HEAVY WATER ORGANIC COOLED REACTOR

COMPATIBILITY OF HYPERSTOICHIOMETRIC UC AND SINTERED ALUMINUM POWDER (SAP)

By
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A Joint Venture for Heavy Water Organic Cooled Reactors

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ABSTRACT

The status of hyperstoichiometric UC fuel - SAP cladding compatibility studies, applicable to HWOCR conditions, is presented. Diffusion couple interfaces were evaluated, both metallurgically and statistically. Regression equations established correlations between test conditions and the dependent variables of "total reaction thickness" and "uniform reaction thickness." An incubation period, which occurs early in the compatibility reaction, is described. A U-Al-Si phase and impurity elements, including Si and Fe, were detected in the reaction zone by electron beam microprobe analysis. UAl_3 and C (graphite) were detected by X-ray diffraction. A comparison of in-pile (i.e., NRU-305 Experiment) and out-of-pile compatibility data suggests an absence of irradiation effects. The influence of diffusion couple interfacial pressure on the compatibility reaction is discussed. Six steps are suggested to define the compatibility reaction process.

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I. INTRODUCTION

The reference fuel element for the HWOCR development program utilizes a cast and ground cylindrical uranium carbide fuel rod. The rod is contact-bonded (helium gas-bonded initially) to a finned sintered aluminum product (SAP) alloy cladding tube. The fuel rods are designed to allow for fuel slug growth during the course of reaction operation. As the fuel continues to grow after cladding contact is made, high fuel-cladding interfacial pressures are attained. Since the pressures will eventually strain the cladding, knowledge is needed of the SAP cladding integrity and of the SAP-UC interface compatibility.

Early screening tests at Atomics International concluded that neither hypostoichiometric UC-SAP nor stoichiometric UC-SAP are compatible fuel-cladding combinations for HWOCR. These UC-SAP compatibility evaluations led to the selection of hyperstoichiometric UC as the reference fuel for HWOCR, though HWOCR design verification required additional information concerning the compatibility relationships of hyperstoichiometric UC fuel and SAP cladding.

The reactor design is based on a maximum cladding temperature of 870°F, including allowance for surface film formation (hot pin, hot channel), and the in-core lifetime of the fuel assembly ranges from almost three years for the central core elements to about six years for peripheral core elements. The SAP-UC compatibility tests were designed to study the environmental conditions required to promote reaction, the nature of the reactions, and the extent and rate of the reactions. Primary emphasis was on hyperstoichiometric UC fuel in the temperature range between 850 and 950°F. The investigation was performed by metallographical evaluation of the fuel-cladding interface reaction that results from thermal histories of selected fuel compositions. Capsules were exposed to temperatures from 700 to 1150°F for times ranging up to 17,500 hours.

Historically, work on the compatibility of UC and SAP has been conducted at several free world sites, including the Danish Atomic Energy Commission at Risö and the Orgel Program of Euratom's Scientific Activities. In the United States, studies have been conducted by the Atomic Energy Commission at Oak Ridge National Laboratory and at Atomics International.

For several reasons, all sites have found it difficult to describe the reaction kinetics of the compatibility reaction. First, the chemistry of the reaction is not sufficiently well-defined. To date, the reaction products of UAl_3 , UAl_4 , and UAl_5C_4 have been identified. Of these, only two of the three have been detected at one site at one time. At no one time have all three been detected. There is agreement that aluminum is involved in the reaction; however, the influence of carbon and Al_2O_3 is not clearly understood. Second, an adequate quantitative description of the compatibility reaction had not been established. In many studies a reaction was categorized as large, small, major, minor, etc. based on intended engineering application. This limitation restricted the evaluation of results generated at other sites. Finally, the variation in test conditions and evaluations at different sites hindered direct comparison of UC-SAP compatibility data.

In January of 1967, J. T. Venard⁽¹⁾ summarized the results of twelve UC-SAP compatibility investigations. Figure 1 gives the consensus view of times and temperatures that produce either none, acceptable, or not acceptable degrees of reaction. The figure presents only data for the SAP-UC system where the carbon concentration is greater than 4.8 wt %.⁽¹⁾

Figure 1. Temperature - Time Compatibility Limits for SAP vs UC (4.8 wt% C) System⁽¹⁾

A primary objective of the AI study was to determine the influence of hyperstoichiometric UC-SAP compatibility on the performance of the HWOCR. The ability to accurately predict the degree of interface reaction was necessary to satisfy this need. Meaningful compatibility predictions require that a quantitative determination of the reaction product (dependent variable) be given for a specific set of operating conditions (independent variables). The following sequence was used to accomplish this goal.

- 1) Develop a quantitative description of the compatibility reaction. Both metallurgical considerations (e. g. hardness) and simple measurement of reaction zone photomicrographs were used.
- 2) Determine any mathematical relationship between the UC-SAP interface reaction and test conditions of time, temperature, method of surface preparation, and UC chemical composition. The multiple regression analysis technique was used to make this determination and to provide a regression equation.
- 3) The importance of each regression equation correlation was judged, compared, and ranked by the statistical measurements of standard deviation, correlation coefficient, and the number of terms found in each regression equation.

An equally important, but secondary goal was to gain insight into the kinetics and mechanics of the UC-SAP interface reaction. The following work was conducted to attain this objective.

- 1) Metallurgical evaluation of the interface reaction zone
- 2) Electron beam microprobe analysis of the reaction zones
- 3) Laser beam microprobe analysis of selected reaction zone areas
- 4) Comparison with the NRU-305 in-pile experimental results.

II. EXPERIMENTAL DESIGN

Figure 2 defines the limiting time and temperature conditions for the hyperstoichiometric UC-SAP compatibility study. It was planned to use a total of 88 capsules. Each capsule is represented in Figure 2. The "close-out" of the HWO CR program in FY 1967, however, restricted evaluations to those capsules

Figure 2. Hyperstoichiometric UC-SAP Compatibility Studies, Capsule No. DH-1 Through DH-88

shown in Figure 3. The duration of long-term tests was shortened, preventing the examination of other capsules. In all, 66 capsules (292 interfaces) were studied.

Figure 3. Hyperstoichiometric UC-SAP Compatibility Studies, Capsules Evaluated

The compatibility study was performed by metallographically evaluating the fuel-cladding interface reaction that resulted from selected thermal histories. Based solely upon engineering judgment, each hyperstoichiometric UC-SAP couple was then categorized as a "major," "minor," or "no-reaction" interface.

In an attempt to more fully understand the interface reaction, Capsules DH-54 to DH-88 were more stringently evaluated to study the dependent variables of reaction as a function of the experimental (independent) variables. The approach used a multiple regression analysis and calculations were made by the IBM-360 computer. The capsules included in the statistical computer study are given in Figure 4.

The independent variables used in the computer study of Capsules DH-54 to DH-88 were: The impurity level and stoichiometry of the UC, the SAP surface preparation technique, the assembly contact pressure, and the test conditions of time and temperature. The chemical composition of the SAP used in the tests was assumed to be constant. Ten potential dependent variables were selected to describe UC-SAP compatibility and were evaluated statistically.

Figure 4. Capsules Used in Statistical Computer Evaluation of Hyperstoichiometric UC-SAP Compatibility Studies

Of these, the thickness of uniform reaction, and the total reaction thickness, gave good correlations with the independent variables, where total reaction thickness was defined as the sum of uniform reaction thickness plus any projections of interface reaction or SAP into the UC.

The test conditions were selected to simulate and exceed the reference design of the HWO CR demonstration plant, specifically a coolant outlet temperature of 900°F, a fuel element life of 12,000 hours, and a 4.85 to 5.35 wt % C concentration in the UC. Correspondingly, the compatibility studies included test temperatures ranging from 700 to 1150°F, a maximum test duration of 17,500 hours (original plans were 20,000 hours), and a 4.80 to 5.82 wt % C concentration in the UC.

III. TEST CONDITIONS

A. PREPARATION FOR TEST

1. Materials

a. SAP

The SAP alloy used in all of the experiments was XAP-001. The shapes received were extruded 0.5-in. or 1.5-in. diameter rods, and the 1.5-in. diameter rods were subsequently reduced in diameter to 0.5-in. by extrusion. These rods were the starting material for the preparation of SAP diffusion couple wafers. First, the rods were cut to form 0.5-in. diameter discs about 0.415-in. thick. These were then mounted, ten at a time, for surface preparation. The wafers were ground uniformly flat by grinding on 400 and 600 grit silicon carbide paper. The polishing process was started with 14μ , and concluded with 6μ , diamond paste. The SAP discs were then turned and the surface preparation repeated. This technique insured flat, parallel surfaces about 0.412-in. apart, with surface finishes less than 5 rms. The SAP wafers were then ultrasonically cleaned in isopropyl alcohol, washed in hexane and dried with forced hot air.

The UC-SAP compatibility study evaluated the effect of three SAP surface treatments on the rate of the interface reaction. The first was the surface preparation just described. This was called the "as-received" surface. The second treatment was called an "oxidized" surface. This condition was achieved by taking "as-received" SAP discs and oxidizing them in an air atmosphere furnace at 500°C (932°F) for 15 minutes. The third treatment produced a "passivated" surface. Again the "as-received" surface was used as the starting point. Passivation was accomplished by the procedure outlined below.

- 1) Degrease in acetone for 5 minutes
- 2) Clean surface for one hour in an Oakite No. 160 solution (3 oz/gal) at 130 to 140°F .
- 3) Rinse in tap water.
- 4) Dip for 1 to 2 minutes in a 50 vol % nitric acid solution at room temperature.

- 5) Rinse in tap water, followed with spray of distilled water.
- 6) Rinse for 30 seconds in methanol.
- 7) Dry surface with forced warm air.

The above "passivation" treatment was incorporated as the reference HWO CR procedure for fuel rod irradiation experiments. Table 1 gives the typical SAP alloy composition and impurities. For the compatibility studies, the chemical composition of the SAP was considered constant, though the alloy is not completely homogeneous. As shown in Table 1, the alumina concentration may vary from 5 to 8 wt %.

TABLE 1
TYPICAL SAP ALLOY COMPOSITIONS AND IMPURITIES
(wt %)

SAP Alloy	Nominal Al ₂ O ₃ Content (wt %)	Impurities									
		Fe	Si	C	B	Cd	H	N	Cu	Mg	Ti
XAP 001	5 to 8	0.2	0.18	0.5	0.001	0.001	0.001	0.002	0	0	0

b. UC

The hyperstoichiometric UC rods used in these tests were manufactured by arc melting depleted uranium and carbon in a UC skull. This method uses a non-consumable graphite electrode and a 10 to 12 psia furnace pressure in an argon atmosphere. A typical melt was between 320 and 340 gm. The melt was cast into 6- to 8-in. long, 1/2-in. diameter cylindrical rods, and the UC castings provided the starting material for the preparation of diffusion couple wafers.

The castings were Eloxed to make 1/2-in. diameter by 0.420-in. thick discs, and the discs were ground and polished in groups of ten. Silicon carbide paper, 400 grit followed by 600 grit, was used for grinding. This was followed by polishing with 30, 14, and 6 μ diamond paste. To prevent water reactions, kerosene was used as the cooling fluid for all grinding, while "lapping oil" was used for the rough polishing.

TABLE 2

CHEMICAL COMPOSITION OF URANIUM CARBIDE
USED IN COMPATIBILITY STUDIES

Chemical Elements with Constant Concentrations			
Element	ppm	Element	ppm
Ag	<1	Mg	<4
B	<0.5	Mn	<5
Ba	<4	Na	<50
Be	<1	Ti	<25
Ca	<20	Zn	<25
Co	<2	Cb	<50
Li	<5		

Upper and Lower Limits in the Concentration
Range for Chemical Elements which Varies

Analytical Element	Upper Concentration Limit (ppm)	Lower Concentration Limit (ppm)
Al	50.0	10.0
Bi	35.0	2.0
Cd	5.0	0.5
Cr	20.0	<5.0
Cu	15.0	2.0
Fe	175.0	5.0
Mo	20.0	<4.0
Ni	30.0	<5.0
Pb	20.0	<2.0
Si	25.0	10.0
Sn	7.0	2.0
V	10.0	<2.0
N	200.0	85.0
O	400.0	17.0

Once the surfaces were flat and smooth, the specimen was turned and the other side was processed. When both sides were polished they were ultrasonically cleaned in isopropyl alcohol in preparation for final polishing. The last polishing step used Linde "B" (alumina), kerosene, and a 10 vol % oxalic acid solution. This step produced a bright surface with a 3 to 5 rms surface finish. All UC wafer specimens were cleaned in acetone, rinsed in methanol, vacuum outgassed using a dynamic vacuum (1×10^{-5} torr) at 600°C for one hour, and stored in 1×10^{-5} torr vacuum when not in processing. The purpose of the vacuum storage was to reduce any moisture or air contamination. Upon removal from outgassing, the specimens could either be stored under vacuum or directly loaded into capsules for testing.

The chemical composition of the UC used in the compatibility test had a carbon range between 4.80 and 5.82 wt %. Table 2 gives the chemical concentration of the impurities found in the starting UC. A chemical determination of the impurity concentration divided the elements into those which remained constant and those which varied in concentration. The upper and lower limits in the range of concentration are presented for the elements which varied.

2. Capsule Assembly

Diffusion couples were used to study the compatibility of UC and SAP. A "cross-section" of the assembled capsule is given in Figure 5. As shown, the tests were conducted in a heavy-walled Inconel X capsule containing ten specimen wafers. The UC and SAP specimens were alternately stacked to simulate the fuel-cladding interface found in the reactor. Assembly pressure was imposed by the threaded Type 304 Stainless Steel end plug. Initially, 75 ft-lb of torque were used in capsule assemblies; later, to eliminate UC wafer cracking, a torque of only 25 ft-lb was used. Because of the different thermal expansions of the test specimens and capsule components, the compression increases at test conditions. This aspect of the capsule design insures intimate contact between specimens. The final closure of the capsule was made by welding the Type 304 Stainless Steel end plug to the Inconel X capsule wall. All capsule assembly work was done in a glove box under a protective helium atmosphere at 10 to 12 psig pressure.

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Figure 5. UC-SAP Compatibility Capsule As Loaded
(Capsules DH-1 through DH-88 sealed in helium
atmosphere)

B. OPERATION

Resistance-type electrical furnaces were used to thermally soak the capsules. To insure accurate temperature control, Chromel-Alumel thermocouples were attached to the outer surface of compatibility tests capsules and were held in place by wire bands. Generally, the furnace temperature was controlled to $\pm 5^{\circ}\text{F}$ of the nominal test temperature.

C. SECTIONING, MOUNTING, AND SAMPLE PREPARATION

The compatibility capsules were sectioned longitudinally by the Elox process. After the appropriate heat treatment, all surface oil was removed with acetone and methanol. The exposed surfaces were then impregnated with epoxy resin to fill any voids found in the UC. Coarse grinding began on a Buehler high speed disc grinder, starting with 180 grit and finishing with 320 grit silicon carbide paper. Fine grinding was done with 400 and 600 grit silicon carbide paper. Kerosene was used as the fluid coolant. After the capsule surface had been made uniformly flat by grinding, the surface was coarse-polished on a metallography cloth, using 6μ diamond paste suspended in lapping oil. A Microcloth with Linde B alumina, 10 vol % oxalic acid solution, and a small quantity of kerosene, were used for final polishing.

After a satisfactory polish had been achieved, the UC segments of the capsule were etched with a solution of equal parts of acetic acid, nitric acid, and water. The sample was then repolished and etched as just described. This sequence was repeated as many times as necessary to attain a high polish and a clear delineation of the microstructure. To etch the SAP, the aluminum segments were swabbed for one to two seconds with a solution of Murakami's Reagent* followed by a quick rinse. This reagent will also etch the SAP-UC reaction zone which is an aluminum based matrix.

The photographic sequence used in preparing the UC-SAP interfaces for evaluation was:

- 1) A 2.5 X photograph of the overall capsule surface was made. This allowed comparison of all 9 interfaces and depicted the general condition of the capsule.

*Murakami's Reagent is a 10% solution of potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$, 10% solution of sodium hydroxide, NaOH . Solutions are separately made, then mixed in equal parts for use as needed. Mixed reagents will decay on standing.

TABLE 3
CHEMICAL COMPOSITION OF URANIUM CARBIDE USED
IN COMPUTER STUDIES OF 198 UC-SAP INTERFACES

Elements with Constant Chemical Impurity Concentration			
Element	ppm	Element	ppm
Ag	<1	Li	<2.5
Al	<10	Mg	<4
Ba	<4	Mn	<5
Be	<0.5	Na	<50
B	<0.5	Ti	<20
Ca	<20	Zn	<25
Cr	<5	Mo	<4
Co	<2	Cb	<50

Maximum and Minimum Concentration for Chemical
Impurity Elements Which Varied

Element	Maximum Concentration (ppm)	Minimum Concentration (ppm)
Bi	30.0	2.0
Cd	5.0	0.5
Cu	15.0	2.0
Fe	25.0	5.0
Ni	30.0	5.0
Pb	7.0	2.0
Si	25.0	10.0
Sn	4.0	2.0
V	5.0	2.0
T. I. V. C. C. *	561.5	179.5

*T.I.V.C.C. = Total independent variable chemistry content

- 2) Each interface was carefully studied at 150 X magnification. For each interface the "worst case" condition was selected and photographed at 150 X magnification. If "no reaction" was found, or if there was an area of particular interest, the total interface was reevaluated at 1000 X magnification. Worthy conditions were photographed at 1000 X magnification.

D. CHEMICAL COMPOSITION OF URANIUM CARBIDE AND SAP USED IN STATISTICAL ANALYSIS

It has long been known that small variations in alloying elements and impurities have great effects on the properties of engineering materials. Prediction of threshold concentrations for a specific material use is initially difficult and usually requires extensive testing. Therefore, the statistical analysis included all known chemical variations, no matter how slight. All elements of metallurgical importance were mathematically evaluated, and elements found to be of questionable significance were noted for subsequent study.

Table 3 gives the metallic impurity level of the uranium carbide specimen used in the statistical studies. Both those elements considered constants and those which vary are shown.

The SAP alloy used in all diffusion couples was XAP-001, with a typical Al_2O_3 constant of 5 to 8 wt %. Although the SAP alloy was considered a constant, its composition was not totally homogeneous. When the metallic impurities were evaluated, by multiple regression analysis, for their contribution to the UC-SAP compatibility reaction, only silicon and nickel were found to be statistically significant.

Figure 6. Hyperstoichiometric UC-SAP Compatibility Studies, Capsules and Interfaces Evaluated

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. INTRODUCTION

The goal of the UC-SAP Compatibility Study Project has been to define the nature and extent of the reaction between hyperstoichiometric UC fuel and SAP cladding. Specific knowledge of the extent of the reaction at various operational design levels is needed to satisfy pragmatic engineering requirements, two of which are to: (1) provide information to help determine fuel element reliability for reactor application, and (2) establish a method which will allow the prediction of the UC fuel - SAP cladding reaction under various conditions of time and temperature. These goals were accomplished by using the engineering test approach. Another objective of the task, however, was to study the nature of UC-SAP compatibility reactions. To satisfy this latter requirement, a more basic approach, concerned with mechanisms and reaction products, was also incorporated within the study. The technique of integrating the engineering and basic approach has provided additional insight into the understanding of the compatibility reactions of UC and SAP. Interpretation and evaluation of the experimental results were aided by the use of probabilistic models and statistical inference.

B. ENGINEERING EVALUATION

1. Visual Evaluation

The results of the visual evaluations of the compatibility study are summarized in Figure 6 illustrating the regions where the "major," "minor" and "no" reactions occur. The results, in general, agree with prior AI investigations and studies at other sites; nevertheless, as shown in Figure 6, these areas are not simply a function of reaction time and temperature. The overlapping of different regions clearly illustrates the importance of other unknown variables. Hence, a more stringent statistical approach was attempted to more fully understand the interface reaction.

2. Numerical Value for Compatibility Interaction

Quantitative definition of the compatibility interaction between hyperstoichiometric UC and SAP has been difficult. Generally, the reaction at the interface does not lend itself to simple measurement. For this reason, many past

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Figure 7. Major Reaction Interface

- a. Knoop Hardness vs Traverse Across UC-SAP Interface
- b. Photomicrograph

studies have used engineering judgment to describe the metallographically observed interaction; these evaluations gave verbal descriptions of reactions, such as "small," "large," "major," "minor," etc. More recently, investigations have measured the reaction zone width, using these measurements in conjunction with microhardness traverses and verbal descriptions. Early in the subject compatibility studies, however, the need for meaningful numerical values became quite clear since any statistical approach requires numerical values for the dependent variables.

One disadvantage of studies involving UC is that exposure to moisture and air deteriorates the surfaces of specimens. This evaluation limitation can necessitate repolishing of surfaces, with the possible loss of the area of interest. However, for this compatibility study, photography was extensively used to remove the dependence on repeated visual observation of the specimen surface. Once specimens were prepared, standard 150 X magnification photomicrographs were taken. In addition, areas of specific interest were recorded at 1000 X magnification. This technique provided permanent records for subsequent evaluations.

It was important to establish what measurements of the reaction interface were significant. The first attempt used a detailed metallurgical evaluation to quantitatively describe the compatibility reaction. This approach met with limited success, since it was limited by the engineering judgment required to differentiate between reaction categories. Nevertheless, the technique allowed a more quantitative approach than previously used. In general, the broad divisions of "major," "minor," and "no" reaction at the interfaces were established.

The metallurgical examination consisted of the following steps: (1) establishment of microhardness profiles across the interface of interest, (2) measurement and recording the size of the reaction zone at 150 X, and (3) preparation of photomicrographs of the area of study to typify each definition. Figures 7, 8, and 9 give the results from major, minor, and no-reaction interfaces evaluated, respectively. The identification of the compatibility capsule selected for study, the experimental test conditions, the carbon concentration found in the UC, and the hardness traverses are shown in each figure.

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Figure 8. Minor Reaction Interface

- Knoop Hardness vs Traverse Across UC-SAP Interface
- Photomicrograph

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Figure 9. No-Reaction Interface

- Knoop Hardness vs Traverse Across UC-SAP Interface
- Photomicrograph

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Figure 10. Types of UC-SAP Compatibility Reactions, and Locations of Descriptive Measurements

At this juncture, we did not know which attributes of the UC-SAP interface were significant enough to measure. No correlations were known between the dependent variables of the compatibility reaction and the independent test variables. A visual overview of the interface area revealed characteristics by which the reactions could be typified and measured. Figure 10 describes each type of compatibility reaction and gives the measurements used in its numerical definition. A total of eight reaction measurements were used to describe the four interface reaction types: no reaction, isolated reaction, uniform reaction, uniform reaction - SAP intrusion, and major reaction. Yet, the prime design parameter of "maximum reaction" thickness was missing. To fulfill this need, the reaction thickness and depth of penetration were added. This sum created a new dependent variable called "total reaction thickness" (TRT).

In brief, nine values were used to describe the compatibility reaction. When arranged as shown in Table 4, they produce a numerical value free of verbal adjectives, i.e., the larger the number, the more the interface reaction. Also presented are the largest and mean numerical values for each dependent variable measurement of the compatibility reaction.

The statistical significance of each reaction measurement was determined by multiple regression analysis. The evaluation used an experimental data set containing 191 data points or interfaces. An 85% probability level was selected

TABLE 4
DEPENDENT VARIABLES OF THE UC-SAP COMPATIBILITY REACTION

Dependent Variable Measurement	Total Reaction Thickness (mils) (A + E)	Uniform Reaction Thickness (mils) (A)	Reaction Zone Width (mils) (B)	Depth of Penetration (mils) (E)	Width of Penetration (mils) (F)	Width of UC Islands in SAP (mils) (H)	Thickness of UC Islands in SAP (mils) (G)	Distance Between Reaction Zones (mils) (C)	Thickness of 2nd Phase Reaction (mils) (D)
Maximum Value of Reaction Variable	124	110.5	500	32.4	150	30	15.8	16.0	0.0
Mean Value of Variable (Typical Reaction)	10.99	5.788	299.4	5.206	16.450	1.312	0.7979	0.34	0.0
Regression Equation Correlation Coefficient	0.9781	0.9738	0.7923	0.8734	0.8804	0.8744	0.8887	0.5332	Constant
Regression Standard Equation Deviation	5.27	4.63	162.0	3.57	11.28	1.874	1.162	0.72	
Number of Terms in Regression Equation	48	51	26	35	32	33	31	30	

for the significance level for the terms of the regression equation. Each dependent variable was correlated with 79 independent variable terms. The first 17 terms describing the independent variables were linear terms of UC chemistry, time, temperature, and SAP surface preparation technique. The next 17 (terms 18 through 34) were the squares of linear terms. The final 35 terms (terms 35 through 79) were the cross products of UC chemistry, time, temperature, and SAP surface preparation. As shown in Table 4, two measurements showed important correlations: the total reaction thickness and the uniform reaction thickness, which had correlation coefficients of 0.9781 and 0.9738, respectively. Only these two dependent variables were considered worthy of additional study.

Table 3 gives the metallic impurity level of the uranium carbide used in the compatibility studies. The figure is divided into those elements considered constants and those which vary.

3. Regression Analysis

The mathematical tool of multiple regression analysis allows determination of the relationship between the dependent variables of a compatibility reaction and the independent variables of test conditions. The technique also provides the F ratio method for evaluating the significance of each independent variable term. The greater the value of the F ratio, the more important is its contribution to the correlation. The test of a particular input variable's significance is made by testing individual F ratios at a preselected fixed probability level.

The Weighted Regression Analysis Program (WRAP)⁽²⁾ which was used in this study is capable of correlating up to 80 independent variables with the dependent variable. This latitude permits the input of several mathematical forms for the same basic variable. For example, the input for the silicon concentration in uranium carbide had the following five terms: Si, e^{Si} , (Si) (time), (Si) (temperature), and (Si) (SAP Surface Treatment); the regression analysis for the total reaction thickness evaluation included 17 independent variables using 79 mathematical terms. Trial and error iterations, which were conducted to improve statistical measurements, resulted in the following regression equation:

$$\begin{aligned}
\text{TRT} = & 1712.894 + 24.51518 (\text{Cu}) - 0.4196207 (\text{Ni}) \\
& + 9.613975 (\text{N}) - 0.06503935 (\text{O}) + 13.72196 (\text{Si}) \\
& - 124.1250 (\text{Sn}) - 217.1851 (\text{V}) - 0.02875682 (\text{time}) \\
& - 4.894131 (\text{temperature}) - 0.05254102 e^{\text{Cd}} \\
& - 158.7392 e^{\text{N}/100} + 2.437303 e^{\text{V}} \\
& + 1233.397 e^{\frac{(\text{temperature})}{1000}} + 0.0001225488 (\text{time} \times \text{Bi}) \\
& - 0.0001166089 (\text{time} \times \text{N}) + 0.00001361177 (\text{time} \times \text{O}) \\
& - 0.0001458983 (\text{time} \times \text{Si}) \\
& + 0.00003170006 (\text{time} \times \text{temperature}) \\
& - 0.01839457 (\text{temperature} \times \text{Cu}) \\
& - 0.002758569 (\text{temperature} \times \text{N}) \\
& - 0.009165977 (\text{temperature} \times \text{Si}) \\
& + 0.09037355 (\text{temperature} \times \text{Sn}) \\
& + 0.1392548 (\text{temperature} \times \text{V}) \quad \dots(1)
\end{aligned}$$

The mathematical units for the chemistry elements are ppm, time is given in hours, and temperature is in °R. Concentrations of elements refers to uranium carbide; SAP composition is assumed constant. This 24-term equation is derived from 198 data points. The analysis was conducted at a 0.999 probability level. The correlation coefficient and the standard deviation for the regression equation are 0.975 and 5.16 mils, respectively. This equation allows the comparison of candidate uranium carbide materials based on their predicted total reaction thickness values.

A much simpler equation can be obtained by selecting a specific uranium carbide chemistry. Given the most representative chemistry (Table 5) Equation 1 reduces to a function of time (hr) and temperature (°R) having only five terms, Equation 2:

$$\begin{aligned}
\text{TRT} = & 1930.0102 - 0.042383 (\text{time}) - 4.95182 (\text{temperature}) \\
& + 0.0000317 (\text{time} \times \text{temperature}) \\
& + 1233.397 e^{\frac{(\text{temperature})}{1000}} \quad \dots(2)
\end{aligned}$$

TABLE 5
MOST REPRESENTATIVE CHEMISTRY OF
URANIUM CARBIDE

Element	ppm	Element	ppm
Pb	2.0	N	105.0
V	2.0	O	35.0
Sn	2.0	Ni	5.0
Cd	0.5	Cu	5.0
Bi	5.0	(T.I.V.C.C.)*	171.5
Si	10.0		

*Total Independent Variable Chemistry Content is defined as the most representative value of the sums of chemical independent variables.

Figure 11 gives the total reaction thickness vs time at a number of constant temperature levels for the most representative uranium carbide chemistry. A threshold reaction temperature of about 875°F is observed, where threshold temperature is defined as the temperature below which no increase in

Figure 11. Total Reaction Thickness vs Time at Constant
Temperatures for Most Representative Chemistry

compatibility reaction will occur at infinite time. Selection of 10,000 hours was made as equivalent to infinity.

A like approach was used in the regression analysis of the dependent variable, uniform reaction thickness (URT). The regression equation for the uniform reaction contains 18 terms and is:

$$\begin{aligned}
 \text{URT} = & 1596.136 + 2.27495 (\text{N}) + 13.37659 (\text{Si}) - 238.0981 (\text{V}) \\
 & - 0.0269485 (\text{time}) - 3.961027 (\text{temperature}) \\
 & + 0.4348057 (e^{\text{Bi}}) - 0.20508 (e^{\text{Cd}}) \\
 & + 960.1025 e^{\frac{(\text{temperature})}{1000}} - 0.00006182936 (\text{time} \times \text{N}) \\
 & + 0.0002742025 (\text{time} \times \text{Pb}) - 0.0000943583 (\text{time} \times \text{Si}) \\
 & + 0.000006966734 (\text{time} \times \text{T.I.V.C.C.}) \\
 & + 0.00001991592 (\text{time} \times \text{temperature}) \\
 & + 0.002625247 (\text{temperature} \times \text{Cd}) \\
 & - 0.001512752 (\text{temperature} \times \text{N}) \\
 & - 0.009475542 (\text{temperature} \times \text{Si}) \\
 & + 0.178447 (\text{temperature} \times \text{V}) \quad \dots(3)
 \end{aligned}$$

where chemical concentration is in ppm, time is in hr, and temperature in °R. The statistical dimensions of the equation are: 198 data points, a correlation coefficient of 0.953, a standard deviation of 5.438 mils, and a regression equation probability level of 0.999.

Again, using the most representative UC chemistry, the preceding regression equation can be expressed in the following terms of time and temperature,

$$\begin{aligned}
 \text{URT} = & 1492.9543 - 0.026386 (\text{time}) - 3.856421 (\text{temperature}) \\
 & + 0.0000199 (\text{time} \times \text{temperature}) \\
 & + 960.1025 e^{\frac{(\text{temperature})}{1000}} \quad \dots(4)
 \end{aligned}$$

Figure 12 shows the relationship between URT and time at a number of constant temperature levels for the most representative UC chemistry. Although

Figure 12. Uniform Reaction Thickness vs Time at Constant Temperatures for Most Representative Chemistry

some values for compatibility reaction are negative, some understanding of a threshold reaction temperature can be obtained. The temperature for which uniform reaction thickness would not increase (a horizontal line) is again about 875°F. Additional weight can be given to this 875°F level since similar threshold temperatures were generated by two separate and independent regression analyses.

Venard,⁽¹⁾ in January 1967, reviewed the available literature associated with the compatibility of UC and SAP. The consensus viewpoint of Venard for temperature-time compatibility limits for the SAP vs UC (> 4.8 wt % C) system is shown in Figure 1. The times and temperatures of 9600, 6000, and 2700 hours and 950, 975, and 1000°F, respectively, were used to translate the compatibility limit to Figure 12. This translation gives a constant URT of 4 mils as the consensus of engineering acceptability.

C. BASIC RESULTS

1. Metallurgical Evaluation

a. Electron Microprobe X-Ray Analysis

During the course of our investigation, several reaction interface samples (Table 6) were examined by electron microprobe X-ray analysis (EMXA).

TABLE 6
REACTION INTERFACE SAMPLES EXAMINED BY EMXA

Capsule-Interface Number	Time (hr)	Temperature (°F)
DH-70-3	500	1050
DH-65-4	8,000	925
DH-81-3	4,000	950
DH-66-7	10,000	925

Samples removed from capsules by core-drilling were mounted, ground, and polished for EMXA examination. Sample DH-70-3 was the first sample examined, representing an example of a major reaction between UC and SAP. The investigation of this sample was purely exploratory. The major finding in DH-70-3 was that both Al and U were present, in varying proportions, throughout the area called the "reaction zone."

A more detailed analysis of Samples DH-81-3 and DH-65-4 was made (Figures 13 and 14). Both of these samples were selected because their time-temperature test fell somewhat above the anticipated HWO CR operating conditions. Both samples were typical of minor reactions with a number of intrusion reactions into the UC. The EMXA results of this investigation follow.

- 1) The elements, Ca, Cu, Fe, Mo, Nb, Ni, Si, Sn, and Zn, all of which may be present as impurities in either or both the SAP and UC, were examined to determine whether they had precipitated or segregated from their host materials. Fe and Si were found to be present in amounts greater than 1%, in the following locations.

1

2

3

4

5

6

a. Al X-rays

b. U X-rays

c. Si X-rays

d. Ca X-rays

Figure 13. Area Scans of U, Si, Al, and Ca X-rays, Sample DH-81-3 [Si-containing region (U-Al-Si) at UC-SAP interface and in intrusion reaction zone; Ca-Si-Al inclusion optically fluoresces under electron beam (probably an oxide); dark region within UC (b.) corresponds to cracks in fuel.]

a. Specimen Current

b. Al X-rays

c. U X-rays

d. Si X-rays

Figure 14. Area Scans of Specimen Current, U, Si, and Al X-rays, Sample DH-65-4 [Si-containing region (U-Al-Si) at UC-SAP interface and at start of intrusion reaction zone; U-Al region for remaining reaction zone.]

Figure 15. Line Profiles of U, Si, and Al X-rays, Sample DH-65-4, Taken Perpendicular to SAP-UC Interface (U-Al region away from SAP)

- 2) Analysis of the SAP showed nodules of an Fe-rich phase.
- 3) There is, in addition to an intrusion reaction, an interface reaction between the UC and the SAP. This interface reaction zone contains ~74 wt % U, ~20 wt % Al, and ~6 wt % Si. The Si in the interface reaction can be seen, for example, in Figures 13c and 14d. We thought that the interface reaction had not been previously observed on photomicrographs because of the relatively low magnifications employed for our investigation, but subsequent investigation at higher magnifications showed that it was difficult to identify interface reaction between the UC and the SAP.
- 4) The intrusion reaction contains U-Al-Si and U-Al. This can be clearly seen by comparing Figures 14b and 14d, where the U-Al-Si region is closest to the SAP and the remaining intrusion reaction in the UC is U-Al. Figure 15 shows the distribution (one dimensional) of U, Al, and Si, and identifies the U-Al-Si at the UC-SAP interface, and the U-Al farther into the UC. Subsequent light microscope examination at high magnification revealed that some slight distinction could be made between regions of U-Al-Si and U-Al in the intrusion reaction, namely, that the U-Al-Si region would appear slightly "gray" relative to the "white" U-Al region.

The analysis of DH-66-7 (10,000 hr at 925°F) offered something in the way of unusual results. Photomicrographs of the area in question show the following characteristics:

- 1) A noticeable phase segregation in the SAP alloy (light versus gray regions)
- 2) A white SAP area adjacent to the UC interface where a major intrusion occurred
- 3) The observation, in the body of the intrusion, of many particles which appeared to be precipitates
- 4) Islands of UC in the intrusion
- 5) Colored phases in the intrusion.

The complexity of the reaction was further illustrated by EMXA which showed that:

- 1) The light areas in the SAP were richer in Al than was the gray.
- 2) The white area at the mouth of the intrusion was also Al-rich.
- 3) The body of the intrusion was almost entirely Al; no alloyed U or Si was present.
- 4) The inclusions or precipitates were rich in iron.
- 5) The colored area was lower in Al and showed traces of Si and Fe.

In this sample, the composition and testing of which compare with those of DH-65-4 and DH-81-3, there was no observation of reaction. The only characteristic in common with the other samples was the intrusion of SAP into UC.

b. Laser Beam Microprobe Analysis

A laser-excited spectrographic analysis was used for the purpose of identification and semi-quantitative measurement of the chemical composition across the UC-SAP diffusion couples. Fourteen interfaces, each representing a different reaction condition, were chosen for study. The interfaces selected ranged from no reaction to a major reaction having a width of 0.040-in.

The data revealed strong emission lines for aluminum and uranium only, with silicon and iron as common impurities. Repeated measurements, variations of technique, and precision realignment of the equipment did not lead to reproducibility of data. To some degree, all analyses of uranium carbide and reaction zones were marked by an intensified background. This condition was caused by the high concentration of uranium, which has many emission lines. The light element, carbon, was difficult to determine because the dense background had a large adverse influence on the sensitivity needed for detection.

The composition and concentration data obtained by laser microprobe were plotted against the dimension across the interface. When applicable, curves were made for Al, U, Fe, Si, Cr, Ca, and Ni. Comparison of these graphs, between those of the same region of the same interface, showed little consistency. However, observations generally confirming the EMXA data were that: (1) the impurities of Fe and Si tended to concentrate in or near the interface region, and (2) the aluminum concentration of the major reaction found at Interface 9 of

Capsule 70 decreased slightly from the parent SAP to the reaction zone. Observation (1) gives independent evidence that, again, silicon has a role in the UC-SAP compatibility reaction.

c. X-ray Diffraction

X-ray diffraction was used to identify the crystallographic or phase characteristics of a major reaction interface. The samples of the reaction zone submitted for study came from Capsule DH-55-4 which had a thermal history of 8000 hours at 1050°F. The specimen was ground to powder and x-ray photographed by the Debye-Sherer method. Twenty-seven of the 38 lines found on the x-ray photograph were identified as UAl_3 , Al, and C (graphite). However, the detection of Al in the reaction zone may be misleading. Its presence is probably associated with parental SAP accidentally introduced into the specimen during preparation. The compounds Al_2O_3 , UO_2 , U_3O_8 , UAl_2 , and UAl_4 were not detected.

To establish and categorize better x-ray lines, another specimen from the same interface was subjected to $120^\circ\text{-}2\theta$ x-ray diffractometer analysis. In this analysis, 41 peaks were determined, with UAl_3 , UC, C (graphite), and Al_3C_4 accounting for 27 of them. The presence of UC in the sample again suggested the introduction of parent material during specimen preparation.

Because of the previous detection of silicon by an electron beam and laser beam microprobe analyzer, the x-ray diffraction results were evaluated for the presence of silicon compounds. Although identification was limited by the availability of standards for the U-Si system, it was determined that U_3Si and USi_3 were conceivable possibilities. However, the major lines for these intermetallics are obscured by the U-Al system lines. Further investigation gave no evidence to support the presence of U_3Si_2 or USi . The lack of standards data for the U-Al-Si and U-Al-Si-C system made identification of any ternary or quaternary phases impossible.

In brief, x-ray diffraction studies of a major reaction zone between hyperstoichiometric UC and SAP revealed the presence of UAl_3 , C (graphite), and possibly Al_3C_4 , U_3Si , and USi_3 .

Figure 16. Small Spherical Fuel Particle (~ 0.002 -in. diameter) Embedded in Cladding

Etched

85-4-2

7866-4-1

Figure 17. Local Reaction Occurring Intermittently at SAP-UC Interface

d. NRU-305 In-Pile Experience*

The evaluation of UC fuel - SAP cladding compatibility in the NRU-305 Fuel Element Irradiation Experiment has given no results that conflict with out-of-pile experimental data. The test environment of the NRU-305 Irradiation Experiment is described below.

- 1) UC fuel centerline temperature was 1900 to 2100°F, with peak temperatures of 2100°F.
- 2) The average SAP cladding outer surface temperature was 850°F, with peak temperature of 870°F.
- 3) The test duration was equivalent to about 213 full power days (~9650 Mwd/MTU).
- 4) All UC fuel in the experiment was hyperstoichiometric.
- 5) The integrated neutron flux at the fuel-cladding interface was:
 - a) Fast neutron (> 1 Mev) nvt = 8×10^{20} , and
 - b) Thermal neutrons, 2.1×10^{21} nvt for the outer ring of fuel element rods.

The UC-SAP interaction zone observed in the irradiated fuel rods was discontinuous and limited to the area of fuel-cladding contact. The interaction zone extended from the UC-SAP interface only into the fuel. All fuel rods selected for interface examination were taken from Bundle LTA of NRU-305. The minimum, maximum, and average thicknesses of the UC-SAP interaction zone found in Bundle LTA (i.e., Rods B, H, J, N, and P) were 0.0005, 0.001, and 0.0008 inches, respectively. These results give good agreement with out-of-pile data. For example, compare metallurgical structure of the reaction zone of Figure 16, where a small spherical fuel particle is embedded in the cladding, with the local reaction shown in Figure 17.

e. Stages of UC-SAP Compatibility Reaction

A total of 292 UC-SAP interfaces covering a wide range of thermal histories were evaluated in measuring values for the dependent variables of TRT and URT.

*The specific details of the NRU-305 Experiment are reported in AI-CE-76.

UC Etched

7530-1-1

Type A. No Reaction at UC-SAP Interface

7486-3-4

B. No Reaction at UC-SAP Interface or at SAP Intrusion into UC

Figure 18. Step 1 – No Reaction

These determinations led to detailed comparisons, classifications, and groupings of interfaces. Finally, the evaluation suggested the stepwise reaction sequence described below.

Step 1 — No Reaction (Figure 18)

Type A — No reaction found at the UC-SAP interface

Type B — No reaction found at the UC-SAP interface or at the interface of a SAP intrusion into the UC

Step 2 — Isolated Reaction (Figure 19)

Type A — Local reaction found occurring intermittently at the UC-SAP interface

Type B — Local reaction found at the UC-SAP interface of a SAP intrusion into UC

Step 3 — Uniform Reaction (Figure 20)

A uniform reaction found along the entire UC-SAP interface

Step 4 — Uniform Reaction — SAP Intrusion (Figure 21)

A uniform reaction found along the entire UC-SAP interface and at the interface between the SAP intrusion and UC

Step 5 — Major Reaction — Early Stages (Figure 22)

A uniform reaction along the entire UC-SAP interface and at the interface between the SAP intrusions and UC. The SAP penetrations into the UC connect and form UC islands surrounded by compatibility reaction products.

Step 6 — Major Reaction — Latter Stages (Figures 23 and 24)

A uniform reaction along the entire UC-SAP interface and at the interface between the SAP intrusions and UC. The SAP penetrations into the UC connect and form UC islands surrounded by compatibility reaction products. There is evidence of material depleted from the parent SAP surface. Sometimes there is branching of the SAP intrusions. Close examination of reaction products shows fern-like structure.

7866-4-1

Type A. Local Reaction Occurring Intermittently at UC-SAP Interface

7495-3-2

Type B. Reaction Product at SAP-UC Intrusion Interface

Figure 19. Step 2 - Isolated Reaction

7866-8-1

Figure 20. Step 3 — Uniform Reaction Located Along Entire UC-SAP Interface

7815-7-2

Figure 21. Step 4 — Uniform Reaction Along UC-SAP Interface With SAP Intrusion Into UC

7934-2-1

Figure 22. Step 5 — Major Reaction (Early stages) UC Island Formation

7934-9-1,-2

Figure 23. Major Reaction (Latter stages)

6330-6-7-2

Figure 24. Major Reaction (Latter stages) Showing Fern-Like Structure

The depletion of parent SAP at the diffusion couple interface occurs in the latter stages of the reaction process, as indicated in Figure 25, where capsules having interfaces with visually observed SAP depletion are noted among the capsules evaluated. A curve separates the capsules with and without SAP surface depletion.

Figure 25. Capsules Showing Visual SAP Depletion at Interface

Mathematical analysis can be used to help establish the importance of specific chemical elements in the compatibility reaction. This can be done by F ratios, which are used to compare the relative importance of each term found in the total reaction thickness and uniform reaction thickness regression equations (see Table 7). Some measure of relative weight of a particular term can be obtained by comparing the term F ratio to the largest F ratio (i.e., ranking the F ratios for the various terms in the regression equation). Regression terms whose F value is less than one-tenth of the largest F term are considered of questionable contribution, and will not be discussed here. Future UC-SAP compatibility tests, however, should not dismiss their effects.

TABLE 7
F RATIOS FOR REGRESSION EQUATION OF TOTAL REACTION
THICKNESS AND UNIFORM REACTION THICKNESS

Total Reaction Thickness			Uniform Reaction Thickness		
Order of Rank	Term	F Ratio Value	Order of Rank	Term	F Ratio Value
1.	e^{Temp^*}	421.3	1.	Temp	262.9
2.	Temp	400.0	2.	e^{Temp}	254.7
3.	Constant	186.0	3.	Constant	191.9
4.	(Time [†])(Temp)	161.9	4.	(Time)(Temp)	65.2
5.	N	63.1	5.	(Temp)(V)	58.6
6.	(Time)(N)	59.7	6.	(Time)(TIVCC) [§]	56.8
7.	(Time)(O)	59.4	7.	V	52.5
8.	Time	57.9	8.	e^{Cd}	47.5
9.	(Time)(Si)	49.8	9.	(Time)(N)	43.3
10.	O	41.0	10.	(Temp)(Si)	35.7
11.	V	37.3	11.	Si	35.2
12.	e^V	36.6	12.	Time	30.4
13.	e^N	34.9	13.	(Time)(Si)	25.6
14.	(Temp)(Sn)	33.5	14.	(Temp)(Cd)	18.2
15.	Sn	33.3	15.	e^{Bi}	15.8
16.	Si	32.3	16.	N	13.3
17.	(Temp)(N)	30.7	17.	(Time)(Pb)	12.1
18.	(Time)(Bi)	29.2	18.	(Temp)(N)	11.8
19.	(Temp)(V)	28.9			
20.	(Temp)(Si)	28.3			
21.	Ni	23.0			
22.	(Temp)(Cu)	22.8			
23.	Cu	22.3			
24.	e^{Cd}	17.4			

*Temp = Temperature (°R) (absolute)

†Time = Hours

§TIVCC = Total Independent Variable Chemistry Content (ppm)

Temperature is the first order of importance in both equations, because of the strong dependence of chemical and diffusion reactions on temperature. For the TRT equation, the terms of next importance are the concentrations of nitrogen and oxygen. For the third parameter, no mathematically significant correlation was found between carbon content of UC and the compatibility reaction. Time ranks as the fourth independent variable cited, as might be expected from the large influence of time in diffusion reactions. The fifth consideration is the cross product term of time and silicon concentration in the UC starting material.

As previously stated, temperature is the independent variable contributing most to the regression equation for URT. Review of the regression equation shows that temperature contributes to three out of the first four ranked terms, and to seven of the total eighteen terms. Time is the second most frequent independent variable to appear in the URT equation. Its metallurgical importance is known and requires no discussion. Third in the order of mathematical importance is vanadium concentration, even though the element is present in only very small quantities. While it is difficult to accept that concentration changes from 2 to 5 ppm can have metallurgical merit, it is possible that vanadium concentration indirectly represents the influence of other unspecified elements. Ranked fourth is the total independent variable chemistry content. Metallurgically, impurity content can be a measure of alloy cleanliness. For uranium carbide it may well be a quantitative measurement of impurities located at the grain boundaries. Photomicrographs of the interface reaction suggest that reaction may well start at the grain or phase boundaries. Cadmium is ranked fifth in order of F ratio values. It, like vanadium, also has a narrow range in concentration. The minimum value is 0.5 ppm, and the maximum value is 5.0 ppm. The metallurgical justification for this mathematical rank is not clear. Thus, the contribution of cadmium to the interface reaction is of questionable merit. However, the mathematical ranking of cadmium indicates it should be considered in future studies. Nitrogen and silicon are the remaining elements with F ratios greater than one-tenth the value of the largest F term.

Bismuth and lead are of questionable mathematical and metallurgical significance. They do not have F values greater than one-tenth the largest F ratio. The absence of oxygen from the uniform reaction thickness regression

equation is noteworthy, although not understood. The contribution of impurity elements formed in UC as the result of the fission process has not been defined to date. It is discussed elsewhere in this report.

In summary, the independent variables found to be mathematically significant in both equations are temperature, time, nitrogen, and silicon. In addition, vanadium, cadmium, and total independent variable chemistry were important in the URT regression equation. For the TRT equation dependent variables, the only additional element of significance was oxygen.

The "unit value" analysis is another technique that permits additional information to be obtained about the relative importance of equation terms. The first step of this method is the selection of a unit value. In our case, this was a concentration of 1 ppm. Next, the influence of the unit value change is tested by holding all independent variables constant and varying only the independent variable being evaluated by the unit value. The results are measured by the net change in the dependent variable (i.e., TRT and URT).

When the chemical impurity composition of the UC was evaluated by this technique, the temperature and time were held constant at 900°F and 10,000 hours. Table 8 ranks the impurity elements from "most important" to "least important."

TABLE 8
RANKING OF REGRESSION EQUATION CHEMISTRY TERMS
(Importance* Established by the Unit Value Analysis Technique)

Dependent Variable: TRT	Dependent Variable: URT
V	V
Sn	Si
Si	N
N	Cd
Bi	Pb
O	Bi
Cd	T. I. V. C. C.
Ni	
Cu	

*Ranked in importance from most important element down to least important

Many of the same elements previously determined by mathematical analysis to be important are high in the order of ranking. For example, V, Si, N, and Cd are the first four elements ranked for uniform reaction thickness and V, Si, and N account for three of the first four elements in the ranking of total reaction thickness. These results give additional support to the importance of UC chemical impurity levels in the compatibility reaction between UC and SAP.

f. Incubation Period of the Compatibility Reaction

The relationship between starting test conditions and the onset of the UC - SAP compatibility reaction has been the subject of much conjecture. Among the considerations are the influence of initial surface roughness, interfacial pressure, activation energy, and adsorbed surface gases or reaction products.

Statistical evaluations at AI verified the existence of an incubation reaction period and reaction threshold temperature. Figure 26 defines, in general, the extent of the incubation reaction and the reaction bounds of time and temperature for the dependent variable of TRT (using the case of the most representative uranium carbide chemistry). The first indication of an incubation reaction period came from the plot of the observed TRT vs its difference from the regression equation shown in Figure 27. This figure shows a much larger than

Figure 26. Total Reaction Thickness vs Time at Constant Temperature for Most Representative Chemistry, Showing Incubation Reaction Time and Temperature

Figure 27. Actual Total Reaction Thickness Data vs Actual Data Minus Predicted Data

normal variation in the smaller values of the TRT. Two separate and distinct population sets are suggested. As illustrated, a division seems to occur somewhere about an actual TRT value of five mils. The plot of the actual value for uniform reaction against the difference between the actual and the predicted value from regression equation value gives a similar graph; two population sets are again found.

Another way to demonstrate an incubation period was to group the compatibility data by constant temperature. The same statistical "yardsticks" of standard deviation and correlation coefficient were used to compare regression analyses. The evaluations used the regression equations developed for the TRT. Multiple regressions were conducted at five constant temperatures: 850, 875, 925, 950, and 1000°F. Table 9 gives the temperature constant, correlation coefficient, standard deviation, average value, and number of data points used in each regression. No significant correlation coefficients are shown in the table at 850 and 875°F, though the correlation coefficient improves with increases in temperature. A highly significant correlation coefficient is attained at a constant temperature of 950°F. These results again suggest a temperature-time dependent threshold, below which an unpredictable interface reaction takes place.

TABLE 9
STATISTICAL MEASUREMENTS OF MULTIPLE REGRESSION ANALYSIS
OF TEMPERATURE CONSTANT DATA
(Total Reaction Thickness)

Temperature Constants	Number of Data Points	Correlation Coefficient (R)	Standard Deviation (σ , mils)	Average Value of Dependent Variable ($\bar{y}$, mils)
850	48	0.380	2.07	2.48
875	47	0.574	1.54	2.32
925	36	0.790	4.08	5.40
950	28	0.974	1.92	3.74
1000	24	0.940	10.4	27.1

7495 1-11

Figure 28. Intrusion of SAP Into Surface
Cracks of UC

7620 4710

Figure 29. Intrusion of Aluminum Alloy
Into UC

D. EFFECT OF INTERFACIAL PRESSURE

It is apparent that extreme interfacial pressures in the UC-SAP couples markedly affect the compatibility test results. The specific relationship between pressure and the compatibility reaction, however, is not clearly understood. Lack of relevant experimental data contributes to the uncertainty associated with the incubation period of the compatibility reaction, though it is known that the pressures associated with the test environment far surpass reactor design conditions. In discussing this point, Lauritzen and Knudsen⁽³⁾ have stated: "The interfacial pressures during the tests have, in general, been more severe than would be expected in fuel rods irradiated in a reactor. On account of the extremely low ductility of SAP, very little, if any, strain of the fuel-rod cladding can be tolerated. Thus, the contact pressure between fuel and cladding should be kept low. The extent of the interaction is, therefore, likely to be more limited under actual fuel-rod conditions than in the compatibility tests."

In the HWO CR fuel element, the pressure exerted on the cladding due to fuel growth, swelling, and fission gas release will be about 1200 psi maximum; the reactor design allows only 0.5% cladding strain for the worst case of adverse assembly tolerances and operating conditions. By contrast, the test capsules in the current series undergo contact pressures in excess of the yield strength of SAP. This contact pressure is a combination of initial assembly pressure and pressure due to differential thermal expansion of capsule components. Generally, the SAP wafers in the capsules are actually deformed at exposure condition. Thus, the diffusion couple contact pressure far exceeds that anticipated for the SAP cladding in the HWO CR fuel elements.

Uranium carbide is hard and brittle at room temperature, and cracks can form quite easily in UC. As thermal treatment proceeds, surface cracks allow SAP under pressure to intrude into the UC. Figure 28 illustrates this condition. As shown, SAP material under pressure intruded into a narrow ($\sim 1 \times 10^{-4}$ in. wide) crevice of the UC surface. This example is from Interface 1 of Capsule 72 which had a thermal history of 4000 hours at 850°F. At 4000 hours, the 850°F temperature is within the incubation period for the compatibility reaction for the case of the most representative UC chemistry.

It is noteworthy that Figure 28 does not show any significant reaction at the SAP-UC interface, though some slight reaction between the intruded SAP and UC can be detected. This "minor" reaction was due to the high surface-to-mass ratios resulting from the SAP intrusion. This type of reaction had been previously observed. For example, Elkins and Kerr⁽⁴⁾ described these as "local" reactions (Figure 29).

V. CONCLUSIONS AND RESULTS

The main conclusion from the study of compatibility reactions between hyperstoichiometric UC fuel and SAP cladding is that the data indicate no significant UC-SAP compatibility problem in the operating regime considered for the HWO CR. Other conclusions and results of the compatibility study are listed below.

- 1) Mathematical equations were developed which give correlations between the test conditions and the dependent variables of total reaction thickness and uniform reaction thickness.
- 2) A technique for numerically describing the UC-SAP compatibility reaction has been established.
- 3) A description of the compatibility reaction process having six sequential steps has been suggested.
- 4) The presence of an incubation period in the early stages of the compatibility reaction has been confirmed. The general bounds of reaction time and temperature, including a reaction threshold temperature, are defined.
- 5) The compatibility study identified the following intermetallic compounds in the UC-SAP interaction zone: UAl_3 , C (graphite), and U-Al-Si phase. Intermetallic compounds tentatively identified were Al_3C_4 , USi_3 , and U_3Si .
- 6) The post-reaction chemical composition at the UC-SAP interface indicates that impurity elements may play a significant part in the compatibility reaction. Key impurity elements, found in the UC and evaluated by regression analysis, were N, Si, V, Cd, and O. Important impurity elements found by metallurgical examination were Si and Fe. The specific reaction mechanisms involving these impurity elements have not been established to date.
- 7) In-pile and out-of-pile UC-SAP compatibility results are in agreement. Within experimental error, and within the range of reactor operation examined to date, no change in compatibility behavior can be attributed to the reactor radiation environment.
- 8) UC fuel and SAP cladding interface pressures in excess of HWO CR reactor conditions enhance the conditions favoring interaction.

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