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WANL-TME-564
October, 1963

MASTER

PRELIMINARY REPORT ON THE USE OF NITROGEN AND
AIR FOR REACTOR SHUTDOWN
(Title Unclassified)

E. Kochka

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MASTER

Westinghouse Electric Corporation

Astronuclear Laboratory

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May 25, 1964

* Mr. R. W. Schroeder
Space Nuclear Propulsion Office
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SPECIAL REREVIEW FINAL DETERMINATION Class: <u>U</u>	Reviewers	Class.	Date
	<u>KAW</u>	<u>4</u>	<u>5-3-82</u>

Subject: WANL-TME-564, Preliminary Report on the Use of Nitrogen and Air for
Reactor Shutdown, dated October, 1963

Dear Mr. Schroeder:

Transmitted herewith are three (3) copies of the subject report.

This report is transmitted for your information.

Respectfully,

H. F. Faught
amw

H. F. Faught
Program Manager
NERVA Nuclear Subsystem

Enclosures - 3

cc: Mr. R. Wilke, SNPO-C Resident Office at WANL
Mr. G. O'Brien, SNPO-C Resident Office at WANL

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23

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PRELIMINARY REPORT ON THE USE OF NITROGEN AND
AIR FOR REACTOR SHUTDOWN
(Title Unclassified)

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Abstract

The effects of nitrogen and air coolants on NERVA reference fuel elements and fuel element constituents was studied. Post-reactor hot test operation was simulated by using sections from hydrogen tested fuel elements. Exposure at hydrogen corrosion test temperatures in excess of 2200°C increased the susceptibility of the element to attack by the coolant gases. In such cases, exposure to air at 200°C with as low as 20 ppm water caused the element to crack as a result of bulk volume changes accompanying the oxidation and/or hydrolysis of diffused uranium carbide. Air and/or water vapor were also observed to damage the niobium carbide liners at temperatures as low as 200°C and when present as impurities in nitrogen lead to a possible adverse effect on the liners at temperatures as low as 300°C .

I. Introduction

Post-shutdown cooling is needed to remove the heat continually generated in a reactor core as a result of the decay of radioactive fission products formed during reactor operation. The amount of decay heat generated drops off rapidly after the reactor becomes sub-critical, but remains substantial for several hours or even days depending upon the total burnup achieved during the run.

The removal of decay heat after a NERVA reactor hot test poses a particularly serious problem. Large quantities of coolant gases must be used, and, in order not to interfere with the post-mortem examination of the core, these gases must be relatively inert. Nitrogen and air are being considered because of safety considerations, availability, and their relative inertness to graphite at the temperatures required for adequate reactor shutdown cooling.

The present plan for the NRX-A2 power run calls for displacing 500°R (4°C) gaseous hydrogen at a maximum fuel element temperature of 1225°R (407°C) by gaseous nitrogen at 200°R (-162°C). The nitrogen will be introduced at a rate (5 lb/sec) that should bring the maximum fuel element temperature to 585°R (52°C) in 24 hours. Air will then be introduced to the reactor prior to disassembly.

This report discusses preliminary findings of the effects of nitrogen and air upon the individual constituents of the NERVA reference fuel and upon the fuel element itself. Particular emphasis is placed upon the thermal history of the fuel element and the relationship this bears to the effects of the coolant gases.

II. Test Procedures

The effect of the coolant gases on graphite only was studied using uncoated, unfueled element sections obtained from the Astrofuel Facility. Niobium carbide powder (Firth Sterling, Incorporated) and pellets (compacted powder hot pressed at 3000°C) provided information on the possible effects of coolant gases on the element

liners. Data on uranium carbide was obtained from the literature. The bulk of the experimental data came from tests on samples of sectioned (fueled and coated) elements that had previously been subjected to hydrogen corrosion testing.

Test samples of one to two inches in length were cut from fueled elements approximately 50 inches from the S/N end. After recording the initial weight of the samples, they were placed in a temperature calibrated tube furnace which had been equilibrated at the reaction temperature. Gas of known purity and water content was passed over the samples at a known controlled flow rate (1 liter/min.) well below required rates of coolant flow through the reactor core. Also, the fact that the gas flow in these experiments is not confined to the channels is another departure from actual post-test reactor operation. This led to a greater contact between the matrix and the coolant, and may exaggerate the effects of the coolant gases upon the fuel element.

The samples are periodically removed from the furnace, cooled, and weighed. A visual inspection was performed at the time of weighing and if significant changes were observed, the samples were photographed and examined in detail microscopically.

III. Behavior of Fuel Element Constituents in Nitrogen and Air

Graphite is relatively inert to pure nitrogen even at moderately high temperatures. The useful temperature range of nitrogen, however, can be lowered by the oxygen and water impurities present in the gas, and these impurities should be reduced to a practical minimum. Typical specifications of commercial grade gases used in these tests are given in Table I.

The reaction of oxygen with graphite may become serious as low as 300°C, but the use of air as a reactor coolant can be effective below this temperature and also be economically desirable. However, because water reacts rapidly with graphite, it is essential that air or any other gas be dried prior to its introduction into the reactor. ⁽¹⁾

(1) T. J. Clark, et. al., "Gas-Graphite Systems" in R. E. Nightingale, Nuclear Graphite, Academic Press, N. Y., 1962, pp. 387-437.

Table I

Nitrogen Specifications

Prepurified Nitrogen

<u>Component</u>	<u>Maximum</u>	<u>Typical</u>
Oxygen	20 ppm	5 - 10 ppm
Hydrogen	20 ppm	0 - 5 ppm
Dew Point	-76°F	-85° to -90°F
Water	22 ppm	6 - 12 ppm

Dry Nitrogen

Oxygen	0.2% by vol.
Dew Point	-76°F
Water	22 ppm

Oil Pumped Nitrogen

Specifications same as dry, however, there is no moisture specification.

Test data on the effect of nitrogen and air on uncoated, unfueled element sections are given in Table II. Negligible weight changes were obtained in tests using gases known to be dry. The data shows that the largest weight loss in these tests came from the use of oil pumped nitrogen for which no moisture specification was available.

In reacting niobium carbide with nitrogen or air, it is reasonable to expect to form a nitride, carbonitride, or oxide. Many references state that niobium carbide is susceptible to nitride formation, and nitrides, carbonitrides, oxides, and oxycarbides are reported in the literature. However, a recent reference⁽²⁾ showed that in nitrogen at one atmosphere, niobium carbide is stable indefinitely at temperatures below 1400°C. Above 1400°C, carbon will react with either pure niobium metal in the presence of nitrogen or solid carbide-nitride solutions and convert them completely to carbide⁽²⁾. In view of this it may be necessary to attribute the weight gains shown in Table III to the nitrogen impurity level (some indication of this is given in Table III) or to nitride formation by an as yet unknown mechanism. The considerably larger weight gain shown by niobium carbide powder in contrast to the small weight gains of the compacted material shows the relationship of the reactivity of niobium carbide to surface area. Additional data obtained at 700°C, as shown in Figure 1, indicates that the reaction products do not inhibit the reaction rate.

Table IV gives data on the effect of dry nitrogen on coated, unfueled element sections at 550°C. There is less apparent effect on these samples than on niobium carbide or graphite separately insofar as weight changes are concerned, but the reaction of impurities in the nitrogen with the liner or nitride formation is observed in these tests and may be capable of causing physical damage upon prolonged exposure.

The effect of nitrogen, oxygen, and water vapor on uranium carbide has been covered in the literature.⁽³⁾ Of these reactants, water vapor would probably

(2) K. I. Portnoi and Yu. V. Levinskii, "Reactions in the Systems Refractory Metals-Carbon-Nitrogen," Issled. Splavov Tsvetn. Metal., Akad. Nauk SSSR, Inst. Met., No. 4, 279-85 (1963) (C.A. 60, 1395 (1964)).

(3) A. B. Tripler, Jr., et. al., "Further Studies of Sintered Refractory Uranium Compounds," BMI-1313 (January 27, 1959).

FIGURE 1 REACTION OF DRY NITROGEN (1 L/ M) WITH NIOBIUM CARBIDE PELLETS AT 700 °C

Table II

Uncoated Unfueled Element Sections Treated in Nitrogen and Air

<u>Gas⁽¹⁾</u>	<u>Temperature (°C)</u>	<u>Time hrs.</u>	<u>Weight Change mg/g</u>
Prepurified N ₂	550	10	-0.1
Dry N ₂	550	10	0.8
		20	0.8
Oil Pumped N ₂	550	10	-2.0
		20	-1.3
Air (Dry)	300	6	-0.43

(1) Flow Rate = 1 liter/min

Table III
Reaction of Nitrogen and Air with Niobium Carbide

<u>Gas⁽¹⁾</u>	<u>Form</u>	<u>Temperature (°C)</u>	<u>Time hrs.</u>	<u>Weight Change mg/g</u>
Prepurified N ₂	Powder ⁽²⁾	550	10	2.40
			20	2.80
	Pellets	550	10	0.00
			20	0.60
Oil Pumped N ₂	Powder	550	10	6.30
			20	14.50
Dry N ₂	Powder	550	10	1.50
			20	3.10
	Pellets	550	10	0.50
			20	0.60
Dry N ₂	Powder	700	7	0.80
			48	3.20
Dry N ₂	Pellets	700	8	0.02
			20	0.22
			60	1.55
Air	Pellets	300	8	0.07

(1) Flow rate = 1 l/min.

(2) 325 mesh and finer.

(3) Compacted powder hot pressed at 3000°C.

Table IV

Coated Unfueled Element Sections in Dry Nitrogen at 550°C

<u>Treatment Time hrs.</u>	<u>Flow Rate liter/min</u>	<u>Weight Change mg/g</u>
24	1	-0.2
87	1	0.0
120	1	+0.2

cause the most severe damage in reacting with uranium migrated from fuel particles. At the temperatures being considered for the introduction of the coolant gases, the effect of water vapor on uranium dicarbide is catastrophic in comparison to the effects of nitrogen and oxygen, although these latter two gases can also react in a damaging manner.

IV. Fuel Element Testing

After the preliminary tests previously considered were completed, tests were continued to provide information on the effects of nitrogen and air on elements that were exposed to hydrogen for short times at elevated temperatures.⁽⁴⁾ These were production elements from the Astrofuel Facility, most of which had uranium loadings of 417 to 440 mg/cc. The effects of dry nitrogen on hydrogen tested fueled elements is shown in Table V. These tests indicate that nitrogen may cause severe coating damage upon prolonged exposure or when test specimens had previously been exposed to temperatures causing extensive uranium migration and possible diffusion into the liner. Although tests were performed using only dry nitrogen, it will become evident from subsequent data that the presence of moisture would cause hydrolysis of migrated uranium dicarbide and accentuate the damage being caused by the nitrogen.

The predominant effect of nitrogen is to attack the liner. Air, however, is found to be more damaging than nitrogen to the element as a whole. The damage manifests itself as longitudinal cracks apparently emanating from the hot end of the sample and/or element and generally located between a hole and a face or an edge. Figure 2 shows a severely cracked sample containing both an edge and a face crack. Figure 3 also shows severe cracking in the web area, and one of the views shows a part of the liner still intact. The elements pictured in Figures 2 and 3 were subjected to hydrogen corrosion above 2300°C. The temperature of the air test

(4) For details of the hydrogen test see M. B. Blinn, "Hydrogen Corrosion Testing of NERVA Reference Fuel," WANL-TNR-129, September 16, 1963, pp. 12-19.

Table V

Behavior of Hydrogen Corroded Fuel Elements in Dry Nitrogen at
One Liter per Minute and 300°C

Element No.	Section (in)	Hydrogen Pretreatment		Test Conditions and Effects			Remarks
		Temp. (°C)	Time (min)	Water Content (ppm)	Time (days)	Weight Change (mg/g)	
AC 99-4438	45-46	2440	4	20	2.0	0.80	Coating discoloration
AC 99-4438	46.5- 47.5	2440	4	20	2.0	38.80	Coating turned blue and some of it fell out.
AC 99-5243	--	2240	5	20	1.0	0.00	No physical damage was observed. Coating discoloration was evident in each test.
AC 99-5532	45-46	2200	5	20	5.3	0.80	
AC 99-5532	46.5- 47.5	2200	5	20	5.3	2.03	
AC 99-5532	48-49	2200	5	20	5.3	2.58	
AC 99-6457	45-46	2330	5	20	4.0	1.78	
AC 99-6457	46-47	2330	5	20	4.0	2.71	
AC 99-6457	47-48	2330	5	20	4.0	11.20

Figure 2 - Effect of Exposure to Air at 300°C and 21,000 ppm
Water Vapor for 48 Hours
(Element hydrogen tested for 3 minutes at surface
temperature of 2311°C - Element No. AC-99-4902)

Figure 3 - Effect of Exposure to Air at 300°C and 2,500 ppm Water Vapor for 48 Hours
(Element hydrogen tested for 3 minutes at a surface temperature of 2460°C - Element No. AC-99-4866)

was 300°C. Figure 4 shows an element that was also hydrogen corrosion tested above 2300°C, but tested in air at 200°C. It is seen that test conditions have an effect upon the severity of the damage done by cracking. Figure 5 shows cross sections of elements that did not fail. The polished surface of these specimens fail to reveal the presence of micro-cracks. The data from these trials are shown in Table VI. Figure 6 is a somewhat idealized diagram showing some of the crack parameters.

Tests are still needed to better define the effect of the parameters responsible for cracking. The important parameters (not necessarily independent) appear to be (1) the reported surface temperature* of the fuel element during the hydrogen corrosion test; (2) the location from which the sample is taken from the fuel element; (3) the length of time the element is at elevated temperatures during the hydrogen corrosion test; (4) the constitution, temperature, and relative humidity of the coolant gas; and (5) the time of the post-hydrogen corrosion air or nitrogen test and/or rate of weight gain.

The likelihood that an element will crack on exposure to air is greater if the element had been previously exposed to surface temperatures in excess of 2200°C during hydrogen corrosion testing. The tendency to crack is apparently related to the high rate of uranium migration above surface temperatures of 2200°C and gives rise to the suggestion that cracking is caused by the bulk volume change resulting from the oxidation and/or hydrolysis of exposed uranium compounds. The probability that an element will crack upon exposure to air of a certain temperature and humidity and the rate at which it cracks depend upon the temperatures attained in the locations of the fuel element from which the samples were taken. Figure 7 shows this relationship using three adjacent samples from the same element. (The surface temperature could vary from the reported temperature of 2200°C to about 2150°C at 46 inches and 2230°C at 49 inches.) The graph shows the difference in weight increase with

* The hydrogen corrosion test procedure used at WANL up to the time of writing this report leads to a central region to surface temperature gradient of 250°-300°C depending on the highest surface temperature of the element. Thus, a substantial portion of an element tested at a surface temperature of 2200°-2300°C actually reaches temperatures of 2400°-2600°C, which is near or above the temperature where substantial uranium migration is observed on the production coated fuel particles.

Table VI

Behavior of Hydrogen Corroded Fuel Elements in Air at One Liter per Minute

Element No.	(in)	Hydrogen Pretreatment		Test Condition and Effects				Remarks
		Temp. (°C)	Time (min)	Water Content (ppm)	Temp. (°C)	(days)	(mg/g)	
AC 99-5143	--	2475	4	43,000	37.5	23.0	7.10	No cracks
AC 99-3982	--	--	--	43,000	37.5	21.0	0.50	Uncoated, leached in HCl-He atmos. for 30 min. at 1745°C
AC 99-5166	47-48	2000	5	20	100	5.7	-0.28	No cracks; no change in coating
AC 99-4868	43-44	2550(av.)	2	20	100	25.0	1.41	H ₂ test at 2350°C for 1 min. and 2700°C for 1 min; no cracks.
AC 99-4868	44-45	2550(av.)	2	20	200	6.0	10.30	Cracked after six days.
AC 99-6346	46-47	2200	5	10,500	200	12.5	+0.20	No cracks
AC 99-6346	47-48	2200	5	10,500	200	12.5	+0.18	No cracks
AC 99-6346	48.5-49.5	2200	5	10,500	200	12.5	+0.40	No cracks
AC 99-5982	46-47	2200	5	22,200	200	10.5	2.96	Cracked at 10.5 days; crack did not traverse sample length
AC 99-5982	47-48	2200	5	22,200	200	10.5	4.09	Cracked after 3.75 days after gaining 3.14 mg/g
AC 99-5982	48-49	2200	5	22,200	200	10.5	6.00	Cracked after 2.75 days after gaining 4.31 mg/g
AC 99-5166	48-49	2000	5	20	300	2.0	2.03	Coating turned blue; no cracks
AC 99-4875	46-47	2110	5	20	300	2.0	-0.61	No cracks, coating turned blue
AC 99-5196	45-46	2200	5	20	300	17.0	0.35	No cracks
AC 99-5196	46-47	2200	5	20	300	17.0	0.14	No cracks
AC 99-5196	47-48	2200	5	20	300	17.0	0.23	No cracks
AC 99-5199	45-46	2350	5	20	300	1.0	20.4	Cracked
AC 99-5199	46.5-47.5	2350	5	20	300	1.0	20.6	Cracked
AC 99-5199	48-49	2350	5	20	300	1.0	20.5	Cracked
AC 99-4866	44-45	2460	3	20	300	2.0	14.90	Coating turned blue and some fell out; cracked after 1 day

Table VI
Behavior of Hydrogen Corroded Fuel Elements in Air at One Liter
Per Minute (cont.)

Element No.	Section (in)	Hydrogen Pretreatment		Test Condition and Effects				Remarks
		Temp. (°C)	Time (min)	Water Content (ppm)	Temp. (°C)	(days)	(mg/g)	
AC 99-4866	42-43	2460	3	2,500	300	2.0	9.52	Coating turned blue, some fell out; cracked after 1 day.
AC 99-6749	46-47	2210	5	2,500	300	20.5	+0.28	No cracks
AC 99-6749	47-48	2210	5	2,500	300	20.5	+0.16	No cracks
AC 99-6749	48-49	2210	5	2,500	300	20.5	+0.32	No cracks
AC 99-4902	47-49	2311	6	21,000	300	2.0	9.57	Coating turned blue, some fell out; cracked after 1 day.
AC 59-1747	47 -48.5	2200	5	21,000	300	1.0	6.60	No cracks; coating turned red, green, and blue.
AC 59-1747	48.5-50.0	2200	5	21,000	300	2.0	7.10	No cracks; but cracked after two weeks at room temperature.

Figure 4 - Effect of Exposure to Air at 200°C and 20 ppm Water Vapor for 48 Hours

(Element hydrogen tested for 1 minute at a surface temperature of 2350°C and 1 minute at a surface temperature of 2700°C - Element No. AC-99-4868)

- a) Element No. 1747; hydrogen tested for 5 minutes at 2200°C ; tested in air containing 21,000 ppm water vapor for 1 day at 300°C .

- b) Element No. 5166; hydrogen tested for 5 minutes at 2000°C ; tested in air containing 20 ppm water vapor for 2 days at 300°C .

Figure 5 - Polished Cross-section of Elements Showing No Microcracks

FIGURE 6 SCHEMATIC DIAGRAM SHOWING SOME OF THE HYDROGEN AND AIR TEST PARAMETERS RESPONSIBLE FOR ELEMENT CRACKING DURING COOLANT TRIALS

FIGURE 7 CRACKING OF AN ELEMENT HYDROGEN CORROSION
TESTED FOR 5 MIN. AT 2200 C; TESTED IN AIR CONTAINING
22,200 ppm WATER VAPOR AT 200 C

time for these three elements as well as the weight at which cracking was first observed. The photographs show the difference in crack width. Further testing caused very little additional damage after the cracks had formed even though the weight continued to increase at a reduced rate. It is seen that the crack in the 46-47 inch section does not pass through the sample. Microscopic examination of the crack revealed that it followed boundaries between flour particles and traveled around fuel particles.

Figure 8 generalizes the effect of air upon fuel elements with respect to the oxidation and/or hydrolysis of migrated uranium dicarbide. It is seen that the hydrolysis reactions proceed more slowly than oxidation reactions. Although the bulk volume change accompanying the conversion of uranium dicarbide to the oxide by either hydrolysis or oxidation is probably the cause of element cracking, the residual stress pattern in the fuel element must also have a contributory effect.

The stress condition of fuel elements at room temperature was deduced from a number of observations which show that the exterior is in compression and the interior in tension. ⁽⁵⁾ Differences in particle orientation and consequent differences in the coefficient of thermal expansion between the inner and outer webs of a fuel element are believed to be responsible for this stress configuration. The swelling of fuel particles upon oxidation and/or hydrolysis creates additional stress raisers. The exact manner in which the stresses contribute to crack formation and propagation is not yet fully understood, but it is believed that the combined stresses are transmitted to areas of low strength and are eventually relieved by cracking.

(5) C. A. Andersson, "Mechanical Properties of NERVA Fuel Material, " WANL-TNR-130, September 16, 1963, pp. 47-48.

FIGURE 8 RATE AND PROPOSED MECHANISM OF ATTACK LEADING TO CRACKING OF FUEL ELEMENTS IN AIR

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Mr. J. L. Dooling
NERVA Subcontract Manager
Rocket Engine Operations - Nuclear
Department 7140
Aerojet-General Corporation
Post Office Box 1947
Sacramento, California 95809

Attention: Mr. R. J. Pickering

Subject: Nitrogen Cooling Temperature Limit

Reference: 1. WANL-TME-564, "Preliminary Report on the Use of Nitrogen and Air for Reactor Cooldown", dated October, 1963, (C-RD).
2. AGC letter, RJP:se:7433:1878L, August 26, 1965.
3. AGC letter, RJP:se:7433:1902L, September 30, 1965.
4. WANL letter, dated September 10, 1965.

Gentlemen:

It is the purpose of this letter to give a report of the results and conclusions arrived at from the fuel testing with nitrogen gas and to establish a basis for future investigations if required.

The established temperature limit for nitrogen cooling of the core is established as 1400°F maximum by Reference 1. References 2 and 3 requested that this limit be re-evaluated to alleviate an ETS-1 facility problem. It is understood that this problem exists due to insufficient helium to handle an emergency shutdown.

Reference 4 stated that laboratory tests (small scale) and hydrogen corrosion facility tests (full scale) would be required. The minimum test conditions agreed to with Mr. P. J. Pickering were a fuel temperature of 2250°F with 10 minute exposure to nitrogen gas having 20 to 25 ppm of O₂ and H₂O. The 10 minute exposure time at 25% flow is equivalent to ETS case of 150 seconds at 100 lb/sec.

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-2-

It is concluded from the results of the laboratory tests that these minimum test conditions are unacceptable as explained in the following discussion of the test results:

A total of twenty-six test runs have been made in the course of the recent study. Of these, the first twelve (12) were expended in a study of the effects of nitrogen coolants at a fuel temperature of approximately 2500°R (1120°C). Two basic levels of nitrogen purity were used in the experiments. The first, which shall be designated as pre-purified, was shown by analysis to contain 3-4 ppm H₂O and about 20-25 ppm O₂. The second, which shall be designated as "special" was shown by analysis to contain 30-35 ppm H₂O and 60-70 ppm O₂. Test times varied from 10 to 60 minutes at flows on a per channel basis approximating 1-4 per cent of maximum anticipated reactor flows. The pressure, however, was only 8-14 psig compared to the 150-200 psi predicted for the maximum reactor case. The results of these runs, which invariably resulted in coating damage, indicated that lower temperatures should be investigated.

Fourteen additional tests at a lower temperature (2250°R) have now been completed. The same two grades of nitrogen were used, but test durations did not exceed ten (10) minutes. Two tests at higher pressures (180 and 220 psi, runs 25 and 26 respectively) were also accomplished. Of these tests, the last five (5) were selected for detailed discussion in this memo. A pertinent data summary on these runs is given in Table I.

Two types of fuel element damage have been found upon metallographic examination of the test samples. The first is direct attack of the NbC coating. In all cases a surface attack is indicated by the dark or multicolored surface on the NbC channel surface. More significant, however, is a form of grain boundary attack which seems to be strongly related to the total impurities to which the sample is exposed. The second type of damage, oxidation or nitriding of fuel beads adjacent to the coating substrate interface, is more difficult to relate to impurity exposure. It has been observed in the least severe run (run 23) and in the most severe (run 25).

The various types of damage observed and the relationships to the nitrogen treatments can best be demonstrated by reference to the attached photomicrographs:

Figures 1 and 2 were included to demonstrate "problem beads". These two figures depict representative examples of beads near the surface of the channel which have been affected by the NbC coating operation. It is apparent that consumption of the pyrocarbon shell surrounding the UC₂ core by the coating has resulted in exposure of the UC₂ cores. In neither case is there any evidence of hydrolysis or oxidation, although the bead shown in Figure 2 is partially leached. It is after the subsequent nitrogen treatment where oxidation and swelling of the bead is observed.

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-3-

Figures 3 and 4 were included to illustrate the serious coating damage which occurred during the earlier 2500°R runs. Oxidation of the NbC liners had progressed to where essentially no NbC remained except in the blocked channel shown at the bottom of Figure 4. The data for the corresponding nitrogen run (run 2) is given in Table I.

Run no. 22, where all the flow was directed through channel 10, represents a relatively high flow low pressure test with the high impurity nitrogen. Figure 5 shows how channel 10 was darkened during the nitrogen test. That the surface was reacted to a measurable depth can be readily demonstrated by a careful inspection of the NbC coating (top surface) of Figure 6. The dark material (presumably some form of oxide) shows up as the thin gray phase between the light NbC and the dark mounting material. The NbC coating shown in Figure 6 also illustrates the grain boundary attack referred to previously. This can be seen by noting the light gray lines running from the bottom of the gray phase into the NbC coating. More advanced examples of grain boundary attack will be illustrated subsequently.

The effects of low impurity nitrogen were studied in runs 23 and 24. The main difference between the two runs was the flow, through 17 channels in run 23 and a single channel in run 24. Bead damage was observed in both runs. Figure 7 shows such a bead; in this case the reaction has proceeded to the point where the NbC coating has been partially lifted. Figures 8 and 9 were included to show that the coating damage in these runs was minimal, although the surface of the exposed NbC was slightly tarnished.

The effect of higher pressures (180-220 psi), higher flows, and higher impurity levels is illustrated by Figures 10, 11, 12, 13, and 14. These photos, which represent runs 25 and 26, show examples of dark surface reactions on the exposed NbC bores, severe grain boundary attack, and reacted beads. The grain boundary attack relative to the preceding example (Figure 6) is most striking.

In summary, the experiments performed to date indicate the use of nitrogen with impurities in the range of 20-40 ppm O₂ (as O₂ or H₂O) cannot be given unequivocal approval. Potentially deleterious reactions of both beads and coating have been shown to result, even at relatively low impurity levels and at low equivalent reactor flows. Under more severe conditions, virtually catastrophic reactions were observed.

It is our understanding that by a modest investment in molecular sieves it might be possible to lower the O₂ and H₂O impurities of the present nitrogen to quite low values (~5 ppm or less). The previous experiments indicate that very low impurity levels should be satisfactory in preventing damage to NbC coatings. Several additional runs are planned in our laboratory to study lower temperatures with the pre-purified nitrogen

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-4-

(1800 and 2000°R) and at 2250°R with the use of very pure nitrogen (less than 10 ppm total H₂O and O₂). These experiments are expected to be useful in the formulation of further recommendations along the lines of lower impurity gases or lower temperatures.

The reactions of nitrogen or impurities with exposed UC₂ appear to be the biggest problem. Recent communications between M. Wright (WANL) and G. Ross (AGC) and between G. Kilp (WANL) and G. Ross (AGC) have revealed references to a potentially damaging reaction between nitrogen and UC₂ between 600°C and 1100°C. The implications of the new information have not been fully explored. However, in light of the experimental data discussed above it would seem to indicate that the present temperature limitation for use of nitrogen coolants should be maintained for the present.

Respectfully,

H. Faught
Program Manager
NERVA Nuclear Subsystem

Enclosures - 1 set

cc: R. W. Schroeder, SNPO-C, w/1 set of enclosures
L. C. Corrington, SNPO-C, w/1 set of enclosures
SNPO Resident Office at WANL, w/1 set of enclosures
AGC Resident Office at WANL, w/1 set of enclosures
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Table I
Nitrogen Test Data Summary

<u>Test Run No.</u>	<u>Nitrogen Designation</u> ^(a)	<u>Time (min)</u>	<u>Temp. (°F)</u>	<u>Nominal Pressure (psig)</u>	<u>Nominal Flow % of Reactor Max.</u>
2*	Special	45	2500	14.0	1
22	Special	10	2250	12.8	25
23	Pre-purified	10	2250	11.0	1
24	Pre-purified	10	2250	14.4	22
25	Special	10	2250	180.0	40
26	Special	5	2250	220.0	25

(a) The oxygen and water concentrations in the nitrogen were as follows:

Special nitrogen: O₂, 60-70 ppm; H₂O, 30-35 ppm

Pre-purified nitrogen: O₂, 20-25 ppm; H₂O, 3-4 ppm

* Test run no. 2 was included for comparison purposes.

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Figure 1. Not Treated 200X

Figure 2. Not Treated 200X

Figure 3. Exit End
Run No. 2 3X

Figure 4. Slit View
Run No. 2 2X

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Figure 5. Slit View
Run No. 22 2X

Figure 6. Ch. 10 400X
Run No. 22

Figure 7. Run No. 23
200X

Figure 8. Slit View
Run No. 24 2X

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Figure 9. Ch. 10 200X
Run No. 21

Figure 10. Slit View
Run No. 25 2Y

Figure 11. Ch. 10 200X
Run No. 25

Figure 12. Ch. 10 200X
Run No. 25

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Figure 13. Ch. 10 400X
Run No. 25

Figure 14. Slit View
Run No. 26 2X

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