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### A REVIEW OF CARBIDE FUEL CORROSION FOR NUCLEAR THERMAL PROPULSION APPLICATIONS

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# Abstract

At the operation conditions of interest in nuclear thermal propulsion reactors, carbide materials have been known to exhibit a number of life limiting phenomena. These include the formation of liquid, loss by vaporization, creep and corresponding gas flow restrictions, and local corrosion and fuel structure degradation due to excessive mechanical and/or thermal loading. In addition, the radiation environment in the reactor core can produce a substantial change in its local physical properties, which can produce high thermal stresses and corresponding stress fractures (cracking). Time-temperature history and cyclic operation of the nuclear reactor can also accelerate some of these processes. The University of New Mexico's Institute for Space Nuclear Power Studies, under NASA sponsorship has recently initiated a study to model the complicated hydrogen corrosion process. In support of this effort, an extensive review of the open literature was performed, and a technical expert workshop was conducted. This paper summarizes the results of this review.

#### **INTRODUCTION**

Nuclear Thermal Propulsion (NTP) engine systems are attractive options for orbit transfer and planetary exploration applications because of their high performance (Bussard and DeLauer 1965, Borowski et al. 1992, and Stafford et al. 1991). To achieve such performance, which is typically over twice that associated within chemical propulsion systems, hydrogen is used as the NTP engine system working fluid because of its low molecular weight. In the operation of such systems, NTP reactor chamber temperatures and pressures are typically greater than 2500 K and 3 MPa, respectively. Additionally, to minimize the weight, NTP reactors operate at high power densities. Power densities of up to 2.7 MW/liter have been demonstrated, while future generation solid-core reactor concepts could conceivability operate at power densities as high as 10 MW/liter or greater for single burn, short operation time applications (Koenig 1986 and Clark et al. 1993). Operating at these high power densities produces a high radiation flux environment in the reactor core. These characteristics provide a bostile environment for NTP reactor core materials in which to survive. To meet this engineering challenge, Uranium-Zirconium Carbon (U-Zr-C) and Uranium-Nioblum-Carbon (U-Nb-C) material systems have been considered for such applications (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, Matthews et al. 1991, Carmack et al. 1991, Homan et al. 1991 and Storms et al. 1991). Carbide inaterial systems are attractive due to their favorable nuclear properties, high melting point, thermal stability, low volatibility, high moderation properties, and low density.

At the operation conditions of interest in NTP reactors, carbide materials have been known to exhibit a number of life limiting phenomena (Storms et al. 1991). These include the formation of liquid, loss by vaporization, creep and corresponding gas flow restrictions, and local corrosion and fuel structure degradation due to excessive mechanical and/or thermal loading. In addition, the radiation in the reactor core environment can produce a substantial change in its local physical properties, producing high thermal stresses and corresponding stress fractures (cracking). Time-temperature history and cyclic operation of the nuclear reactor can also accelerate some of these processes.

Degradation of NTP reactor fuel integrity by the physical processes just mentioned, has been the subject of research and development during reactor testing associated with the Rover and NERVA programs (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, and Homan et al. 1991). Of most concern was the core material mass loss associated with localized corrosion of the prismatic design fuel elements used in these programs. Material mass loss occurred at temperatures substantially lower than the fuel material melting temperature (2500 K vs. 3200 K) and accounted for a large percentage of the core material loss during operation. This highly complex phenomena encompassed many of the life-initing processes previously discussed, and made engineering solutions to correct this

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problem difficult to identify and implement. The hydrogen corrosion process substantially reduces NTP engine system performance and life, which directly influences overall mission safety reliability, and cost.

### **OBJECTIVE**

The University of New Mexico's (UNM) Institute for Space Nuclear Power Studies (ISNPS), under NASA sponsorship has recently initiated a study to model the complicated hydrogen corrosion process. In support of this effort, an extensive review of the open literature was performed and a technical expert workshop was conducted. These study activities helped to provide the foundation to establish the state-of-the-art understanding of the physical processes and modeling of corrosion of carbide material systems when exposed to hot hydrogen at conditions typical of NTP reactors. Additionally, the review assessed the applicability of available experimental data to benchmark (verify) future corrosion models. This paper summarizes the results of the review.

An extensive open literature review was performed during this initial study. In this effort, literature was gathered and reviewed principally in the areas of carbide thermochemistry and in related research and development work associated with the NERVA and Rover programs. In addition, extensive discussions were held with many technical experts in this field. Based on this data gathering activity, assessment was made on of the technical community's past experience, fundamental understanding of the complex corrosion process, and the adequacy of available experimental data to properly benchmark the next generation of corrosion model(s). The following section summarizes the results of this review.

## RESULTS

Corrosion of carbide fuel materials, due to their exposure to hot hydrogen in NTP systems greatly impacts the engine performance, thrust-to-weight, and operation life and is considered by many to be a critical development issue. Experience from the Rover and NERVA programs have shown the effects of corrosion to be substantial and to be highly complex. Hydrogen corrosion phenomena of carbon-based structual materials and carbide fuels are driven by many highly coupled and interrelated physical processes. These processes include: (1) exposure to hot hydrogen gas which produces thermo-chemical reactions of various types, (2) preload and non-uniform heating and mechanical loading, (3) exposure to nuclear radiation, and (4) high temperature effects such as creep. Coatings have been used in the past to combat corrosion, but with only moderate success.

As shown in Figure 1, corrosion has a major impact on NTP engine system design, development, and operation, including: (1) specific impulse, (2) engine system thrust-to-weight ratio, (3) reactor control, (4) operational life, and/or duty cycle, and (5) ground testing complexity and cost.

For solid-core reactor engine systems, hydrogen corrosion limits the reactor exit gas temperature for a given operational lifetime and duty cycle. Corrosion of high-temperature carbide solid-solution systems have been found to exist at temperatures (<2400 K) substantially less than their melting points (>3200 K). The reactor exit (chamber) temperature substantially impacts engine system performance, and specific impulse (Bussard and DeLauer 1965). Thus, as the propellant exit temperature increases, mission propellant mass and support (launch system) infrastructure requirements decrease, reducing the overall mission life cycle cost. Additionally, the occurrence of corrosion during operation can slightly reduce the engine system performance by increasing the molecular weight of the propellant gas working fluid by entrainment of the heavier reactor fuel and structual material and its reaction byproducts (Bussard and DeLauer 1965).

Hydrogen corrosion affects the thrust-to-weight ratio of the engine system in twr ways: (a) it increases the initial reactor core mass to compensate for mass loss during its operation lifetime, and (b) it lowers the reactor power density, resulting in a lower engine system thrust-to-weight ratio and/or limits on given system operational lifetime and duty cycle. The relationship between power density and critical size of the core greatly influences engine system life for a given fuel design.

Mass loss of the reactor core fuel by corrosion also increases the demand (adaptative response) of the reactor control system which can reduce the reliability and safety of the NTP engine system (Koenig 1986 and Taub 1975). The reactor core neutronics will vary as a function of operating time (parasitic absorption and scattering will change) within the core as the moderator and/or fuel material is removed by corrosion. These factors, which change the reactivity feedback characteristics and reactor period, will likely challenge its control system.



FIGURE 1. Effects of Hydrogen Corrosion on a Nuclear Thermal Propulsion Engine System.

For a given NTP reactor design with a particular set of operating conditions, duty cycle life-limiting effects such as residual stress buildup and/or low temperature hydriding of the carbide fuel, coupled with corrosion, can reduce the operational life of the system. (Koenig 1986, Finseth 1991, Taub 1975 and Lyon 1973). The release of NTP reactor fuel (fission products) into the atmosphere and surrounding ground test area is unacceptable from an environmental viewpoint. Thus, containment and collection of NTP system fission byproducts effluent requires that an effluent exhaust gas treatment system be used, increasing the complexity and cost of the test system.

U-Zr-C fuel material has been used in a number of fuel element designs for NTP reactor systems which are summarized in Table 1. A particular core fuel design can affect the local propellant (hydrogen) flow, material temperature, radiation flux, surface area-to-volume characteristics, size and mass of the reactor, and internal stress considerations. These inherit design traits interact in a highly-coupled, integrated manner with the many competing corrosion processes, on both a local (micro) and global (macro) scale.

The first fuel element design shown in Table 1 were developed and studied extensively during the Rover and NERVA programs (Clark et al. 1993, Finseth 1991, Taub 1975, and Lyon 1973). Typically, each fuel element contains 19 small, axial circular coolant channels. Fuel elements of this type were fabricated and tested with different U-Zr-C fuel designs and compositions. Figure 2 displays the principle fuel design examined in the Rover and NERVA programs. Uranium fuels in the past were embedded in: a graphite matrix in the form of UO<sub>2</sub> (not shown) or UC<sub>2</sub> particles as a continuous UC webbed dispersion, and as a U-Zr-C solid-solution. Development test reactor experience showed these types of fuel designs to be susceptible to hydrogen corrosion. Hydrogen corrosion was found to occur primarily in the small coolant channels, about the outer periphery of the fuel element, where hydrogen gas leakage was observed, and at the fuel element support cup region, (see Figure 2) (Koenig 1986, Finseth 1991, and Taub 1975). The graphite fuel elements associated with NRX-A6 reactor test of the NERVA program, were considered the most successful (Koenig 1986, Finseth 1991 and Taub 1975). The Nuclear Furnace-1 (NF-1) demonstrated better hot end corrosion than the graphite fuel elements previously tested in the Rover and NERVA program, but still exhibited a significant degree of mid-band (relatively low temperature) corrosion (Koenig 1986, Taub 1975 and Lyon 1973).

Because of the high chemical reactivity of carbon with hot hydrogen, numerous surface coating strategies were investigated. Much of the past Rover and NERVA program efforts in this area focused on the development of effective surface over coatings, to reduce the corrosion and corresponding degradation in structural integrity of the fuel elements and non nuclear reactor core components (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, Homan et al. 1991, Wagner 1992, and Wallace 1991). Monocarbides such as NbC and ZrC, as well as others, were considered as protective coating material candidates because of their stable interface (contact) adherence with graphite at high temperature, high eutectic temperature, relative resistance to attack by hydrogen at NTP reactor operation conditions, and low neutron cross-section (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, Homan et al. 1991, and Wallace 1991). Fabrication processing and quality control, thermal expansion compliance between the surface coating and the fuel form substrate, and the presence of initial surface micro-cracks were found to be the key factors which influenced the effectiveness of a coating to combat corrosion (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, Lyon 1973, Lyon 1973, Homan et al. 1991, Wallace 1991, and Kochka 1969).

TABLE 1.	Typical US Nuclear Thermal Propulsion Reactor Carbide Fuel Form Designs
	Considered in the Past.

FUEL FORM DESIGN	COMMENTS	HYDROGEN FLOW	REACTOR TYPE
	<ul> <li>Hexagoral shaped fuel element approximataly 0.025 m wide, 0.9 to 1.5 m in length. Each fuel element contains 19 small axial flow circular coolant charnels.</li> <li>Fuel elements are assembled to form fuel bundles which are held together in a tie-tube assembly.</li> <li>Development efforts focused on coated UC particle/graphite matrix fuel designs. Research on composition matrix and carbide solid-solution fuel designs was conducted.</li> </ul>	Axial	ROVER Test Reactors     NERVA Engine     Small Nuclear     Space Engine     NERVA-Derived     Reactors
BUTER BUTTRAM ALC SALICON BURGEL MERNEL BURTER HAS	<ul> <li>TRISO-type microsphere, 500 to 1000 µm diameter fuel particles. Fuel design approach derived from past terrestrial high temperature gas reactor effores.</li> <li>Battermal costing (NbC or ZrO combate corrosion contain gaseous fusion products.</li> <li>Advanced fuel designs considered uncludes ZrC, (U,Nb)C, NbC, and (U,Zr)C.</li> </ul>	Radia	<ul> <li>Perucie Bed</li> <li>Rotating Bed</li> </ul>
	<ul> <li>Spherical diameter fuel peliets, 6-10mm in diameter, encapsulates many TRISO type microspheres.</li> <li>Fuel design provides additional barrier(s) againal hydrogen corrosion, while improving its structural integrity.</li> </ul>	Radial	• Pellet Bed



EVOLUTIONARY DEVLEOPMENT (INCREASED TEMPERATURE AND/OR LIFE)

FIGURE 2. Types of Carbide Based Fuel Matrix Designs Previously Considered.

The NbC surface coating was first investigated in the Rover program because of their high eutectic temperature (-3575 K), which is approximatly 450 K higher than that of ZrC (-3123 K) (Taub 1975, Homan et al. 1991, and Wallace 1991). Early tests showed NbC coatings to have some problems associated with surface cracking and adherence with the graphite matrix fuel substrate (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, Homan et al. 1991, Wallace 1991, and Kochka 1969). Initial research on ZrC coatings were found to adhere better to the fuel substrate than NbC coating. Based on this experience ZrC coatings were incoporated in many fuel element designs in later Rover and NERVA test reactors and engine designs. Composite fuel elements for the NF-1 tests also employed ZrC surface coatings (Taub 1975, Lyon 1973). Even with the lower eutectic temperature associated with ZrC, these coatings were found to have good resistance to carbon diffusion at high temperatures (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, Homan et al. 1991, and Wallace 1991). Though fuel mass loss was shown to be reduced by using ZrC coatings, significant coatings surface cracking was still observed (Koenig 1986, Finseth 1991, Taub 1975, Lyon 1973, Homan et al. 1991, and Wallace 1991). The presence of these surface cracks in the coatings of fuel elements was primarily attributed to differences in the coefficients of thermal expansion (CTE) of the coating and fuel substrate materials. The CTE characteristics of some candidate fuel compositions and surface Rover and NERVA programs are summarized in Table 2. Additionally, factors such as the coatings considered. operational environment and duty cycle that a reactor core experiences, can also contribute to surface coating cracking.

MATERIAL	APPLICATION*	CTE (µm/m K) / TEMPERATURE (K)
Flour-Type Graphites	F	5.3 - 6.5 / 298 - 2273
Unfueled Graphite Extrusions	F	2 - 4 / 293 - 2273
NDC	Ç	6.6/
ZrC	Ç	7.7/
(U, Zr)C Composite Fuel Elements	F	6 - 7 / 293 - 2300
(U, Zr)C Carbide Fuel Elements	F	- 7.8 / 293 - 2273

 TABLE 2.
 Typical Coefficient of Thermal Expansion (CTE) Values of Candidate

 Nuclear Thermal Propulsion Fuel Materials (Taub 1975).

C = Coating, F = Fuel Substrate

Substantial interface surface stress mismatch(es), between the surface coating and the fuel substrate material, is possible due to creep of the two different materials at temperatures other than their deposition temperature (Taub 1975, Wallace 1991, Dobranich and El-Genk 1990, and Bernard et al. 1958). Table 3 summarizes many of the conting/fuel substrate surface integrity states which are possible as a carbide fuel material is thermally cycled. Typically, coating application temperatures ranged from 1473 to 1673 K (Taub 1975). CTE compliance will only occur at the temperature at which the coating material was applied, Tfc. At other temperatures residual surface stresses will likely be present. If the surface coating/fuel substrate temperature is less than Tfc, the coating is in tension relative to the fuel substrate, which eventually leads to surface coating cracks, as well as enhancing the propagation of cracks which were initially present. Conditions such as this are present after fuel element fabrication is completed, as well as during NTP engine system start-up and shut-down. This surface response will likely increase the rate of corrosion and decrease the structural integrity of graphite-based fuel elements. Conversely, when the surface coating/fuel substrate temperature is greater than Tfc, the coating is in compression relative to the fuel substrate. This surface condition, which typically occurs during NTP full power engine operation, tends to close up any surface cracks which were initially present, as well as structurally strengthen the coating. The surface coating when operated under such CTE compliance conditions, tends to be highly effective in minimizing the effect of hydrogen corrosion.

Experience from the Rover and NERVA programs, based on room temperature observations, showed that it was almost unpossible to fabricate fuel elements which were crack free, because of the CTE interface compliance issue (Taub 1975). Typically, surface coating micro-cracks were present on newly fabricated fuel elements. Only in rare instances was it possible to produce fuel elements which had surface coatings that were essentially crack free. This condition was found to occur only when the fuel substrate's CTE matched that of the coating. In general, the coating's CTE was shown to be highly dependent on it's carbon-to-metal ratio, as well as the impurity content (Taub 1975).

To address the issues of surface coating cracking and its corresponding influence on corrosion, two surface coating strategies were examined in the Rover and NERVA programs (Koenig 1986 and Taub 1975). One approach studied the use of a Mo coating which was applied over ZrC coated fuel element coolant channels in





the lorward (low temperature) fuel element region. Overall surface coating strength was increased in this region of the luel element, where the surface coating is under high tension due to a CTE interface mismatch. This coating design approach was tested in a Rover Phoebes reactor and in NERVA development test reactors. Results showed the Mo outer coatings reduced the presence of surface cracks, increased the structural integrity of the fuel element and reduced fuel mass loss (Koenig 1986 and Taub 1975). The Mo-ZrC coating approach was baselined for the NERVA light engine reactor design which used a carbide particle matrix composition (Koenig 1986). The other coating strategy investigated focused on developing a fuel element which minimized and/or eliminated any difference in the CTE between the substrate and the coating (Koenig 1986 and Taub 1975). Near the end of the Rover program, fuel elements which exhibited such physical characteristics were fabricated, but were never tested in a reactor due to the termination of the program.

Flow instabilities, as well as substantial levels of nonuniform mechanical and thermal loading were also observed to be present in Rover type fuel designs (Koenig 1986 and Finseth 1991). On the positive side, this type of fuel design exhibited a rather low surface area-to-volume ratio which tends to reduce the overall effect of corrosion on the operation of the NTP engine system. Much of the fuel technology and experience base gained from the Rover and NERVA programs has applicability to the fundamental understanding and development of other emerging NTP reactor concepts.

The use of small microsphere fuel particles has also been considered for a number of packed bed NTP reactor concepts (Clark et al. 1993, Botts et al. 1983, and El-Genk et al. 1993). Typically these particles, shown in Table 1, are approximately 500 to 1000  $\mu$ m in diameter and are composed of an inner fuel kernel made up of UC<sub>x</sub>/ZrC or UC<sub>x</sub>/NbC hydrogen corrosion resistant materials which are multicoated with high strength, high temperature over coatings such as porous carbon, pyrolytic carbon, and ZrC. These particles are designed to withstand the internal pressure buildup due to fission gas (mostly Xe and Kr) production, as well as to withstand the reactor core environment. Such small particles possess a high surface area-to-volume ratio, which can enable operation at high power densities, but at the expense of rapid mass loss by hydrogen corrosion (Storms 1991 and Clark et al. 1993).

Another carbide fuel form design that has been examined in the past is the fuel pellet (Clark et al. 1993 and El-Genk et al. 1993). The fuel pellet, shown in Table 1, is typically 5 to 10 mm in diameter, which is made up of many UC-ZrC or UC-NbC fuel, TRISO-type, microspheres, and has an over coat of ZrC or NbC, respectively. This fuel particles are then encapsulated in a ZrC matrix which is also coated with an additional layer of ZrC to provide additional protection against hydrogen corrosion. The fuel pellet design provides a more uniform temperature distribution, avoids high contact point stresses between microspheres, offers multiple structural barriers to ensure full lission product retention, and provides high resistance to corrosion by hydrogen. Packed bed reactor concepts that use this tuel form typically exhibit a medium fuel surface area-to-volume ratio, and produce reactor power densities (2-4 MW/liter) that are greater than those demonstrated in the Rover and NERVA programs. Because of the substantially lower surface-to-volume ratio of these pellets, they would exhibit substantially less fuel mass loss by corrosion than in a particle bed reactor.

The development test reactors, the NERVA, and Small Nuclear Space Engine flight designs, all used fuel elements that were based on the coated-particle matrix design (Figure 2) (Koenig 1986). Tests results showed that fuel mass loss and mechanical degradation were major development issues and the potential of increasing the reactor operating temperature was marginal. Hence, The composite matrix and solid-solution fuel designs were pursued (Figure 2) during the later portion of the Rover program. These fuel designs have the potential to operate at higher temperatures, as well as being more resistant to hydrogen corrosion than coated-particle designs. The high temperature potential of a solid-solution fuel composition can be understood by examining a pseudo-binary phase diagram of such a carbide material,  $(U_{0,1}, Zr_{0,9})C_x$ , which is displayed in Figure 3 (Lyon 1973). With in a small carbon atom ratio range (~0.92 to 0.96), material temperatures greater than 3100 K are possible. Conversely, Figure 3 shows that the melting point of  $(U_{0,1}, Zr_{0,9})C_x$  is sensitive to a change in carbon content, which could vary during operation if hydrogen corrosion takes place. By increasing interspersion of the fuel into the graphite matrix a closely packed webbed type structure is produced (Figure 2), the propagation of cracks can be limited. Limited development testing of these alternative fuel designs were performed in the Nuclear Furnace research reactor. Based on these limited results for modest NTP operation life, these alternative fuel compositions could likely operate at reactor gas temperatures  $\ge$  2700 K for the composite design and  $\ge$  2900 K for the  $\therefore$  slid-tolution design (Taub 1975). Operating temperatures for these advanced fuel designs can be compared to the coated-particle matrix fuel which operate up to a maximum gas temperature of 2500 K. These temperatures are also a few hundred degrees higher than that associated with coated fuel microspheres. The increased operating temperature capability of these advanced fuel designs can translate into increased NTP engine system performance, design margin (reliability and safety) and/or life

A comparison of the mass loss rate, as a function of fuel element axial position, for Pewee-1 graphite and NF-1 composite test reactor elements are displayed in Figure 4 (Lyon 1973). Figure 4 shows the average mass loss rate as a function of coolant channel position for (A) 102 Pewee-1 graphite fuel elements coated with NbC, (B) 12 Pewee-1 graphite fuel elements coated with ZrC, and (C) 23 NF-1 composite fuel elements coated with ZrC. The data has

been adjusted to take into account the differences in operating temperatures between the 2 reactors. The Pewee-1 fuel elements had coolant channel surfaces which were coated with either NbC or ZrC, while the NF-1 test composite tuel was coated with ZrC. Peak mass loss rates in the mid-band corrosion region, (at low temperature) for the composite fuel element were 13 to 17 percent lower, depending on the Pewee-1 fuel element design considered. The high mass loss rates observed in the low temperature region have been attributed to the presence of initial surface coating cracks and the difference in CTE's of the coating and the fuel substrate materials. The reduction in observed mass loss rate downstream of the peak rate region (at higher fuel temperature) indicates that the differential in the CTE of the coating and the fuel substrate materials are such that the surface coating is in compression relative to the fuel substrate. This condition tends to close surface cracks which are potential corrosion sites. Likewise, the corrosion byproducts, such as CH4 and C2H2, in the hydrogen coolant gas stream, the deposite of these byproducts on the coolant channel surface, as well as the shifting surface composition, can reduce the chemical driving potential for corrosion (Koenig 1986, Taub 1975, Wallace 1991, MacMillan 1991, Storms 1992 and Butt 1992).

Composite fuel element mass loss rates at the hotter, downstream axial element positions are also substantially lower than those typical for the Pewee-1 elements (Figure 4). Mass loss observed in the high temperature regions is dominated by the vaporization of it's elemental material constitutes (Koenig 1986, Taub 1975, Wallace 1991, MacMillan 1991, Storms 1992 and Butt 1992). Like the mid-band corrosion region, surface coating integrity, and the chemical composition of the coolant gas and the fuel surface, are major factors which influence the corrosion process in this region



FIGURE 3. Pseudo-binary Phase Diagram of  $(U_{0,1}, Zr_{0,9})C_X$  (Lyon 1973).



It was fuel mass loss observations like those just discussed, throughout the Rover and NERVA programs, which indicated to the scientist and engineers at the time that the hydrogen corrosion process associated with NTP reactor fuels is highly complex and is difficult to quantify fully from a fundamental viewpoint. In addition to the complex chemical corrosion processes inherent with a carbide/hot hydrogen gas system, other physical/mechanical processes such as fuel/material design and fabrication, nuclear radiation exposure, and local coolant flow conditions, can greatly influence the corrosion processes (and corresponding fuel mass loss). Because of the many highly interrelated, complex physical processes and mechanical design features which influence the corrosion of NTP carbide systems, accurate fundamental modeling of the overall process is a major challenge, especially for coated fuel designs. The availability of relevant experimental data to benchmark corrosion model(s) is limited (Table 4). It should be noted that this data base summarized in Table 4, is based principally on open literature on the United State's (US) past experience. The University of New Mexico plans on continuing this effort by augmenting this data base with the Russian experience. A joint research and development effort between UNM-ISNPS and the Russian Research and Development Institute of Power Engineering (RDIPE) was initiated in the Fall of 1993. Results from this joint effort will be reported at a later date.

Subscale thermochemical, arcjet, and heated tube, single-effects experiments (Table 4) provide data on one or more fundamental aspects of the hydrogen corrosion process with carbide materials. Many of these experiments were conducted at test (exposure) conditions less demanding than those typically encountered in an operational NTP reactor, but were well controlled. This data is valuable, but lacks quantitative insight into some of the fundamental competing (highly coupled) processes associated with hydrogen corrosion. Also, scaling laws for applying these tests results to operational NTP reactor conditions have not been developed. This would be a difficult task because of the complexity (and coupling) of the many corrosion processes at work. Thus, the usefullness of this data to benchmark corrosion models is highly uncertain, but would likely be used as a surting point for future modeling efforts.

The data base associated with past research and engine reactor tests contains a wealth of information, but is of a qualitative nature (Koenig 1986, Finseth 1991 and Taub 1975). Many of the qualitative observations pertaining to fuel corrosion and integrity from the prototype engine reactor tests are summarized in Table 5. Because these tests were performed with NTP reactors, at true operational conditions, instrumentation measurements, and independent control of reactor parameters were limited. Much of this experimental data base is of little use for initial corrosion model verification, because single cause and effects corresponding to a particular corrosion process is difficult to deduce. The data associated with the NF-1 test is believed to be the best quantitative data available on hydrogen corresion and structural performance of NTP fuels at true operational conditions (Taub 1975 and Lyon 1973). Unfortunately this data base is limited in terms of quantity.

CATEGORY	REFERENCES
Research Reactor/Prototype Engine Reactor Tests • Rover and NERVA Programs	Finseth (1991) <sup>*</sup> , Koenig (1986) <sup>*</sup> , Lyon (1973) <sup>*</sup> , Taub (1975) <sup>*</sup> , Wagner (1992) <sup>*</sup> .
Subscale Hydrogen/Carbide Material Experiments Primarily Based on Arcjet and Heated Tube Experiments (Part of the Rover Program)	Burghardt (1965) <sup>*</sup> (1965) <sup>*</sup> , Juveland et al. (1963), MacMillan (1991) <sup>*</sup> o (1975) <sup>*</sup> , Wagner (1992) <sup>*</sup> .
Supporting Physical Fundamental Properties of Carbide and Related Materials • Phase States • Vaporization • Diffusion • Thermal Conductivity • Coefficient of Thermal Expansion • Creep	Andrievski et al. 969), Butt (1992), Butt et al. (1993), Fedrov etal. (1972), Fries (1962), Green (1959), Kempter et al. (1960), Lyon (1973)*, Nikol'akaya et al. (1968), Samsonov (1974), Santandrea (1993), Storms (1967, 1992), Storms et al. (1969, 1973a, 1973b, 1973c), Tobin et al. (1965), Wallace (1991), Wallace et al. (1993).
Effects of Radiation of Carbide and Related Materials Primarily Based on the Radiation Effects of Graphite Material Property Behavior of Fission Products Included	Bokor et al. (1991), Childs et al. (1963a, 1963b), Dahl et al. (1965), Dahl (1966), Davidson et al. (1965, 1966), Degal'tev et al. (1987), Freas et al. (1961), Hunter (1959), Lyon (1973), Nightingale (1962, 1964), Roberston (1969), Rossmer et al. (1967)*, Sayers et al. (1963), Simmons et al. (1965), Taylor et al. (1969), Taub (1975)*.
<ul> <li>Hydrogen Reaction Kinetics</li> <li>Almost All Work Has Focus on the Hydrogen-Carbon Chemical Reaction System</li> </ul>	Burghardt (1965) <sup>*</sup> , Chi (1965) <sup>*</sup> , Chi et al. (1968) <sup>*</sup> , Clarke et al. (1967), Krakowski et al. (1968), Rodgera et al. (1986) <sup>*</sup> , Sanders (1965).

TABLE 4. Sources of Supporting Data and Literature Related to Hydrogen Corrosion of Carbides.

\*Highly Applicable to Hydrogen Corrosion of Carbides for Nuclear Thermal Propulsion Applications.

Past work on the behavior of fissior products in carbide NTP fuels provides some useful insight into issues perlaining to fuel material integrity, solid-solution molecular processes and potential hydrogen corrosion mechanisms (Roesmer et al. 1967 and Bokor et al. 1991). Fundamental out-of-pile (non nuclear) corrosion reaction data is also available on related material systems, such as hot hydrogen with carbon or graphite materials (Table 4). Some of this work (Chi 1965, Chi and Landahl 1968, Burghardt 1965, and Rogers and Sesonske 1986) was performed at the high pressures and temperatures of interest to NTP reactor systems. In-depth characterization of carbon-hydrogen chemical reaction systems is critical to the fundamental understanding and modeling of the hydrogen corrosion process. Additionally, general reactor fuel technology data in the areas of nuclear radiation effects on similar materials, basic fuel form designs that incorporate materials such as uranium carbide, carbon, graphite, and high temoerature gas reactor fuel designs, is available (Table 4). These sources of supporting fundamental data provides meaningful insight on many of the competing physical processes which must be considered in the formulation and validation of future carbide hydrogen corrosion modeling effort(s).

ТҮРЕ	OBSERVATIONS
	• In NERVA Program: 1.0 to 0.2 g/minute per Fuel Element.
Fuel Mass Loss	• Mass loss of 0.2 g/minute per Fuel Element Achieved at the End of the NERVA Frogram.
	<ul> <li>Fundamental Understanding on the Impact of Fuel Design on Corrosion Was Lacking.</li> </ul>
	<ul> <li>Substantial Cracking/Desintegration Coating the Low to Medium Temperature (Mid-Axial Element Positions) and Hot End Regions.</li> </ul>
Structural/Material Integrity	<ul> <li>Substantial Fuel Element Coolant Channel Surface Cracking.</li> </ul>
	<ul> <li>Thermal Conductivity Change: Measured in the High Radiation Flux (Mid-Axial Element Position) Region.</li> </ul>

TABLE 5. General Past Engine System Testing Observations from Post-Test Inspections.

Another major outstanding technical issue identified in the review addresses the value of non-nuclear carbide material/hydrogen compatibility testing. This issue could have a major potential impact on material compatibility testing complexity and cost. It was the consensus of a forum of international technical specialists in this area that the question of nuclear versus non-nuclear material compatibility testing is still an important, open ended issue. They also stated that even if non-nuclear material compatibility tests are considered valid, the method of heating the test sample, typically induction or ohmic heating, has produced conflicting results in the past (D'yakov 1993 and Taub 1975). Such conflicting results are likely due to the difference in the thermal gradients prduced in a given material from the induction and ohmic heating methods. It is recommended that a simple, small scale experiments be performed at conditions close to those associated with NTP reactors to address this critical research testing issue. These experiments could give valuable insight into scaling non-nuclear test data to realistic NTP reactor environmental conditions, if it is possible at all.

## **CONCLUSIONS**

Based on the initial findings of this review, it is recommended that future efforts focus on: (1) developing a corrosion model that includes all major interrelated physical process mechanisms, previously discussed, even if they are only included on a first-principle level basis, (2) acquiring fundamental single effect(s) data at rea<sup>11</sup>er<sup>1</sup>. NTP reactor operational conditions, and (3) determining the validity of non-nuclear experimental results to the characterization of carbide material compatibility with hydrogen in NTP reactors. The first recommendation would provide guidance and direction to the proposed fundamental data gathering experimental program in Item 2. Insight from such an effort would likely minimize the investment required to support such a test program. The experimental program, in addition to providing data to benchmark corrosion models, will contribute greatly to the understanding of the complex hydrogen corrosion phenomena. The non-nuclear testing issue has been identified as a separate, near-term item because of its potential impact on testing complexity and cost.

A starting point for any new modeling effort should include initial corrosion process scoping analysis that addresses critical issues in parametric fashion. Possible issues to be addressed include areas such as the rate of corrosion and surface cracking, and surface coating crack development and propagation if coated fuel designs are considered. Initial modeling efforts should also focus on solid-solution U-Zr-C fuel designs because of their simplicity compared to coated fuel designs. As future modeling efforts evolve more competing interrelated physical process mechanisms and capabilities to analyze complex fuel designs should be incorporated into the model.

Once an accurate corrosion model is developed and verified, it could be integrated into the initial NTP engine system design process. The investment required to produce a robust, accurate corrosion model and corresponding optimization design capability will likely pay for itself many times over in terms of NTP engine system safety, reliability, and low development cost.

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