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# SHIELDING REACTOR CORROSION STUDIES

Arnold R. OLSEN

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REACTOR EXPERIMENTAL ENGINEERING DIVISION

# SHIELDING REACTOR CORROSION STUDIES

Arnold R. Olsen

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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.

## 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:

| Type | Composition % | | | | |
|---|---|---|---|---|---|
| | Al | Zn | Si | Cu | All Others |
| 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 |

## TABLE I

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

| Concentration of All Constituents in Sample | Units | Ave. | Max. | Min. |
|---|---|---|---|---|
| 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 x $10^3$ | 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 | | |

## TABLE II

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

| Sample | pH | Cl ppm | Al ppm | Resistivity ohms x $10^3$ |
|---|---|---|---|---|
| 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.

## 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-phosfate 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.

## 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

| Sample | Inhibitor | Weight Change (MDM*) | Pit Count Per Sq. Cm. | Maximum Pit Depth, mils |
|---|---|---|---|---|
| 2S Al | -- | -14.8 | 0.15 | 1.0 |
| 2S Al | -- | - 9.2 | Neg | Neg |
| 2S Al | $Na_2CrO_4$ 60 ppm | + 3.0 | Neg | Neg |
| 2S Al | $Na_2CrO_4$ 60 ppm | + 3.0 | Neg | Neg |
| Std. Alodized 2S Al | -- | + 3.6 | Neg | Neg |
| Std. Alodized 2S 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.

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.

## TABLE IV

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

| Sample | Weight Change (MDM) 1 Month | 2 Months | 3 Months | 4 Months | 5 Months | 6 Months | Defilmed |
|---|---|---|---|---|---|---|---|
| 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 | +287.3 | +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 ($Na_2CrO_4$) | 0 | 0 | 0 | 0 | 0 | 0 | Nil | Nil |
| 2S ($Na_2CrO_4$) | 0 | 0 | 0 | 0 | 0 | 0 | Nil | Nil |
| 2S ($K_2CrO_4$) | 0 | 0 | | | | | Nil | Nil |
| 2S ($K_2CrO_4$) | 0 | 0 | | | | | Nil | Nil |
| 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 | | | | | | | |
| 2S-72S ($HNO_3$) | Tiny Pits | | | | | | | |

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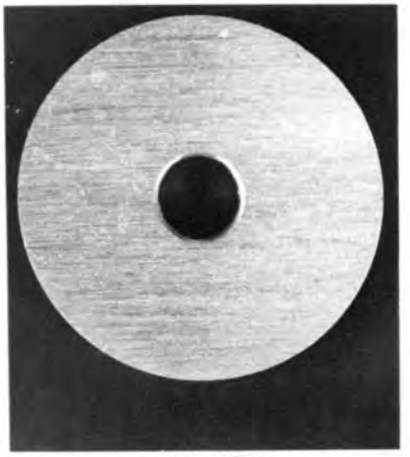
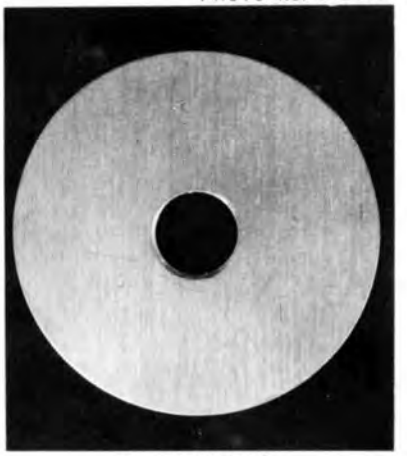
PHOTO NO. 6-2500



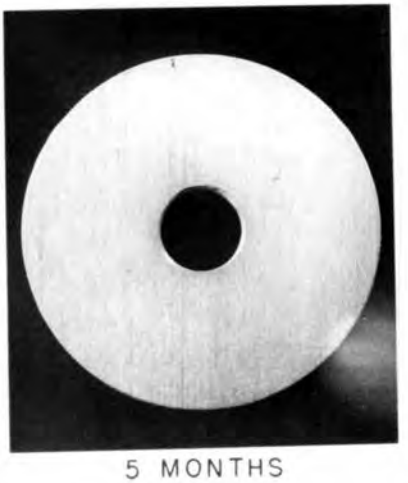
1 MONTH



2 MONTHS

3 MONTHS

4 MONTHS



5 MONTHS

6 MONTHS
DEFILMED

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

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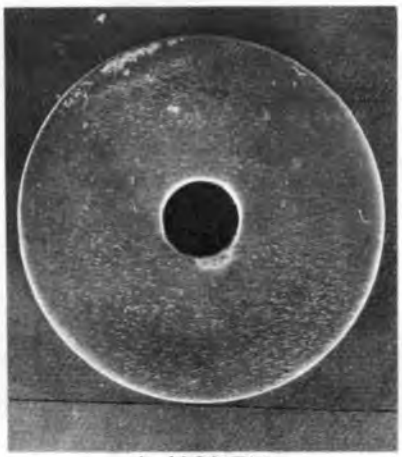


1 MONTH

2 MONTHS

3 MONTHS

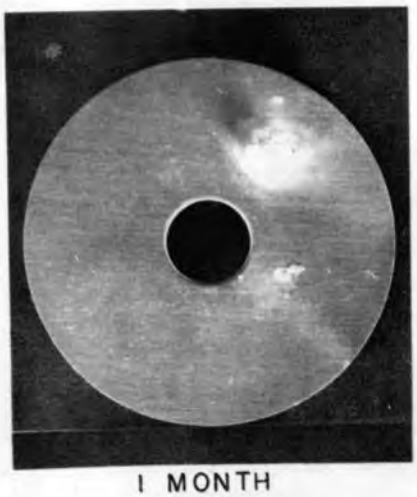
4 MONTHS

5 MONTHS

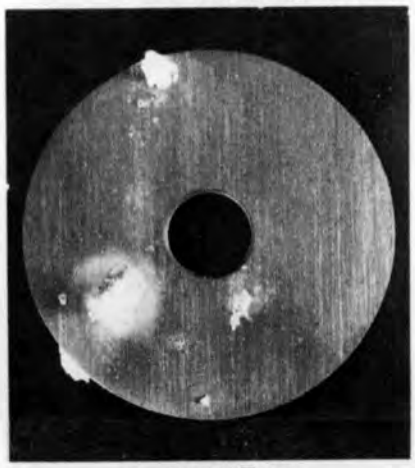
6 MONTHS
DEFILMED

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

UNCLASSIFIED
PHOTO NO. 6-2502



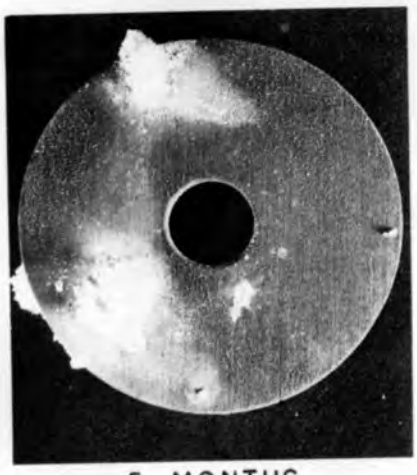
1 MONTH



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

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

UNCLASSIFIED
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

UNCLASSIFIED
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 TEMPERATURE (EDGES WAXED)

UNCLASSIFIED
PHOTO NO. 6-2506

1 MONTH

2 MONTHS

3 MONTHS

4 MONTHS

5 MONTHS

DEFILMED

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

## 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

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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.

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