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ORNL 967

METALLURGY AND CERAMICS

Contract No. W-7405, Eng 26

REACTOR EXPERIMENTAL ENGINEERING DIVISION

SHIELDING REACTOR CORROSION STUDIES

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Price \$ 0.25

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

CLASSIFICATION CANCELLED

DATE MAR 2 1957 *pl*

For The Atomic Energy Commission

H. R. Canale

Chief, Declassification Branch

Date Issued:

JUL 9 1951

OAK RIDGE NATIONAL LABORATORY

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CARBIDE AND CARBON CHEMICALS COMPANY

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Oak Ridge, Tennessee

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ABSTRACT

The investigation of corrosion on MTR type fuel elements for the Shielding Reactor in filtered water is reported.

The study included two basic types of protection: Element pretreatment, by either anodizing or alodizing; and solution control, using nitric acid to maintain a pH of 5.5 to 6.5 or the addition of 60 ppm sodium chromate as an inhibitor.

No pretreatment was effective in stopping pitting attack for more than four months as a maximum. Control of the pH tended to reduce pitting attack but did not stop it. However the addition of sodium chromate was found to stop all pitting attack and at the same time reduce the overall corrosion rate to essentially zero.

INTRODUCTION

In August of 1950 the Corrosion Group was asked to investigate the effect of filtered water as a corrosive media on fuel elements of the Shielding Reactor. Plans had originally called for demineralized water but the additional cost involved seemed excessive. Consequently the investigation of filtered water was begun. The need for some passivation treatment or protective measure was known before the tests were started and various alternatives were included in the original group.

The construction and start-up schedule was so far advanced at the time of the decision to use filtered water that only two week corrosion tests were available when it was decided to use alodizing as the pretreatment for added protection. The inherent risk involved in using short term tests as a basis for long term exposures was realized and consequently the tests were continued for a period of some months. Both the short term and the longer term tests are reported here.

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TEST PROCEDURE

Corrosion Media

Filtered water as supplied to the Laboratory was used in these tests. Table I contains an average analysis together with the maximum and minimum values obtained from analysis of this water over a five month period.

In addition to these analysis certain components were also checked in the water at the end of one month exposure when the water was changed. Results of these analyses are listed in Table II. The only significant figures from these data are the marked rise in aluminum content in the final solutions in which unprotected 2S aluminum and 2S-72S aluminum were exposed. The reason for the similar pick up in aluminum during the first two months of exposure in the Na_2CrO_4 treated water is probably due to a slight attack involved in establishing the passive surface.

In only three tests were additions made to the water; these were Na_2CrO_4 - 60 ppm, K_2CrO_4 - 60 ppm, and HNO_3 sufficient to lower and maintain the pH in the 5.5 to 6.5 range.

Test Materials

Types of Aluminum

Three classes of aluminum are involved in the make up of the fuel assemblies. These classes together with typical composition are:

<u>Type</u>	<u>Composition %</u>				
	<u>Al</u>	<u>Zn</u>	<u>Si</u>	<u>Cu</u>	<u>All Others</u>
2S	99 +	0.10 max	0.25	0.20 max	0.05
72S	Bal	1.0	-	0.1 max	0.05
Brazing Alloy	Bal	0.10 max	11.5	0.20 max	0.05

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TABLE I

Filtered Water Analysis From Five Samples Taken at One Month
Intervals From August Through December 1950

<u>Concentration of All Constituents</u> <u>in Sample</u>	<u>Units</u>	<u>Ave.</u>	<u>Max.</u>	<u>Min.</u>
pH	pH	8.0	8.3	7.4
Ppm. Alkalinity as CaCO_3	ppm	5.0	10.0	0.0
M.O. Alkalinity as CaCO_3	ppm	98.0	106.0	95.0
Specific Resistance, 25°C	ohm-cm $\times 10^3$	6.92	8.26	4.95
Soap Hardness as CaCO_3 detn.	ppm	112.0	120.0	106.0
Soap Hardness as CaCO_3 calc.	ppm	101.0	117.0	90.0
Dissolved CO_2	ppm	3.0	6.0	0
Dissolved Solids	ppm	138.0	164.0	112.0
Non-Volatile Solids	ppm	80.0	131.0	35.0
SiO_2	ppm	5.3	9.2	2.7
Fe	ppm	0.02	0.08	0.01
Al	ppm	0.08	0.14	0.02
Cu	ppm	0.02		
Ni	ppm	0.02		
Cr	ppm	0.02		
Ca	ppm	30.0	34.0	27.8
Mg	ppm	7.2	8.6	4.7
Na	ppm	9.6	14.0	6.6
SO_4	ppm	25.1	39.6	5.4
Cl	ppm	4.2	5.0	3.3
CO_3	ppm	58.2	63.6	56.4
HCO_3	ppm	118.8	129.3	114.7
NO_3	ppm	1.1	2.3	0.4
PO_4	ppm	0.8	1.7	0.2
F	ppm	0.02		

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TABLE II

Comparative Analysis Before and After 30-Day
Intervals of Corrosion Testing

<u>Sample</u>	<u>pH</u>	<u>Cl ppm</u>	<u>Al ppm</u>	<u>Resistivity ohms x 10³</u>
Initial	8.3	5.0	.09	8.26
a* - 1F	8.2	4.4	0.3	7.69
b - 1F	8.2	3.8	2.1	6.0
c - 1F	8.3	4.2	0.24	6.96
d - 1F	8.4	3.9	0.23	6.94
e - 1F	8.5	4.2	0.5	7.80
Initial	8.3	4.4	.14	8.26
a - 2F	8.1	4.3	0.3	7.69
b - 2F	8.2	4.5	1.9	5.31
c - 2F	8.4	3.9	0.29	7.08
d - 2F	8.3	3.9	0.2	6.94
e - 2F	8.5	3.9	0.6	8.13
Initial	7.7	4.6	0.1	7.84
a - 3F	8.3	4.3	1.2	7.8
b - 3F	8.4	4.2	0.25	4.93
c - 3F	8.1	2.4	0.23	6.94
d - 3F	8.3	4.8	0.33	7.17
e - 3F	8.4	3.8	1.5	6.72
Initial	7.4	3.3	0.7	4.95
a - 4F	8.0	4.4	1.0	4.95
b - 4F	8.0	4.4	0.15	3.41
c - 4F	7.6	3.7	0.3	5.17
d - 4F	8.0	2.8	0.24	4.4
e - 4F	7.9	4.4	0.64	5.28
Initial	7.7	3.8	0.02	5.31
a - 5F	8.2	4.3	0.7	4.76
b - 5F	8.0	2.2	0.32	3.54
c - 5F	8.2	2.9	0.16	5.07
d - 5F	8.0	5.7	0.05	4.96
e - 5F	8.1	4.2	1.4	5.31

*a - 2S Aluminum

b - 2S Aluminum (Na_2CrO_4)

c - 2S Aluminum (Standard Alodized)

d - 2S Aluminum (Anodized)

e - 2S-72S Aluminum

1F - First month final solution

2F - Second month final solution, etc.

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Pretreatments

In all, three classes of pretreatment for enhanced corrosion resistance were tested. These were Anodizing, Standard Alodine*, and Hot-Dry Alodine*.

Anodizing was the straight anodic treatment of 2S aluminum sheet. The sheared edges of the coupons were protected with a high temperature wax. The protection is from the extra thick oxide coat that is formed by the anodic treatment.

The alodized samples were of two different varieties; simple circular samples of 2S aluminum were given both the Hot-Dry and Standard Alodizing procedures, while a mock assembly involving two sheets of 72S clad 2S aluminum brazed together with 11.5% silicon alloy were only hot-dry alodized. These samples were alodized by Mr. R. P. Spruance of the American Chemical Paint Company. The protective coating is a mixed aluminum oxide-chromate-phosphate type of film.

Samples marked 72S-2S refer to roll bonded sheets of 72S aluminum on one side and 2S aluminum on the other side. Thus both types were exposed to the water during these tests.

Test Operation

The actual testing consisted of suspending a dried and weighed specimen of known area on a glass hook so that it was totally immersed in four liters of filtered water in a covered three-neck, five-liter distilling flask.

Samples were removed monthly, dried, weighed and photographed before being returned to test. The water was changed at the inspection period.

The defilmed sample weights were obtained only at the end of the test period. This defilming process involves the use of a 5% by volume phosphoric acid - 4% by weight chromic acid solution at 50°C for 20 minutes. The principle purpose of the defilming process was to make possible an accurate count and investigation of the pits.

*Alodine - Patented process of the American Chemical Paint Company.

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RESULTS OF INITIAL TWO-WEEK TESTS

As the time schedule involved did not permit a thorough investigation before some protective treatment was decided upon, the original tests were only two weeks in duration.

The results of these tests are given in Table III.

TABLE III

Two-Week Tests in Filtered Water at Room Temperature

<u>Sample</u>	<u>Inhibitor</u>	<u>Weight Change (MDM*)</u>	<u>Pit Count Per Sq. Cm.</u>	<u>Maximum Pit Depth, mils</u>
2S Al	--	-14.8	0.15	1.0
2S Al	--	- 9.2	Neg	Neg
2S Al	Na ₂ CrO ₄ 60 ppm	+ 3.0	Neg	Neg
2S Al	Na ₂ CrO ₄ 60 ppm	+ 3.0	Neg	Neg
Std. Alodized 2S Al	--	+ 3.6	Neg	Neg
Std. Alodized 23 Al	--	Neg	Neg	Neg
2S-72S Al	--	-47.2	0.2	2.6
2S-72S Al	--	-43.6	0.25	6

*Milligrams per square decimeter per month

The untreated 2S aluminum and the 2S-72S bonded aluminum were stained dark gray on all surfaces. The major pitting attack on the bonded material was in the 72S aluminum; however, one pit did occur on the 2S aluminum side.

In view of these results and from the reported improvement in protection provided by the Hot-Dry Alodine process, it was decided to use this type of protection, but also, to continue the tests to determine, if possible, the life expectancy. In addition the tests with the remaining samples were continued for comparison.

RECORDED

RESULTS OF TESTS OF LONGER DURATION

Table IV gives the results of the continuation of tests as previously reported (Results of Initial Two-Week Tests) and all new tests which were started and run for various lengths of time. All tests were tested at least long enough to prove their worth.

Since the prime criterion for this application is pitting which might penetrate to the core and release the highly active fission products, it can readily be seen that no pretreatment offered satisfactory protection for long periods of time. A better idea of what this type of corrosion means may be obtained from the accompanying photographs, Figures 1 through 7.

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TABLE IV

Results of Corrosion Tests on Various Aluminum Samples
Exposed to Filtered Water at Room Temperature

Sample	Weight Change (MDM)						Defilmed
	1 Month	2 Months	3 Months	4 Months	5 Months	6 Months	
2S Al	+8.8	+15.1	+12.4	+31.2	+26.4		-32.0
2S Al	+7.3	+11.4	+13.0	+27.5	+18.3		-27.8
2S-72S	+2.3	+23.4	+58.8	+91.9	+79.6		-54.7
2S-72S	+5.1	+207.3	+37.4	+75.6	+69.0		-53.7
2S Anodized	-9.3	-4.2	-7.7	-5.6	-4.65	-4.1	
2S Anodized	-13.4	-12.5	-13.6	-9.8	-7.9	-5.7	
2S (Na_2CrO_4)	+0.8	+2.2	+0.7	+0.0	+0.1	-1.1	+0.3
2S (Na_2CrO_4)	+3.2	+3.4	+1.3	+0.7	+0.3	-0.5	+0.2
2S (K_2CrO_4)	-0.5	-2.5					-1.5
2S (K_2CrO_4)	-2.4	-2.9					-2.5
2S Std Alodized	-3.0	-0.9	-1.1	+0.9	+2.9	-6.6	
2S Std Alodized	-3.7	-1.2	+0.3	+0.2	-5.2	-7.1	
Mock Assembly	+7.7	+5.6	+7.0				
Mock Assembly	+6.1	+5.0	+1.9				
2S Hot Dry	+0.5	-1.5					
Alodized at X-10	+3.9	-0.8					
2S (HNO_3)	+5.9						
2S (HNO_3)	+2.5						
2S-72S (HNO_3)	+2.0						
2S-72S (HNO_3)	+3.8						

TABLE IV (CONT'D)

Results of Corrosion Tests on Various Aluminum Samples
Exposed to Filtered Water at Room Temperature

Sample	Number of Pits Per Sample						Max. Pit Depth (mils)	Max Pit Dia. (mils)
	1 Month	2 Months	3 Months	4 Months	5 Months	6 Months		
2S Al	1	8	12	12	12		46	40
2S Al	2	8	12	12	12		38	80
2S-72S	1	4	5	6	6		19	120
2S-72S	1	1	2	4	6		19	80
2S Anodized	0	0	0	0	3	16	1	20
2S Anodized	0	0	0	0	2	38	1	4
2S (Na ₂ CrO ₄)	0	0	0	0	0	0	N11	N11
2S (Na ₂ CrO ₄)	0	0	0	0	0	0	N11	N11
2S (K ₂ CrO ₄)	0	0					N11	N11
2S (K ₂ CrO ₄)	0	0					N11	N11
2S Std Alodized	0	0	0	8	8	9	40	20
2S Std Alodized	0	1	5	5	9	15	34	40
Mock Assembly			5				7	40
Mock Assembly			0				Neg	Neg
2S Hot Dry	1	5					7	40
Alodized at X-10	1	4					18	20
2S (HNO ₃)	4							
2S (HNO ₃)	6							
2S-72S (HNO ₃)	Numerous Tiny Pits							
2S-72S (HNO ₃)

1 MONTH

2 MONTHS

3 MONTHS

4 MONTHS

5 MONTHS

6 MONTHS
DEFILMED

FIGURE 1. CORROSION OF UNPROTECTED 2 S
ALUMINUM SAMPLES EXPOSED TO FILTERED
WATER CONTAINING 60ppm Na_2CrO_4 AT ROOM
TEMPERATURE

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1 MONTH

2 MONTHS

3 MONTHS

4 MONTHS

5 MONTHS

6 MONTHS
DEFILMED

FIGURE 2. CORROSION OF 2S ALUMINUM PRETREAT-
ED BY THE STANDARD ALODINE PROCESS AND
EXPOSED TO FILTERED WATER AT ROOM
TEMPERATURE

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PHOTO NO. 6-2502

1 MONTH

2 MONTHS

3 MONTHS

4 MONTHS

5 MONTHS

DEFILMED

FIGURE 3. CORROSION OF UNPROTECTED 2 S
ALUMINUM SAMPLES EXPOSED TO FILTERED
WATER AT ROOM TEMPERATURE

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UNCLASSIFIED
PHOTO NO. 6-2503

1 MONTH

2 MONTHS

3 MONTHS

DEFILMED

**FIGURE 4. CORROSION OF MOCK FUEL ASSEMBLIES
PRETREATED BY THE HOT DRY ALODINE
PROCESS AND EXPOSED TO FILTERED WATER
AT ROOM TEMPERATURE**

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PHOTO NO. 6-2504

1 MONTH

2 MONTHS

DEFILMED

**FIGURE 5. CORROSION OF 2 S ALUMINUM
PRETREATED BY THE HOT DRY ALODINE
PROCESS AND EXPOSED TO FILTERED
WATER AT ROOM TEMPERATURE**

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PHOTO NO. 6-2505

1 MONTH

2 MONTHS

3 MONTHS

4 MONTHS

5 MONTHS

6 MONTHS

FIGURE 6. CORROSION OF ANODIZED 2S
ALUMINUM SAMPLES EXPOSED TO
FILTERED WATER AT ROOM TEMPER-
ATURE (EDGES WAXED)

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1 MONTH

2 MONTHS

3 MONTHS

4 MONTHS

5 MONTHS

DEFILMED

FIGURE 7. CORROSION OF 2 S-72 S
ROLL BONDED ALUMINUM SHEETS
EXPOSED TO FILTERED WATER AT
ROOM TEMPERATURE -72 S SIDE
SHOWN

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CONCLUSIONS

On the basis of the results of these tests, it was decided to add 60 ppm Na_2CrO_4 to the cooling water in the shielding reactor.

No pretreatment tested was found to be effective in preventing pit formation for more than four months. The anodized 2S aluminum samples showed no pits at the end of four months, but were pitted at the five month inspection. Alodized samples which appeared satisfactory at the end of two weeks, failed by pit formation between 60 and 90 days.

Although pit depth was shown to stop at the 2S-72S aluminum interface because of the sacrificial effect of the 72S aluminum, the accumulation of corrosion products was high. Such accumulation could effectively block the cooling channels, with subsequent formation of hot spots and consequent rapid corrosion.

Time and space did not permit investigation of lower concentrations of the sodium chromate inhibitor. Operation of the reactor for three months has shown that there is negligible effect of the Na_2CrO_4 on background activity, making consideration of lower concentrations unnecessary.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to the following people for their assistance in making these tests.

Mr. J. Brown and Mr. L. L. Fairchild for the handling of the specimens and test media.

Miss Helen Barker for the photographs of the test samples.

Mr. J. H. Edgerton of the Analytical Chemistry Division for chemical analysis of the test media.

END