

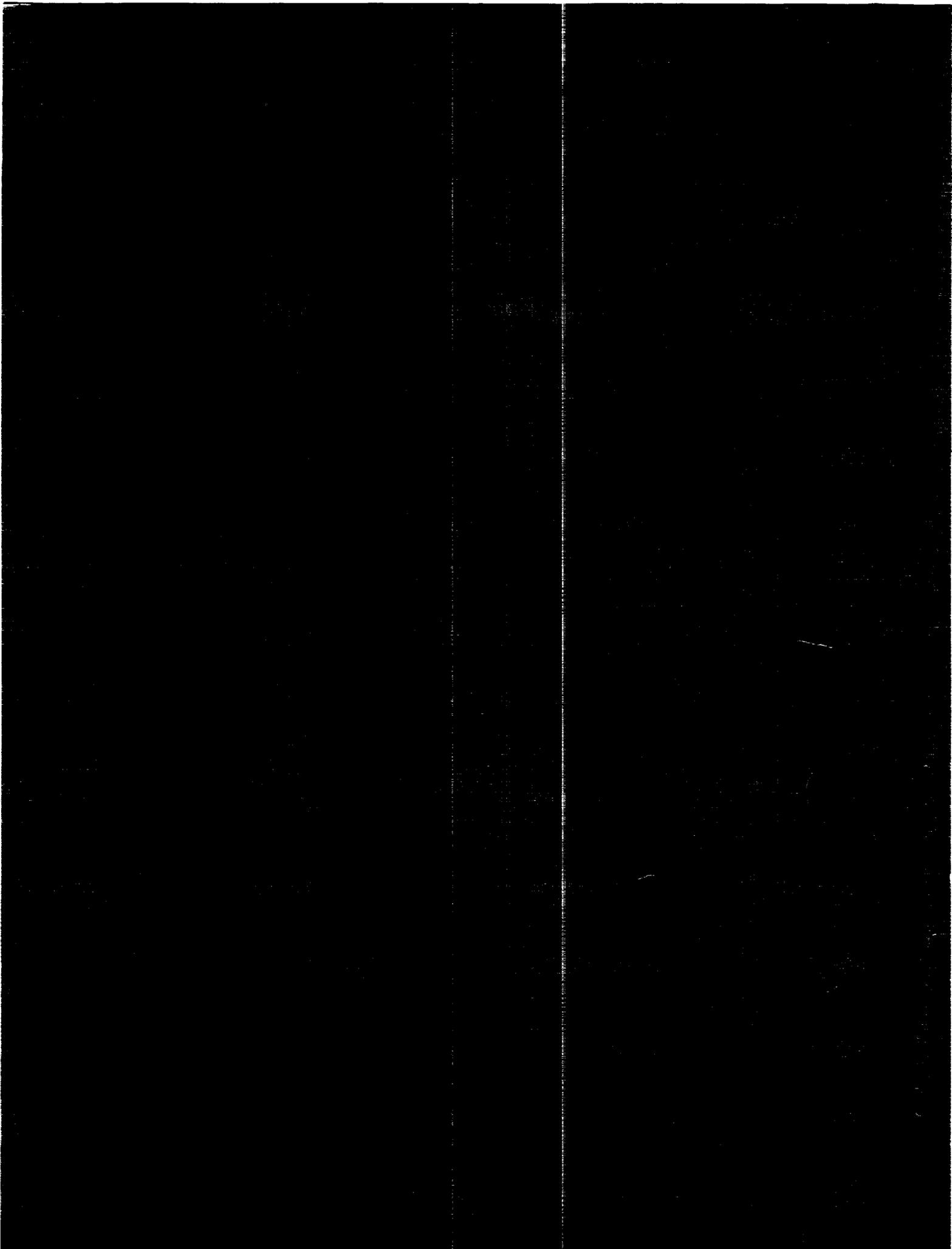
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(NASA-CR-197533) A REVIEW OF  
NUCLEAR THERMAL PROPULSION CARBIDE  
FUEL CORROSION AND KEY ISSUES Final  
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## ABSTRACT

Corrosion (mass loss) of carbide nuclear fuels due to their exposure to hot hydrogen in nuclear thermal propulsion engine systems greatly impacts the performance, thrust-to-weight and life of such systems. This report provides an overview of key issues and processes associated with the corrosion of carbide materials. Additionally, past pertinent development reactor test observations, as well as related experimental work and analysis modeling efforts are reviewed. At the conclusion, recommendations are presented, which provide the foundation for future corrosion modeling and verification efforts.



## ACKNOWLEDGMENTS

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## 1.0 INTRODUCTION

Nuclear Thermal Propulsion (NTP) engine systems are attractive options for orbit transfer and planetary exploration applications because of their high performance.<sup>1-3</sup> They typically exhibit a specific impulse ( $> 800$  lbf-sec/lbm or  $7840$  N-sec/kg) over twice that associated with chemical propulsion systems. To achieve such a high performance level, hydrogen is used as the NTP engine system working fluid propellant because of its low molecular weight. Hydrogen at pressure is heated in an NTP nuclear reactor to high temperature before it is expanded through a supersonic nozzle to create thrust.

Hydrogen temperatures and pressures in a NTP reactor chamber are typically greater than  $2500$  K and  $3$  MPa, respectively. Since NTP engine system specific impulse is directly proportional to the reactor chamber temperature, engine systems that operate at chamber temperatures in the range of  $3000$  K or greater, are of great interest today because they reduce overall mission launch (infrastructure) weight requirements and corresponding cost.<sup>1-5</sup> Additionally, to minimize mass, which is a key consideration in any space system design, NTP reactors operate at high power densities. Power densities of up to  $2.7$  MW/liter have been demonstrated, while next generation solid-core reactor concepts could operate at power densities greater than  $10$  MW/liter for a single burn, short operation time applications.<sup>4,5</sup> Operating at these high power densities produces a high radiation flux environment in the reactor core. To meet this engineering challenge, Uranium-Zirconium-Carbon (U-Zr-C) and Uranium-Niobium-Carbon (U-Nb-C) material systems have been considered for such applications.<sup>4-11</sup> The exposure to high nuclear radiation, plus the high temperature and pressure, provide an extremely hostile environment for NTP reactor core materials. Carbide material systems are considered in NTP reactors due to their favorable nuclear properties (relatively small absorption nuclear cross-section(s)), high melting point, thermal stability, low volatility, high moderation ratio, high fuel fraction and low density ( $<10$  g/cm<sup>3</sup>).<sup>12</sup>

At the operation conditions of interest in NTP reactors, carbide materials have been known to exhibit a number of life limiting phenomena.<sup>4,6-8,11,12</sup> These include the formation of liquid, loss by vaporization, creep and local corrosion. Substantial fuel structure degradation and/or mass loss can result from these material interaction phenomena. The high chemical reactivity (corrosion) of carbon when exposed to hot hydrogen was well known at the start of the NTP development program in the early 1960's.<sup>4,6-8,11,12</sup> Thus, many of the NTP fuel designs pursued have incorporated high temperature, corrosion resistant coatings, such as ZrC, NbC, TiC and Mo thin surface coatings.<sup>4,6-8,11,12</sup> The integrity of these complex fuel designs have been challenged by many of the combined (coupled) effect of reactor environmental and design

operational factors such as excessive mechanical and/or thermal loading and nuclear radiation exposure.<sup>4,6-8,11</sup> The high radiation environment associated with NTP reactor operation was found to produce a substantial change in local physical properties of the fuel materials, and high thermal stresses that contributed to the stress fracturing (cracking) of the surface coating and/or the fuel form. Such observations were initially considered surprising because of the low reactor burnup which is typical of NTP system operation.<sup>4,6-8,11</sup> It has also been observed that time-temperature history and cyclic operation of the nuclear reactor can accelerate many of these processes.<sup>4,6-8,11</sup>

Degradation of the nuclear 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<sup>4,6-8,11</sup>. Of most concern was the core material mass loss associated with 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 at 60 minutes life vs. 3200 K), and accounted for a large percentage of the core material loss during operation. This highly complex phenomena encompassing many of the life-limiting processes previously discussed, made engineering solutions to correct this 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.

The University of New Mexico's Institute for Space Nuclear Power Studies (ISNPS), under NASA sponsorship, has recently conducted a study to examine the complicated hydrogen corrosion process. As part of this effort, an extensive review of relevant past work in the open literature was performed. The results of this review are presented in this report. Additionally, this report provides detailed insight into the hydrogen/carbide corrosion issue associated with NTP reactor systems and its impact on the engine system design. Much of the discussion focuses on the design and corrosion issues of U-Zr-C material fuel systems for NTP reactor applications, but it is also considered relevant to other related high temperature carbide material systems.

In this report the competing physical processes associated with the hydrogen corrosion of carbides are discussed in some detail. The thermodynamics of carbide are addressed, to provide greater insight into carbide material physical states and properties, its operation limitations, as well as the reaction kinetics of carbides in flowing hot hydrogen. Past carbide hydrogen corrosion research experiments are reviewed to provide insight of the applicability of the present database to realistic NTP reactor conditions, and benchmark verify current and future corrosion model(s). The state-of-the-art (SOA) modeling (prediction) of hydrogen corrosion of carbide material systems is

addressed to establish the requirements for further research work in this area. The report then presents a discussion on how to design, with the use of an accurate corrosion model, future NTP reactor systems that can be optimized in terms of performance, weight, and lifetime. Future proposed areas of research associated with carbide/hydrogen corrosion modeling is presented at the conclusion of the report.



## 2.0 HYDROGEN CORROSION ISSUE

The hydrogen corrosion phenomena of carbide fuels considered for NTP reactors are highly complex, and greatly impacts the design, development, operations, performance and life of such systems. The following discussion highlights the influence hydrogen corrosion has on the design and operation of an NTP engine system. Key NTP development test reactor observations and technology/design issues are discussed. Relevant past fundamental process experimental and corrosion modeling efforts are identified and qualitatively assessed in terms of their applicability to support future corrosion modeling development efforts. The remaining discussion in this section identifies the major physical processes associated with hydrogen corrosion of NTP fuels and their complex interrelationships. This global understanding of the NTP fuel corrosion process is of critical important in assessing the limitations of current models, as well as to identify the overall direction and requirements of future modeling development efforts.

### 2.1 Background

Corrosion has a major impact on NTP engine system design, development, and operation, as shown in Figure 1. These impact areas are: 1.) specific impulse; 2.) engine system thrust-to-weight ratio; 3.) reactor control; 4.) operational life, and/or duty cycle; and 5.) ground development 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 substantially less (~2400 K) than their melting points (>3200 K). The reactor exit (chamber) temperature has a substantial impact on overall engine system performance, as shown in Figure 2. An increase in chamber temperature increases the engine specific impulse. Thus, as the propellant exit temperature increases, mission propellant mass and support (launch system) infrastructure requirements decrease. This correspondingly reduces 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 material and its reaction byproducts. The thrust-to-weight ratio of the engine system can be affected by hydrogen corrosion in two ways. One effect is by increasing the initial reactor core mass, to compensate for mass loss during its operation lifetime. Thus, the engine system thrust-to-weight ratio is less than that of a system that has had no corrosion. Secondly, due to corrosion, the specific energy density of the reactor, can be limited to meet a given operational lifetime and/or

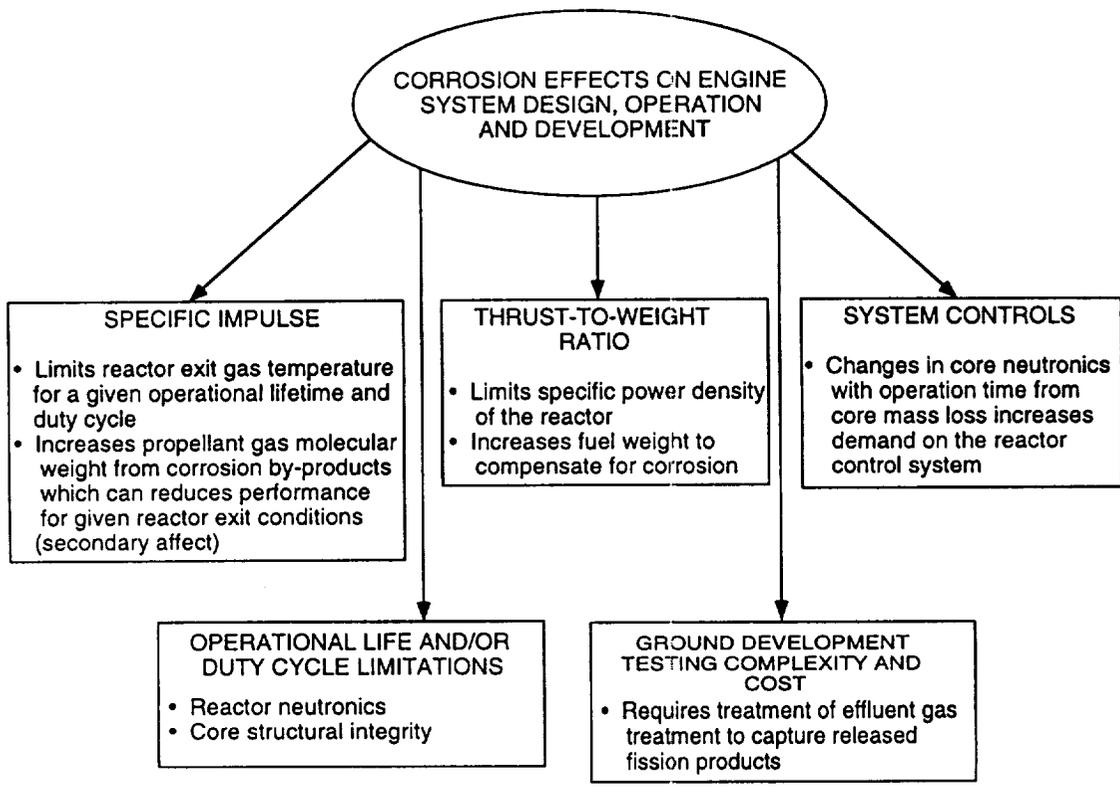


Figure 1. Effects of Hydrogen Corrosion on a Nuclear Thermal Propulsion Engine System.

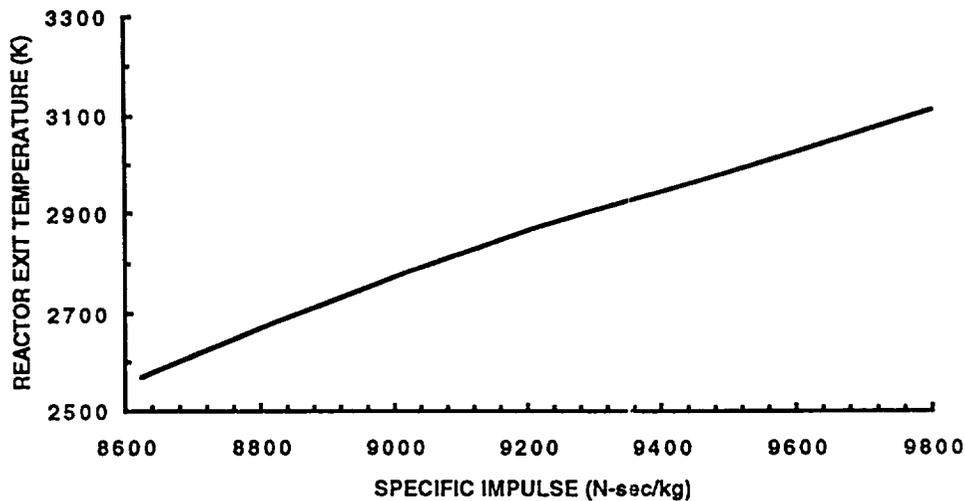


Figure 2. The Effect of Reactor Exit Temperature on Engine System Performance; High Pressure Hydrogen Expanded Through a 100:1 Area Nozzle (Gas Kinetics, Divergence and Boundary Layer Losses are Included).

duty cycle, which also limits the thrust-to-weight ratio of the engine system. The relationship between power density and area-to-volume ratio of the core greatly influences engine system life, for a given fuel design.

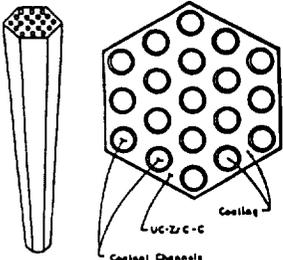
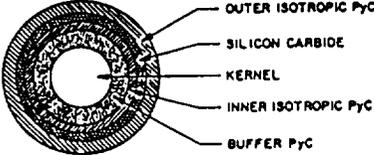
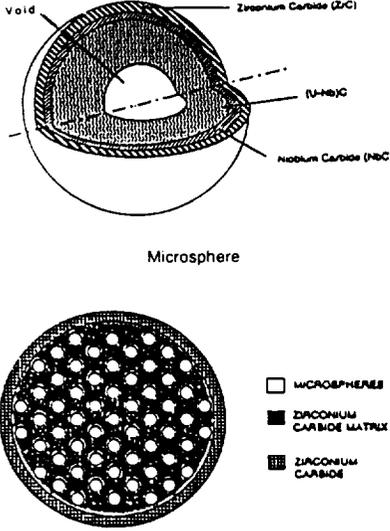
Mass loss of the reactor core fuel by corrosion also affects the reactor control as operation time increases.<sup>4,7</sup> This effect increases the demand (adaptive response) of the reactor control system which can reduce the reliability and safety of the NTP engine system. The reactor core neutronics will change as a function of operating time. Parasitic absorption and scattering changes within the core as 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.

For a given NTP reactor design with a particular set of operating conditions, corrosion can limit the overall engine system operational life and/or duty cycle. 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.<sup>4,6-8</sup> Corrosion also has a major influence on NTP reactor fuel and engine system development testing, complexity, and cost. 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 is required. This dictates that an effluent exhaust gas treatment system be used, increasing the complexity and cost of the test system.

U-Zr-C fuel materials have been used in a number of NTP reactor system fuel element (form) designs. These fuel designs are summarized in Table 1. It is important to understand the fuel form and the design of its matrix material composition. A particular core fuel design can affect the local propellant (hydrogen) flow, material temperature, radiation flux, surface area-to-volume characteristics, 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 was developed and studied extensively during the Rover and NERVA programs. These fuel element forms are hexagonally shaped, approximately 2.5 centimeters wide and 0.9 to 1.5 meters in length.<sup>5-8</sup> 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 3 displayed the principle fuel design examined in the Rover and NERVA programs. Uranium fuels in the past

Table 1. Typical US Nuclear Thermal Propulsion Reactor Carbide Fuel Form Design Considered in the Past

FUEL FORM DESIGN	COMMENTS	HYDROGEN FLOW	REACTOR TYPE
	<ul style="list-style-type: none"> <li>Hexagonal shaped fuel element approximately 0.025 m wide, 0.9 to 1.5 m in length. Each fuel element contains 19 small axial flow circular coolant channels.</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	<ul style="list-style-type: none"> <li>ROVER Test Reactors</li> <li>NERVA Engine</li> <li>Small Nuclear Space Engine</li> <li>NERVA-Derived Reactors</li> </ul>
	<ul style="list-style-type: none"> <li>TRISO-type microsphere, 500 to 1000 <math>\mu\text{m}</math> diameter fuel particles. Fuel design approach derived from past terrestrial high temperature gas reactor efforts.</li> <li>External coating (NbC or ZrC) combats corrosion contain gaseous fission products.</li> <li>Advanced fuel designs considered includes ZrC, (U,Nb)C, NbC, and (U,Zr)C.</li> </ul>	Radial	<ul style="list-style-type: none"> <li>Particle Bed</li> <li>Rotating Bed</li> </ul>
	<ul style="list-style-type: none"> <li>Spherical diameter fuel pellets, 6-10 mm in diameter, encapsulates many microspheres.</li> <li>Fuel design provides additional barrier(s) against hydrogen corrosion, while improving its structural integrity.</li> </ul>	Radial	<ul style="list-style-type: none"> <li>Pellet Bed</li> </ul>

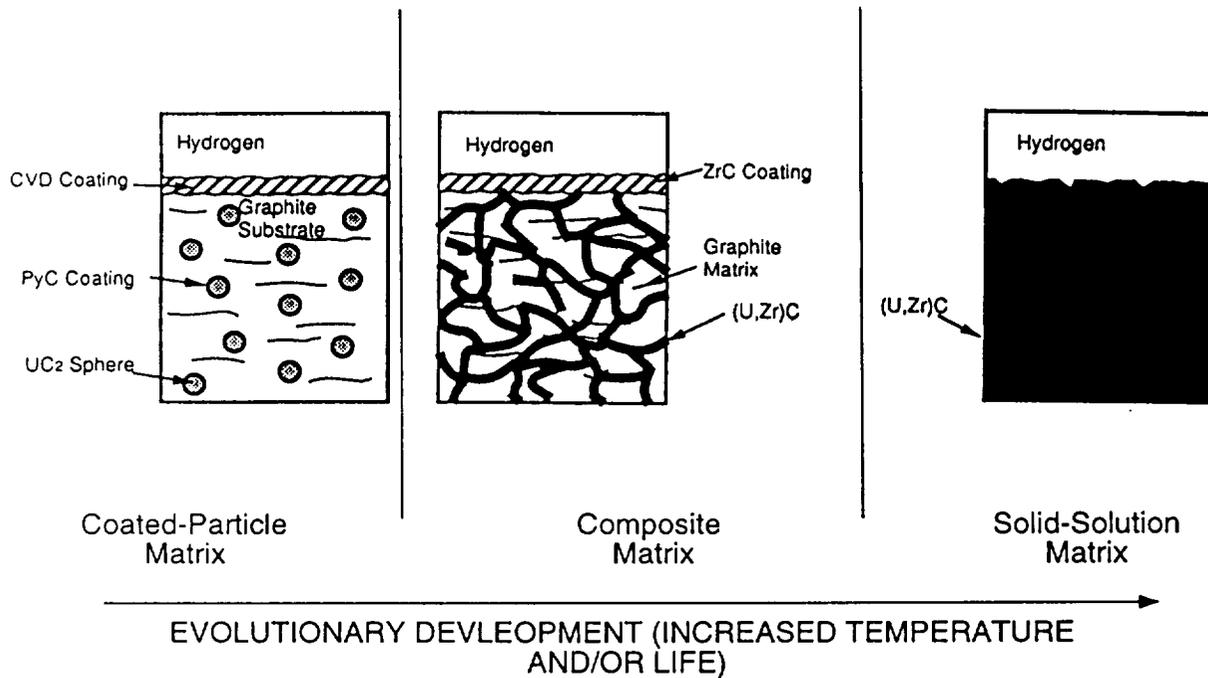


Figure 3. Types of Carbide Based Fuel Matrix Designs Previously Considered.

were embedded in: a graphite matrix in the form of  $\text{UO}_2$  (not shown) or  $\text{UC}_2$  particles, as a continuous UC webbed dispersion, and as a U-Zr-C solid solution. Development test reactor experience showed these fuel designs to be susceptible to hydrogen corrosion. Hydrogen corrosion was found to occur primarily in the small fuel element coolant channels; about the outer periphery of the fuel element, where leakage of hydrogen gas was observed; and at the fuel element support cup region, (see Figure 3).<sup>4,6,7</sup> Table 2 provides some key reference points from this past fuel element development experience. The graphite fuel elements associated with NRX-A6 reactor test of the NERVA program, were considered the most successful which was conducted near the conclusion of the program.<sup>4,6,7</sup> The Nuclear Furnace-1 (NF-1) test fuel elements demonstrated better hot end corrosion than the graphite fuel elements previously tested in the Rover and NERVA program, but they still exhibited a significant degree of mid-band (relatively low temperature) corrosion.<sup>4,7,8</sup>

Because of the high chemical reactivity of carbon, which is a principle element of a carbide material system, 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

Table 2. Key Past Fuel Mass Loss Reference Points<sup>4,7,8 and 15</sup>

REACTOR TEST	FUEL EXIT TEMP. (K)	TIME (min)	CYCLES	TOTAL LOSS (g)	MID-BAND (g)	HOT END (g)	PERCENT LOSS (MID-BAND) (%)
NF-1 *	2444	108.8	4	13.7	8.6	5.1	63
NRX-A6 **	2556	62.7	1	12.8	2.3	10.5	18
NRX-XI **	2450	10.3	28	7.3	0.6	6.7	8

\* Replacement composite fuel elements with crack free ZrC coating

\*\* Graphite fuel elements with NbC coating and Mo overcoat

effective NbC, ZrC and/or Mo surface over coatings, to reduce the corrosion and corresponding degradation in structural integrity of the fuel elements and non nuclear reactor core components.<sup>4,6-8,11,17,18</sup> 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; their relative resistance to attack by hydrogen at NTP reactor operation conditions; and low neutron cross-section.<sup>4,6-8,11,18</sup> 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.<sup>4,6-8,11,18,19</sup>

NbC surface coatings were first investigated early in the Rover program because of their high eutectic temperature. The eutectic temperature of NbC (~3575 K) is approximately 450 K higher than ZrC (~3123 K).<sup>7,11,18</sup> Early tests showed NbC coatings to have some problems associated with surface cracking and adherence with the graphite matrix fuel substrate.<sup>4,6-8,11,18,19</sup> Initial research on ZrC coatings were found to adhere better to the fuel substrate than NbC. ZrC coatings were incorporated in many fuel element designs associated with later Rover and NERVA program test reactors and engine designs. Composite fuel elements for the NF-1 tests also employed ZrC surface coatings.<sup>7,8</sup> Even with the lower eutectic temperature associated with ZrC, like NbC, was found to have good resistance to carbon diffusion at high temperatures.<sup>4,6-8,11,18</sup> Though, fuel mass loss was shown to be reduced by using ZrC fuel element coatings, significant coatings surface cracking was still observed.<sup>4,6-8,11,18</sup> The presence of these surface cracks with the ZrC fuel elements, as well as with the NbC coated fuel elements, were primarily attributed to the difference in the coefficient of thermal expansion (CTE) between the coating and fuel substrate materials, and the operation environment and duty cycle the reactor core experiences.<sup>4,6-8,11,18</sup> The CTE characteristics of some candidate fuel compositions and surface coatings considered in

the Rover and NERVA programs are summarized in Table 3.

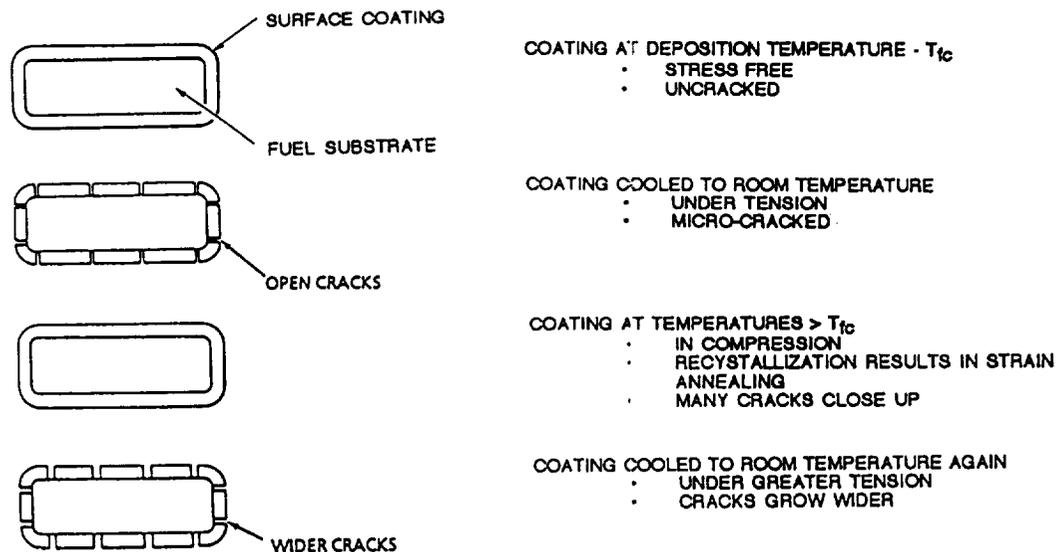
These factors can produce substantial interface surface stress mismatch(es) between the surface coating and the fuel substrate material is due to creep of the two different materials at temperatures other than their deposition temperature.<sup>7,18,20,21</sup> Table 4 summarizes many of the coating/fuel substrate surface integrity states which are possible as a carbide fuel material is thermally cycled. Typically, coating fabrication application temperatures ranged from 1473 to 1673 K.<sup>7</sup> CTE compliance will only occur at the temperature at which the coating material was applied to the fuel substrate during fabrication. At temperatures other than the coating fabrication compliance temperature,  $T_{fc}$ , residue surface stresses will be present. If the surface coating/fuel substrate temperature is less than  $T_{fc}$ , the coating is in tension relative to the fuel substrate. Such a condition can make the surface coating crack, as well as enhance the propagation of cracks which were initially present. This surface response will likely increase the rate of corrosion and decrease the structural integrity of the fuel element. When the opposite is true, the surface coating/fuel substrate temperature is greater than  $T_{fc}$ , the coating is in compression relative to the fuel substrate. This surface condition tends to close up any surface cracks which were initially present, as well as

TABLE 3. Typical Coefficient of Thermal Expansion (CTE) Values of Candidate Nuclear Thermal Propulsion Fuel Materials<sup>7</sup>

MATERIAL	APPLICATION*	CTE ( $\mu\text{m}/\text{m K}$ ) / TEMPERATURE (K)
Flour-Type Graphites	F	5.3 - 6.5 / 298 - 2273
Unfueled Graphite Extrusions	F	2 - 4 / 293 - 2273
NbC	C	6.6 / -----
ZrC	C	7.7 / -----
(U, Zr)C Composite Fuel Elements	F	6 - 7 / 293 - 2300
(U, Zr)C Carbide Fuel Elements	F	~ 7.8 / 293 - 2273

\* C = Coating, F = Fuel Substrate

Table 4. Possible Coated Fuel Structural Integrity States as it is Thermally Cycled



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 on the fuel material.

Experience from the Rover and NERVA programs showed that it was almost impossible to fabricate fuel elements which were crack free, because of the CTE interface compliance issue.<sup>7</sup> 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 its coating. In general, the coating's CTE was shown to be highly dependant on its carbon-to-metal ratio, as well as on its impurity content.<sup>7</sup>

Two major fuel element surface coating strategies to address the issues of surface coating cracking and its corresponding influence on corrosion were examined in the Rover and NERVA programs.<sup>4,7</sup> One approach studied the use of a Mo coating which was applied over ZrC coated fuel element coolant channels in the forward (low temperature) fuel element region. Overall surface coating strength was increased in this region of the fuel 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 from these tests showed that the Mo outer coatings reduced the presence of surface cracks, increased the structural integrity of the fuel element and reduce fuel mass loss.<sup>4,7</sup> The Mo-ZrC fuel element coating

approach was baselined for the NERVA flight engine reactor design which used a carbide particle matrix composition.<sup>4</sup>

The other major surface coating strategy investigated focused on developing a fuel element design which minimized and/or eliminate any difference in the CTE between the fuel form substrate and its' surface coating.<sup>4,7</sup> 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.<sup>4,7</sup>

Flow instabilities, as well as substantial levels of non-uniform mechanical and thermal loading were also observed to be present in this class of fuel form design.<sup>4,6</sup> On the positive side, this type of fuel form design exhibits 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 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.<sup>5,14</sup> Typically, these particles, shown in Table 1, are approximately 500 to 1000  $\mu\text{m}$  in diameter and are composed of an inner fuel kernel made up of  $\text{UC}_x/\text{ZrC}$  or  $\text{UC}_x/\text{NbC}$  which are multicoated with high strength, high temperature, hydrogen corrosion resistant materials such as porous carbon, pyrolytic carbon, and  $\text{ZrC}$ .<sup>9,13-16</sup> These particles are designed to withstand the internal pressure buildup due to fission gas (mostly Xe and Kr) production, as well as the reactor core environment. These small particles possess a high surface area-to-volume ratio, which enabled operation at high power densities, but leads to more rapid mass loss by hydrogen corrosion.<sup>12,15</sup>

Another carbide fuel form design that has been examined in the past is the fuel pellet.<sup>5,14,15</sup> The fuel pellet, see Table 1, is typically 5 to 10 mm in diameter, which is made up of many  $\text{UC-ZrC}$  or  $\text{UC-NbC}$  fuel, TRISO-type, microspheres, and has an over coat of  $\text{ZrC}$  or  $\text{NbC}$ , respectively. This fuel particles are then encapsulated in a  $\text{ZrC}$  matrix which is also coated with an additional layer of  $\text{ZrC}$  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 fission product retention, and provides high resistance to corrosion by hydrogen. Packed bed reactor concepts that use this fuel 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 reactor designs, as well as the NERVA and Small Nuclear Space Engine flight designs, used fuel elements that were based on the coated-particle matrix design approach, see Figure 3. Tests results showed that fuel mass loss and mechanical degradation were major development issues and that the potential of increasing the reactor operating temperature was marginal. Hence, alternate fuel element composition/ design approaches were pursued, see Figure 3, 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 4.<sup>8</sup> Within a small carbon atom ratio range ( $\sim 0.92$  to  $0.96$ ), material temperatures greater than 3100 K are possible. Conversely, Figure 4 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 interspersions of the fuel into the graphite matrix a closely packed webbed type structure is produced, see Figure 3, 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  $\geq 2700$  K for the composite design and  $\geq 2900$  K for the solid-solution design.<sup>7,8</sup> 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 shown in Figure 5.<sup>8</sup> The Pewee-1 fuel elements had coolant channel surfaces which were coated with either NbC or ZrC; while the NF-1 test composite fuel was coated with ZrC. The data shown in Figure 5 has been adjusted to take into account the differences in operating temperatures between the 2 reactors. 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 has been attributed to the presence of initial surface coating cracks and the difference in CTE's of the coating and the fuel substrate materials which

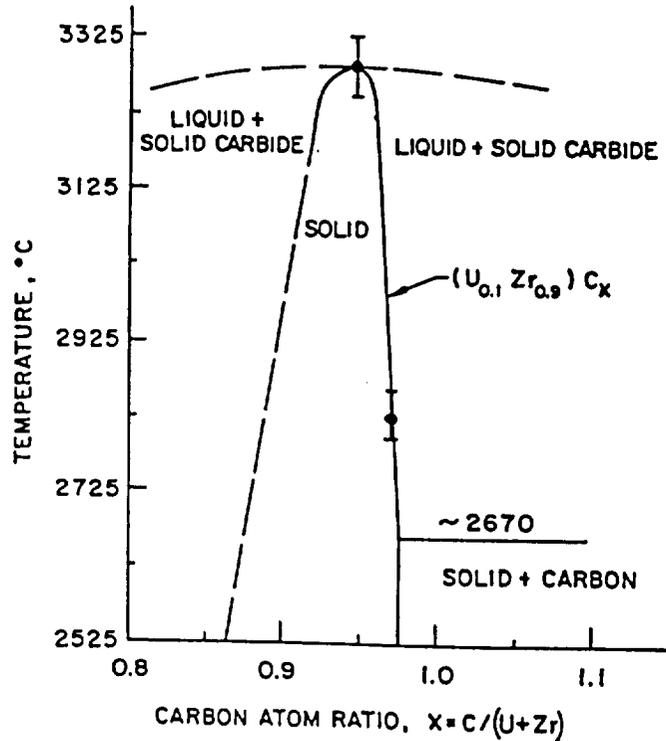


Figure 4. Pseudo - binary Phase Diagram of  $(U_{0.1}, Zr_{0.9})C_x$ .<sup>8</sup>

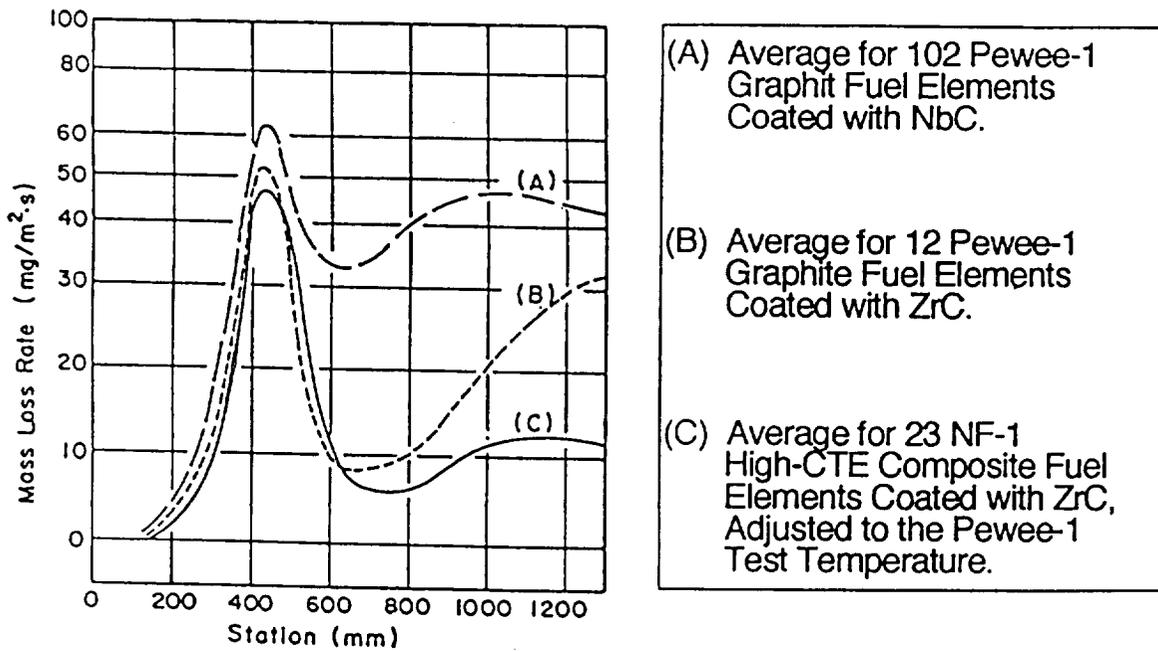


Figure 5. Mass Loss Rate for Graphite and Composite Fuel Elements.<sup>7,8</sup>

places the surface in tension relative to the fuel substrate, as previously mentioned.<sup>4,7,8</sup> 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.<sup>4,7,8</sup> Likewise, the presence of corrosion byproducts, such as CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>, in the hydrogen coolant gas stream, the deposition of these byproducts on the coolant channel surface, as well as the gas/fuel interface composition, can reduce the chemical driving potential for corrosion to occur.<sup>4,7,12,,22-24</sup>

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, see Figure 5. Mass loss observed in the high temperature regions axial fuel element positions is typically dominated by the vaporization of its elemental material constituents.<sup>4,7,12,,22-24</sup> Like the mid-band corrosion region, surface coating integrity, and the chemical composition of the coolant gas and the fuel surface, are also major factors which influence the corrosion process in this region.

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 carbide 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 design processes and features such as fuel/material system design and fabrication, nuclear radiation exposure, and local coolant flow conditions, can greatly influence the corrosion process (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.

The availability of relevant experimental data is extremely important to verify the accuracy of present and future analytical corrosion model(s). To quantify the carbide material, hydrogen corrosion process in terms of test data and global observations, a limited number of directly related data sources are available. These sources of data, plus others which summarize related data, are provided in Table 5. It should be noted that this data base is based principally on open literature on the United State's (US) past experience. For completeness, in the future, one should augment this database with the Russian experience base. The Russians have been very active in addressing hydrogen corrosion of high temperature carbide materials from an experimental perspective.<sup>25</sup>

Table 5. Sources of Supporting Data and Literature Related to Hydrogen Corrosion of Carbides

CATEGORY	REFERENCES
<p>Research Reactor/Prototype Engine Reactor Tests</p> <ul style="list-style-type: none"> <li>Rover and NERVA Programs</li> </ul>	<p>4,* 6,* 7,* 8,* 17.*</p>
<p>Subscale Hydrogen/Carbide Material Experiments</p> <ul style="list-style-type: none"> <li>Primarily Based on Arcjet and Heated Tube Experiments (Part of the Rover Program)</li> </ul>	<p>7*, 17* 41*, 46*, 47.</p>
<p>Supporting Physical Fundamental Properties of Carbide and Related Materials</p> <ul style="list-style-type: none"> <li>Phase States, Vaporization, Diffusion, Thermal Conductivity, Coefficient of Thermal Expansion, Ductility, and Creep</li> </ul>	<p>8*, 18, 23, 24, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35,36, 37, 38, 39, 40, 68.</p>
<p>Effects of Radiation of Carbide and Related Materials</p> <ul style="list-style-type: none"> <li>Primarily Based on the Radiation Effects of Graphite Material Property</li> <li>Behavior of Fission Products Included</li> </ul>	<p>7,* 8, 42,* 43, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 63, 65, 69, 70.</p>
<p>Hydrogen Reaction Kinetics</p> <ul style="list-style-type: none"> <li>Almost All Work Has Focus on the Hydrogen-Carbon Chemical Reaction System</li> </ul>	<p>44, 45,* 46,* 47,* 48,* 49, 50.</p>

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

Subscale thermo-chemical, arcjet, and heated tube, single-effects experiments shown in Table 5, provide data on one or more fundamental aspects of the hydrogen corrosion process with carbide material systems. Many of these experiments were conducted at test (exposure) conditions less demanding than those typically encountered in an operational NTP reactor. This data is

valuable, but does not provide insight into some of the fundamental competing processes associated with hydrogen corrosion process. 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 usefulness of this data to benchmark corrosion models is highly uncertain, but would likely be used as a starting 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.<sup>4,6,7</sup> Many of these qualitative observations pertaining to fuel corrosion and integrity from the prototype engine reactor tests are summarized in Table 6. 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 effect corresponding to a particular corrosion process is difficult to deduce. The data associated with the NF-1 test, which tested advanced fuel element materials, previously mentioned, is believed to be the best quantitative data available on hydrogen corrosion and structural performance of NTP fuels at true operational conditions.<sup>7,8</sup> Unfortunately this data base is limited in terms of quantity.

Past work which examined the behavior of nuclear reaction fission products of carbide NTP fuels is available.<sup>42,43</sup> Review of this work provides some useful insight issues pertaining to fuel material integrity, solid-solution molecular processes and potential hydrogen corrosion mechanisms. Fundamental out-of-pile (non nuclear) corrosion reaction data is also available, see Table 5, on related material systems, such as hot hydrogen with carbon or graphite materials.<sup>40-50</sup> Some of this past work was performed at the high pressures and temperatures of interest to NTP reactor systems.<sup>45-48</sup> In-depth characterization of chemical reaction systems of this type, 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 which incorporate materials such as uranium carbide, carbon, graphite, and high temperature gas reactor fuel designs, is available.<sup>51-70</sup> 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).

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 potent-

Table 6. General Past Engine System Testing Observations from Post-Test Inspections

TYPE	OBSERVATIONS
Fuel Mass Loss	<ul style="list-style-type: none"> <li>• In NERVA Program: 1.0 to 0.2 g/minute per Fuel Element.</li> <li>• Mass loss of 0.2 g/minute per Fuel Element Achieved at the End of the NERVA Program.</li> <li>• Fundamental Understanding on the Impact of Fuel Design on Corrosion Was Lacking.</li> </ul>
Structural/Material Integrity	<ul style="list-style-type: none"> <li>• Substantial Cracking/Desintegration Coating the Low to Medium Temperature (Mid-Axial Element Positions) and Hot End Regions.</li> <li>• Substantial Fuel Element Coolant Channel Surface Cracking.</li> <li>• Thermal Conductivity Changes Measured in the High Radiation Flux (Mid-Axial Element Position) Region.</li> </ul>

ial 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.<sup>25</sup> 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.<sup>7,25</sup> Such conflicting results are likely due to the difference in the thermal gradients produced 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.

## 2.2 Corrosion and Interrelated Process(es) Description

Observations of NTP carbide fuel materials exposed to hot hydrogen showed that many interrelated, competing physical processes which were at work have degraded the structural integrity and/or produces mass loss of these materials. Review of past Rover and NERVA program data indicated that hydrogen corrosion in general, depends on the following parameters: 1.) operation time, 2.) duty cycle (on-off cycles), 3.) local material temperature, 4.) local gas flow conditions, 5.) fuel material location in reactor, 6.) reactor power density, and 7.) fuel material/coating design compatibility. From first principles, one expects corrosion to be highest at the maximum surface temperature location of the fuel material. This expectation was not found to be the case, as previously discussed and as is shown in Figure 5. In Figure 5, the maximum mass loss rate typically occurred in the moderate temperature region (<2000 K) of an NTP fuel element. This observation, plus others from post-test inspections, indicated that numerous competing processes are at play.

A schematic of hydrogen corrosion phenomena of carbide fuels that displays its many interrelated, competing physical processes is shown in Figure 6a (also see Figures 2b and 2c). There are 4 major coupled, reaction and/or healing (slowing down) processes which drive corrosion. They are: 1.) exposure to hydrogen gas, 2.) non-uniform loading and/or cycling of the fuel material, 3.) radiation exposure and 4.) creep of material defects. These processes interact with each other, depending on the local conditions, and the fuel design. The first physical process listed is directly associated with the actual transport/chemical corrosion reaction mechanisms which are responsible for the mass loss of fuel material. The other physical processes, while not directly related to the corrosion reaction process, greatly influences the fuel material surface area exposed to the hydrogen gas which intern impacts the magnitude (and rate) of fuel material mass loss. It is essential that these fundamental physical interrelated processes be well understood and be considered, where appropriate, in future corrosion modeling efforts. These processes are discussed in more detail in the following subsections.

**Exposure to Hot Hydrogen Gas.** Carbide materials when exposed to hot hydrogen can experience mass loss by two mechanisms, depending on the local temperature of the material and/or the chemical composition of the flowing gas stream. These mechanisms are: 1.) diffusion and chemical reaction of the carbide material constitutes with the hot hydrogen gas stream, and 2.) vaporization (sublimation) of the material constituents. For temperatures less than 1500 K, little, if any, chemical reactions between hydrogen and carbide material takes place. However, at temperatures typically between 1500 and 2900 K, which is well below the vaporization tempera-

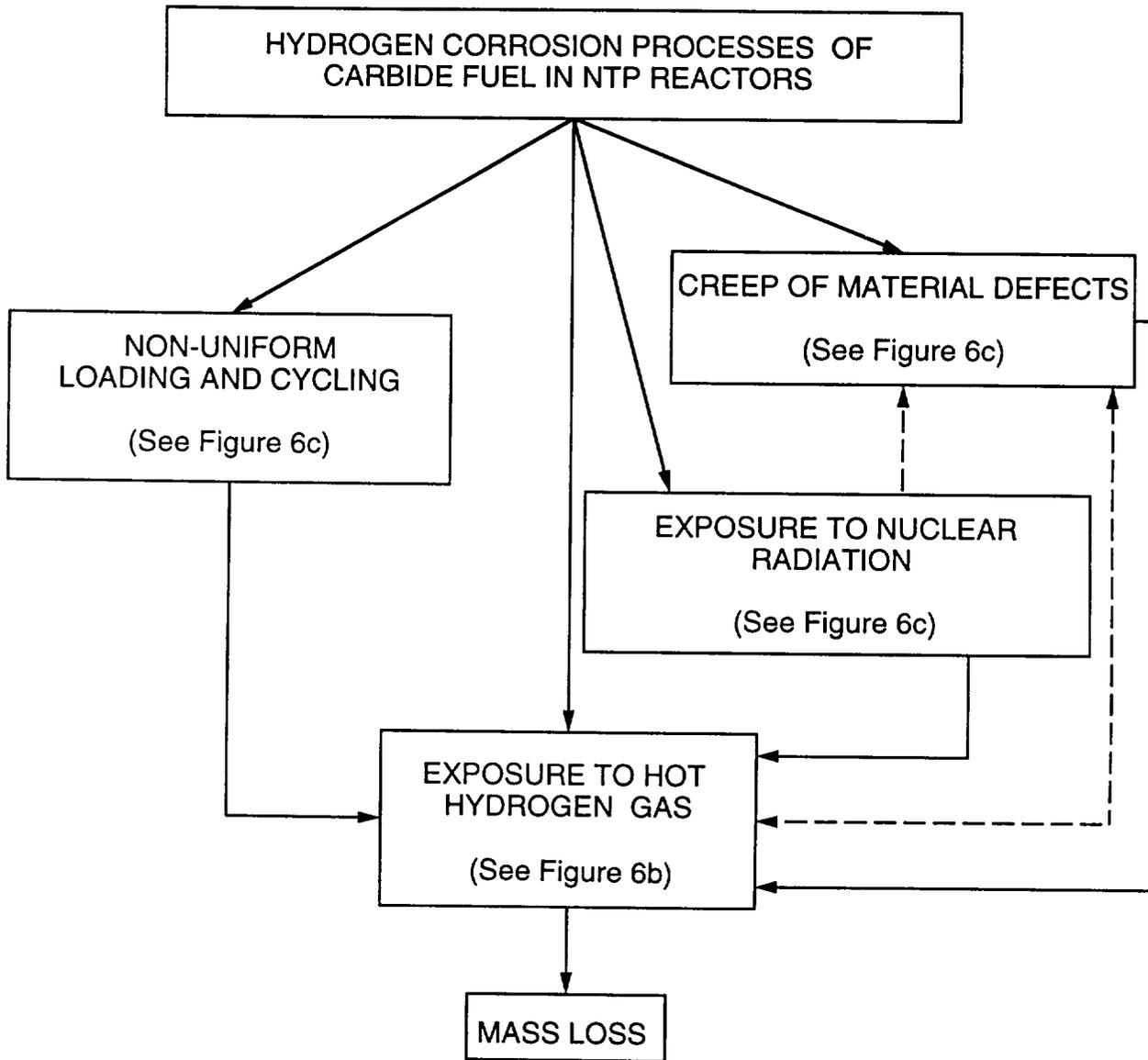
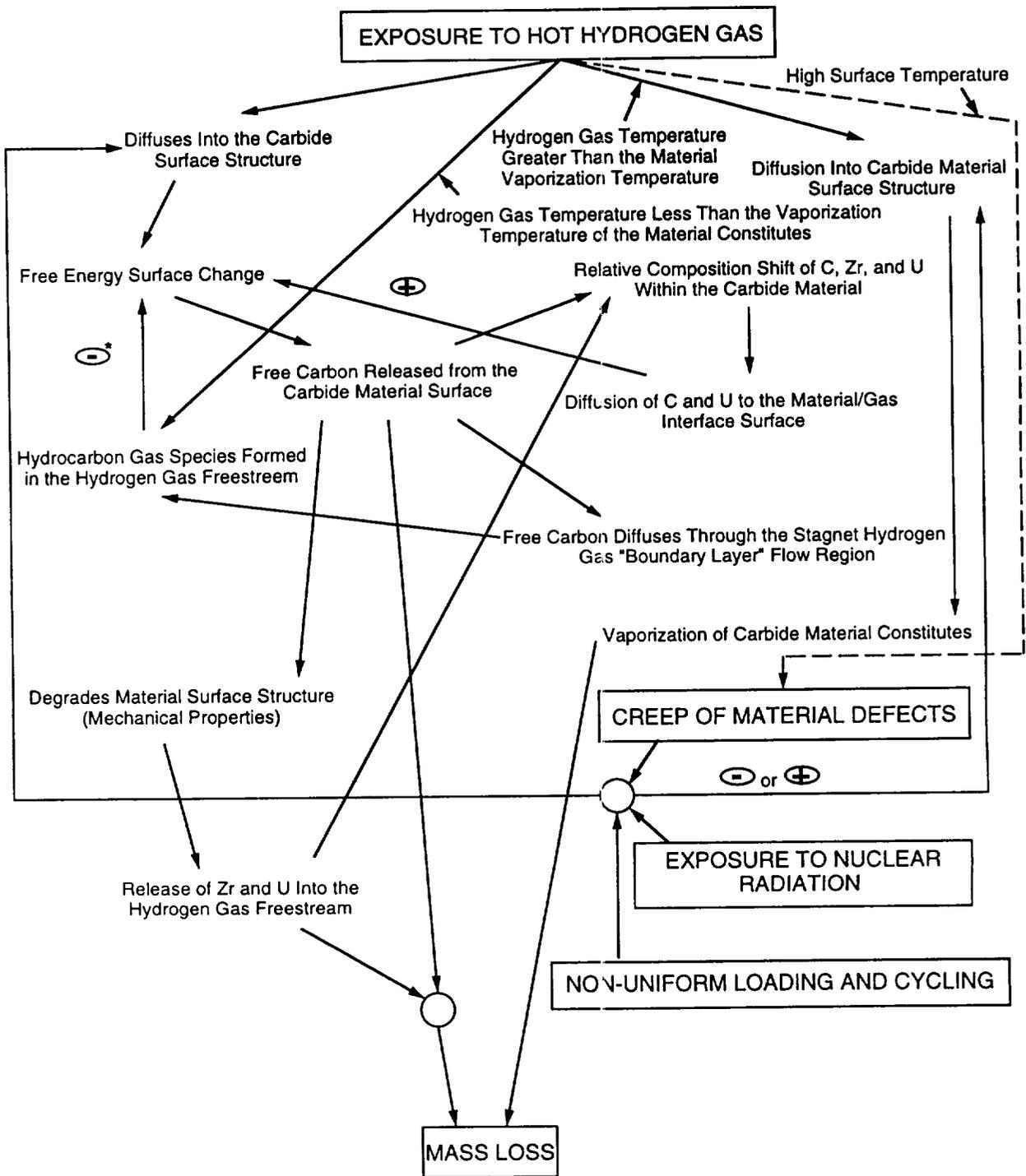


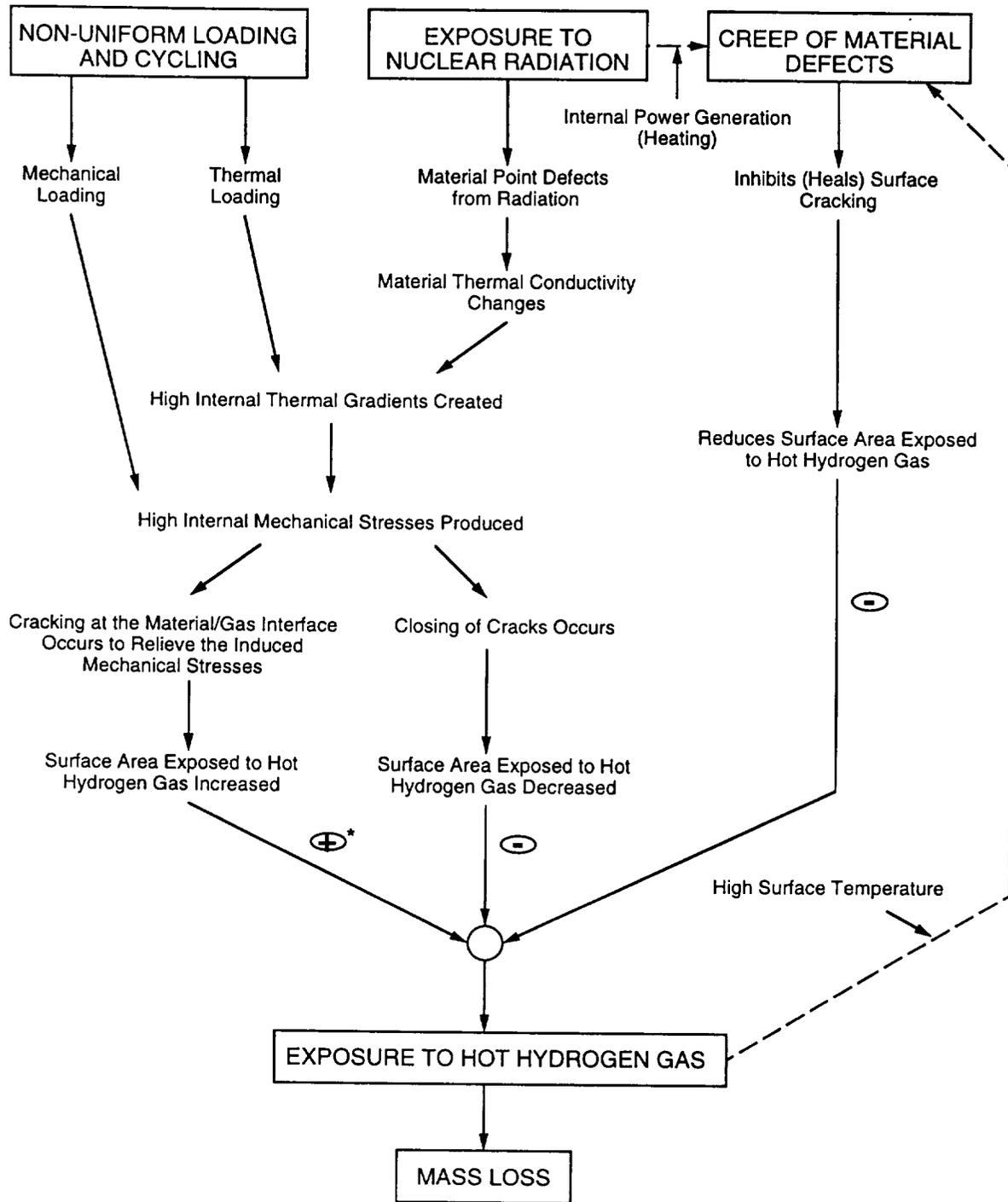
Figure 6a. A Schematic Representation of the Major Interrelated Physical Process Mechanisms that Influence Hydrogen Corrosion of Carbide Fuel.

ture of candidate NTP carbide fuel materials, the chemical reaction process branch, as shown in Figure 6a, will predominate. This corrosion process is highly complex and has been studied in the past in some detail.<sup>23,24</sup>



\*NOTE: ⊕ = Enhanced Mass Loss; ⊖ = Reduced Mass Loss

Figure 6b. A Schematic Representation of the Major Interrelated Physical Process Mechanisms that Influence Hydrogen Corrosion of Carbide Fuel (Con't) - Hot Hydrogen Gas Exposure.



\*NOTE: ⊕ = Enhanced Mass Loss; ⊖ = Reduced Mass Loss

Figure 6c. A Schematic Representation of the Major Interrelated Physical Process Mechanisms that Influence Hydrogen Corrosion of Carbide Fuel (Con't) - Non-uniform Loading and Cycling, Nuclear Radiation Exposure and Creep of Material Defects.

In this process the hot hydrogen gas interacts with both the material substrate and with the freed surface products, see Figure 7. For example, carbon forms hydrocarbon gas species byproducts, such as  $\text{CH}_4$  and  $\text{C}_2\text{H}_2$ , in the hydrogen gas free stream. The released free carbon at surface must first diffuse through the low velocity/stagnant hydrogen gas boundary layer, for hydrocarbon species formation to occur. The formation of hydrocarbons will be affected principally by the local temperature, and to a lesser extent the pressure of the hydrogen gas, as shown in Figures 6a, 6b and 7.<sup>22-24,44-50</sup> Based on thermodynamic equilibrium considerations it has been shown in a recent study, at low-to-moderate pressures with temperatures greater than 1500 K, the formation of  $\text{CH}_4$  becomes increasingly unstable.<sup>71</sup> While at these conditions the presents of  $\text{C}_2\text{H}_2$  was found to be stable. At higher pressures the opposite was found to be true.

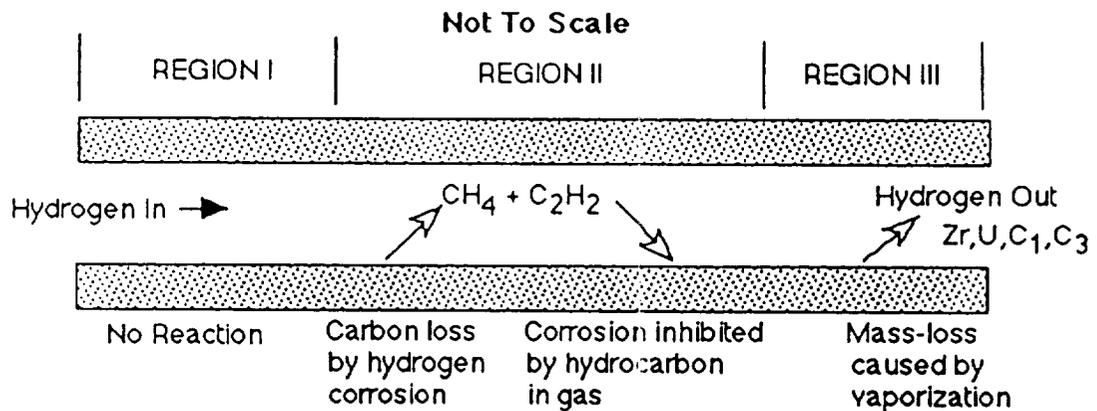


Figure 7. Hot Hydrogen Interaction Process Along a Zr-U-C Material Duct.<sup>23</sup>

The gas flow structure, as well as the replenishment of fresh (clean) hydrogen, can also impact the corrosion process. Rover and NERVA reactor fuel elements operated at Reynolds Numbers in the range of  $10^4$ , which is in the high mixing, turbulent flow region. Radial flow, packed particle (or pellet) bed reactors also operate in the turbulent flow region. It should be noted that during start-up, shut-down and/or throttling, the transient flow structure within the reactor core could be in the laminar or the transition flow regime, which could also affect the corrosion of the fuel material.

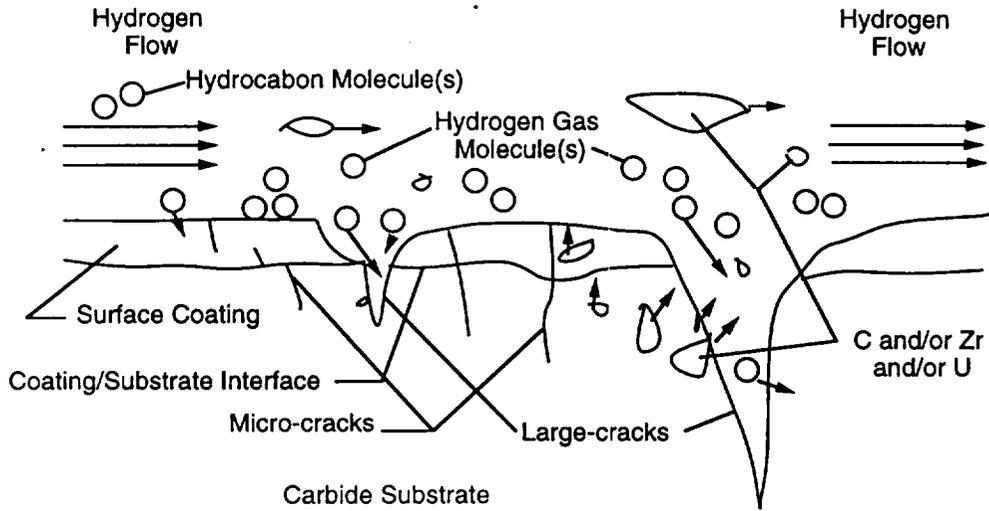
To initiate these fundamental corrosion processes, hot hydrogen gas comes in contact with the carbide material surface structure. Due to the small size of the hydrogen gas species (molecules), which is present in significant quantities in both molecular and dissociated forms at the temperature range of interest, it is possible for them to diffuse into the material. Small cracks present on the outer surface of the fuel will only enhance these processes by increasing the exposed surface area, see Figure 8. At the surface, the material composition will change owing to Le

Chatelier's principle of minimum free energy.<sup>23,24,27,72</sup> This composition change is due, in a sense, to the differences in the equilibrium partial pressures of the constituents of the system, i.e., vaporization occurs incongruently. The partial pressure of predominant chemical reaction species of such a system, which includes U(g), Zr(g) and various hydrocarbons, are displayed in Figure 9.<sup>24</sup> Partial pressure relationships of the reaction species of interest are discussed in more detail in References 23 and 24. For U-Zr-C carbide material systems, the change in surface chemical composition releases free carbon from the surface. This reaction process was known to be prevalent during initial Rover and NERVA program reactor start-up operations and is the predominate mass loss mechanism for this corrosion process branch. The fuel elements used in these programs were hyperstoichiometric ("rich") in carbon in order to enhance their productibility during fabrication.<sup>7</sup>

Mass loss by corrosion may also degrade the fuel structural (mechanical) surface properties, and physically loosen or erode the fuel by removing particles, such as grains or agglomerations containing Zr and U, from the surface.<sup>6,7</sup> These particles are swept away into the gas free stream. Thus, material mass loss is enhanced even further. Due to the heavy molecular weight associated with Zr and U, a small material loss percentage can represent a high percentage of the overall mass loss. This was found to indeed be the true in some past Rover and NERVA tests.<sup>6,7</sup>

In addition to the released free carbon, the surface composition changes as shown in Figure 6a. This tends to enhance the diffusion of C and U to the surface owing to the shift in the U/Zr/C ratio at the surface. At high temperature, the diffusion of C and U can be substantial, particularly in the vaporization corrosion controlled process, which is discussed later. This mechanism drives the free energy change at the surface, releasing additional free carbon into the hydrogen gas stream. Conversely, this release of carbon leads to a change in fuel surface composition. This in turn changes the free energy of fuel surface/hydrogen gas boundary layer reacting system locally. As the free energy of the material changes due to the rapid release of free carbon, in particular, hydrocarbon gas species are formed, as previously mentioned. The presence of these hydrocarbons tend to reduce the release rate of free carbon downstream, decreasing the rate of fuel material mass loss.<sup>22-24</sup> It is believed that this effect provides a partial explanation for the lower mass loss rates observed at the downstream, high temperature positions on the fuel element, see Figure 6a, compared to the mass loss at the lower temperature, upstream positions.

While mass loss occurs, to a varying degree, by the vaporization process in the moderate to high temperature range, it is typically the predominate mechanism of mass loss for U-Zr-C carbide material at surface temperatures which are greater than 2900 K. Hydrogen diffuses into



NOT TO SCALE

Figure 8. Effects of Surface Cracks on Corrosion.

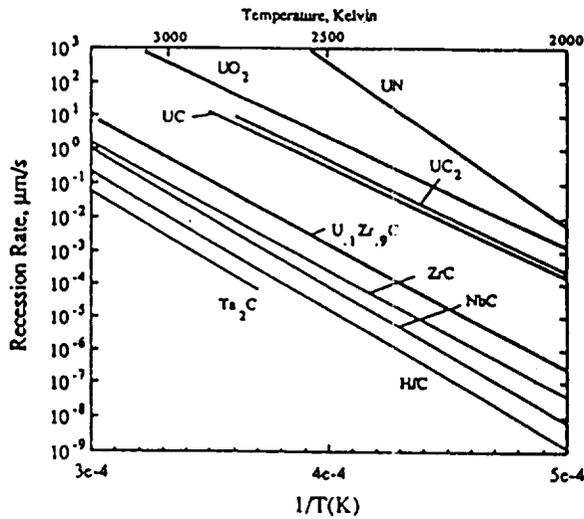


Figure 9. Recession Rate of U<sub>0.1</sub>Zr<sub>0.9</sub>C Compared to Other Uranium Compounds and Stable Refractory Carbide Materials as a Function of Temperature.

the exposed hot carbide material surface causing its constituents, such as Zr, U and C, to vaporize. In Figure 9, the recession rates of U, Zr and C are compared to other uranium compounds and stable refractory carbide materials as a function of temperature. The large recession rates of these high molecular weight compounds correlate into high mass loss rates. At the high temperatures associated with this corrosion process, the high diffusion rate of C relative to Zr and U (which are approximately the same) promotes its movement to the surface.<sup>23,24,37</sup> Additionally, the large

shifts in surface composition would locally change the carbide material's phase properties, which can lower or raise their melting points depending on the its starting composition and the shift in the surface congruent vaporization composition during NTP system operation. Based on past NF-1 composite fuel element data, which is displayed in Figure 10, the mass loss rate in the high temperature, vaporization region, has been reasonably correlated as a function of temperature at realistic NTP operating conditions.

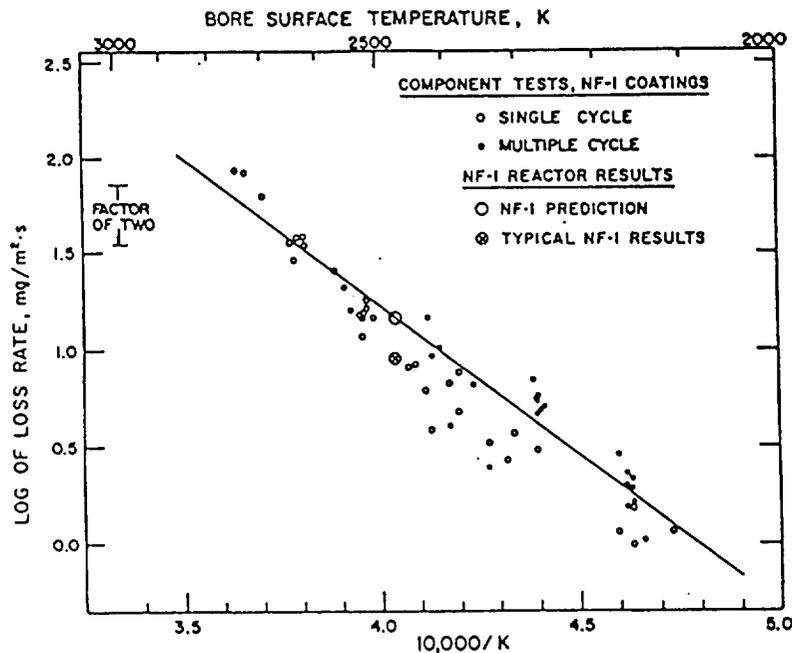


Figure 10. Component and Nuclear Furnace-1 Reactor Test Results for Hot-end Mass Loss Rates of Composite Elements. Mass Rate is Based on a Square Meter of Fuel Element Coolant Channel Surface Area.<sup>8</sup>

In the vaporization loss region hydrocarbon species would also be present in the bulk gas stream due to the hydrogen/free carbon reactions that occur upstream, see Figure 7. The presence of hydrocarbons tends to reduce the vaporization rate of the fuel/carbide surface material.<sup>23,24,27</sup> High mass loss rates were not observed at the high temperature axial positions in the Rover and NERVA fuel elements, see Figure 5. However, it is highly probable that other competing corrosion processes helped control material mass loss in this high temperature operating regime. An example of such a process is reduction (healing) of material defects by creep, which occurs readily at high temperatures. This competing phenomena can help relieve surface coating/fuel substrate interface stresses which intern reduces surface coating cracking, and, hence the rate of mass loss, see Figure 6a. Alternatively, the healing effect of creep can be hindered by the stresses caused by atom(s) dislocation and defects induced by the exposure to nuclear radiation; particularly

by the interaction of fast neutrons with the material.<sup>56,72</sup>

It should be noted that the presence of material defects can reduce the local thermal conductivity of the material, producing locally high thermal stresses and corresponding surface coating/fuel substrate stress mismatches. Such conditions encourage the formation of surface coating cracks and sequentially accelerates material corrosion, see Table 4. Substantial surface coating cracking was believed to be present during operation in modest temperature, high radiation flux regions of the Rover and NERVA program reactor fuel elements.<sup>6-8,72</sup> Due to the hostile operation environment, which is characteristic of such reactors, no direct measurement(s) of surface coating cracking during operation in these test programs, were possible. Typically, a substantial degree of surface cracking was observed during post test examination of Rover/NERVA fuel elements in their upstream, low-to-moderate temperature region, which could have happened in part during cooling of the material at shutdown. An example of this is displayed in Figure 11, where the number of cracks in a Zr-C coolant channel coating as a function of length for a NF-1 composite fuel element is shown.<sup>7,8</sup> This data, which has been examined in great detail in the past, likely is of little use to correlate fuel element surface coating cracking during operation because of the high thermal and structural loading experienced by the fuel elements during test reactor shutdown.

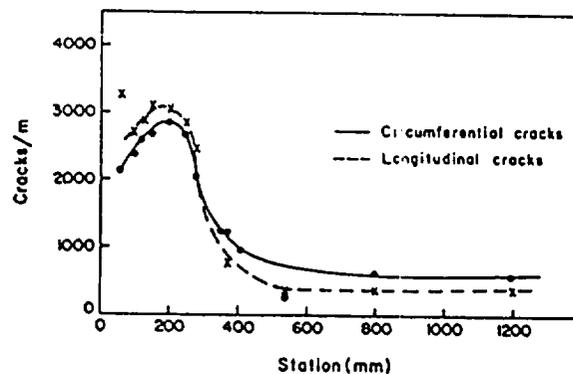


Figure 11. Number of Cracks in ZrC Coolant Channel Coatings as a Function of Length for a Nuclear Furnace-1 Composite Fuel Element.<sup>8</sup>

**Non-uniform Loading and Cycling.** Another major hydrogen corrosion initiator is non-uniform loading and/or cycling of the fuel material. Non-uniform loading of the fuel material can be induced by mechanical and/or thermal loading means. Mechanical loading of this type can be induced by: 1.) the presence of preload stresses in the fuel material during assembly or application of a material coating(s), and 2.) the presence of non-uniform and/or unsteady pressure (flow) and non-uniform axial temperature distribution(s) during operation. Non-uniform, varying pressure(s)

are always present during NTP engine system transient operation conditions. Non-uniform thermal loading conditions are typically present, due to non-uniform axial and radial fission profiles in the reactor core, when non-uniform/unsteady flow is present, as well as when local core coolant flow and reactor power generation profile(s) are mismatched. Cycling of the fuel material can also introduce residual stresses. For example, heating the material to high temperature during operation could cause it to undergo some degree of creep. When this material cools down, depending on the fuel design configuration, it may experience high compression and large tensile stresses. These conditions can produce high internal material thermal and/or mechanical stresses, which can amplify a mismatch in stresses (generate induced stress), between in the surface coating and fuel substrate. As previously mentioned, such a condition typically favors cracking of the surface coating. This increase in surface area from cracking, enhances corrosion and accelerate the mass loss rate. It has also been shown in the Rover program that non-uniform loading and steady-state thermal expansion of the material can help reduce corrosion locally.<sup>7</sup> This process tends to close up surface coating cracks, hence retarding corrosion from occurring.

Significant non-uniform and cyclic loading effects were present in the Rover and NERVA program reactors and have contributed both in a positive and a negative sense to fuel corrosion.<sup>6,7</sup> Due to the axial flow fuel element design associated with these reactors, substantial mechanical preloading of the elements was required to hold them in place within a tie-tube assembly. This assembly was supported from a plate located at the forward end of the reactor, see Figure 12.<sup>4</sup> Unsteady, channel flows and high thermal gradients were observed in the reactor core because of the non-uniform axial and radial fission power profiles.<sup>4,6</sup> Non-uniform loading and material expansion effects are also considered major contributors in reducing the fuel mass loss rate at the fuel element axial position just downstream of the peak rate, see Figure 5. This is attributed to the closing a large number of coolant channel surface coating cracks.

**Radiation Exposure.** The exposure of carbide fuel materials to nuclear radiation, expressed in terms of fluence (fluence =  $\phi \times t$ ; where  $\phi$  is the neutron flux and  $t$  is the exposure time) and neutron energy spectrum can be major corrosion drivers. If radiation exposure is great enough, material point defects can be produced locally, reducing the thermal conductivity and ductility of the material. The lower thermal conductivity and ductility can produce high thermal gradients and cause cracking of fuel coatings and/or the fuel, if uncoated, at the surface. This cracking can increase local corrosion, as previously discussed. This hydrogen corrosion enhancement process is likely to occur in high neutron flux regions of the NTP reactor. At high local core temperatures, it may be possible to heal many of the radiation induced defects by creep and, hence reduce local corrosion in these high flux regions.

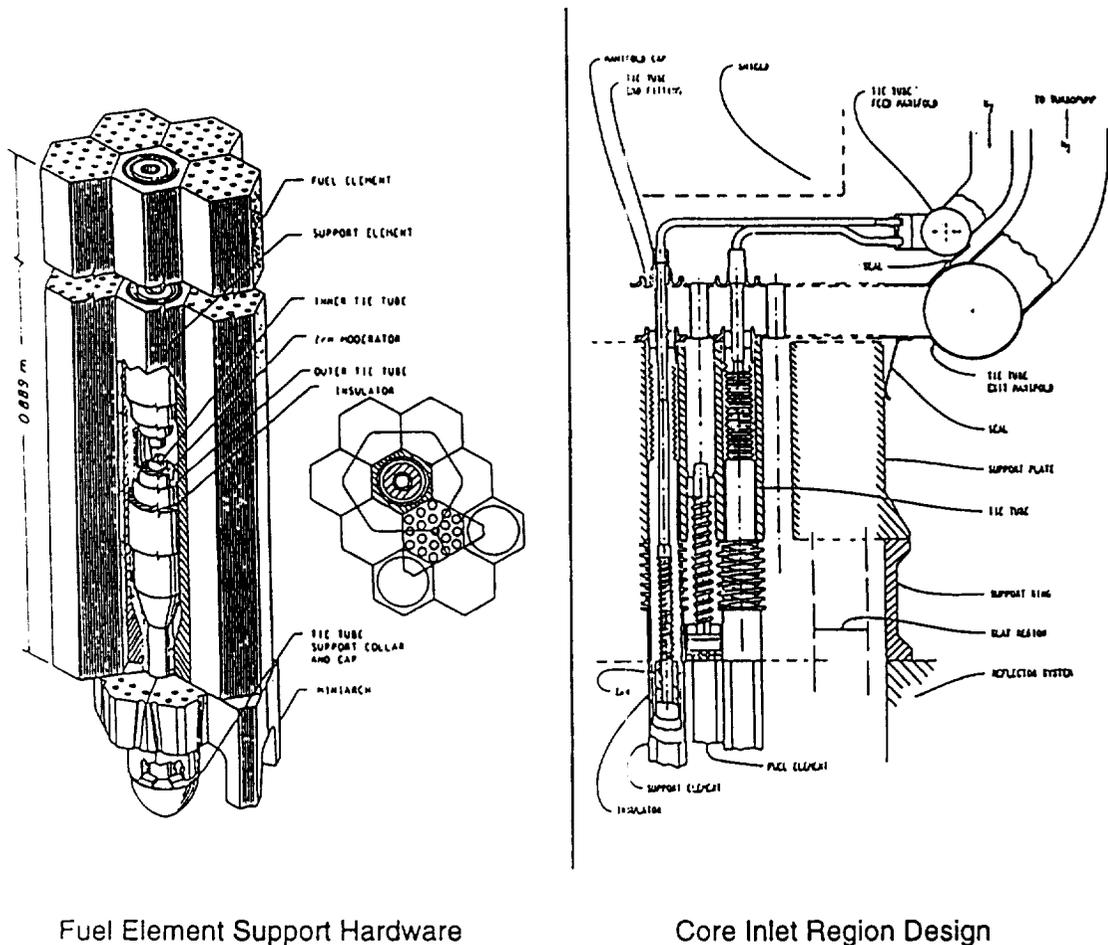


Figure 12. Typical Axial Reactor Core Fuel Tie-Tube Assembly (Small Space Engine Example).<sup>4</sup>

Initially, during the Rover program it was felt that radiation effects on carbide fuels, which are high in carbon content, would be minimal, because of the high resistance of carbon to radiation and the short total operation time of an NTP engine system.<sup>8</sup> This was found not to be the case because of the high power densities in these reactors. Post-test inspection of Rover and NERVA reactor fuel elements, has shown that material defects caused by radiation exposure, reduces local thermal conductivity and material ductility, and were considered likely mechanism to promote cracking.<sup>6-8</sup> The resulted cracking could be correlated to radiation flux profile in the reactor as shown in Figure 13, but as previously discussed, one must consider the fuel shutdown and fuel operation duty cycle effects in interpreting this data and form a conclusion. Interpretation of these observations back then, indicated that the radiation-induced property changes were likely caused by the interaction of fission fragments with the fuel element's graphite lattice.<sup>8</sup> A recent evaluation of the NF-1 test data indicates that radiation embrittlement (a reduction in material ductility) likely

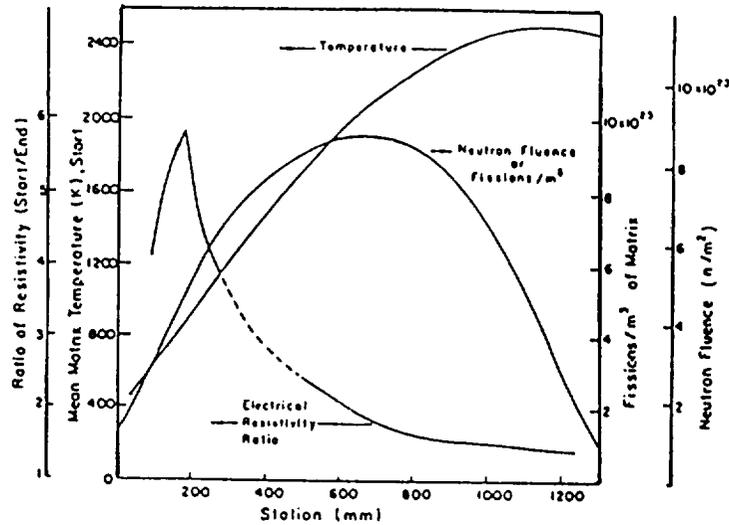


Figure 13. Fuel Element Environment versus Length: Temperature, Fission, and Fast Neutron Fluence (>0.18 MeV), as well as the Change in Room Temperature Electrical Resistivity Ratio for a Nuclear Furnace-1 Test Composite Fuel Element from Pre- and Post-Test Observations.<sup>8</sup>

occurred.<sup>73</sup> It was concluded from this assessment that radiation embrittlement was likely one of many mechanisms, which also contributed to surface coating cracking.

**Creep of Material Defects.** In reactor regions where high material temperatures are present, healing of material defects is likely due to creep. This competing corrosion process shown in Figure 6a, can close surface cracks, as well as reduce material defects internal to the fuel substrate. Stress relieve and physical transport material properties associated with this competing mechanism, can help reduce and/or close, or inhibit the growth of preexisting or newly formed surface cracks.<sup>71</sup> Likewise, this phenomena tends to reduce interface stress mismatches between the surface coating and the fuel substrate and internal fuel substrate stress gradients which are caused by radiation exposure and/or non-uniform external mechanical and thermal loading. These process features tend to reduce the effective surface area exposed to the hot hydrogen, which intern inhibits (slowdown) corrosion. Recent analysis of NF-1 test data indicates that the influence of creep can be less than expected when one considers thermal cycling affects.<sup>73</sup>

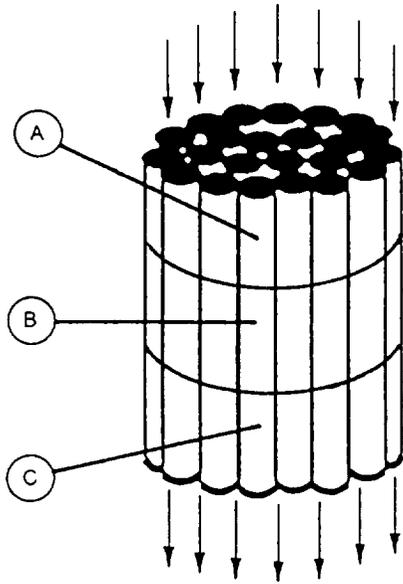
**Other Considerations.** Many of the physical mechanisms which affect hydrogen corrosion are difficult to characterize due to their inherent complex nature. In addition to the difficulty of understanding these mechanisms at traditional benign conditions, such as those typical of terrestrial power reactor systems, they are magnified at conditions which are characteristic of

NTP reactors. Many of these processes, such as material creep and carbon/hydrogen chemical kinetics for example, can be influenced by the high radiation fluxes encountered in NTP reactors.<sup>56,72</sup> These effects should also be considered in future corrosion modeling efforts.

As shown in Figure 6a, the hydrogen corrosion reaction process branch is the only process path where carbide material mass loss occurs. The mass loss from this process path will likely weaken the materials lattice structure, and hence, will further contribute to enhancing to the fuel material mass loss rate by erosion. This fuel mass loss process path is not shown in Figure 6a, because it was not considered as a fundamental process mechanism that directly influences the corrosion process. It should be noted that it may be possible for fuel erosion to indirectly influence corrosion by affecting the surface area exposed to hydrogen.

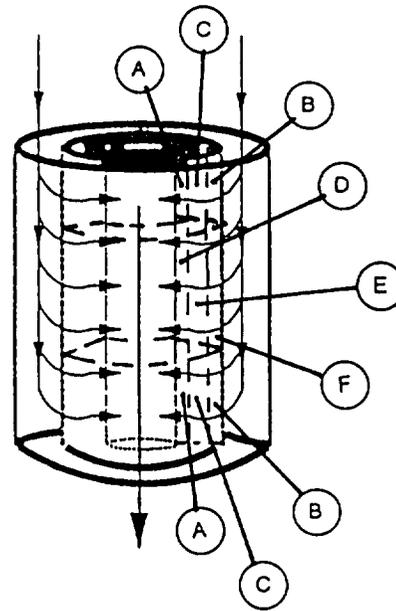
Creep of high carbide content materials at high temperatures is believed to be a major contributing factor on why fuel mass loss observations were typically lower than that expected at the downstream, high temperature location of Rover/NERVA fuel elements, as shown in the Figure 5 example.<sup>4,6-8</sup> Other corrosion inhibiting processes, which support the mass loss observations in the development reactor tests, are the presence of hydrocarbon species in the hydrogen coolant gas in the downstream fuel element region, as previously discussed. These hydrocarbons are produced in the low-to-moderate temperature, radiation exposure region and are carried away by the upstream flow and deposited on the surface of the fuel material in the downstream fuel element region. Because of the cosine axial fission power generation profile typical of these reactors, the fuel temperature peaks slightly above the core mid-plane, see Figure 13. Therefore, it is expected that the corrosion rate will be the highest in the lower half of the reactor core. These results suggest that flattening the fission power profiles in the reactor core could help reduce the material mass loss.

By understanding the many competing physical processes associated with hydrogen corrosion of the carbide materials, one may be able to interpret the fuel mass loss profiles and corresponding observations at conditions typical of past Rover and NERVA reactor tests, see Figure 5. Such understanding will also provide qualitative engineering insight into the potential of corrosion occurring and its impact on future NTP carbide fuel reactor designs. Dominate hydrogen corrosion processes typical of carbide fuel solid-core reactors employing either axial or radial flow designs are shown in Figure 14. Due to their dissimilar flow paths and corresponding temperature profiles, the dominate hydrogen corrosion mechanisms in these solid-core concepts could be quite different.



REGION	PROCESS MECHANISM
A	Non-uniform Loading, Thermochemistry
B	Radiation, Thermochemistry
C	Vaporization, Creep

**AXIAL FLOW**



REGION	PROCESS MECHANISM
A	Vaporization, Creep
B	Thermochemistry
C	Non-uniform Loading, Thermochemistry
D	Radiation, Vaporization, Creep
E	Radiation, Thermochemistry
F	Radiation, Non-uniform Loading, Thermochemistry

**RADIAL FLOW**

Figure 14. Dominate Corrosion Process Mechanisms Associated with Various Regions of Axial and Radial Flow Reactor Cores.

One must also consider the numerous interrelated corrosion mechanisms on a smaller scale. The orderly (predictable) channel flow characteristics and past experience base of axial flow geometries establishes a basis to begin corrosion prediction modeling of more complex radial flow packed particle bed reactor configurations. The complexity and the highly turbulent nature of the flow field in packed particle bed reactors, and the higher surface area-to-volume ratio of the fuel core design (microspheres or pellets) can greatly affect its corrosion characteristics and rate.



### 3.0 CORROSION MODELING AND FUTURE REQUIREMENTS

Previous discussion, see Section 2.0, has shown that hydrogen corrosion of carbide fuel materials is complex and can be influenced by numerous fuel design and reactor operation parameters. Past modeling efforts have focused on the thermo-chemical aspects of this process.<sup>23,24,37</sup> No modeling effort to date has been accomplished which integrates the other interrelated physical processes discussed earlier. Development of such an inclusive corrosion model presents many challenges both in terms of accurately quantifying the various complex processes, coupling them appropriately, and to also benchmark the model predictions. Such fuel mechanical integrity response models have been successfully accomplished for terrestrial reactor applications.<sup>74</sup> The following discussion in this section addresses corrosion modeling issues and considerations which were identified during this review, and the impact of developing such a robust, accurate model based on fundamental physical principles to support the development of future NTP engine systems.

In order to model the vaporization behavior of refractory carbide fuels, it is necessary to know the equilibrium partial pressures of important vapor species. When, for example, a  $U_xZr_{1-x}C_y$  fuel is undergoing hydrogen corrosion, the most important vapor products are U, Zr, and hydrocarbons. Initially these gaseous products leave the fuel surface at different rates. Because this solid solution exhibits a wide range of stoichiometry, the fuel composition can change significantly during vaporization or corrosion. Of course, any change in composition will affect the equilibrium vapor pressures. Figures 15 and 16 show the binary phase diagrams for the U-C and Zr-C systems, respectively; while Figure 17 displays an isothermal ternary phase diagram for the U-Zr-C system at 2473 K. For all the carbide material systems shown, the physical phase states are highly dependent on their chemical composition and stoichiometry.

To be able to model the vaporization or corrosion of a gas/solid reaction a priori, it is necessary to know specifically the rate controlling mechanism or mechanisms. Mass loss may be transport controlled, reaction rate controlled, or may be caused by a combination of two or more mechanisms. Table 7 lists many of the possible reaction mechanisms one must consider in developing a corrosion model.

Two models were developed at Los Alamos National Laboratory (LANL) that describe the corrosion kinetics of a solid-solution  $U_xZr_{1-x}C_y$  nuclear fuel materials in hydrogen gas at 1 atm, in the range of 2500 to 3000 K.<sup>23,24</sup> Both models suggest that the corrosion is controlled by vapor transport. In the later model, it was found that the corrosion of  $U_xZr_{1-x}C_y$  is rate limited

by the gaseous transport of  $Zr(g)$  away from the solid surface through a gaseous boundary layer where the partial pressure of  $Zr(g)$  at the surface is determined by the congruently vaporizing surface composition.<sup>24</sup> More recent modeling work at LANL also addresses the effectiveness of carbide coating on graphite to impede hydrogen corrosion.<sup>37</sup>

Based on the extensive review of available literature performed over the past year in the areas of corrosion of NTP reactor carbide materials, modeling, supporting experimental databases and related reactor design practices and technologies, a number of major outstanding technical issues have been identified, as outlined in Table 8. These issues must be addressed to support initial development of an accurate corrosion model. To address these issues, a modest, sustained research investment will be required to develop fundamental understanding and a supporting experimental database. The following discussion provides the rationale in the selection of these outstanding issues.

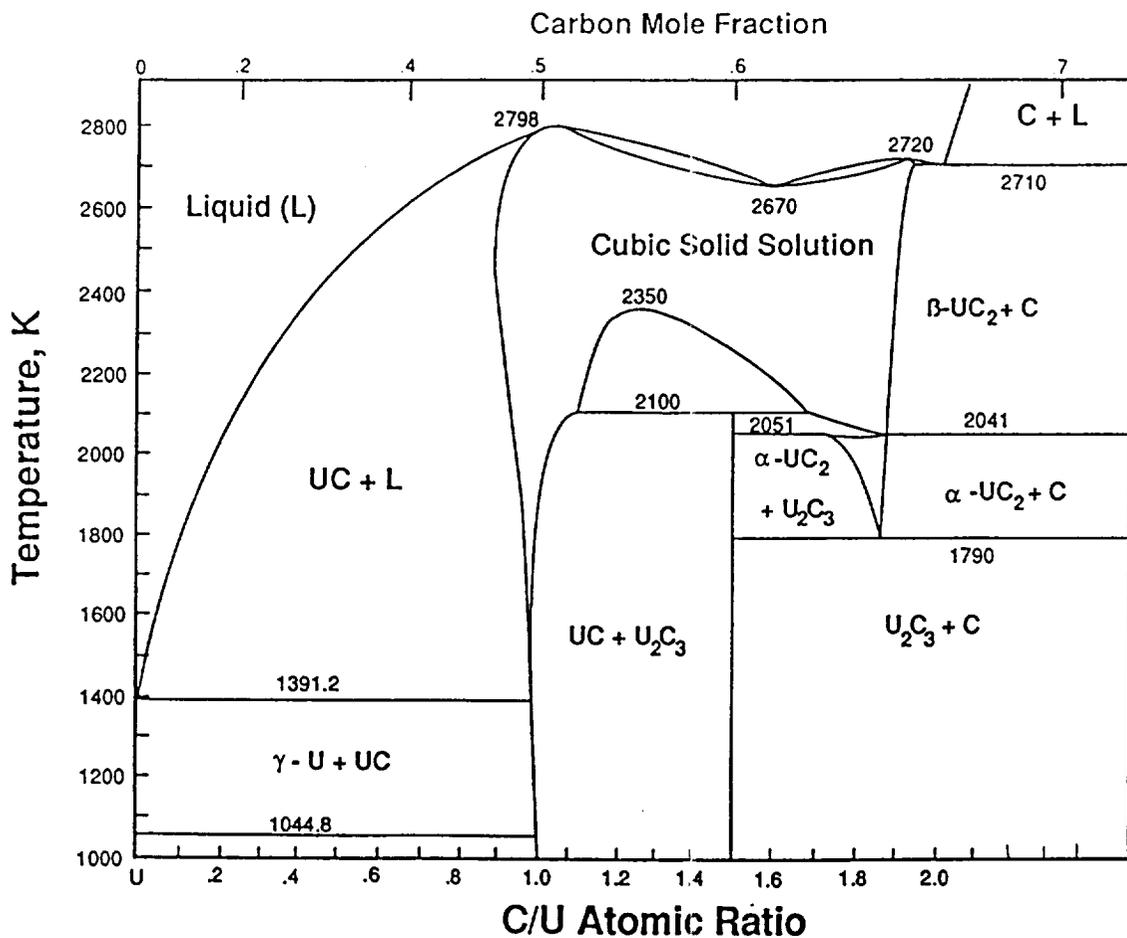


Figure 15. The U-C Binary Phase Diagram.

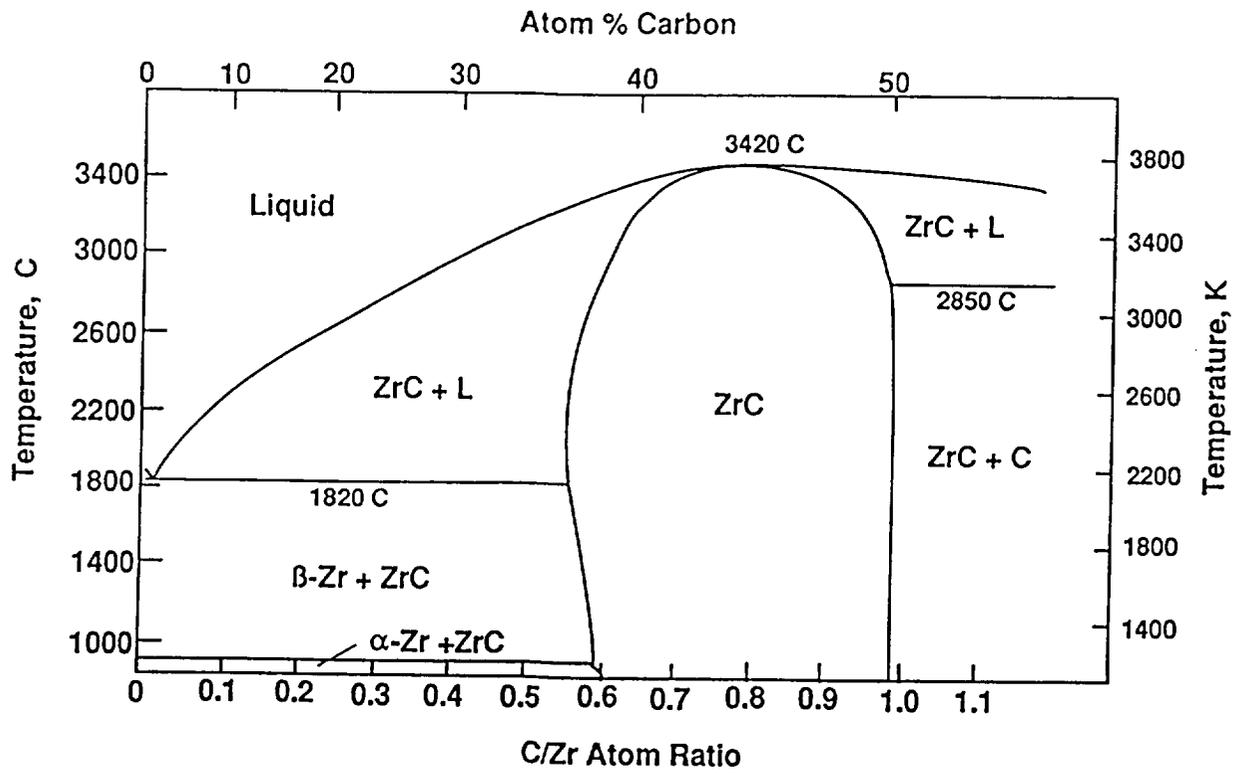


Figure 16. The Zr-C Binary Phase Diagram.

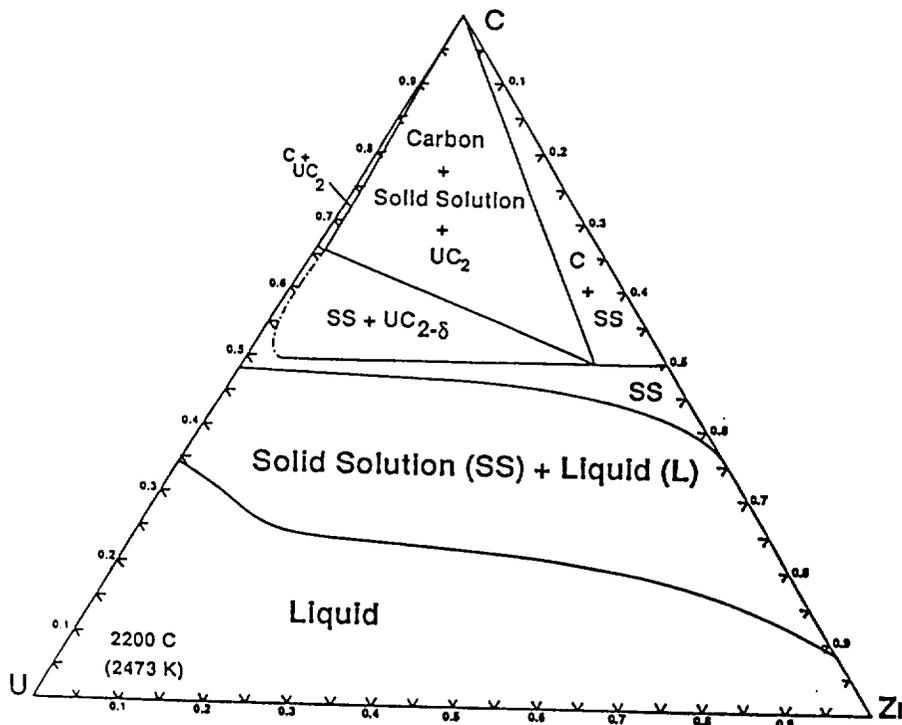


Figure 17. Isothermal Ternary Phase Diagram for the U-Zr-C Material System at 2473 K.<sup>27</sup>

Table 7. Possible Corrosion Model Reaction Mechanisms

Transport Controlled	Surface Reaction Rate Controlled
<ul style="list-style-type: none"> <li>• Diffusion of reactant gas species from the gas stream to the solid surface through a solid, liquid, or gaseous boundary layer.</li> <li>• Diffusion of product gas species from the solid surface to the gas stream through a solid, liquid, or gaseous boundary layer.</li> </ul>	<ul style="list-style-type: none"> <li>• Adsorption of the reactant gas species on the solid surface.</li> <li>• Desorption of the product gas species from the solid surface to the gas stream or boundary layer.</li> <li>• Surface diffusion of adsorbed gas species on the solid surface to achieve sites for reaction or to sites where other adsorbed species are present, the combination of which can induce a reaction (e.g., a localized catalysis event).</li> <li>• Cracking or dissociation of gas species to more reactive forms.</li> </ul>

Table 8. Major Outstanding Technical Issues Identified Which Need to be Addressed to Support Future Corrosion Model Development(s)

<ul style="list-style-type: none"> <li>• Lack of qualitative (integrated) understanding of radiation, preloads/non-uniform loading, creep, and flow structure effects on the overall corrosion processes.</li> <li>• Lack of single effects data for the various competing corrosion processes at realistic NTP engine system operating conditions.</li> <li>• The validity and/or scaling of nonnuclear testing for material compatibility testing.</li> </ul>
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Current carbide corrosion models lack an integrated approach to quantify the effects of the different corrosion mechanisms such as exposure to nuclear radiation, preload/non-uniform loading, annealing and flow structure effects. Instead, modeling of hydrogen corrosion has focused on thermo-chemical corrosion mechanisms, as previously mentioned. Although thermo-chemical processes are important, other competing corrosion mechanisms, previously discussed, are also major contributors to hydrogen corrosion and mass loss of reactor materials of this type. This fact was confirmed by detailed post-test examination of Rover and NERVA reactor fuel elements.<sup>4,6-8</sup> The importance of all the competing corrosion processes were recognized by the reactor scientific team that supported the fuel and reactor design developments. Even with this knowledge, no multi-process modeling of the hydrogen corrosion phenomena has been attempted to date. It is only speculation at this time by the authors, but we feel that such modeling was likely not previously attempted due to constraints on funding support and/or on the limited computational capabilities available at that time. Hence, the current corrosion modeling capabilities need to be revised to include many of the physical processes identified, ideally to at least a first-principle level basis. Sensitivity studies should then be performed to provide the necessary insight into the coupling of the various, competing corrosion mechanisms. Results from such studies will also be useful in identifying the critical tests required to supply the benchmark data necessary to properly verify the modeling approach and assumptions.

Another key issue is the lack of fundamental single effects data associated with the various corrosion mechanisms expected at typical NTP operation conditions. Such data is required to support both modeling development and verification activities. As previously mentioned, the availability of such data is limited and is at best marginal, due to the disparity between the test conditions and those typical of NTP reactors. It can not be emphasized more the importance of having this fundamental data. By defining the model verification data requirements in conjunction with initial first-principle model sensitivity studies, investment requirements to support the proposed data collection effort can be kept to a minimum. If fundamental experimental studies are to be conducted at the demanding operational conditions typical of NTP reactors, an assessment of instrumentation requirements and experimental techniques is recommended.

The third and last major outstanding technical issue identified 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. A review of past Rover and NERVA data indicated that radiation damage does affect hydrogen corrosion, as previously mentioned.<sup>4,6-8</sup> Additionally, 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.<sup>25</sup> 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. It is recommended that a simple, small scale experiments be considered, at conditions close to those associated with NTP reactors, to address this critical 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.

The overall goal of future NTP reactor fuels corrosion modeling effort(s) is to develop a phenomenological model, based on fundamental physical processes. Such a model should accurately characterize the corrosion rate of candidate carbide-based fuels with hydrogen at typical NTP reactor temperature, gas pressure and local velocity conditions. To verify the system of equations and boundary conditions used in the model, benchmark verification with previous and hopefully new test data will be required.

Once such a model is developed, it can then be used to assess the impact of corrosion on candidate NTP engine systems.<sup>5,15</sup> An additional goal is to integrate this model into an NTP engine system design process. A computer program would be developed and used to optimize NTP systems in terms of hydrogen corrosion to meet demanding performance and lifetime requirements in the preliminary phase of design development. Corrosion modeling of the NTP reactor, of the types discussed herein, can also be highly useful in supporting the development of many ground test facilities of such a system. Accurate characterization of the reactor materials released (due to corrosion and other means) from the NTP engine system can greatly help in the design of the complex and costly effluent treatment/containment system(s) required. Hence, it is of great interest to be able to characterize and optimize (minimize) corrosion in the initial design phase of an NTP reactor design. Based on past experience, such a design capability could significantly reduce NTP engine system development cost.

Figure 18 shows such a design process. The NTP reactor design goals and approach are defined to initialize the corrosion optimization model. Table 9 lists the NTP reactor design parameters required to initiate the design process for minimizing hydrogen corrosion. The proposed design model uses a robust, accurate corrosion model to optimize the surface area of the reactor core fuel form and operation conditions to meet engine system lifetime and duty cycle requirements. E. Storms of LANL has discussed the idea of such a design optimization model in the past.<sup>12,25</sup> To make such a design capability a reality, fundamental understanding and accurate analytical modeling of the complex corrosion process is required. The evolutionary development of such a corrosion modeling capability is displayed in Figure 19.

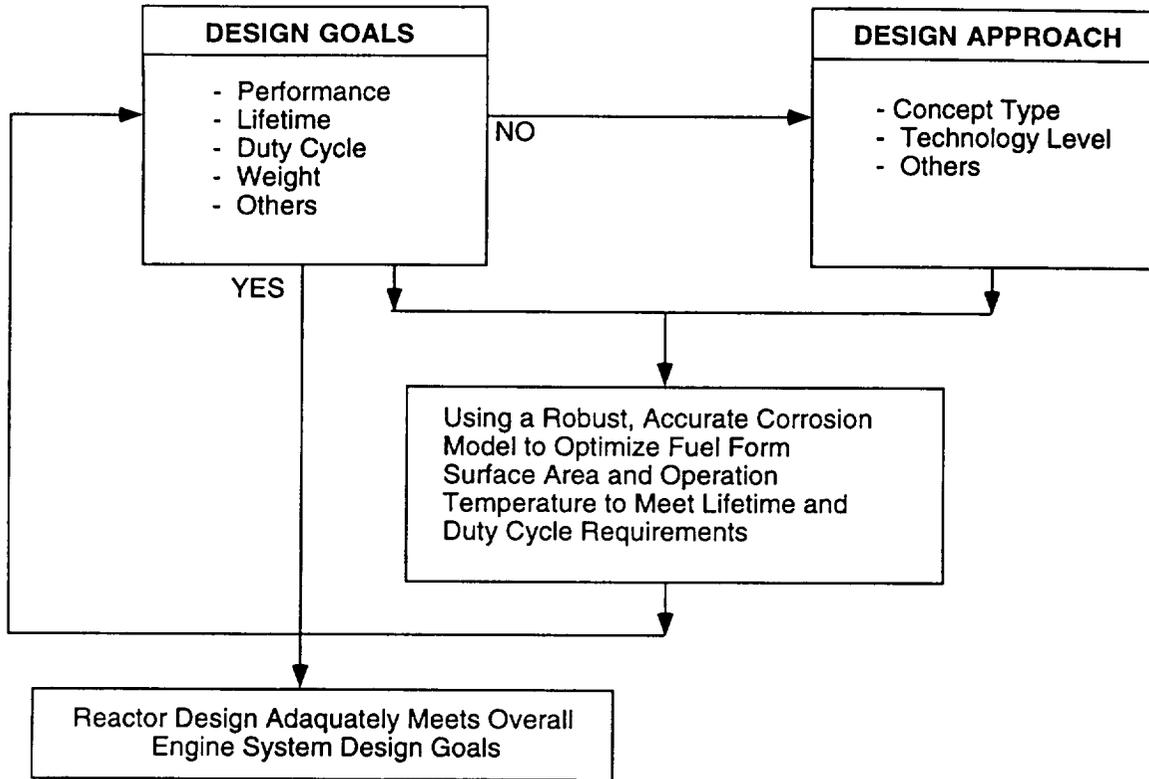


Figure 18. The Future Goal of Corrosion Modeling is to be an Integral Part of the Design Process Associated with Future Nuclear Thermal Propulsion Design/Development Efforts.

Table 9. Nuclear Thermal Propulsion Reactor Design Factors Which Influence the Hydrogen Corrosion Process

<ul style="list-style-type: none"> <li>• Fuel Matrix Composition</li> <li>• Fuel Form Design               <ul style="list-style-type: none"> <li>- Amount of Surface Area Exposed to Hydrogen</li> <li>- Mechanical Stresses                   <ul style="list-style-type: none"> <li>-- Preloaded</li> <li>-- Induced</li> </ul> </li> <li>- Thermal Stresses                   <ul style="list-style-type: none"> <li>-- Induced</li> </ul> </li> </ul> </li> <li>• Propellant Temperature</li> <li>• Fuel Material Position in the Reactor               <ul style="list-style-type: none"> <li>- Location in the Propellant Coolant Path</li> <li>- Location in the Reactor's Nuclear Radiation Field</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>• Propellant Pressure</li> <li>• Propellant Mass Flow</li> <li>• Nuclear Radiation Exposure               <ul style="list-style-type: none"> <li>- Flux Energy Distribution</li> <li>- Flux Field Strength</li> </ul> </li> <li>• Operation Time</li> <li>• Duty Cycle</li> </ul>
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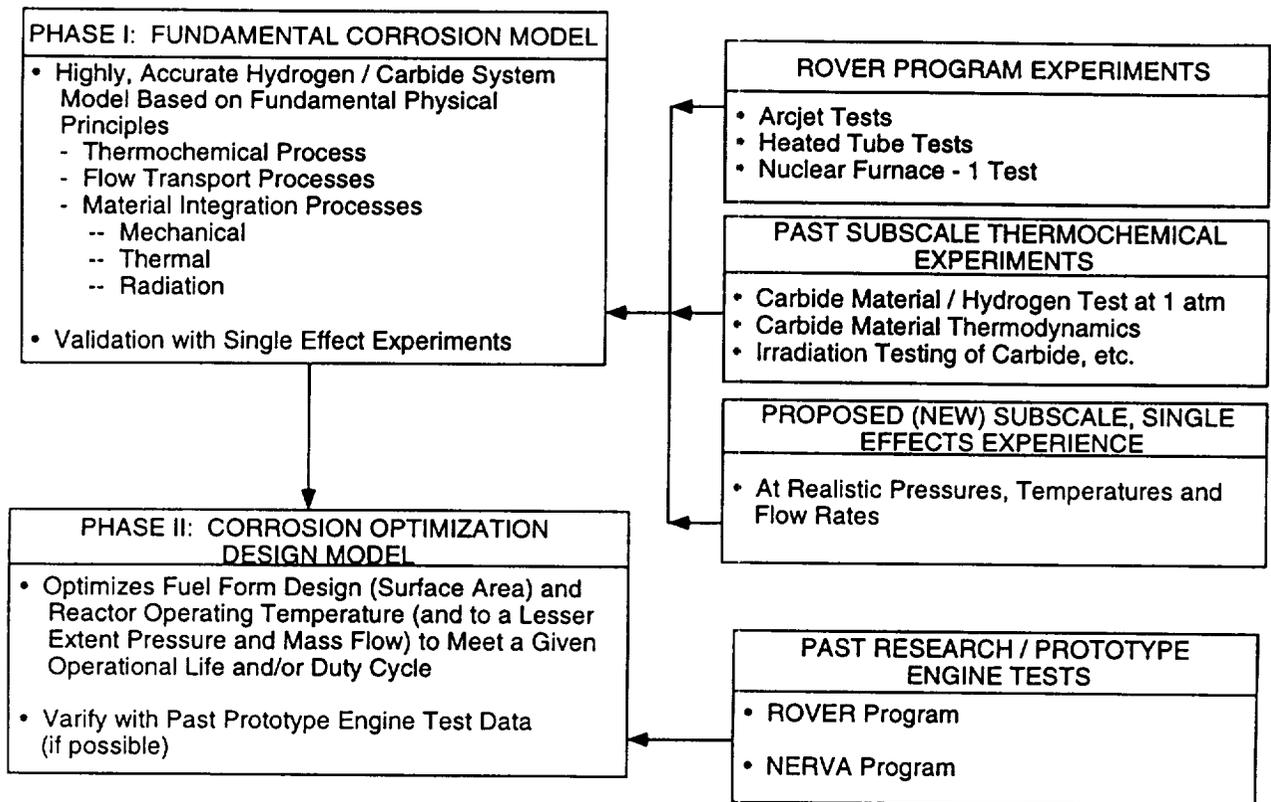


Figure 19. Hydrogen/Carbide Corrosion Model Evolutionary Development Process and Supporting Requirements.

Due to the hostile environment associated with NTP reactor operation, little fundamental single effects data are available at realistic conditions to support model validation. Past subscale thermochemistry and Rover program experiments have provided an existing data base which is marginal for model validation. It is recommended that a new subscale, single effect(s) experimental program be considered at conditions which are more representative of NTP reactor operation conditions, than in the past. The initial investment in supporting this experimental research will pay for itself many times in terms of savings during the costly NTP engine system development program.

It is envisioned that once the fundamental process-based corrosion model is established, it will be integrated with a design optimization model during the second phase of model development, as shown in Figure 19 and discussed earlier. In support of this effort, it may be possible to validate this model with data from past research and prototype engine tests associated with the Rover and

NERVA programs. Acquiring such a design capability would increase NTP engine system operational safety and reliability and would likely produce a substantial development cost saving over current design approaches.



#### 4.0. CONCLUDING REMARKS

Hydrogen corrosion of carbide fuel materials 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 has shown the effects of corrosion to be substantial and highly complex. Hydrogen corrosion phenomena 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 creep. Coatings have been used in the past to combat corrosion, but only moderate success has been achieved. This level of success can be attributed to the complex nature and the degree of (or lack of) understanding of the many interrelated fuel design and operation factors and their influence on corrosion.

Because of the complexity of the hydrogen corrosion phenomena, detailed modeling has not been accomplished. Past modeling efforts have focused on the important thermo-chemical reactions with some success, but they lack inclusion of many of the other interrelated physical processes contributing to hydrogen corrosion in NTP reactors. Benchmark verification of past models have been hampered by the lack of applicable, single effect(s) data on the physical corrosion processes of interest.

Based on the initial findings of this review, it is recommended that future corrosion modeling and supporting characterization efforts focus on:

- 1.) developing a corrosion model that couples all major interrelated physical process mechanisms, even if they are only included on a first-principle level basis,
- 2.) acquiring fundamental single effect(s) data at realistic 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. This insight could likely minimize the investment required to support such a test program. The proposed experimental program, in addition to

providing data to check corrosion model accuracy, 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.

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 development cost.

It is recommended that future corrosion modeling efforts initially address two of the three technical issue areas previously mentioned. An initial near-term effort should focus on developing a first-principle corrosion model, which includes all major corrosion processes identified in this study. One possible approach to this effort could focus on upgrading the LANL thermo-chemical corrosion model, previously discussed in Section 3.0, to include the other physical corrosion processes. Based on this review 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, (including 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 could be incorporated into the model. Once completed, sensitivity studies should be initiated to provide guidance for further model development and experimental verification efforts. These analytical analysis effort(s) should be followed by small, simple, single effect(s) experiments to address particular corrosion issues, which are identified from the sensitivity studies.

In addition to these efforts, UNM-ISNPS also recommends that a future dedicated effort be undertaken to capture the vast experience of the Russians (former Soviet Union) in this area, and integrate it with the United States knowledge base. Only then can a true assessment of this complex technical area be assured.

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