the Be-BeO equilibrium relative to the expected values for nuclear fuel has two additional benefits. First, the beryllium is strongly oxidized, so there will be a very low pressure of Be vapor. Second, uranium is also strongly oxidized, so it is extremely unlikely that the intermetallic compound UBe_{13} can form.

Fig. 1.10. Oxidation stability diagram for beryllium

References for subtask 1.4

- [1] Ihsan Barin, *Thermochemical Data of Pure Substances*, third edition (VCH Verlagsgesellschaft: Weinheim, Germany, 1995)
- [2] Terrence B. Lindemer and Theodore M. Besmann, "Chemical Thermodynamic Representation of $\langle \text{UO}_{2\pm x} \rangle$ ", *Journal of Nuclear Materials*, vol. 130, pp. 473-488 (1985).

Task 2: Develop processing methods and produce pellets (Purdue)

Subtask 2.1: The Polymer Impregnation and Pyrolysis or PIP Method.

SiC is a refractory compound that is resistant to many alkalis and acids, and is highly resistant to oxidation even at high temperatures because of the formation of SiO₂ under highly oxidizing conditions. It is chemically compatible with zircaloy up to 1200°C [1], possesses very high thermal conductivity when pure and fully-dense, has a low neutron absorption cross section, good radiation stability, and it is compatible with many oxides even at reasonably high temperatures [1, 2]. However, its reaction with UO₂ at T>1370 °C [3] was a key problem for the present research, and could not be overcome in processing. Nevertheless, SiC-based ceramics find a variety of high temperature fuel applications. Its high thermal conductivity make it an excellent candidate for the inert matrix phase in dispersion fuels [2, 3]. However, pure SiC powders can be consolidated into dense bodies only at very high temperatures of ~2000°C, or at somewhat lower temperatures with the addition of a large quantity of sintering aids [1], which would reduce its thermal conductivity.

Hence, the development of cost-effective and commercially feasible fabrication methods for the consolidation of SiC-based ceramics continues to be a promising area of research. The *Polymer Impregnation and Pyrolysis or PIP*, has been demonstrated to be a versatile, simple and cost-effective route to consolidate ceramic matrix composites [4], as well as to join compatible ceramics [5, 6, 7, 8, 9, 10, 11], but has not heretofore been used in nuclear fuels fabrication. Essentially the procedure usually involves vacuum impregnation of a liquid polymeric ceramic precursor into a porous solid or a fiber “preform” followed by the pyrolysis of the polymer, and crystallization to a relatively dense ceramic. For composite fabrication, the density need only be sufficient to transfer the load to the reinforcements, but for fuels, higher density and purity are desired. One underlying processing issue is the release of the decomposition gases upon pyrolysis and the shrinkage of the product which necessitates multiple impregnations to achieve high density.

Even though many such organic precursors are available, the one that is most widely-used and well-studied is allylhydridopolycarbosilane, commercially known as SMP-10 [10]. The use of a commercial source also allowed us to obtain a current cost for the precursor of \$550/kg [Starfire Systems]. The absence of oxygen prevents the oxidation of the SiC phase if all processing is carefully done under UHP argon. Moreover, this precursor gives a high ceramic “yield” on a weight basis of ~80% of stoichiometric, pure cubic β-SiC [11, 12, 13]. The cubic crystal structure has the important advantage of isotropic irradiation growth, as witnessed by the irradiation stability of CVD deposited β-SiC as the diffusion barrier on TRISO fuels [14]. Therefore, the use of PIP-SiC as a high conductivity matrix is advantageous for actinide burning in fast reactors where the fast neutron fluxes are high.

The primary objective of this work was to develop a procedure based on the PIP technique, to produce a two phase fuel containing a continuous minor SiC phase in UO₂. We have called these *Enhanced Conductivity Oxide or “ECO”* fuels. It has been shown by Ishimoto *et al.* [15] that a continuous BeO phase at the grain boundaries in UO₂ can significantly improve thermal conductivity much more than a dispersed BeO phase. Secondly, we were interested in the use of PIP to consolidate *Inert Matrix Fuels*. The microstructure of the processed bodies was examined, and the thermal properties and thermal shock resistance measured.

2.1.1: Polymer impregnation

An experimental system was developed to degas and impregnate the polymer into porous samples under vacuum. A schematic diagram of this system is shown in **Fig. 2.1**. It consists of two independent but interconnected chambers (“A” and “B”). Chamber “A” was used to degas the polymer while “B” was used for vacuum impregnation. Ultra high purity argon gas (UHP Ar) was used in order to avoid the reaction of the polymer with oxygen and, even more importantly, moisture which degrades the polymer.

Prior to impregnation, the precursor was evacuated to ~50 μ m and back-filled three times with UHP argon while holding at 60°C and stirring with a magnetic bar, in order to remove the gas generated during cold storage at -4°C. (Storage at this temperature is necessary to prevent degradation of the polymer. We did not see any degradation over a 3 year period.) This step also helped reduce the viscosity and improve the rate of penetration of the precursor into porous UO₂. The measured values of the viscosity of the precursor specimens in the as-received, de-gassed and used condition were found to be 0.10, 0.08 and 0.14 Pa-s, respectively, **Fig. 2.2**.

The heated and de-gassed precursor was then transferred to the pellet chamber to cover the pellets, and the system backfilled with UHP argon at atmospheric pressure for one hour. In order to insure that even the finest pores were filled with the precursor, a pressurization step was found necessary. This was carried out in a pressure vessel by pressurizing the vacuum impregnated sample with a slight excess of the polymer with argon or helium.

It was found that at high pressures, a measurable quantity of He dissolved in the precursor, which could cause swelling of the precursor during subsequent processing, resulting in a porous product. Hence, the maximum pressure that could be employed for the impregnation had to be determined experimentally. The weight gain of a known volume of the polymer held under different pressures of the inert gas was measured, and the saturated weight was recorded. The results obtained, **Fig. 2.3**, show that for UHP helium, there is an abrupt increase in the quantity of the gas dissolved in the precursor at pressures above 3 MPa. Therefore, this represented the maximum pressure for He. For UHP argon, 4 MPa was identified as an acceptable pressure.

To determine the time necessary for an impregnation at high pressure, the Hagen-Poiseuille equation (1) was used to estimate the steady state flow rate, Q, through a capillary with a fluid of known viscosity in the laminar flow regime. The time required to impregnate an evacuated porous sample was estimated using the relations (1) to (4) assuming that the effects of gravity and capillarity were negligible. The latter assumption was certainly conservative since wetting behavior was clearly observed.

$$Q = \frac{\Delta P \pi D^4}{128 \mu L}, \text{ (m}^3 \text{ / s)} \quad (1)$$

$$V = \frac{\pi D^2}{4} L, \text{ (m}^3 \text{)} \quad (2)$$

$$t_{\text{Hagen-Poiseuille}} = \frac{32 \mu L^2}{\Delta P D^2}, \text{ (sec)} \quad (3)$$

$$t_{practical} = Tortuosity \times t_{Hagen-Poiseuille}, (\text{sec}) \quad (4)$$

where V is the volume of the flow tube or pore of a certain length, and $t_{Hagen-Poiseuille}$ is the time to flow into as assumed length L of 5 mm (half the specimen diameter) and pore diameter D . This is an overestimate for our disk-shaped specimens.

Assuming that the tortuosity factor is ~ 2 (since the range of tortuosity is 1~2 [16,17] and the viscosity μ as 0.08 Pa-s, a pore diameter of 0.1 micron is expected to be fully impregnated at 4 MPa in 60 minutes. Hence, the high pressure impregnation was carried out for an hour at pressures ≥ 4 MPa. Of course, the pore diameters can vary greatly, but during successive impregnations they progressively fill and eventually close off, so 0.1 μm represents the pore diameter very near pore closure.

2.1.2: Pyrolysis and crystallization

The steps involved in the pyrolysis and crystallization of the polymer precursor are well-established [5, 6, 7, 8, 9, 10, 11, 12, 13]. These are as follows:

- (1) Removal of moisture and volatile oligomers,
- (2) Loss of H_2 from SiH_2 groups leading to cross-linking of the polymer and the formation of a network structure,
- (3) extensive structural rearrangement, accompanied by the loss of H_2 along with a small quantity some species containing C and Si,
- (4) formation of amorphous SiC and
- (5) crystallization leading to the formation of nano-crystallites of β -SiC.

In terms of volume filling, there are critical temperature regimes where the polymer decomposes and large volumes of gas must exit the structure. These temperatures were determined by thermogravimetry (TG) measurements on small samples [10, 11, 12, 13]. We also observed the gas evolution and polymerization process by filling the degassed polymer in glass vials and slowly heating 240°C in box furnace with a window. The bubbling of polymer starts at about 200°C .

It is important in the gas evolution stage, to allow the competing reaction of polymerization to become important, so slow heating is required in this stage [10]. These investigations revealed that the cross-linking of the polymer (SMP-10) occurs at $\sim 400^\circ\text{C}$, followed by the formation of an amorphous SiC at $\sim 900^\circ\text{C}$, and crystallization which commences at $\sim 1200^\circ\text{C}$.

In view of the fact that the sample sizes involved in the present study were considerably larger than those reported in the published thermogravimetric investigations, it was necessary to validate the applicability of these findings by carrying out the following experiments: The precursor by itself was pyrolyzed at temperatures from 100 to 1200°C under UHP argon. A typical hold time of about 2 h was used at each temperature and a heating rate of $0.5 \sim 3^\circ\text{C}/\text{min}$ was employed. Subsequently, the density of the product was measured. The results obtained in these experiments which are shown in **2.4(a)**, revealed that a significant weight loss occurs

between 300 and 600 °C. The density of the SiC-PIP product fragments pyrolyzed at various temperatures is shown in **2.4(b)**. The maximum density in the PIP product crystallized at 1300°C is about 80%TD. An improvement in the density to 88%TD is expected for 1600°C temperature crystallizations with SiC filler particles [10].

Earlier studies [18,19] also showed that in order to improve the cross linking, minimize losses due to premature evaporation of low molecular weight intermediates, minimize porosity [19] and improve the ceramic yield [18] a low heating rate of about 0.5 ~ 3 K/min needs to be employed up to 873 K. The temperature profile used for the experiments is shown in **Fig. 2.5**, with 0.5 C/min in the critical gas release stage.

Optical micrographs of the mounted and polished fragments, **Fig. 2.6**, indicate that below 600 C, the precursor possesses channel-like narrow pores, while those obtained by crystallization at 1300°C, appear to have larger pores. Earlier high magnification SEM work done at Cadarache by the PI, shows that there is a very fine microporosity and grain size for such low temperature crystallizations. Nevertheless, the large pores, which usually dominate the volume can be filled in the subsequent PIP cycles, as long as they remain open. This suggests doing crystallization after each impregnation, although we only saw a small increase in density doing this vs. the usual practice of doing a crystallization after every 3 impregnations. The reason for this will become apparent below.

The crystallization of SMP-10 is reported to start at ~1200°C [10]. The XRD pattern of PIP product after crystallization at 1300°C for 5h is shown in **2.7(a)**. The three broad peaks in the pattern are of β -SiC. The broadening of these peaks indicates that the β -SiC produced at 1300°C has a very small crystallite size, consistent with the SEM observations. The broadening decreases with the crystallization time. On the other hand, the formation of cristobalite (SiO_2) or of graphite (C) appears to increase with time.

The half width of (111) peaks is related to the crystallite size by the Debye-Scherrer formula [21]. As shown in **Fig. 2.7(b)**, the crystallite size is a function of the crystallization time and temperature. The trend of crystallite size shows that no increase in the size was observed for up to 7 h at 1300 C. However, a one hour crystallization at 1500°C yields the same size (~ 50 nm) as 45 h crystallization at 1300°C, but even then, the grain size remains small. This result is consistent with the earlier SEM observations at Cadarache.

2.1.3: Characterization of the SiC-PIP product

The microstructure and density of the products obtained at different stages of the processing were examined. Optical microscopy and SEM with EDAX were used for obtaining the microstructures and phase composition. The geometric density of some of the specimens was determined by measuring their weights and dimensions. Porosity (both open and closed) and density were determined using immersion density measurements.

The density of the SiC phase and the fraction of volume filled during each PIP run were calculated assuming that the matrix phase did not undergo any physical or chemical change during PIP processing. An artifact in the measurement is the SiC layer that is formed on the sample surface. Although this layer is interesting for providing a protection from the Zry/ UO_2 reaction, as contrasted with the difficult SiC encapsulation method of Lippmann *et al.*[2], it was not fully characterized in the present study. For the present calculations, the SiC layer on the surface is excluded by taking the volume of the SiC within the porosity as the volume difference between the initial open porosity and the final open porosity.

$$W_{SiC} = W_1 - W_{1_{initial}}, \quad (5)$$

(W_1 : dry sample weight)

$$V_{SiC} = V_{open-initial} - V_{open}, \quad (6)$$

(V_{open} : open pore volume)

$$SiC_{filling} (\%) = \frac{V_{SiC}}{V_{open-initial}} \times 100 \quad (7)$$

Whereas the density of the SiC phase (which includes only closed porosity) and the bulk density (which includes all open porosity), are calculated by the following equations:

$$\rho_{SiC} (\%TD) = \frac{W_{SiC}}{3.21 \times V_{SiC}} \times 100 \quad (8)$$

, and

$$\rho_{SiC,bulk} (\%TD) = SiC_{filling} / 100 \times \rho_{SiC} (\%TD) \quad (9)$$

The latter definition assigns all of the open porosity to the SiC phase which must be known for modeling purposes. As shown below, the porosity that is observed after processing is completed usually consists of large cracks or pores in the larger pockets of the SiC, so it really belongs to the SiC phase. So the latter definition is of more interest and relevance.

Then, the open and the closed porosities of SiC phase and the fraction of volume filled were calculated as follows:

$$oP_{SiC} (\%) = 100 - SiC_{filling} (\%) \quad (10)$$

$$cP_{SiC} (\%) = 100 - \rho_{SiC,bulk} (\%) - oP_{SiC} \quad (11)$$

Using these equations, the characteristics of the crystallized SiC phase in the UO₂ sample can be quantitatively characterized.

2.1.4: Fabrication of ECO and IMF samples by the PIP process

2.1.4.1 Materials

β -SiC powders, 10 μ m and submicron, were procured from Superior Graphite and H.C. Starck, respectively. A highly sinterable depleted UO₂ powder (DUO₂), was obtained from the Siemens Corporation in hammer-milled condition.

2.1.4.2 “SiC-SiC” processing (SiC-PIP+SiC powder)

To simulate the matrix phase, we formed pure SiC samples by either casting SiC powders with the precursor, or by pelletizing the SiC powders and precursor. The composition of the samples prepared in this study is presented in **Table 2.1** along with the conditions used

for processing them. β -SiC powders (~ 55 vol%) were mixed with the polymer in a stainless steel mold and then pyrolyzed at 850°C. After the pyrolyzing, the density of these samples was found to be about 60 %TD, and because of shrinkage, could be easily removed from the mold for subsequent impregnations. PIP processing was carried out with these pellets until no appreciable increase in density was observed after a PIP cycle.

2.1.4.3 ECO fuel processing

To obtain a UO_2 / SiC sample with a continuous SiC phase in a dense UO_2 matrix, it was necessary to first form a dense UO_2 pellet but with an open pore structure. High density UO_2 was desired so as not to reduce the fissile atom content too much in spite of the second phase. A “slug/bisque” method was developed involved the following steps:

- 1 High pressure pelletizing at 650 MPa, of the as-received UO_2 powder.
- 2 Granulation in a mortar and pestle into granules.
- 3 Sizing the granules to 75 to 500 μm by sieving.
- 4 Spheroidizing the granules in the 200 to 500 μm size range by a “self milling” procedure in which they are simply rolled against each other in a ball mill.
- 5 Pre-sintering or “bisqueing” them at 1000°C in Ar-5% H_2 for 2 h to get semi-hard granules.
- 6 Pelletizing at 200 MPa, and
- 7 Sintering at 1600°C for 5h in flowing Ar-5% H_2 in a tungsten mesh furnace.

The pre-slugged pellet thus obtained had a high density UO_2 phase of ~98%TD with large-scale interconnected porosity for easy impregnation. The oxygen partial pressure of the gas phase during an entire PIP cycle was measured at the exit of the tube furnace using our solid electrolyte based oxygen meter (Ametek, Model CG 1000). Since the oxygen partial pressure was much lower than the measurement range of the meter, the partial pressure was estimated by the following extrapolated equation given by Ametek:

$$\text{Oxygen content (atm)} = 0.20705 \times \exp(-0.0522 E_{\text{cell}} (\text{mV})) \quad (12)$$

.Using this equation, the oxygen partial pressure of Ar-5% H_2 was estimated to be about 10^{-20} atm, which was reproducible but it's absolute accuracy at this level is questionable.

2.1.5: UO_2 / SiC Compatibility Experiments.

Several investigators have studied the reaction between UO_2 and SiC. The formation of several phases was reported at temperatures above 1370 C by Allen *et al.* [22]. However, Lippmann *et al.* [2] reported that no solid reaction products were observed up to a maximum temperature of 1800°C when UO_2 pellets were heated in *sealed* SiC capsules, showing that the reaction between SiC and UO_2 can be halted in closed systems once the equilibrium partial pressures are attained. We have calculated the equilibrium partial pressures of the two volatile species, SiO and CO, and determined that their equilibrium partial pressures are considerably less than 1 atm. We have examined the reaction products and propose the following reaction [3]:

Therefore, in open systems it was necessary to limit the maximum PIP processing temperature to $\leq 1370^\circ\text{C}$, and for safety we selected 1300°C for all our UO_2/SiC processing.

We made one attempt to overcome this problem using specially-fabricated *nested* Ytria-stabilized zirconia tapered crucibles. The specimens were placed between the crucibles to minimize the diffusion of CO and SiO out of the lower crucible. However, the reactions still could not be prevented at higher temperatures. While the alternative of using pressure vessels to sinter was a possibility, we decided that this approach would not be feasible on an industrial setting.

2.1.6: Production of IMF fuel forms

The problem of chemical reactions is avoided when SiC is used with UC or PuC fuel forms. Therefore we produced UC microspheres by first intimately mixing graphite powder with our UO_2 powder in a ball mill for 7 hrs, followed by pressing, granulation and self-milling. The granules were then carbothermally reduced in flowing Ar to produce the spheres shown in **Fig. 2.8a**, and their microstructures, **Fig. 2.8b**. The spheres were then consolidated by PIP-SiC but crystallized at $1600^\circ\text{C}/5\text{h}$, **Fig. 2.9**.

2.1.7: Characterization methodology

The pore size distributions were determined using the BET method [23] (TriStar 3000, Micromeritics Instrument Corporation).

Thermal diffusivity measurement were performed using the Anter Flashline 5000 laser flash method at the Idaho National Laboratory on specimens listed in Table 2.3. The thermal diffusivity is measured 5 times at a number of temperatures. The thermal conductivity κ is then determined using the following relationship:

$$k = \alpha \rho C_p, \quad (12)$$

Where α = thermal diffusivity, m^2/s and ρ = density, g/m^3 .

The measured densities are corrected for thermal expansion using the values for the majority phase, UO_2 , and the specific heats are calculated on a mass-weighted mixture of the phases.

2.1.8: Results

2.1.8.1: Calculated impregnation profiles

The evolution of porosity, volume and density at various stages during PIP processing was evaluated using the measured values of weight loss and density change in the products obtained by pyrolysing pure SMP-10.

The evolution of the density and porosity during the successive process cycles, were calculated using the experimentally determined “yield” of the solid obtained by pyrolysing the pure precursor in an alumina crucible at 1300°C for 5h. This solid was found to have a density of 80 % TD, **Fig. 2.4(b)**. It was then determined that each PIP cycle done up to the crystallization temperature, filled ~29.4 % of the volume of the *accessible* pores with the PIP-SiC phase, 22.9% of which was solid SiC, and the other 6.5 % was closed porosity in the SiC as determined by immersion density.

Using these data, the *calculated* evolution in the open pore volume, closed pore volume, density of the SiC phase, and the overall density of the solid during a typical multi-cycle PIP processing with crystallization for each cycle is shown in **Fig. 2.10**. This idealized estimate indicates that after 9 PIP cycles 95% of the initial open porosity in the solid would be filled with a SiC phase which has a *bulk* density of 75 % TD. Within this SiC phase space, 21% of the volume would be occupied by inaccessible closed pores and 4% by open pores. Since the starting sintered UO₂ sample has an open porosity of about 10%, the open porosity in the UO₂-SiC sample after 9 PIP cycles would be 0.4%, and the closed porosity would be $0.1 \times 21\% + 0.9 \times 2\% = 4\%$.

However, this theoretical calculation does not take into account that some of the small pore channels may become blocked during the impregnation cycles, and thus the pores inboard can no longer be filled. Therefore, the maximum shrinkage of the pyrolyzed product by crystallization would be desirable to open such channels.

2.1.8.2: “SiC-SiC” cast samples (SiC-PIP+SiC filler particles)

The dependence of the density of the SiC-SiC cast samples prepared using different size filler particles (see Table 1) on the maximum processing temperature is shown in **Fig 2.11**. It is evident that the maximum crystallization temperature has a strong influence on the density. When submicron particles, and low pressure impregnation was used for preparing the samples, a maximum density of 75 %TD was obtained after only 3 PIP cycles. No further improvement in the overall density of the composite was observed in the subsequent PIP cycles. However, compacts with a higher density (about 80 % TD) could be obtained by impregnating the polymer precursor at a higher pressure (after 6 PIP cycles). A maximum density of about 85 % TD could be achieved under similar conditions after 12 PIP cycles.

2.1.8.3: UO₂/PIP-SiC samples

The dependence of the pelletized density and sintered density on the final compaction pressure for the UO₂ pellets prepared by the SB route is shown in **Fig. 2.12**. The small scatter in the data is due to the variation in the length to diameter ratio among the samples investigated, with longer pellets having lower density. In general it was observed that the sintered pellets consisted of well-sintered granules (> 98%TD), with 5 to 15 % interconnected pores and 1 to 2 % closed pores.

The thermally-etched microstructures are shown in **Fig. 2.13**. The grain size is ~20 μm, and the porosity is coarse to permit easy impregnation. (Our finite element modeling indicated that over the ranges of microstructures investigated, the thermal conductivity depended primarily on the volume fraction of the high conductivity phase, and was relatively insensitive to the *scale* of the microstructure.) No noticeable change in the microstructure and the immersion density was observed even at the repeated sintering cycles, showing that the pore structure is stable after the initial sintering.

The evolution of the overall density of various $\text{UO}_2/\text{PIP-SiC}$ specimens with the different impregnation pressures (**Table 2.2**) is shown in **Fig. 2.14**. Assuming no change in the UO_2 pore structure during the PIP cycles, it is expected that the *maximum* density of the SiC phase formed at a processing temperature of 1300°C would be about 80% TD since this is the density obtained when the polymer alone was crystallized at 1300°C . The different curves (a) to (d) correspond to impregnation pressures at 1 to 3 MPa He and up to 4 MPa argon, showing the importance of the impregnation pressure, so long as the pressurizing gas does not dissolve in the polymer. The degree of He dissolution at the higher pressures was unexpected.

SEM observations reveal that the polymer is well-impregnated into the whole specimen especially for very narrow passages (less than 1 micron in diameter), as shown in **Fig. 2.15** after 6 and after 9 cycles, in which the pyrolyzed product appears to be in intimate contact with the UO_2 phase indicating good wetting of the precursor. With 6 impregnation cycles, shrinkage cracks are dominant in large pockets of the SiC phase. More impregnation cycles lead to still higher SiC density and less cracks.

X-ray mapping shows that there is no trace of Si in UO_2 phase or U in SiC phase. It supports the observation of no interdiffusion of Si at 1300°C [4]. This was again confirmed when a $\text{UO}_2/\text{SiC-PIP}$ sample was examined with XRD to determine the phases and degree of crystallinity since no other peaks from reaction products were observed except those from SiO_2 and C after extended periods.

The temperature dependence of the thermal conductivity of the various specimens prepared in this study is shown in **Fig. 2.16**. From these data it is evident that the $\text{UO}_2/\text{SiC-PIP}$ samples did not show a higher thermal conductivity than the measured and published values for UO_2 . The reason for this is shown in **Fig. 2.17**. The low processing temperatures necessary for compatibility with UO_2 yielded a low conductivity SiC phase that we measured for the first time. This null result was confirmed by our finite element modeling. On the other hand, if normal crystallization temperatures could be used, for example if the fuel were carbide or nitride, they would exhibit significant improvements in thermal conductivity as witnessed by the BeO/UO_2 co-sintered specimens to be discussed below. The low temperature crystallization may also lead to residual carbon or Si leading to non-stoichiometry as well as crystal defects all of which may also reduce thermal conductivity.

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Table 2.1. Description of SiC/SiC samples

Specimen	SiC Filler particles	Polymer Impregnation Pressure
SiC 1	Sub micron	1 MPa (He gas)
SiC 2	10 μm	1 MPa (He gas)
SiC 3	10 μm	4 MPa (Ar gas)
SiC 4	10 μm	4 MPa (Ar gas)

Table 2.2. Effect of pressurization conditions on UO_2 / PIP-SiC samples shown in Fig. 2.14

	Initial condition of porous UO_2	Polymer impregnation pressure and gas	
	%TD	oP%	
UO_2 /SiC-a	87.9	10.5	0.1 MPa (Ar)
UO_2 /SiC-b	87.4	10.7	1~3 MPa (He)
UO_2 /SiC-c	86.3	12.5	1 MPa (He)
UO_2 /SiC-d	87.3	11.9	4 MPa (Ar)

Table 2.3. Samples used in the thermal conductivity measurements

Specimen	SiC powder	Polymer Impregnation Conditions	Crystallization temperature/time	Relative Density, %
SiC/SiC 1	10 μm (55vol%)	Vacuum / 4 MPa (Ar)	1300°C / 5h	81.2
SiC/SiC 2	10 μm (55vol%)	Vacuum / 4 MPa (Ar)	1500°C / 5h	81.2
UO ₂	none	--	1600°C / 5h	97
UO ₂ /SiC- PIP	none	Vacuum / 4 MPa (Ar)	1300°C / 5h	10 vol% of SiC-PIP, 87% UO ₂ , 3 vol% porosity

Fig. 2.1. Schematic of the polymer impregnation system. The vessel on left is for degassing, and the vessel on the right is for vacuum/impregnation

Fig. 2.2. Viscosity of SMP-10 for different conditions

Fig. 2.3. Pressure dependence of the solubility of He and Ar in SMP-10.

(a)

(b)

Fig. 2.4. (a) Weight loss and (b) density change of SMP-10 with heating

Fig. 2.5. Thermal cycle used for PIP thermal processing in blue, with measured oxygen concentrations. “IPX” is the entire Impregnation / pyrolysis / crystallization cycle.

Fig. 2.6. Optical micrographs of the SMP-10 polymer pyrolyzed to (a) 600°C and (b) 1300°C. Finer porosity and grain size is seen in the SEM

(a)

(b)

Fig. 2.7. (a) XRD pattern of SiC crystallized at 1300°C for various times showing the formation of SiO₂ and free carbon, (b) Variation of the crystallite size by X-ray line broadening.

Fig. 2.8 (a) UC spheres produced by granulating UO_2 and graphite powders followed by carbothermic reduction, and (b) polished and etched microstructures of the UC spheres

Fig. 2.9. UC spheres consolidated with SMP-10 at 1600°C showing the SEM image and the scans for U on the left and Si on the right.

Fig. 2.10 Calculated evolution of the density and porosity during successive PIP cycles.

Fig. 2.11. Evolution of density in the cast “SiC-SiC” samples. SiC 1 is with the submicron powder, and SiC 2 and 3 are with the 20 μm powder

Fig. 2.12. Effect of final compaction pressure of the SB granules after pelletizing, and after sintering at 1600°C for 5 hrs.

Fig. 2.13. Polished and thermally-etched microstructure of the sintered Slug Bisque UO₂ sample showing the large scale porosity which, from immersion density measurements, is almost entirely open.

Fig. 2.14. Measured evolution of SiC density with number of impregnations and impregnation pressure.

Fig. 2.15. UO₂/PIP-SiC specimens after 6 impregnations (left), and after 9 impregnations (right). Good contact between the two phases and penetration of the polymer are observed, but some residual shrinkage cracks are seen for lower numbers of impregnations

Fig. 2.16. Measured thermal conductivity of UO_2 and $\text{UO}_2/\text{PIP-SiC}$, and published compilation for UO_2 (Fink 2000)

Fig. 2.17. Measured thermal conductivity of cast samples of SiC powders impregnated 9 times with PIP-SiC, crystallized at 1300 and 1500°C

Fig. 2.18 Inert Matrix Fuel pellets with 6 vol% UC spheres in a SiC matrix produced by the PIP processing at 1500°C.

Sub task 2.2: BeO-based ECO and IMF Fuels by Co-sintering

2.2.1: History of BeO use in reactor applications

In the past, the choice of BeO amongst other high conductivity ceramics was motivated by several characteristics. Besides being the oxide with the highest thermal conductivity [1], it is, first and foremost, compatible and insoluble with UO_2 up to 2160°C, at which temperature it forms a eutectic, **Fig. 2.19**, [2]. It is also compatible with Zircaloy cladding up to 1200°C [3], does not react with water [4] and very weakly with nitric acid. The latter characteristics allow both open and closed fuel cycles. It also has a low neutron capture cross section [5], good neutron moderation and, as shown below in the fuels performance section, an appreciable fast neutron multiplication via an $(n, 2n)$ reaction with a threshold energy of 1.85 MeV [5] that is shown in the fuel performance section, to have an important impact on neutronics.

Beryllium occurs naturally in the earth surface in about 30 minerals. The United States is the world's leading producer, processor, and consumer of beryllium. It is used in large quantities for Aerospace and Defense applications and for many other electrical applications in Cu-Be alloys in metallic form, and, as BeO, for electronic applications because of its combination of high thermal but low electrical conductivity,

The Department of Energy has had a long history of beryllium use because of the broad application to many nuclear operations and processes for:

- 1 Nuclear weapons
- 2 Nuclear reactor moderators / reflectors
- 3 Nuclear fuel element cladding

Fig. 2.19 Phase diagram for the BeO – UO₂ system. Ordinate is in °C. Solid line indicates a theoretical curve. [2]

Because of its high chemical stability and compatibility, the oxide form has been preferred for reactor applications. In the early 60's, BeO was used as a reflector and/or moderator, and as an inert matrix [6-9]. However, BeO was somewhat more costly than graphite, suffered radiation degradation like graphite because of its non-cubic crystal structure, reacted with steam, and raised issues in chemical reprocessing. On the other hand, it did not cause carbothermic reduction of UO₂, and was stable against catastrophic fires.

In 1945, Farrington Daniels presented the first high temperature Pebble Bed Reactor, PBR, with BeO as moderator, reflector and fuel matrix with helium as coolant [3]. Clinton laboratory in Oak Ridge built a 12 MW plant, but the project ended in 1947 from lack of knowledge on the high pressure behavior of BeO.

Renewed interest in BeO arose in the early 50's with a US program for nuclear propulsion [3]. The Aircraft Reactor Experiment, ARE, used BeO as moderator and reflector, but the information was classified.

In another US program, the Maritime Gas-Cooled Reactor, MGCR with a closed-cycle gas-turbine was investigated. In this project, BeO was selected for both moderator and reflector. This led to the EBOR reactor.

In 1960, the Experimental Beryllium Oxide Reactor (EBOR) was launched in Idaho. This 10 MW reactor was to be fueled with UO₂ – BeO pellets, 62.5 % enriched but the project was terminated in 1967 before producing any power.

BeO was also selected as the matrix phase for UO₂ in the Aerojet-General nucleonic army gas-cooled Mobile Low power reactor (ML-1) [3]. BeO was also used to remove heat from the pellets and thus reduce the temperature gradients.

Also in the 60's, the Australian Atomic Energy Commission Research Establishment (AAECRE) pursued a high temperature gas-cooled reactor concept using BeO. Their initial

study focused on a *PBR* fueled reactor with a dispersion of ThO₂ and PuO₂ in a BeO matrix. The choice of BeO was made because [4]:

- 1 BeO allows a very high gas-outlet temperature to efficiently drive a gas turbine.
- 2 For the same fuel load and the same specific power, a BeO-moderated core is smaller than a graphite one
- 3 BeO has a low n capture cross-section, and a (n, 2n) multiplication reaction
- 4 A high integrity, high conductivity uncracked dispersion fuel type would retain the fission products, could eliminate the need for metallic cladding, and permit high fissile loading
- 5 BeO is compatible with CO₂ up to very high temperatures, and
- 6 The somewhat higher cost of BeO compared to graphite could be offset by a higher burn up and lower fuel cycle costs.

The United Kingdom Atomic Energy Agency (UKAEA) designed and ran a prototype *Advanced Gas-cooled Reactor, AGR*, for 10 months using another dispersion fuel of 30 vol% UO₂ in BeO [3]. The use of the UO₂ / BeO dispersion fuel was designed to eliminate the cladding and improve the thermal efficiency. They estimated a reduction in electricity cost of £1/kWe per 20°C increase in fuel temperature.

2.2.2: Irradiation behavior of BeO

Under fast neutron flux ($E > 1.85$ MeV) Be undergoes an (n, 2n) reaction [9]:

and an (n, α) reaction with a threshold neutron energy of 0.71 MeV, and a cross section of 25 mb, leading to ⁶He production:

⁶He decays very quickly to ⁶Li with a half-life of 0.82s. And finally, tritium is produced by an (n, α) reaction on ⁶Li with a very high cross section of 950 barns. The net neutron production from Be depends on whether, ⁶Li, ³He or ³H escape by diffusion, or are removed from the system by reprocessing or both [10].

In terms of radiation stability, fast neutron doses cause anisotropic crystal growth in BeO because of its hexagonal crystal structure. G.W. Keilholtz [10] showed powdering of a specimen at a fast neutron dose of 1.5×10^{21} nvt ($E > 1$ MeV) at 100°C, but simple fractures at fast doses of 2×10^{21} nvt at temperature between 800 and 1000°C. At a lower dose of 2×10^{20} nvt ($E > 1$ MeV) micro-cracking initiated at ~100 C in BeO [11]. Thus, very low temperature irradiations are problematic for BeO.

The tritium is retained below 250°C, but almost completely lost above that temperature. Helium loss was measured to be about 50% from samples receiving doses higher than 3×10^{21}

nvt at temperatures between 750 and 1100°C. The helium generation rate has been evaluated at 10^{21} nvt ($E > 1$ MeV) as 205 μl per g of BeO [12].

J. Elston [13] measured the ^3He and ^3H production rate as a function of the fast n dose. ^3He was measured at 50 – 60 mm^3 / g of BeO / 10^{20} nvt ($E > 1$ MeV), and ^3H was measured at 0.5 mm^3 / g of BeO. They argued that BeO can be used as moderator between 1100 and 1300°C. Below 1100°C, anisotropic growth induces micro-cracking, and above 1300°C, the ^3H loss rate is too high.

Hickman and Pryor [11] concluded that the production of ^3H and ^3He is unlikely to cause property changes up to at least 700°C, but might become significant at higher temperatures. However they estimated that the limiting condition of BeO is the fast neutron dose that eventually induces micro-cracking. However, they examined the onset cracking as a function of grain size, temperature and the dose rate. They observed no visible cracking with 2 – 3 μm grain size, irradiated at 10^{21} nvt at a flux of 4×10^{13} nv, at 100°C, but there were significant variations between specimens that are still not understood. Hickman, also noted rate effects: lattice expansion was significantly reduced when fast neutron flux was lowered from 10^{14} to 10^{13} $\text{n.cm}^{-2}\text{s}^{-1}$. They suggested different limits for the use of BeO as a function of grain size and flux as shown in **Fig. 2.20**. They also showed data for the dose and temperature dependence of the thermal conductivity of BeO up to the microcracking threshold, **Fig. 2.21**. Although end-of-life fast neutron doses in a typical LWR are on the order of 10^{22} nvt, this is slightly reduced by the presence of BeO. As seen below for the hot spot in the reactor, the fuel temperatures vary from 576 to 1100°C which means that the cracking threshold may be passed in some locations. However, there are additional factors to consider besides the fast neutron damage.

For ECO fuels, there is also the issue of fission fragment damage, since the fragments may penetrate through the thickness of the BeO phase and produce damage as well as intense local heating. Hanna *et al.* [14] examined fission-fragment damage in BeO by irradiating (U, Th) O_2 dispersed in a BeO matrix. The irradiation was done in thermal fluxes between 1.6 and 2.7×10^{13} $\text{n.cm}^{-2}\text{s}^{-1}$, and negligible fast fluxes at temperatures of 600 and 850°C. Fission densities were between 2×10^{19} and 1.8×10^{20} fissions per cm^3 . Samples were apparently unaffected by the thermal stresses that in some cases could exceed the modulus of rupture of the material. They concluded that fission-fragment damage produces volume increases of the specimen and strain in the BeO matrix. They observed that the strain appeared to be greater with fine (~ 1 μm) fuel particles, but this greater strain did not seem to affect the specimens with a small BeO grain size of 5 μm . Later, Hanna *et al.* [14] even observed that the fission fragment bombardment *reduces* the effect of the fast neutron damage. They argued that the fission fragment local heating can either anneal the neutron-induced defects or simply enhance the creep process that relieves the growth strains.

Recent experiments [15] compared thermal conductivity degradation with neutron irradiation of several high thermal conductivity ceramics. BeO was the least affected by neutron damage for irradiation at temperature below 300°C, and for low doses up to 0.1 dpa. Similar results obtain for higher doses, but eventually, if microcracking occurs at high doses, the conductivity would likely be severely reduced.

Fig. 2.20. Limiting fast neutron doses predicted for BeO [11]

Fig. 2.21. Effects of fast neutron damage on the thermal conductivity of BeO at various temperatures [11]

2.2.3: Consolidation of UO_2 in a BeO matrix

Many techniques have been used to consolidate UO_2 particles in a BeO matrix including

- 1 cold uniaxial pressing and sintering
- 2 extrusion and sintering
- 3 uniaxial hot pressing

Reeve [16] investigated cold pressing and sintering. Their investigation showed that when using sintered fuel particles, large voids were created around the particles, whereas by using unsintered particles, they could reach very high density with no voids. However, the unsintered particles were too weak to allow adequate mixing and thus, they added a low temperature sintering step for the fuel particles before mixing with BeO. The co-sintering of BeO and $(\text{UTh})\text{O}_2$ was successful to get high density ($> 2.86 \text{ g/cc}$) specimens with no open porosity, but grain size control of the BeO was more difficult to achieve.

Christie *et al.* [17] investigated the possibility of fabricating UO_2 /BeO fuel rods by extrusion and sintering. They studied the influence of UO_2 pre-sintering on the final density and on the mixing conditions. They concluded that a short pre-sintering above 800°C improves mixing without decreasing the final density too much. They could fabricate 20 cm long rod with this technique but did not achieve the desired $5 \mu\text{m}$ grain size.

Nishigaki and Maekawa, [18] studied the fabrication of BeO / UO_2 / Be fuel pellets using vacuum hot pressing. Their results show an improvement of the densification behavior, reduction in grain growth, high mechanical strength and no influence on the thermal conductivity. However our experiments showed that Be vaporization can be a problem, and vacuum hot pressing is a very costly process for production.

Hammer *et al* [19] fabricated and irradiated dispersed UO_2 in BeO similar to our co-sintering to get a relative density of 93% with $12 \mu\text{m}$ grain size BeO and $6 - 21 \mu\text{m}$ grain size for UO_2 . They tested the thermal stability of the fuel by heating 124 days at 1100°C without any noticeable changes in microstructure. They then irradiated the fuel for 125 days at 1100°C to a fast neutron dose of $1 \times 10^{20} \text{ nvt}$ ($E > 1 \text{ MeV}$). They observed a steady-state fission gas release fractions between 1.3×10^{-3} for ^{87}Kr and 1.9×10^{-2} for ^{133}Xe . In addition, they observed swelling, macro- and micro-cracking and an anomalous grain growth in the fuel particles. They then developed a method to better disperse the fuel in the matrix and observed a significant reduction of the fission gas release.

2.2.4: Fabrication and characterization of BeO-based ECO fuels

Our finite element modeling calculations, and extrapolation of Ishimoto's results suggested that additions of only 10 vol% of BeO could have a significant effect on fuel conductivity.

The co-sintering of green and presintered UO_2 granules in a BeO matrix has already been successfully used to produce Inert Matrix Fuels (IMF) of high density as described above. The success of these co-sintering studies [16][18][19] were possible because of the similar shrinkage rates and kinetics [20][21][22] of BeO and UO_2 during sintering under reducing atmospheres.

Fig. 2.22. Particle size analysis of BeO and UO₂ powders measured with Laser Analyzer Coulter, after ultra-sounds. Some UO₂ aggregates remains after ultra-sounds but most of the particles are smaller than 10 micron. The BeO particles are comprised between 1 and 10 μm .

For producing the BeO fuel we used the same depleted UO₂ powder described previously, and a UOX grade of BeO powder, courtesy of Brush Wellman. The specific surface area of UO₂ was measured with BET to be $2 \pm 1 \text{ m}^2.\text{g}^{-1}$. Brush Wellman reported a specific surface area of $12 \pm 1 \text{ m}^2.\text{g}^{-1}$ for UOX grade BeO. We also measured the particle size distributions with a Laser scattering particle size analyzer (Coulter LS230) with sonication in the sampling chamber, for both powders. The results are shown in **Fig 2.22**.

One fabrication schedule is shown in **Fig. 2.23**. We first press the UO₂ powder in a single-action press at 300 MPa using no lubricant. The compacts are then granulated by hand in a mortar and pestle, and sieved to a size range of 45 to 500 μm , **Fig. 2.24(a)**. The granules are then “self-milled” in a ball mill without grinding media for 8 hours to smooth the granule surfaces. The spheres may or may not be pre-sintered at 1000°C/ 4h, and are again sieved to remove the fines. BeO powder from 4 to 13 vol% is then added to the granules and mixed for another 30 minutes. The BeO-coated granules are shown in **Fig. 2.24(b)** indicating the very high uniformity of the coating process. The coated granules are indistinguishable from the uncoated granules. The coated granules are then pelletized at 200 MPa in a 9.57 mm diameter die that had been lubricated with stearic acid, and finally sintered up to 1700°C for 5 hours, under flowing Ar / 5% H₂. Sintered pellets are shown in **Fig. 2.25**

The sintered pellet dimensions and immersion densities are measured in ethanol, **Table 2.4** Finally, some pellets are used to prepare specimens for microscopic observation and for thermal diffusivity measurements. The specimens for microscopic observations were mounted and ground with SiC papers, and polished down to 1 μm diamond, and thermally-etched at 1600°C for 2 hours under flowing Ar / 5% H₂.

Fig. 2.23. Flowchart describing the fabrication process for UO_2 / BeO matrix fuel using SB granules. Alternatively, green granules are used

Table 2.4 Density of the pellets made from “green” granules measured before and after sintering.

Sample	UO ₂ (%)	BeO (%)	Density (%)	
			Green	Final
UO ₂	100	0	53	99
UO ₂ / BeO ₅	95	5	-	97
UO ₂ / BeO ₁₀	90	10	54	99
UO ₂ / BeO ₈₀	20	80	-	97
BeO	0	100	56	99

(a)

(b)

Fig. 2.24. (a) Optical micrograph of the UO₂ powder after granulation, and (b) after the self-milling and BeO coating step.

Fig. 2.25. UO_2 / BeO pellets after sintering at 1700°C for 5 h under flowing Ar / 5% H_2 .

The microstructure of the 10 vol% BeO pellet produced with “green” granules is shown in **Fig. 2.27**. The BeO phase appears continuous everywhere and completely fills the granule interstices without cracks or large pores **Fig. 2.27(a)**. There is some evidence of flattening and accommodation of the granules as a result of pressing in the vertical direction on the photo, but the granules appear to remain intact after pressing. It is during this critical compaction process that the UO_2 granules, uniformly coated with the BeO powder, become a space-filling assembly. The BeO powder accommodates the deforming granules and fills the available space between them. A higher magnification in **Fig. 2.27(b)** shows excellent contact between the large-grained UO_2 phase and the fine-grained BeO phase which contains an appreciable quantity of UO_2 , up to 30 vol% as a dispersion, as well as a small fraction of porosity. The UO_2 dispersion is effective in controlling grain growth in the BeO phase to 2 to 5 μm .

When SB granules are used, there is less “contamination” by the UO_2 phase, but some porosity as well as dispersed UO_2 appears next to the granules. Also, the grain size of the BeO becomes comparable to that of the UO_2 or ~20 μm .

Fig. 2.26 (a). SEM picture of a polished section of the UO_2 / BeO sintered pellet using “green” UO_2 granules, and (b) the thermally-etched specimen at higher magnification showing the UO_2 “contamination” (light phase) in the BeO phase .

Fig. 2.27. Optical Microscope pictures of a section of UO_2 / BeO_{80} pellet after polishing and thermal etching at 1600°C . The low magnification picture (a) shows the fair dispersion of the UO_2 in the BeO matrix. The higher magnification picture (b) shows the very good bonding between the two phases.

2.2.5: Fabrication of BeO-based IMF fuels.

Co-sintering may also be used to consolidate IMF type fuels in any desired proportions of the phases. **Table 2.2** shows the various mixtures of phases and the overall densities achieved. Again, because of the sintering compatibility between the green UO_2 and BeO under reducing atmospheres, high density is achieved. However, in this case the BeO phase does not contain the UO_2 dispersion, and large BeO grains are formed which might lead to microcracking at high fast neutron doses as described earlier. Therefore, it would probably be necessary to incorporate a grain growth inhibitor in the BeO phase. Of course, if the fuel is run at temperatures of 1000 to 1300°C , microcracking is not observed in BeO [11].

Sub task 2.3: Prepare pellets with appropriate enrichments, develop conceptual design for test rodlets, and identify test reactor

Verification of the design concepts for ECO fuel requires one or more test programs. Tests on unirradiated material are obviously the less expensive route and various techniques, for example the laser flash technique to measure thermal conductivity, are available to confirm theoretical predictions. However, irradiation tests would ultimately be required to determine whether the physical and chemical stability of the product was sufficient for commercial use. Changes to the chemical composition as a result of irradiation could cause adverse effects on the thermal conductivity and other properties of the fuel. In an ideal situation, reference UO_2 fuel would be irradiated concurrently with ECO fuel to provide a direct comparison, but sufficient information is available in the literature relating to UO_2 fuel properties and performance that this course is not proposed. The purpose of this task is to prepare for future irradiation tests of ECO fuel. The task includes preparation of fuel pellets, development of a conceptual design, and identification of a suitable test reactor. Irradiation will be deferred to a future project.

Test Program

Various concepts might be considered for an irradiation program. A simple approach is to review recent non-proprietary fuel studies in the U.S. The most recent identified test is that on MOX fuel irradiated in the Advanced Test Reactor (ATR) to various burnups and under fluence and flux conditions approximating those experienced in commercial pressurized water reactors. Following irradiation, the rodlets used in the program were transferred to hot cell facilities to perform a variety of tests and to confirm equivalency with UO_2 fuels. This work has been reported by Morris et al. [23].

Fuel pellet/rod design.

If two different types of ECO fuels are to be evaluated, e.g. $\text{UO}_2\text{-SiC}$ and $\text{UO}_2\text{-BeO}$, it would be desirable to test the rodlets at similar linear heat generation rates, and the rodlets should be designed accordingly. For example, the uranium density of $\text{UO}_2\text{-SiC}$ pellets will probably be lower than that of $\text{UO}_2\text{-BeO}$ pellets. Therefore, it may be preferable to choose a lower enrichment for the $\text{UO}_2\text{-BeO}$ pellets. The linear heat generation rate might also be controlled by changing the fuel density. However, a change in density would have other effects, such as an increase in fission gas release, that could confound the results.

The cladding for the rodlets should ideally be a zirconium alloy with a diameter and wall thickness similar to those used in commercial power reactors. Actual dimensions of the components will depend on available materials and the heat ratings required of the test fuel but typical values might be pellet diameters on the order of 0.37 inch, and a diametral gap between the pellet and cladding of about 0.006 inch. The length of the rodlet would be about 8 inches, with a fuel stack of about 6 inches. The actual length of the stack would be calculated to assure that the final rodlet pressure was not excessive after allowing for release of fission gas and other volatile products. Each rodlet would be encapsulated in a stainless steel capsule to prevent contamination of the irradiation loop in the event of a rodlet failure. The gas compositions and pressures, both within the rodlet and between the rodlet and the stainless capsule, would be chosen to provide typical fuel operating temperatures.

Test Reactor

As mentioned earlier, the above proposals are based on the use of the ATR. This reactor has a number of locations that can be used for irradiation studies but the preferred locations for low cost programs are the four small "I-Holes" on the periphery of the core. Individual rodlets are held in a basket assembly. A typical basket assembly has a capacity of nine rodlets, which are arranged in three columns of three. One column is partially shielded from the center of the core by the other two columns, so there are some differences in the burnups achieved within the different columns unless the rodlets are relocated between irradiation cycles. An alternative method for controlling burnup is to modify the fluence by using Inconel or aluminum baskets. A further advantage of an ATR irradiation is that hot cell facilities are available at the Idaho site, so subsequent examination of the rodlets does not incur significant transportation and licensing costs.

A second test reactor that was investigated was the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. It has been used in the past for test irradiation programs but is currently under modification and would only be available on a limited basis. Other research reactors, such as the one at the Massachusetts Institute of Technology, might also be able to handle the irradiations.

Burnup limits

No significant experience is known to exist for irradiation of $\text{UO}_2\text{-SiC}$ fuel, therefore it is proposed that the initial irradiation be limited to relatively low burnups, perhaps 5 or 10 GWd/MTU. At this burnup, fuel densification should be largely complete and chemical reactions between the component parts, if any, should be near equilibrium. Past results with coated-particle fuel for high-temperature gas-cooled reactors might provide information that would be helpful in predicting the performance of $\text{UO}_2\text{-SiC}$ ECO fuel.

The ATR allows irradiation of up to nine rodlets of the type described above in one I-Hole, so multiple rodlets of each composition could be irradiated. Alternatively, the fuel in the rodlets could be produced by different process routes to assess whether one process provides advantages over another. Individual rodlets could be removed and destructively examined at selected burnups. Nondestructive examination by neutron irradiation might also provide useful information. Rodlets that are not destructively examined could be returned to the reactor for irradiation to higher burnups.

Post-Irradiation Examinations

Details of the post-irradiation program should be defined in advance so that appropriate pre-irradiation measurements can be taken. Ideally, archive samples should be retained. Essential examinations are expected to include:

Cladding diameter before and after opening each rodlet. (There have been reports of diameter changes after gas pressure is released.) The ATR rodlets are not in contact with water, and therefore the cladding is not subject to aqueous corrosion or hydrogen pick-up. Better measurements of cladding diameter changes can therefore be obtained.

Rodlet gas pressure and composition. These measurements are used to determine the fission gas release for comparison with predictions.

Fuel density changes.

Fuel microstructure. particularly a comparison between the center and edge of the pellet so that the center line temperature can be estimated. Examination of the interface between the pellet and cladding would also be desirable in order to verify that there are no unexpected reactions. Some oxidation of the inner surface of the zirconium alloy cladding is expected as a result of oxygen release during irradiation, and this can affect the oxygen potential in the fuel pellets.

Radial dependence of elemental fission product composition. Operating temperature can be estimated based on fission product migration.

Additional measurements that could be beneficial are:

Crystal structure determinations to detect possible reactions between UO_2 and SiC in $\text{UO}_2\text{-SiC}$ fuels.

Tests on cladding ductility to determine whether excessive embrittlement has occurred with the $\text{UO}_2\text{-SiC}$ fuel.

The issues of radiation stability of BeO under fast neutron bombardment and fission fragment damage and implantation in ECO fuels needs to be examined by in-pile experiments. For ECO fuels there are a number of special conditions as compared to the previous results on BeO: First, the minor BeO phase is traversed by fission fragments which appear to provide annealing of damage. Second, the grain size is very small with the UO₂ “contamination”. Third, the BeO phase is under swelling constraint by the majority UO₂ phase that occupies 90% of the volume, and is swelling isotropically.

To produce specimens for irradiation, we have shown that our archival 5, 10 and 20% enriched archival UO₂ helices may be oxidized to U₃O₈ to produce powders that when mixed with our depleted UO₂ powder, produces high density specimens.

The challenge then, is producing specimens that have the required dimensions. For the ATR in the LWR-2 series, the diameter requirement is 0.372 ± 0.001 ". This very tight tolerance with a variety of specimens that we would like to irradiate usually can be done commercially by centerless grinding. We did not have such a facility for grinding BeO-containing enriched UO₂ specimens. Therefore we redesigned our die to produce somewhat oversize specimens, and will use a diamond core drill to do the final sizing.

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Task 3.0: Measure Thermal Properties

The specimens fabricated for thermal diffusivity measurements were sent for measurement at the Idaho National Laboratory (INL). The sample dimensions needed to be 6.20 ± 0.15 mm in diameter, and ~ 1.5 mm in height to fit into the Anter Flashline 5000™ carousel sample holder. To make a measurement, the sample is stabilized at a desired temperature T_0 under UHP Ar before the front surface of the specimen is illuminated with a short laser pulse. The temperature rise at the back surface is measured and recorded with an IR detector. All 6 samples in the carousel are measured at one temperature several times before the temperature is increased for the next series of measurements until a maximum temperature of 1200°C. This temperature rise vs. time curve may then be analyzed by one of several analysis methods to determine the thermal diffusivity of the material.

The power of the laser pulse can be manipulated by changing the voltage, which ranges from a few hundred volts up to a few thousand. However, the ideal voltage is one that gives a signal not too weak to detect nor too powerful to cause damage to the sample. The temperature rise on the back face of a sample was measured by a Sb-In IR detector located at the base of the furnace. The data from the detector was analyzed by Anter's analysis software on a desktop PC. However, several analysis methods are possible.

The Parker method [1] is the basic technique for determining the thermal diffusivity of a material by analyzing the back surface temperature rise time curve. This method assumes the measurement is being performed under the following ideal conditions: uniform laser energy density, no radiative heat losses, homogeneous material, and very short laser pulses. The Parker equation for calculating the thermal diffusivity, α , is given below, where the material thickness, L , is known, and the half rise time, $t_{1/2}$, is taken from the temperature rise time curve.

$$A_P = 0.1388 \times L^2 / t_{1/2} \quad (3.1)$$

Although this is the original basis for laser flash measurements, more advanced analysis methods have been developed to account for the non-ideal conditions: (1) the laser energy density varies with position on a sample's surface leading to uneven heating (this problem can not be easily fixed without altering the specifications and improving the design of the laser system), (2) the sides of the sample suffer from radiation heat losses, which can be observed from the temperature rise time curve, (3) our multi-phase ceramic samples are microscopically heterogeneous, but since the sample thickness is much greater than the dimensions of the different phase regions, it can be assumed to be homogeneous [], (4) the laser pulse is not instantaneous, (for the Anter system, it is $\ll 1$ ms which generates less than 1% error in the measurements [2]. But these issues have led to more advanced analysis methods.

The Clark and Taylor method (CT) is used to account for radial heat losses caused by radiation from the sides of the sample [3]. This heat loss term correction is usually the most significant condition that causes measurements to deviate from the ideal.

This method evaluates the shape of the temperature rise time curve by creating a

polynomial fit that accounts for ratios of the three fourths and quarter rise times.

$$A_{CT} = \alpha_{0.5} \times K_R / 0.1388 \quad (3.2)$$

$$\text{with, } K_R = -0.3461467 + 0.361578 (t_{0.75} / t_{0.25}) - 0.06520543 (t_{0.75} / t_{0.25})^2$$

The result of employing this method is that the shape of the rise time curve is taken into consideration, and thus it reflects the amount of heat loss causing a deviation from the ideal shape. All thermal diffusivity data reported below were obtained using the CT analysis method.

The Cowan method [4] uses the heat dissipation (i.e. the tail of the curve) to calculate the correction factor K_C . It has the advantage of avoiding possible short-circuiting through the high conductivity phase.

$$A_C = \alpha_{0.5} \times K_C / 0.1388 \quad (3.3)$$

Sub task 3.1: Thermal Property Measurements

To calculate the relative densities we used the Theoretical Densities of UO_2 (10.96 g.cc⁻¹) and BeO (3.01 g.cc⁻¹), and used a volume-weighted calculation to obtain the overall density.

The density measurements show that we get high density pellets regardless of the ratio of UO_2 to BeO. After the density measurements, thermal diffusivity measurements were performed at the Idaho National Laboratory (INL) on UO_2 , $UO_2 / 10 \text{ vol\%BeO}$ and, BeO.

The CT values were used to calculate the thermal conductivity. The thermal diffusivity, α , is defined by

$$\alpha = k / (\rho \cdot C_p) \quad (3.4)$$

where the thermal conductivity, k , is divided by the specific heat at constant pressure, C_p , and density, ρ , all at the temperature of interest [5]. By manipulation this equation, the thermal conductivity can be calculated if the values for thermal diffusivity, density, and specific heat are known at a specified temperature. The value for thermal expansion of the two phase specimens was assumed to be that for UO_2 . The density of a sample at the temperature in question was calculated from its known mass and geometric dimensions (corrected for thermal expansion). The specific heat was calculated using the law of mixing with reported data on the specific heat of individual components corrected for the densities of the individual phases measured by quantitative image analysis.

Before the measurements, we calibrated the apparatus with a Pyroceram NIST calibration standard. Each sample was then measured at five different temperatures between 400 and 1400 K. The thermal diffusivity for each temperature is the mean value of several measurements at that temperature. The measured thermal conductivities are shown in **Fig. 3.1**. The measured UO_2 and the $UO_2 / 10 \text{ vol\%BeO}$ curves are compared with a compilation of thermal conductivity data given by Fink [6] for standard 95%TD fuel.

The correlation between Fink's compilation and our data for the thermal conductivity of UO_2 is relatively good, which confirms the quality of our specimens and the measurements. The UO_2 / 10 vol%BeO shows about 50% enhancement of the thermal conductivity over standard UO_2 for the range of temperatures measured. We could not measure the BeO specimen because of an equipment failure at INL. As seen in **Fig. 3.2**, this enhancement is consistent with an extrapolation of Ishimoto *et al*'s data for a continuous BeO phase at UO_2 grain boundaries.

References for Subtask 3.1

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Fig. 3.1. Measured thermal conductivities of UO_2 of 97%TD, UO_2 with 10 vol% BeO and the data compilation for UO_2 of 95%TD. There is a ~50% increase in thermal conductivity for the ECO fuel with 10 vol% BeO

Fig. 3.2. Thermal conductivity enhancement relative to UO_2 , measured by Ishimoto *et al.* [7] on UO_2 / BeO specimens for both continuous and discontinuous BeO phases.

Sub task 3.2: Fuel thermal performance

Before proceeding to an irradiation, we did some calculations to predict the fuel temperatures during irradiation and the fuel reactivity, considering the lower UO_2 volume fraction in ECO fuels.

The thermal conductivity curves were used to calculate the *maximum* fuel temperature profiles for a PWR fuel using the following assumptions: The fuel was assigned a linear heat generation rate (LHGR), of 17.5 kW.m^{-1} for the hot channel in a Pressurized Water Reactor (PWR) [36]. This LHGR was then multiplied by a 1.7 peaking factor. The outer radius of the fuel pellet was calculated to be 576°C , and was kept constant to demonstrate the effect of the high conductivity phase under equal power generation and external temperature conditions. This temperature was calculated using PWR data, including the average moderator temperature of 312°C , the fuel's LHGR, and the Dittus – Boetler equation to determine the heat transfer coefficient of the fuel rod [1][2][3].

The relative temperature profiles for UO_2 and UO_2 /10 vol%BeO are shown in **Fig.3.1**. The results show that for the condition examined, the fuel centerline temperature at the “hot spot” is reduced by 300°C , and the mean fuel temperature is reduced about 200°C .

Fig. 3.3. Comparison of temperature profile between UO₂ and UO₂ / BeO₁₀ calculated from thermal conductivity measurements. Fuel surface temperature is 576°C.

References for Section 3.2

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Task 4: Effects of Fuel Properties on Health, Performance, and Cost.

The major issues previously identified with the use of BeO are:

- 1 Cost
- 2 Performance
- 3 Anisotropic expansion and cracking under irradiation
- 4 Beryllium toxicity and cost of instituting control measures
- 5 Waste handling and recycling

Sub task 4.1: Materials Cost

Costs may be analyzed in several ways. First, materials costs: Brush Wellman [1] gives the following cost for their standard grade of BeO in quantities >12.5 Tons, \$115/lb or \$253/Kg. If we consider a normal PWR core with 95%TD UO₂, it represents 75 Tons of 4.6% enriched

uranium (LEU) at about \$860 / Kg and about \$240 / Kg for the fuel fabrication; hence the total cost is M\$82.5

We compare that to ECO fuel in our case with 90 vol% UO_2 of 98%TD, and 10 vol% of BeO of 95%TD. This would represent 69.6 tons of UO_2 which costs M\$59.9 at the same enrichment, and 4.46 tons of BeO which costs M\$1.13 giving a total core cost of M\$ 61 for the ECO core materials. If we add a fabrication cost that is slightly higher, say 20%, or \$298/Kg, we come to a total fuel cost of M\$61+M\$17.8= M\$78.8. This would represent a reduced cost for ECO fuel core of M\$ 3.7, but this doesn't take into account the cost of any increase in enrichment.

On the other hand, this calculation does not include any benefit that would be directly imputable to the greater performance of ECO fuel, like increased flexibility in operation due to increased margins, potential up-rating of the reactor, and/or the possibility of extending the fuel irradiation time. All these elements, separately or combined could greatly reduce the fuel or operational cost.

References for Subtask 4.1

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Sub task 4.2: Industrial hygiene for BeO and UO_2

Historical background

In 1946, Hardy and Tabershow [1] identified for the first time the existence of a lung disease called "Chronic Beryllium Disease", CBD. Sixteen cases were reported as possible at that time among the 20,000 people living near a beryllium facility in Lorain, Ohio (USA). In 1949, 11 patients were clinically diagnosed with CBD, and the source of contamination identified as due to plant gaseous discharge. From these cases, a $2 \mu\text{g.m}^{-3}$ Permissible Exposure Limit (PEL) for air contamination was adopted by the US Department of Energy (DOE). This limit of $2 \mu\text{g.m}^{-3}$ for 8 hours Time Weighted Average (TWA) was adopted by the US Occupational Safety and Health Administration (OSHA) in 1971. The number of reported cases in DOE facilities started to decline in the 80's and 90's, showed strong evidence that the standard had not completely prevented new cases. In 1998, Eisenbud [2] argued that the $2 \mu\text{g.m}^{-3}$ PEL was not protective enough,. In the same year, the American Conference of Governmental Industrial Hygienists (ACGIH) proposed an 8 hour TWA of $0.2 \mu\text{g.m}^{-3}$. In December 1999, this limit became the standard for DOE facilities in 10 CFR 850. Beryllium has also been classified by the International Agency for Research on Cancer (IARC) and ACGIH, as a human carcinogen [?].

Although some 20% of the general population is susceptible to the reaction that causes CBD [], there is no apriori method of detecting the sensitive individuals. Also, those that are sensitive may develop the allergic type reactions of inflamed lung tissue and restricted oxygen uptake long after the exposure, so very stringent controls are necessary. However, BeO is used safely on an industrial scale in the U.S. and elsewhere. In 2001, Johnson et al. studied [3] the results of the beryllium monitoring program at the Atomic Weapons Establishment beryllium facility in Cardiff Wales. This facility has monitored its workers since the beginning of 1981. More than 200,000 personnel samples were collected and showed 98 % of compliance with the higher $2 \mu\text{g/m}^3$ PEL. The Cardiff program resulted in one single case of clinical CBD over 36 years of operation from an unusual event.

Since 1984, personnel sampling data have provided more precise information on occupational exposure to beryllium at DOE sites [10CFR850]. It also indicates that low level of exposure can be achieved in both fabrication and machining, and decommissioning and

decontamination projects [10CFR850]. Engineering improvements and advanced control strategies have significantly reduced occupational beryllium exposure levels.[10CFR850]

Finally, in our laboratory, under the guidance of the Purdue Industrial Hygiene Department, we have successfully handled BeO for more than 2 years producing ECO fuels, as we do UO₂ in fume hoods, but with the extra precaution of using respirators. Air monitoring shows that, without any modification of our laboratory and good housekeeping, we did respect the 0.2 µg.m⁻³ PEL for all our operations (powder mixing, pressing, grinding, firing ...). Surface contamination is also below requirements. Additional controls would be possible when handling larger quantities in a fuel fabrication facility.

The regulatory limits on exposure to beryllium and uranium, the relative amounts of airborne BeO and UO₂ that would be produced from pellet grinding, and the difficulty of complying with regulations for occupational exposures to these materials were evaluated.

Dose calculations

Respirable dusts of BeO and UO₂ are both known to be hazardous. In spite of that, UO₂ fuel pellets are routinely ground to size, and the grinding operation is safe because the resulting dust is strictly controlled. A UO₂-BeO fuel pellet could also be ground safely if the dust were sufficiently well controlled. It is not immediately clear whether grinding such a pellet would require a significant improvement in dust control. A quantitative evaluation of regulatory limits is needed. Such an evaluation is provided below.

Title 10 Code of Federal Regulations Part 850 (10 CFR 850) requires that employers set “an action level that is no greater than 0.2 µg/m³ [for exposure to beryllium], calculated as an 8-hour [time-weighted average] exposure, as measured in the worker’s breathing zone by personal monitoring” (10 CFR 850.23(a)). Higher levels of beryllium are allowed in principle; 10 CFR 850.22 cites the permissible exposure limits of 29 CFR 1910.1000. Table Z-2 in that section specifies a maximum eight-hour time weighted average of 2 µg/m³, an acceptable ceiling concentration of 5 µg/m³, and an acceptable maximum peak above the acceptable ceiling concentration for an eight-hour shift of 25 µg/m³ for 30 minutes. In other words, beryllium concentrations of up to 25 µg/m³ (the “acceptable maximum peak”) are acceptable if the exposure time is not more than 30 minutes during an eight-hour shift. Apart from that 30-minute period, or in the absence of such a period, concentrations of up to 5 µg/m³ (the “acceptable ceiling concentration”) are acceptable as long as the time-weighted average for a full eight-hour shift does not exceed 2 µg/m³. All of the concentrations are specified in terms of elemental beryllium rather than a compound (e.g., BeO).

All of the permissible exposure limits specified in 29 CFR 1910.1000 are substantially greater than the action level in 10 CFR 850.23(a). However, occupational exposures above the action level (an eight-hour time-weighted average of 0.2 µg/m³) require a significantly increased beryllium monitoring program. Employers may therefore prefer to restrict exposures to below the action level in order to simplify their safety programs.

Exposure to uranium is controlled by both chemical and radiological regulations. Chemical exposure for occupational exposures to air contaminants is regulated through 29 CFR 1910.1000. Table Z-1 in that section sets a maximum concentration of 250 µg/m³ for uranium in the form of insoluble compounds (including UO₂). This value is a permissible exposure limit, specified as an eight-hour time-weighted average. The regulations do not set an acceptable ceiling concentration or an acceptable maximum peak concentration for uranium.

Radiological exposure to uranium is regulated by 10 CFR 20. The concentration is expressed in terms of the derived air concentration or DAC. One DAC is “the concentration of a given radionuclide in air which, if breathed by the reference man for a working year of 2,000 hours under conditions of light work (inhalation rate 1.2 cubic meters of air per hour), results in an intake of one ALI” (10 CFR 20.1003). The annual limit on intake (ALI) for airborne uranium is “the smaller value of intake of a given radionuclide in a year by the reference man that would result in a committed effective dose equivalent of 5 rems (0.05 Sv) or a committed dose equivalent of 50 rems (0.5 Sv) to any individual organ or tissue.” Areas with a concentration of airborne radionuclides in excess of one DAC are known as airborne radioactivity areas. Signs must be posted to indicate airborne radioactivity areas (10 CFR 20.1902(d)). Respiratory protection is not necessarily required in airborne radioactivity areas, but the ALARA principle supports their use, particularly if exposure will result in a significant committed effective dose equivalent.

Respirators can provide significant protection against airborne radioactivity. Disposable filtering facepieces (common dust masks) are generally not credited with any protection, but other types of respirators have assigned protection factors that range from 10 to 10,000 (10 CFR 20, App. A).

The value of a DAC depends in general on both the radionuclide in question and its chemical form. For the three uranium isotopes typically present in fresh fuel (^{234}U , ^{235}U , and ^{238}U), one DAC is $2 \times 10^{-11} \mu\text{Ci/ml} = 2 \times 10^{-11} \text{ Ci/m}^3 = 0.74 \text{ Bq/m}^3$ (10 CFR 20, App. B, Table 1, Column 3, Entry Y) for uranium in the form of UO_2 .

The DAC for uranium is expressed in terms of activity ($2 \times 10^{-11} \text{ Ci/m}^3$), but the action level for beryllium is expressed in terms of mass ($0.2 \mu\text{g/m}^3$), so the specific activity of uranium must be used to put these numbers into consistent units. Enrichment processes increase the concentrations of both ^{234}U and ^{235}U in a predictable way, so 10 CFR 20, App. B, footnote 3 provides the following formula for the specific activity of enriched uranium:

$$S = (0.4 + 0.38E + 0.0034E^2) \times 10^{-6} \text{ Ci/g}$$

where S is the specific activity and E is the enrichment expressed in weight percent ^{235}U . Commercial fuel facilities are typically licensed for up to 5% ^{235}U , and specific activity increases with increasing enrichment, so it is conservative to evaluate the specific activity for an enrichment of 5%. The resulting specific activity is $2.39 \times 10^{-6} \text{ Ci/g}$. One DAC for 5% enriched UO_2 is therefore $(2 \times 10^{-11} \text{ Ci/m}^3) / (2.39 \times 10^{-6} \text{ Ci/g U}) = 8.4 \mu\text{g U/m}^3$.

The relative concentrations of airborne beryllium and uranium will depend on the mass fractions of Be and U in the pellet and on the respirable fraction of grinding dust for each element. The respirable fractions for the UO_2 and BeO phases are not known, so it will be assumed that they are equal. Under this assumption the concentrations of airborne beryllium and uranium are proportional to the mass fractions of Be and U, respectively, in the fuel pellet. If the volume fraction of BeO in a UO_2 -BeO fuel pellet is 10%, the ratio of the mass fractions of Be and U is 0.0125. One DAC of airborne uranium is therefore expected to correspond to $0.0125 \times 8.4 \mu\text{g/m}^3 = 0.105 \mu\text{g Be/m}^3$. Since this concentration is about half of the action level for beryllium, it appears that grinding UO_2 -BeO fuel pellets may be practicable. Other aspects of industrial hygiene would have to be examined in detail before a commercial facility could commit to producing such pellets. Adding beryllium could also affect other aspects of pellet production, such as scrap recycling, waste disposal, and environmental releases. These areas would also require evaluation.

It should be noted that in commercial practice, UO_2 pellets are normally ground in the dry condition with a diamond wheel and limited containment around the grinding wheel. The benefit of this procedure to the manufacturer is that material ground from the pellet can be recycled directly into subsequent pellet feeds. However, if there are industrial hygiene concerns with UO_2 -BeO pellets, wet grinding can be used, with either diamond or silicon carbide grinding wheels, to limit the amount of dust. Alternatively, the grinding operation can be undertaken in a hood fitted with HEPA filters. Either solution would be expected to ensure that health criteria are satisfied.

References for 4.2

- [1] Hardy and Tabershow (1946)
- [2] Eisenbud (1998)
- [3] Johnson et al. (2001)

Sub task 4.3: Fuel rod performance modeling

Adding a second phase with high thermal conductivity to a fuel pellet will affect its thermal, physical, chemical, and neutronic properties. The purpose of this task is to determine how those changes will affect fuel performance. Individual subtasks are assigned for the topics of fuel temperatures, fission gas release, LOCA initialization, neutronics, and economics.

The scope of this task has been expanded slightly from what was originally proposed. The use of BeO as the thermally conductive phase in ECO fuels changes the requirements for industrial hygiene. A new subtask has not been defined for this effort, so it is simply reported as part of task 4.

The object of Subtasks 4.3.1 through 4.3.3 is to use the COPENIC computer code (BAW-10231(NP)-A, 2002) for fuel rod performance calculations on ECO fuel. This section briefly describes the COPENIC code and outlines the fuel design and irradiation conditions that were simulated. It also discusses the methods used to adapt COPENIC to ECO fuel. The results of the calculations are reported in the subsections on fuel temperatures and fission gas release.

COPENIC performs the thermal-mechanical analyses necessary to accurately simulate the behavior of a fuel rod during its irradiation. Inputs to COPENIC include rod manufacturing characteristics and irradiation conditions. Irradiation conditions, in turn, include thermal-hydraulic conditions and power histories. Outputs from COPENIC include fuel temperatures, cladding temperatures, stresses and strains, zirconia thicknesses, and internal pressures. The program is licensed for UO_2 , MOX (UO_2 - PuO_2), and UO_2 - Gd_2O_3 fuels. Approved methodologies have been developed for use in calculating fuel rod internal gas pressure, LOCA initialization, centerline fuel melting, cladding strain, cladding creep collapse initialization, and cladding peak oxide thickness.

COPENIC provides a comprehensive description of the thermal-mechanical performance of a fuel rod. Its models cover heat production and transfer, fission gas release, pellet strains, cladding strains, cladding corrosion and hydriding, internal gas pressure, and the irradiation dependence of material properties. The thermal model includes submodels for the fuel pellet radial power profiles, fuel thermal conduction, closure of the diametral gap, heat transfer across the pellet-cladding gap, cladding thermal conduction, and heat transfer from the cladding to the coolant. The models have been extensively benchmarked against experiments.

The COPENIC code architecture reflects the following general concepts. The fuel rod is subdivided into discrete axial regions known as slices. The slices are further subdivided into discrete radial regions known as rings. This slice and ring composite forms the numerical framework (quasi two-dimensional) for the mathematical analysis. The axial slices are individually analyzed for each time step. When all of the slices have been analyzed, they are coupled, and quantities such as internal pressure and axial friction forces are determined. This general mathematical calculation sequence, which is performed at each time step, produces fuel rod predictions that accurately simulate fuel rod behavior.

Comparative calculations of fuel rod performance were performed for UO_2 and ECO fuel. The calculations were based on a previous calculation for irradiation of Mark-B11 fuel in a Babcock & Wilcox reactor. Mark-B11 refers to a 15×15 fuel assembly design in which the fuel rod diameter is nominally 10.5664 mm (0.416 inch) rather than the 10.922 mm (0.430 inch) that is more commonly used in Babcock & Wilcox reactors. The calculations were intended to be typical of the irradiation of Mark-B11 fuel rather than to represent a given batch of fuel assemblies in a given reactor.

Fig. 4.1. Fuel rod average linear heat generation rate (FR Avg. LHGR) as a function of fuel rod average burnup (FR Avg. Burnup) for UO_2 fuel.

The COPENIC code was used to track the conditions and performance of a fuel rod through three cycles of irradiation. The fuel rod geometry and operating conditions were generally nominal, with a few exceptions that were designed to provide conservatism. The most notable of the exceptions were the linear heat generation rate and the imposition of transients. The linear heat generation rate had a burnup dependence as shown in **Fig. 4.1**. The linear heat generation rate does not represent the actual irradiation of any single fuel rod but is a composite of all the rods in the batch of fuel assemblies. The derived LHGR curve is typically used to

conservatively bound actual fuel rod operations for licensing and set point analysis. The composite linear heat generation rate may be conceptually constructed by plotting the actual linear heat generation rate for each of the rods in the batch as a function of the fuel rod average burnup for that rod, and then drawing another curve that is an envelope for all of the curves for individual rods. The envelope is not unique; different envelopes may be used according to the level of conservatism desired.

For the fuel temperature and fission gas release calculations, additional conservatism was provided by imposing three limiting Condition I transients and one (non-limiting) Condition II transient. The condition levels are as defined in ANSI/ANS-57.5. Condition I refers to “events ... that are expected frequently or regularly in the normal course of power operation. The design requirement for these events is that they shall be accommodated with margin between any plant parameter and the value of that parameter which would require either automatic or manual protective action.” Condition II refers to “events ... that are expected to occur during the life of a plant that may result in reactor shutdown. The design requirement for these events is that they shall be accommodated with, at most, a shutdown of the reactor with the plant capable of returning to power operation after corrective action.” Neither Condition I nor Condition II events result in core damage. An example of a Condition I transient would be a xenon transient that results from control rod movements. Both types of transients cause axial power peaking. The axial power shapes applied to the Condition I transients were limiting for Condition I, that is, they were characterized by the most severe axial power peaking that is consistent with Condition I operational limits. In contrast, the axial power shape applied to the Condition II transient was sufficient to cause reactor shutdown but had a less severe axial peak than the Condition I transients. The reduced peaking is due to the actions of the reactor control systems, which limit the transient.

Fig. 4.2. Axial power shapes for transients used in performance calculations.

Axial power shapes for the transients are shown in **Fig. 4.2**. The transients provide

substantial additional conservatism in that they result in high local temperatures and large amounts of fission gas release.

Three axial power shapes were used for normal operation, as shown in **Fig. 4.3**. Shapes 1, 2, and 3, respectively, were used for the beginning, middle, and end of each operating cycle. Shape 1 is centrally peaked, as expected for a core that contains one batch of fresh fuel assemblies. The axial power shape then gradually progresses to shape 2 (flat) and then to shape 3 (end-peaked) as the core is depleted, particularly near the middle of the fuel rods, and the ends take over the load.

Fig. 4.3 Axial power shapes for normal operation.

It was decided at the outset that the initial calculations for ECO fuel should use it as a direct replacement for standard UO_2 fuel. In other words, the intended use of ECO fuel is that it should directly replace standard fuel and should provide (1) the same energy extraction per fuel assembly and (2) the same core thermal power as standard fuel. If ECO fuel were used in this way, the amount of steam provided to the turbine and the number of spent fuel assemblies produced per operating cycle would be identical for standard and ECO fuels. Any improvement in fuel rod performance, such as decreased fuel temperatures or end-of-life internal pressure, could then be used in support of reactor performance improvements, such as increased burnup or a power uprate.

COPERNIC was designed and licensed for commercial fuel. It was, therefore, a significant challenge to use COPERNIC in a way that represents an experimental material such as ECO fuel. **Fig. 4.4** is a schematic comparison of the two materials that explains how the challenge was met. The approach reflects the specific design and capabilities of COPERNIC.

The upper portion of **Fig. 4.4** compares the volume fractions of different materials in the fuel pellets. In ECO fuel, some of the UO_2 is replaced by a neutronically inert material, such as SiC , which does not contribute to power production. However, if ECO fuel is to be a direct replacement for standard fuel, the power produced by the UO_2 must be the same for both fuels, as shown in the lower portion of **Fig. 4.4**. Since the ECO fuel contains less total UO_2 , it must have a greater end-of-life burnup to maintain the energy extraction per fuel assembly.

Fig. 4.4 Schematic comparison of volume fraction and linear power for ECO fuel and standard fuel for calculations with COPENIC.

Various approaches could be used in an attempt to simulate ECO fuel in COPENIC. Most of the relevant variables that can be changed in COPENIC are related to the fuel rod and fuel pellet geometry or to the volume fraction of open and closed porosity. These variables tend to have undesirable side effects. They affect the amount and location of void volume or the thermal conductivity of fuel, and their effect on fuel rod performance is not clearly related to the replacement of UO_2 by a neutronically inert material. The selected approach, which is suggested in Figure 4.4, was to treat the neutronically inert material as if it were additional UO_2 that produced additional (fictitious) power.

The question of how to handle the extra, fictitious power is best answered by a concrete example. For the current calculations, a standard UO_2 fuel pellet was taken to be, by volume, 95.9% UO_2 , 4.0% closed porosity, and 0.1% open porosity. An ECO fuel pellet was taken to be, by volume, 91.9% UO_2 , 4.0% inert material, 4.0% closed porosity, and 0.1% open porosity. The same pellet geometry was used for both fuel materials. The loading of inert material in the ECO fuel is smaller than that used in recent thermal conductivity experiments.

As is shown in **Fig. 4.4**, the UO_2 is assumed to generate the same power in both the ECO and standard fuels. The total power of an ECO fuel rod is therefore $95.9/91.9 = 1.0435$ times that of a standard fuel rod, that is, there is an additional 4.35% of fictitious power that is attributable to the inert material. There is also 4.35% of additional, fictitious, fission gas release. COPENIC [1] allows direct correction for both of these. Fission gas release is adjusted by using a multiplier for the fission gas release model. The multiplier is set to $1/1.0435 = 0.9583$. Linear power is adjusted by using FHEAT, which is the fraction of fission energy generated inside the fuel rod. For standard fuel, FHEAT was 0.973, whereas for ECO fuel, FHEAT was set to $0.973 \times 0.9583 = 0.93243$. This adjustment hinges on the distinction between linear heat generation rate, which is the thermal power (per unit length of fuel rod) that is conducted through the surface of a fuel rod, and linear power, which is the thermal power generated per unit length of fuel rod. COPENIC is designed so that the user specifies the linear heat generation rate. A reduction in FHEAT does not affect the linear heat generation rate; instead, it increases the linear power but at the same time provides for an increase in the amount of heat that is directly transferred to the coolant, e.g., by gamma radiation or neutron kinetic energy.

With the corrections described above, the ECO fuel will achieve an end-of-life burnup that is 1.0435 times that for standard UO_2 fuel. All burnup data in the COPENIC input file were scaled by this amount.

Two additional minor corrections are required. The additional, fictitious thermal power from ECO fuel results in increased changes in coolant temperature as it flows past the fuel rod. The coolant flow rate was multiplied by 1.0435 to maintain the coolant temperature. The increase in coolant flow is fictitious, like the increase in linear power, so no actual changes in reactor coolant flow would be required to accommodate ECO fuel. The second correction is that the increased burnup achieved by ECO fuel will require an increased initial enrichment. On the basis of earlier calculations for UO_2 -SiC fuel, the initial ^{235}U enrichment was increased from 4.8% to 4.928%. These two corrections were found to have only slight effects on fuel rod performance.

References for task 4.3

- [1] BAW-10231(NP)-A, COPENIC Fuel Rod Design Computer Code, June 2002.

4.3.1: Effect on fuel temperatures

COPENIC was used to simulate both standard UO_2 fuel and ECO fuel. It was assumed that the thermal conductivity of ECO fuel was 0%, 5%, or 10% greater than that of standard UO_2 fuel. The treatment of ECO fuel by COPENIC was in accordance with the discussion above. Fuel temperatures as a function of burnup are given in Figure 15. The temperatures are volume averages for the pellets in an entire fuel rod.

It will be observed in **Fig 4.5** that the ECO fuel rods attain an end-of-life burnup of about

67800 MWd/MTU, compared to about 65000 MWd/MTU for standard UO₂ fuel. This is as expected, because the amount of UO₂ is reduced in ECO fuel, and the same energy extraction per fuel assembly is required

Fig. 4.5 Volume-averaged fuel temperatures (FR Vol. Avg. Temperature) as a function of fuel rod average burnup (FR Avg. Burnup) for standard UO₂ fuel and for ECO fuel with thermal conductivity increased by 0%, 5%, and 10%.

The fuel temperature plots start with a small increase, followed by a gradual decrease for burnups up to about 12000 MWd/MTU. These changes in temperature reflect changes in the size of the fuel-cladding gap. The gap initially widens, and its thermal resistance increases, as the fuel pellets densify. The gap subsequently narrows as the cladding creeps down onto the fuel pellets and the fuel pellets swell. As a result, the thermal resistance of the gap decreases, and the fuel temperature drops. The remainder of each temperature plot has a characteristic saw tooth shape. There is a general alternation between gradual increases in temperature and relatively abrupt drops. This shape reflects the plateaus and slopes of the linear heat generation rate, which are shown in **Fig. 4.1**. The gradual increases in temperature correspond to the plateaus in the linear heat generation rate. The increases reflect the gradual degradation of the thermal conductivity of UO₂ with increasing burnup. The relatively abrupt decreases correspond to the slopes in the plot of the linear heat generation rate. Decreases in linear heat generation rate result in decreases in fuel temperature. The occasional spikes in temperature result from the imposition of Condition I and II transients as discussed above.

The standard fuel (designated as “UO₂ base case”) and ECO fuel without increased thermal conductivity (designated as “ECO, 0% ΔTC”) provide a useful comparison. Over certain ranges of burnup, notably 0 to 17000 MWd/MTU and 60000 to 65000 MWd/MTU, these fuels are operated at the same linear heat generation rate. It is observed that, within these ranges,

the two fuels have very similar temperatures for a given burnup. This is exactly as expected. However, because of the gradual degradation of fuel thermal conductivity with burnup, the ECO fuel has a slightly higher temperature at end of life.

An increased thermal conductivity is seen to have a marked effect on fuel temperature. ECO fuel without increased thermal conductivity shows an increase in volume-averaged fuel temperature of about 6 °C at end of life relative to standard fuel. In contrast, ECO fuel with thermal conductivity increased by 5% and 10% has temperatures that are about 15 and 33 °C, respectively, below that of standard fuel at end of life. Further reductions in temperature are expected to provide additional benefits. The plots suggest that an enhancement in thermal conductivity by as little as 2% will provide some reduction in fuel temperature at end of life.

The benefits of increased thermal conductivity on centerline fuel temperatures should not be underestimated. As an example, consider the transient for ECO fuels at a burnup of about 31300 MWd/MTU. At the end of the transient, the ECO fuel with a 5% increase in thermal conductivity has a volume-averaged fuel temperature that is about 18 °C below that of the ECO fuel without an increase in thermal conductivity. In contrast, the corresponding difference in centerline fuel temperature between these cases is greater than 60 °C.

4.3.2: Effect on fission gas release

The results of the COPENIC calculations included fission gas release and fuel rod internal pressure as functions of burnup. The calculations were the same as those reported for subtask 4.1, and the results are plotted in **Fig. 4.6** and **4.7**.

Fig. 4.6 Fission gas release as a function of fuel rod average burnup (FR Avg. Burnup) for standard UO₂ fuel and for ECO fuel with thermal conductivity increased by 0%, 5%, and 10%.

It is notable that **Figs 4.6** and **4.7** both lack the characteristic saw tooth shape of **Fig 4.5**. For fuel rod internal pressure, this might be partially explained by the location of the void volume. The void volume is predominantly in the upper plenum, and the gas temperature in the plenum is decoupled from the fuel temperature. The fission gas release curves, however, show that there is more to the story. For standard fuel, it can be seen from Figure 11 that the linear heat generation rate drops quickly between burnups of 43000 and 44000 MWd/MTU. That drop is reflected by a significant drop in fuel temperature, as shown in Figure 15. However, Figure 16 shows essentially no change in fission gas release over the same range of burnups. The reason appears to be that fission gas release is determined not only by the current temperature but also by microstructural properties, such as the concentration of fission gas on the grain boundaries, that reflect the past history of the fuel.

Figs 4.6 and **4.7** show that, compared to standard fuel, all three ECO fuels have improved performance with regard to fission gas release and fuel rod internal pressure. Relative to standard fuel, ECO fuel with increases in thermal conductivity of 0%, 5%, and 10% have end-of-life fission gas release that is decreased by 1.7%, 4.0%, and 6.0%, respectively. Similarly, the ECO fuels have end-of-life internal pressures that are 0.5, 2.0, and 3.3 MPa (5, 20, and 33 bars) below those of standard fuel.

The plots for fission gas release and fuel rod internal pressure generally diverge with increasing burnup. This is in agreement with the concept of fission gas release as a breakaway phenomenon, that is, release of some fission gas promotes release of more gas.

Fig. 4.7 Fuel rod internal pressure (FR Internal Pressure) as a function of fuel rod average burnup (FR Avg. Burnup) for standard UO₂ fuel and for ECO fuel with thermal conductivity increased by 0%, 5%, and 10%.

The results of the COPENIC calculations show that even relatively small improvements in fuel thermal conductivity provide significant improvements in fuel rod performance. Recent measurements of thermal conductivity indicate that the achievable increases in conductivity for ECO fuel are substantially larger than those discussed here. Correspondingly larger improvements in performance are therefore expected. Such improvements in performance provide the fuel designer with additional flexibility to increase power output or burnup, or to increase conservatism and safety.

4.3.3: Estimate effect on LOCA initialization

Loss of coolant accident (LOCA) initialization calculations were performed to provide a comparison of standard UO_2 fuel and ECO fuel under conditions of LOCA initialization.

LOCA performance is regulated by 10 CFR 50.46, which provides acceptance criteria for emergency core cooling systems for light-water nuclear power reactors. Among the criteria are requirements that the calculated maximum fuel element cladding temperature shall not exceed 2200 °F (1204 °C) (10 CFR 50.46(b)(1)) and that changes in core geometry shall be such that the core remains amenable to cooling (10 CFR 50.46(b)(4)).

Designing to meet the LOCA criteria is complex and requires consideration of various processes and their effects on all of the stages of LOCA. However, some rules of thumb have been developed to help simplify the process. One rule is that if the best-estimate volume average fuel temperature before the LOCA does not exceed 2050 °F (1121 °C), the cladding temperature will not exceed 2200 °F during the LOCA. The difference of 150 °F (83 °C) normally provides adequate margin for uncertainties in the best-estimate temperature and any temperature increase due to decay heat. A second rule of thumb is that, if the pressure inside the fuel rods before the LOCA does not exceed a certain level, the core geometry will remain coolable during the LOCA. The rules of thumb do not replace the full LOCA analysis. Instead, they provide a relatively quick means for setting fuel operational limits. Those limits are then confirmed by a full analysis.

Fuel rod performance is calculated using a best-estimate model for the limiting rod. The linear heat generation rate as a function of burnup was similar to that used for analysis of fuel temperature or fission gas release, but the Condition I and Condition II operational transients were replaced by a single LOCA initialization transient. The strength of the transient is adjusted until the fuel reaches one of the limits given above. In the case of volume average fuel temperature, the average is that for the hottest of COPENIC's slices, which is typically at or just above the elevation of the axial peak for the transient. The fuel rod performance calculation was stopped at the end of the LOCA initialization transient.

Fuel that can sustain a stronger transient without exceeding the limits is preferable because it performs acceptably under a wider range of operating conditions. The increased flexibility in operating conditions promotes plant profitability.

Many individual fuel rod performance calculations are needed for an analysis of LOCA initialization. First, LOCA performance depends on burnup, so the calculations must be performed at various times in life. Second, at each burnup, several transients with different axial shapes are considered because the effect of the transient depends on its elevation in the core. Third, the strength of the transient must be adjusted so that the fuel reaches but does not exceed the rule-of-thumb limits.

The LOCA initialization transients were assumed to occur at 0.002, 18, 35, 45, and 62 GWd/MTU for standard UO₂ fuel or at equivalent energy extractions for ECO fuel. In each case, the burnup specified is that at the end of the transient. Each transient included a short ramp followed by sustained high power for a longer time. In the calculations reported here, duration of the ramp was 0.01 MWd/MTU, which corresponded to about 15 to 25 seconds, depending on the power level. For the transient at beginning of life 0.002 GWd/MTU, the sustained high power portion lasted for a period of 1.00 MWd/MTU, or a time of about 25 minutes. For the other times in life, the duration of the transient was 100 MWd/MTU, or a time in the range of 45 to 65 hours.

The LOCA initialization calculations used the same basis as the previous calculations on fuel temperature and fission gas release. In particular, the same fuel design, enrichments, and linear heat generation rate were used. The volume fractions of UO₂, porosity, and high-conductivity phase were likewise identical to those used previously, as were the corrections to FHEAT, coolant flow rate, and fuel enrichment for ECO fuel. The calculations included standard UO₂ fuel, ECO fuel without an increase in thermal conductivity, and ECO fuel with a 10% increase in thermal conductivity.

Fig. 4.8 Maximum local linear heat generation rate for LOCA initialization

The results of the calculation are shown in **Fig. 4.8**. The reported linear heat generation rate is that at the peak of the transient rather than a fuel rod average. As in the previous calculations on fuel temperature and fission gas release, the burnups for the ECO fuel are slightly greater than those for the standard UO₂ fuel to promote comparisons at the same level of energy extraction.

It is seen from Figure 18 that the results for ECO fuel without an increase in thermal

conductivity are very similar to those for standard UO_2 fuel, with a slight degradation that may be related to the increase in burnup in the ECO fuel because of the reduced uranium loading. This result is as expected. In contrast, the ECO fuel with a 10% increase in thermal conductivity provides a significant benefit. When compared to standard UO_2 fuel, the ECO fuel provides an increase in the maximum linear heat generation rate by 4.9 kW/m at beginning of life and 3.2 kW/m at 62 GWd/MTU.

Subtask 4.4: Effects on neutronics

Adding a second phase with high thermal conductivity to a fuel pellet will affect its neutronic properties. The purpose of this subtask is to determine how those changes will affect fuel performance. To the extent practical, the performance analysis of composite fuel was parallel to the design of a commercial fuel reload. Some aspects of the process were simplified to reflect the exploratory nature of the work. This section describes the neutronic analysis process and provides the results of the analysis.

The approach was to simulate four operating cycles in which a power reactor undergoes a transition from standard UO_2 fuel to ECO fuel. A baseline calculation was first performed in which UO_2 fuel was used for all cycles. This was followed by similar calculations for the transition from UO_2 fuel to ECO fuel. The ECO fuel assemblies were assumed to be the same as the UO_2 fuel assemblies except for the pellet material and ^{235}U enrichment. The calculations considered two types of ECO fuel: $\text{UO}_2\text{-SiC}$ and $\text{UO}_2\text{-BeO}$. It was assumed that each assembly was fueled with one type of fuel: standard UO_2 , $\text{UO}_2\text{-SiC}$ ECO fuel, or $\text{UO}_2\text{-BeO}$ ECO fuel. In other words, there was no mixing of standard UO_2 and ECO fuel rods or of $\text{UO}_2\text{-SiC}$ and $\text{UO}_2\text{-BeO}$ fuel rods in a single assembly. Additional benefits might be realized by using the ECO fuel selectively. For example, it could be used only for the fuel rods with the highest local power.

To make the neutronic calculations as realistic as possible, they were based on four refueling cycles of a 177-assembly Babcock & Wilcox reactor. The reactor was fueled with Mark-B9ZL assemblies. The Mark-B9ZL features zone loading, that is, the fuel rods have two different ^{235}U enrichments. The zoning is as shown in **Fig. 4.9**; there are reduced enrichment rods in the four locations adjacent to the instrument tube and in the twelve locations closest to the corners. Actual operating data for a commercial reactor were used. The reactor was chosen because it met two criteria. First, it has used the same fuel design for several cycles and therefore has an “equilibrium core”. If a non-equilibrium core had been used instead, the comparisons could produce spurious results associated with transition cycles. Second, the reactor does not use integral burnable absorbers, so its fuel enrichments are relatively low. ECO fuel may require increased enrichments, but its enrichments must remain below the 5 wt % license limit that currently applies to commercial fuel facilities.

The reactor that was simulated uses 18-month refueling cycles and a very low leakage fuel shuffle scheme. This scheme is called “in-in-out” because the fuel assemblies spend their first two cycles near the center of the core and are moved to the periphery for the third. Having the most heavily burned fuel on the periphery reduces neutron leakage from the core.

Fig. 4.9 Zoning of Mark-B9ZL fuel assembly

Fig. 4.10 shows a full-core map for the final cycle of the simulations. The map illustrates the in-in-out shuffle scheme. Note that there are too few peripheral locations for all the third-cycle assemblies, so some of them are placed in interior locations.

It is necessary to simulate four cycles because typical reactor reloads replace about one third of the fuel after each cycle. In addition, reinserted fuel was involved from an earlier cycle. For the transition to ECO fuel, the four cycles represent, respectively, reactor operation with 60, 116, 176, and 177 of the core locations occupied by ECO fuel assemblies. Comparisons were made for the fourth cycle, when the reactor was fueled with a full core of either UO_2 fuel or ECO fuel. Utilities will normally not accept fuel that will reduce the length of their operating cycles, so the cycle length and the energy extraction per assembly were kept constant. Part of the fuel volume in ECO fuel is occupied by the high-conductivity second phase, so the ECO fuel has a lower uranium loading than standard UO_2 fuel. As a result, increases in burnup and ^{235}U enrichment are required to maintain cycle length. The loss of UO_2 loading in ECO fuel can be offset to some extent by the reduced fuel temperatures, which reduce Doppler absorption. In the case of $\text{UO}_2\text{-BeO}$ fuel, there is also a neutronic benefit from the $(n, 2n)$ reaction of ^9Be with fast neutrons.

As was mentioned previously, the calculations considered two types of ECO fuel: $\text{UO}_2\text{-SiC}$ and $\text{UO}_2\text{-BeO}$. The calculations for $\text{UO}_2\text{-SiC}$ fuel were performed first. The calculations for $\text{UO}_2\text{-BeO}$ were similar to those for $\text{UO}_2\text{-SiC}$ fuel, but different techniques were required because of the differences between the neutronic properties of SiC and BeO.

Fig. 4.10 Full-Core Map for Final Cycle

UO₂-SiC fuel

CASMO-3 was used for the neutronic calculations for both standard UO₂ and UO₂-SiC fuel. This code represents the core with an averaged fuel assembly and gives the infinite neutron multiplication factor k_{inf} as a function of burnup. The effect of SiC in the UO₂-SiC fuel was assumed to be a reduction in the volume-averaged fuel temperature of 100 K. This corresponds to an assumed increase in the thermal conductivity of the fuel by about 25%. A reduction in fuel temperature also has implications for neutronics, which the CASMO-3 calculations properly reflect. The ²³⁵U enrichment of the UO₂-SiC fuel was increased relative to that of the standard UO₂ fuel so that both fuel types provided the same core-averaged value of k_{inf} at the end of the fourth cycle for the same energy extraction per assembly. This assures that the cycle length is maintained.

UO₂-BeO fuel

The neutronics of UO₂-BeO fuel are more complex than those of UO₂-SiC fuel, most notably because of the (n , $2n$) reaction of ⁹Be with fast neutrons. CASMO-3 was considered unsuitable for these calculations because it does not have suitable cross-section libraries for beryllium. To circumvent this limitation, the depletion calculations were performed using the TRITON control module of SCALE 5.0 with the 238-energy group cross-section library. The TRITON calculations are performed with an appropriate cross-section library for beryllium and to establish the amount of depletion of the beryllium isotope for three cycles of operation.

The TRITON code performs a more detailed calculation with fewer approximations than CASMO-3. For example, it uses a much finer energy-group structure for the cross-section library, and will also perform depletion calculations (with the ORIGEN-S module of SCALE 5.0) for the beryllium. In contrast, CASMO-3 will not treat the beryllium as depletable. Both the finer energy-group structure and the use of ORIGEN-S mean that TRITON is better able to treat (n , $2n$) reactions of beryllium.

Unfortunately, changing codes from CASMO-3 to TRITON entails the possibility of systematic differences in the results. The nature of the systematic difference was explored by running depletion calculations with both CASMO-3 and TRITON on standard UO_2 fuel, and also using both codes on $\text{UO}_2\text{-BeO}$ fuel. The net result was that, for $\text{UO}_2\text{-BeO}$ fuel of a given enrichment, TRITON predicted a k_{inf} at the end of the fourth cycle that was 0.000337 less than that predicted by CASMO-3. Conversion from standard UO_2 fuel to $\text{UO}_2\text{-BeO}$ ECO fuel was found to require a small increase in initial ^{235}U enrichment. The required increase in enrichment was determined by linear interpolation.

Results of neutronic calculations

Information about the core for the fourth cycle is given in Table 4.1. The enrichments given are for standard UO_2 fuel. A comparison of fuel types is given in Table 4.2. The $\text{UO}_2\text{-BeO}$ fuel has smaller volume fractions for both voids and the second phase than the $\text{UO}_2\text{-SiC}$ fuel; this difference reflects differences in processing of the two fuel types. It has generally been observed that it is easier to sinter $\text{UO}_2\text{-BeO}$ fuel to high density and to produce a continuous network of the second phase.

Table 4.1 Fuel Enrichments for Standard UO_2 Fuel Case, Final Cycle

Batch	Irradiation Cycle	# of Assemblies	Average ^{235}U Enrichment
A	3rd burn, reinserted fuel	1	4.027
B	3rd burn	56	4.027
C	2nd burn	60	4.007
D	1st burn	60	4.027

Table 4.2 Fuel Densities for Design Comparisons

	Fuel Type		
	UO ₂ -SiC	UO ₂ -BeO	UO ₂
UO ₂	90%	93.2%	95%
SiC	7%	--	--
BeO	--	4.8%	--
voids	3%	2%	5%

Comparison of the results for the two ECO fuel types revealed a striking difference in their neutronic performance. Substitution of UO₂-SiC fuel for UO₂ fuel required an increase in enrichment by 0.16 wt % to maintain the end-of-cycle value of k_{inf} . In contrast, substitution of UO₂-BeO fuel for UO₂ fuel required an increase in enrichment by only 0.0073 wt % to maintain the end-of-cycle value of k_{inf} . The reasons for the difference were not explored in detail but are presumably related to 1) the greater uranium loading in UO₂-BeO fuel than in UO₂-SiC fuel, 2) the (n , $2n$) reaction of ⁹Be, and 3) the greater moderating effect of BeO than SiC.

The consumption of ⁹Be through (n , $2n$) reactions is small. It was found that the ⁹Be isotopic concentration decreased by only 0.15% over three cycles of irradiation.

Sub task4.5: Estimate effects on economics

Economic comparisons were completed for six cases. Uranium costs were calculated with the SWUCost 2.0 code under the following assumptions: Enrichment was assumed to cost \$110/SWU (separative work unit). Uranium feed was assumed to cost \$53.5/kg U. The enrichment of the tails was assumed to be 0.3 wt % ²³⁵U. The changes in uranium cost for an actual reload will vary. In particular, the cost of uranium feed is subject to strong market fluctuations. The results of the economic comparisons are given in Table 4.3. The changes in uranium cost and total uranium loading are for a full batch of fuel.

Table 4.3 Effect of Changes in Fuel Design on Uranium Cost

Fuel Type	Number of Assemblies	²³⁵ U Enrichment	Change in U Cost, \$	Total U loading, kg
UO ₂ (base)	60	4.027	--	27820
UO ₂ -SiC	60	4.187	-139000	26360
UO ₂ -BeO	60	4.034	-501000	27290
UO ₂ (base)	56	4.277	--	25970
UO ₂ -SiC	56	4.437	-236000	24600
UO ₂ -BeO	56	4.284	-506000	25470

The first three cases provide a direct comparison of UO₂, UO₂-SiC, and UO₂-BeO fuel for the final cycle of the simulation. These cases assumed a reload with 60 assemblies. As was reported previously in the discussion of subtask 4.4, the UO₂-SiC and UO₂-BeO fuels require an

increase in ^{235}U enrichment of 0.16 wt % and 0.0073 wt %, respectively, to maintain cycle length. However, the density of uranium is reduced in the ECO fuels, so the net result is a decrease in uranium cost of about \$139,000 per batch for $\text{UO}_2\text{-SiC}$ fuel and \$501,000 per batch for $\text{UO}_2\text{-BeO}$ fuel.

The remaining three cases are like the first, but it is assumed that a reload of 56 assemblies would be acceptable. A reduction in the reload batch size from 60 to 56 is expected to impose penalties in terms of increased power peaking, but these may be acceptable with ECO fuel because of its improved thermal conductivity. It was also assumed that an increase in the ^{235}U enrichment by 0.25 wt % would be required to maintain cycle length. The same increase in enrichment was assumed to apply for all three fuel types. The increase in enrichment was strictly an engineering judgment and was not supported by a specific neutronic analysis or core design. Therefore, it is not appropriate to compare costs between batches with 56 assemblies and those with 60. The decrease in uranium cost per batch is \$236,000 for $\text{UO}_2\text{-SiC}$ fuel and \$506,000 for $\text{UO}_2\text{-BeO}$ fuel. The relative costs for the three fuel types are broadly similar for both batch sizes. Brush Wellman [39] gives the cost for their standard UOX grade of BeO in quantities >12.5 Tons as \$115/lb or \$253/Kg. Assuming 5 vol% or 1.5 wt% BeO gives an additional cost of \$350,000 for the BeO of 95%TD.

Table 4 does not directly compare the costs of the UO_2 base cases with 60 and 56 assemblies; those cases reflect a change in fuel cycle design rather than in materials. The total change in cost between the two UO_2 cases will reflect a reduction in manufacturing cost and an increase in uranium cost because of the increased enrichment. The net savings from reducing the batch size is estimated to be between \$100,000 and \$200,000.

The discussion above shows that substitution of ECO fuel for UO_2 fuel can result in a reduced uranium cost. The reduction is more notable for $\text{UO}_2\text{-BeO}$ fuel than for $\text{UO}_2\text{-SiC}$ fuel. The cost of a reload will reflect manufacturing costs as well. Manufacturing costs are typically reported in dollars per kilogram of uranium. Table 4 provides the total mass of uranium per fuel batch, so it can be seen that the reduction in uranium cost for $\text{UO}_2\text{-BeO}$ fuel is sufficient to offset an increase in manufacturing cost of nearly \$20/kg U, whereas the reduction in uranium cost for $\text{UO}_2\text{-SiC}$ fuel would offset an increase in manufacturing cost in the range of about \$5/kg U to \$10/kg U.

The economic impact of using ECO fuel extends beyond the fuel cost. The improved thermal performance of the fuel could support less restrictive peaking, operating, and maneuvering limits, and less restrictive limits can contribute to the economic performance of a power plant.

Sub task 4.6 Waste form and recycling

To examine the continuity of the BeO phase, we immersed a sintered ECO pellet with 10 vol% BeO in boiling nitric acid for 60 min. As seen in **Fig. 4.11**, a low magnification photograph shows the complete BeO “skeleton” after the UO_2 dissolution. **(a)**, shows the surprisingly robust skeleton at higher magnification by scanning electron microscopy. **(Fig. 4.12) (b)** shows the EDS with no detectable UO_2 although some dispersed UO_2 would be expected to remain in the BeO phase. However, the bulk of the UO_2 may be dissolved for re-cycling. This shows that the UO_2 phase is also continuous. The remaining BeO skeleton can be crushed to produce powder that can be recycled in new fuel or simply fabricated as an Inert Matrix Fuel with the contained fission products.

Fig.4.11 Picture of ECO fuel before and after dissolution within boiling HNO_3 for 1 hr: the UO_2 is completely dissolved and the BeO skeleton stays intact. The BeO skeleton can easily be crushed to powder.

Fig.4.12 SEM and EDS of the BeO skeleton obtained after UO_2 dissolution. EDS shows almost no remaining U, which confirm the complete dissolution.

Summary and Conclusions

We have succeeded in performing essentially all tasks in the program to produce and characterize high conductivity oxide fuels: finite element modeling, fabrication, characterization

of the microstructure and properties and performance modeling of a new form of oxide fuels with enhanced thermal conductivity. The one task that we have not completed is the actual production of fuel pellets for irradiation, although we have taken the essential steps.

The fuel form we ended with is one that we had considered in our original proposal, but had preferred investigating SiC as the high conductivity phase by the PIP process. The PIP process has many advantages for producing high conductivity matrices for fuel with which they are chemically compatible. However, our compatibility studies showed that SiC is not compatible with UO_2 above 1370°C , and when processed below that temperature we showed that it is not sufficiently conductive to enhance the conductivity of UO_2 . On the other hand, we also showed that with *compatible* fuel forms like carbides, (UC, PuC), for gas-cooled reactors, the necessary crystallization temperatures greater than 1500°C become possible. In addition, we learned much about the processing of such preceramic precursors for these and other nuclear applications. Many such precursors have been developed. For example, an experimental precursor exists for ZrC that is stable to even higher temperatures than SiC.

Therefore our attention shifted to a ceramic system that is highly stable with UO_{2+x} at temperatures as high as 2160°C , at which point a eutectic can form. Because of the very low solubility of BeO in UO_2 , the kinetics of interdiffusion might make the formation of a eutectic very sluggish, but this was not investigated. We supported extensive earlier work that showed that UO_2 and BeO are highly compatible during sintering not only for IMF type fuels, but even for our new application for ECO fuels. Again, our results were consistent with Ishimoto *et al.*'s reported conductivities when extrapolated to our BeO volume fractions in UO_2 . But in contrast to Ishimoto *et al.*, our technique is easily applicable in a commercial setting.

Our coupled neutronics and cost analyses show that the ECO fuel based on BeO as the conductive phase was comparable in cost to standard fuel, but offered many advantages in operating flexibility, longer irradiation times and/or possible uprating, all with significant economic incentive.

But issues remain to be answered. Although BeO appears to suffer less than most ceramics in reduced thermal conductivity under fast neutron bombardment, its hexagonal crystal structure makes it prone to anisotropic crystal growth, and cracking at or near end of life doses of fast neutrons depending on temperature, dose rate, grain size, particle dispersions which act as recombination sites, fission fragment effects and constraint effects. BeO was abandoned in the 60's because of this problem in spite of the unexplained cases where cracking did not occur. This question would need to be resolved by careful irradiation testing using neutrons and protons (for rapid materials simulations).

The second major issue is handling BeO safely. The DOE has had a checkered past in handling very large quantities of BeO during the cold war era, but other organizations that handle commercial quantities have not had such problems even with an order of magnitude higher allowed air concentrations. Our experience and analyses show that BeO can be safely handled, and allows easy fuel reprocessing, if not recycling of the BeO.

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