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WANL-TME-1298

September 1965

Westinghouse Astronuclear Laboratory

CORROSION INHIBITOR TESTS

(Title Unclassified)

TME 1298

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OCT - 6 1965

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

Subject: WANL-TME-1298, "Corrosion Inhibitor Test," dated September 1965

Dear Mr. Dooling:

Transmitted herewith are ten (10) copies of the subject report. This report is transmitted for your information.

Respectfully,

Original Signed By

H. F. Faught *HF*

H. F. Faught

Program Manager

NERVA Nuclear Subsystem

Enclosures - 10

cc: R. W. Schroeder, SNPO-C, w/enclosures (3)
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18

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CORROSION INHIBITOR TESTS
(Title Unclassified)

Classification cancelled (or changed to _____)

by authority of _____

by H. A. C., T/C, date SEP 11 1973

R. R. Burghardt
Fluid Flow Laboratory

Approved:

E. A. WeZubay
E. A. WeZubay, Manager
Fluid Flow Laboratory

INFORMATION CATEGORY

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ABSTRACT

As a means of reducing interstitial corrosion within the NERVA core, it has been proposed that corrosion products be introduced into the hydrogen entering the core radially by controlled corrosion on the periphery. A series of tests has been performed at surface temperatures of 3000°R and 4000°R and a pressure of 600 psia, to determine the effectiveness of one of these products, methane, in inhibiting corrosion. It was concluded that at a surface temperature of 4000°R methane percentages above about 3 percent by volume would inhibit corrosion and produce a pyrolytic graphite deposit, and that at a surface temperature of 3000°R, percentages above about 5 percent would inhibit corrosion and produce a very thin amorphous deposit.

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INTRODUCTION

A problem made apparent in recent reactor tests is corrosion of the outside, uncoated surfaces of the fuel elements, resulting apparently from radial flow of hydrogen into the core. The source of this radial flow is the lateral support system in which hydrogen is maintained at pressures slightly greater than core pressures in order to provide a positive bundling force on the fuel elements. It has been proposed that methane be introduced into this hydrogen by operation of the core periphery at temperatures of 3000°R or higher, allowing limited corrosion to occur at the periphery rather than within the core itself. The result is expected to be a build-up of methane or other corrosion products in the hydrogen before it enters the core with a subsequent decrease in interstitial corrosion within the core.

The chemical kinetics involved in corrosion and deposition are quite complex, but the reaction involving methane can be stated in this simple form:

Both the direction and rate of this reaction are strongly dependent on temperature and pressure. Figure 1 shows the equilibrium concentration of methane (in a hydrogen-methane mixture in the presence of carbon) as a function of temperature at a constant pressure of 600 psia. If at a given temperature the concentration of methane is higher than the equilibrium concentration, the

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reaction will go in the opposite direction, i.e., the methane will break down into hydrogen and carbon, depositing carbon. Under certain temperature conditions and after a sufficient length of time this deposited graphite may be converted into pyrolytic graphite.

As is apparent from the diagram, the equilibrium methane concentration is high at low temperatures and decreases rapidly with increasing temperature. However, since the rate constant is very low at low temperatures no visible corrosion will occur below about 2200°R. Above this temperature, the reaction will proceed with increasing rapidity, dependent on its departure from equilibrium, in addition to temperature and pressure.

The effect of the formation of corrosion products other than methane could alter the expected pattern of corrosion and deposition. Hence it was desired to obtain data for conditions of temperature and pressure of interest in the NERVA reactor. The objective of the tests reported herein was to obtain such data, specifically to study the effectiveness of the addition of methane to hydrogen in inhibiting corrosion.

EXPERIMENTAL EQUIPMENT

The experimental set-up is shown in Figure 2. The test piece itself consisted of a 3/4-inch diameter graphite rod (graphitite G) turned down to a diameter of 0.375 inches for a length of 1.50 inches. The center section served as the primary electrical resistance, having only one-fourth of the cross sectional area of the remainder of the test piece.

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One end of the test piece slid into a copper bushing which was directly attached to the vessel head. The other end slid into a graphite bushing which was attached to a flexible copper braid. The braid was then attached to the vessel head. This method of attachment was developed in order to allow for thermal expansion and to avoid breaking the test piece during assembly. In later tests a graphite bushing was inserted into the copper electrode to minimize damage to the test pieces and facilitate disassembly.

The test piece was placed within a stainless steel pressure vessel constructed of 2-inch, schedule 80 pipe with bolted end flanges. The vessel was designed for operation at 600 psig and 1000°F and has been tested at 800 psig at atmospheric temperature. The water cooled electrodes were brazed to the flat heads of the vessel, which were insulated from the vessel itself by the asbestos gaskets and micarta sleeves around the bolts. Power for electrical heating of the test piece was supplied by a 40 kw, 1000 ampere direct current welder. The hydrogen-methane mixtures were obtained from banks of cylinders mixed and analyzed by the gas manufacturer.

During a test, the system was evacuated to about 28 inches of mercury (vacuum), pressurized with helium and checked for leaks, and then purged with helium. The desired flow was established with helium, the hydrogen-methane mixture was introduced, and power was turned on as soon as the correct flow was re-established. The initial current of about 100 amps was rapidly increased to the required level of 550 to 750 amps within about 15 seconds. The desired

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temperature levels were reached within one to two minutes and the current adjusted as required to obtain the desired temperature, which was read through an optical pyrometer. The hydrogen flow rate and test piece temperature were then held essentially constant for 20 minutes, or as long as possible, after which the power was rapidly decreased and the system purged with helium. A considerable amount of adjustment in input power was required for those test pieces in which substantial corrosion or deposition occurred.

The hydrogen-methane flow rate was measured with a flat plate orifice and differential pressure transmitter and recorded on a strip chart. It was held constant at a volume flow rate equivalent to 0.0032 lb of hydrogen per second.

Recorded on the data sheet were the inlet pressure to the test vessel, the input current and voltage, and the surface temperature of the test piece. Also recorded were the cooling water flow rate and the temperatures of the pressure vessel surface and outlet nozzle.

The weight of the test piece was determined to the tenth of a milligram before and after each test, with the rate of weight loss or gain reported to the nearest tenth of a milligram per minute. The diameter of the test section was measured with a micrometer (accurately to the mil, with the tenth of a mil estimated) in three positions along its length with two measurements at 90° to each other at each position.

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RESULTS AND DISCUSSION

The results of the tests are shown in Table 1 and Figures 3 through 6. Figure 3 showing the weight change as a function of the methane concentration and surface temperature, and Figure 4 showing the surface regression or thickness of deposit as a function of the same variables are of particular interest. At 3000°R and methane concentrations below about 5 percent, there was a moderate amount of corrosion. At higher concentrations there was no corrosion and virtually no deposition. Only a slight amount of sooting was noted and the time available was apparently insufficient for converting this deposition into pyrolytic graphite. The equilibrium concentration is about 4.2 to 4.4 percent at the average temperatures of these tests, so that the data agrees fairly well with the theoretical expectations except that a greater amount of deposition might be expected at the 9 percent concentration.

At 4000°R there is a large amount of corrosion at low concentrations, with deposition occurring at concentration above about 3 percent methane. The amount of deposition increased in a rather orderly fashion with conversion to a hard pyrolytic graphite surface occurring in all cases.

The fact that the point of zero weight change occurred at methane concentrations somewhat higher than the equilibrium concentration at each surface temperature indicates that the surface temperature may not have been the reaction temperature. Also, with an inlet gas temperature of about 550°R and an outlet temperature of about 1000°R, the bulk gas temperature was definitely

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not the reaction temperature. The controlling temperature based on the results of these tests compared with the accepted equilibrium data, appears to be intermediate between the two extremes of surface and gas temperatures. However, the occurrence of reactions other than the formation of methane may have had a significant effect on the overall corrosion rate, tending to shift the curves of Figures 3 and 4 downward.

In addition, the test section was not at a constant temperature over its length, with only the maximum temperature at the center having been observed. In test piece No. 11, which was run at 1.11 percent methane concentration and 4000°R, the corrosion at the center amounted to a surface regression of about 6.2 mils, whereas about 0.3 inches on each side of the center, where the surface temperature was an estimated 3800°R, the surface regression was about 22 mils. A similar result was obtained with test piece No. 7 (100 percent hydrogen, 4000°R) which broke after about 14 minutes because of overheating in the center, but which exhibited considerably less corrosion in the center than about 0.3 inches off-center in each direction. The measured surface regressions in this test were 5 and 29 mils at the center and 0.3 inches from the center respectively. This was for a 14-minute run rather than 20 minutes.

It may be noted here that the maximum internal temperature was calculated to be 4450°R when the maximum surface temperature was 4000°R. A great deal of difficulty was encountered in controlling the temperature of a test piece such as No. 7. Because of the rapid rate of corrosion it was necessary

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to reduce the input current as the temperature increased beyond the desired level. If this was not done quickly enough, the internal temperature increased to such an extent that the test piece was broken by the thermal stresses which ensued.

The mass flow rate of about 0.0032 lb/sec with a Reynolds Number of about 3000 is expected to produce sufficient turbulence to cause a rapid diffusion of corrosion products into the bulk gas stream. With this assumption, the maximum corrosion rate of 108 milligrams per minute which occurred in Test No. 7, would cause a change of 0.02 percent in the molal percentage of methane in the gas stream. The fact that corrosion and deposition were quite symmetrical about the axial center of the test sections also supports the conclusion that the corrosion products were not retained in a boundary layer and that the reaction at any point was independent of the corrosion or deposition that had occurred upstream.

CONCLUSIONS

There were two drawbacks to the tests as conducted which impair the accuracy with which the results can be applied. In the first place the surface temperature was non-uniform, with a variation of 500°R or more along the test length. This non-uniformity makes the weight changes less meaningful although the similarity between the graphs of weight change and surface change overcomes this drawback to some extent. The surface changes at the center point, where the temperature was measured, are independent of the non-uniformity in temperature along the length. The inability to obtain a system in temperature

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equilibrium is a more serious drawback. In the reactor, the gas flowing through narrow gaps between elements will quickly approach the surface temperature. In these tests such temperature equilibrium could not be attained and as previously mentioned, there appeared to be a substantial difference between the surface temperatures and the actual reaction temperatures.

Despite these drawbacks, the test results are essentially consistent with kinetic theory and clearly demonstrate the effectiveness of methane in inhibiting corrosion at least up to the estimated reaction temperatures. The approximate level of the methane concentration required at these temperatures is indicated.

RECOMMENDATIONS

If more exact data or data at higher temperatures is desired, these tests could be upgraded in several ways. The drawback of a non-uniform surface temperature could be overcome by using a longer test section to obtain suitable length at the center having essentially constant temperature. The remainder of the test section could then be coated with niobium carbide. The drawback of having the gas temperature not equal to the surface temperature could be overcome by preheating the inlet gas, but this would require a major redesign of the entire experimental set-up in order to handle such high temperature gases. Minor changes in the present set-up such as better cooling of the electrodes, a larger surface area in contact with the electrodes, and a hollow test section would

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permit testing to about 4500°R. Tests involving the addition of other corrosion products to hydrogen, such as acetylene, ethene, and ethane may also provide useful information, particularly at temperatures near 4500°R. Consideration should also be given to other geometries, such as narrow gaps either straight or with sudden expansions or contractions.

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Figure 1

EQUILIBRIUM DIAGRAM OF METHANE-HYDROGEN-CARBON SYSTEM

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Figure 2

EXPERIMENTAL SET-UP

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Figure 3

RATE OF WEIGHT CHANGE OF TEST PIECES

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Figure 4
SURFACE REGRESSION OR THICKNESS OF DEPOSITION
AT CENTER OF TEST PIECES

Figure 5

Test Pieces Run at 3000°R
Bottom Piece is a Typical Pre-test Specimen

Figure 6

Test Pieces Run at 4000°R
Bottom Piece is a Typical Pre-test Specimen

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16

TABLE I

Summary of Test Conditions and Results

Test Number	Methane Concentration (Percent)	Surface Temperature (°R)	Time of Test (Minutes)	Weight Change (Grams)	Rate of Weight Change (Milligrams/Min)	Surface Regression (-) Surface Thickness (+) (Mils)	
						At Center	Off Center
6	0	3062	20	-0.5580	-27.9	-14.0	-2.7
8	1.11	3053	20	-0.3149	-15.8	- 4.1	-1.4
5	3.20	3068	20	-0.0426	- 2.1	- 0.2	-0.2
14	6.18	3055	20	-0.0166	- 0.8	0.0	-0.1
9	9.06	3031	18 ⁽¹⁾	+0.0004	0.0	0.0	0.0
7	0	4000	14 ⁽²⁾	-1.5183	-108.	- 5.0	-29.
11	1.11	3993	20	-1.1588	-57.9	- 6.2	-22.
10	3.31	3952	20	— ⁽⁴⁾	—	+ 1.3	+1.5
13	3.23	3978	20	-0.0471 ⁽⁵⁾	-2.4	+ 1.0	+1.0
15	6.16	3947	1.5 ⁽³⁾	+0.0622	+41.5	+ 2.0	+1.1
16	6.16	3961	20	+0.8648	+43.2	+24.1	+16.7
12	9.05	3897	5.5 ⁽³⁾	+0.4132	+75.2	+16.0	+10.0

1. Test terminated because of leak in pressure vessel.
2. Test terminated by break in test piece.
3. Test terminated because of damaged electrode, which also caused slight weight loss.
4. Weight change unavailable because of damage at electrode.
5. Test section had pyrolytic coating. Weight loss apparently resulted from corrosion on downstream extension.

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