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ALUMINUM CORROSION IN SUBCRITICAL AND ZERO POWER CRITICAL REACTORS

M. E. BERGSTRESSER

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by

Mack E. Bergstresser

Approved by

T. C. Evans, Superintendent
Engineering Assistance Section
Works Technical Department
Savannah River Plant

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ABSTRACT

Natural uranium aluminum-clad fuel slugs are
subject to corrosion in low temperature ($<100^{\circ}$C)
water during service in subcritical and zero power
nuclear reactors. This report discusses pitting
corrosion and galvanic corrosion of aluminum in
such service. The use of high purity water or the
addition of chromates as inhibitors will minimize
the corrosion rates.

CONTENTS

LIST OF FIGURES

ALUMINUM CORROSION IN SUBCRITICAL AND ZERO POWER CRITICAL REACTORS

INTRODUCTION

Subcritical and zero power critical reactors are used for nuclear research and instruction by agencies outside the Atomic Energy Commission. Such reactors are fueled with slugs of natural uranium clad with type 1100 aluminum, and are moderated by H_2O, D_2O, or graphite. In all cases the fuel slugs are immersed in either H_2O or D_2O and operate at room temperature. Corrosion of the aluminum cladding material occurs during operation of these reactors. This report describes the types of aluminum corrosion that occur in low temperature water (<100°C) and recommends methods of preventing such corrosion. The recommendations, which are based on operating experience at the Savannah River Plant, may be useful to those who operate subcritical and zero power critical reactors.

SUMMARY

Aluminum cladding on slugs, and aluminum reactor components used in small research reactors are subject to pitting and galvanic corrosion while immersed in stagnant H_2O or D_2O at low temperatures (<100°C).

Pitting corrosion is promoted by the presence of chloride ions and heavy metal ions such as Cu, Cr, Hg, and Ag. Removal of such ions from solution prevents pitting.

Galvanic corrosion occurs when dissimilar metals in electrical contact are exposed to an electrolyte. Such couples between aluminum-clad slugs and dissimilar metals should be avoided. Reduction of the conductivity of the electrolyte (by purifying or deionizing the water) reduces the current flow.

RECOMMENDATIONS

The following procedure is recommended to prevent low temperature corrosion of aluminum in H_2O or D_2O.

1. Use high purity water with a conductivity of 0.1-0.2 μmho/cm. Water may be purified and maintained pure through the use of an ion exchange resin column such as is shown in Figure 1.

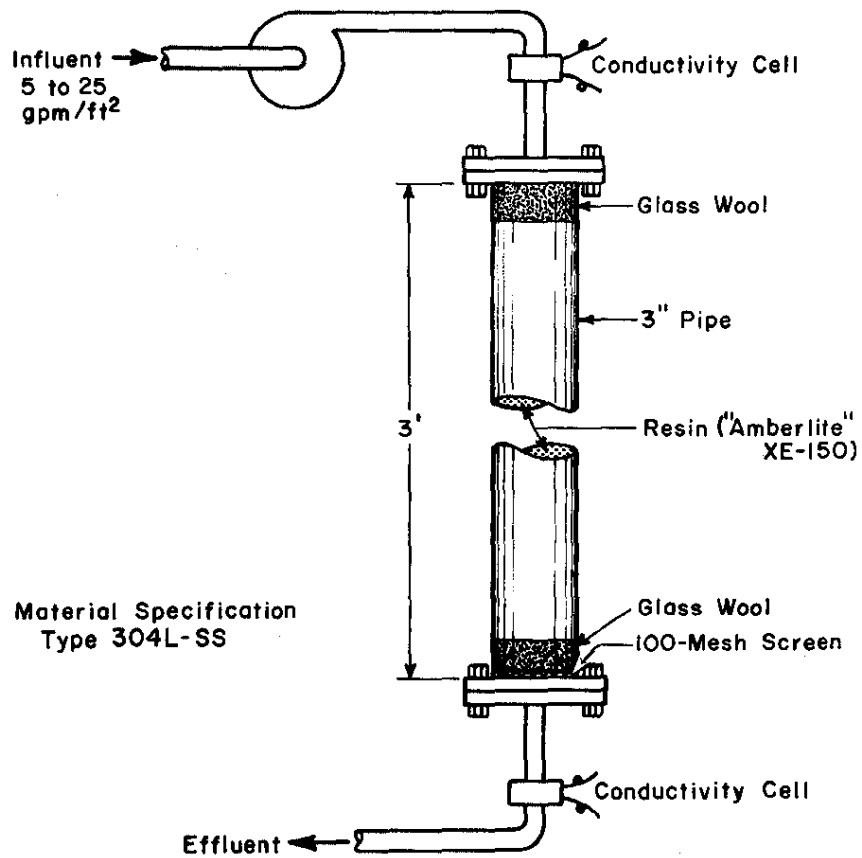Influent
5 to 25
gpm/ft^2

Conductivity Cell

Glass Wool

3" Pipe

3'

Resin ("Amberlite"
XE-150)

Material Specification
Type 304L-SS

Glass Wool
100-Mesh Screen

Conductivity Cell

Effluent

FIG. 1   ION EXCHANGE COLUMN

As an alternative method for preventing
corrosion, $MgCrO_4$ at 0.03M concentration
is preferred. However, $CaCrO_4$ or Na_2CrO_4-
$MgCrO_4$ at 0.03M concentration can be used.
(NOTE: Inhibitors and ion exchange resin
columns cannot be used in the same system.)

2. Avoid couples between aluminum and dis-
similar metals.

3. Handle aluminum-clad slugs with utmost care.
Do not remove, break, or destroy the pro-
tective oxide layer on the aluminum surface.

DISCUSSION

A protective hydrated oxide layer ~0.0001 inch thick
is formed on the aluminum cladding surface of fuel slugs by
steam autoclaving following the fabrication process. This
protective oxide ($\alpha Al_2O_3 \cdot H_2O$) provides a passive surface
that increases the corrosion resistance of aluminum in water.

In service, aluminum cladding and reactor components
are subject to four types of corrosion: pitting, galvanic,
general, and intergranular. Because there are differences
in these corrosion phenomena, "low temperature" corrosion
($<100^\circ C$) is distinguished from "high temperature" corrosion
($>100^\circ C$). Pitting and galvanic corrosion occur generally in
the low temperature range, while general and intergranular
corrosion occur in the high temperature range. Other than
temperature, the principal factor influencing the corrosion
rates of aluminum is the purity of the water.

Low Temperature Corrosion

Pitting Corrosion

Small, normally white, crystalline or gelatinous
deposits on the surface of aluminum are evidence of pitting
corrosion. Pitting[1,2] begins by breakdown of passivity
at a favored nucleus. This breakdown is followed by the
formation of an electrolytic cell where the exposed metal
at the minute area under the broken film is anodic, resulting
in a rapid corrosion rate.

The reactions for the general corrosion of aluminum in
H_2O or D_2O where Al^{+3} is the dominant ion can be expressed
as follows:

- 3 -

$$2Al = 2Al^{+3} + 6e^- \qquad \text{Anodic reaction}$$

$$6e^- + 6H_2O = 3H_2 + 6OH^- \qquad \text{Cathodic reaction}$$

$$2Al^{+3} + 6OH^- = 2Al(OH)_3 \ (\beta\text{-trihydrate}) \qquad \text{Precipitation reaction}$$

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2 \qquad \text{Over-all reaction}$$
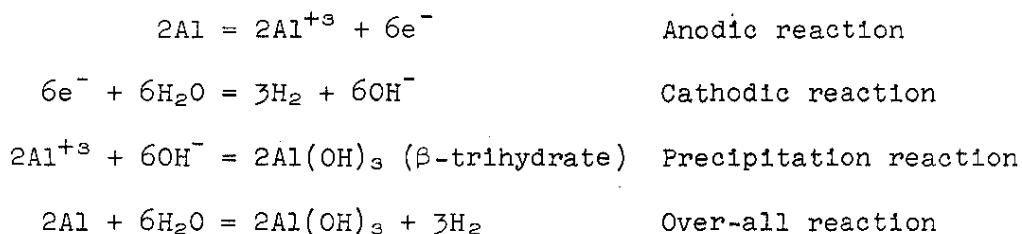
The concentration of aluminum ions in the solution adjacent to the point of failure soon exceeds the solubility of the aluminum hydroxide and a precipitate is formed[1,2]. Initially, the precipitate is gelatinous (Figure 2), which hinders the migration of the aluminum ions from the surface and causes a crystalline deposit to form around the point of attack. The reactions of the aluminum ions, impurity ions, and hydroxyl ions from the water form soluble complexes to produce acidity at the point where no film exists. The acidity prevents formation of a passive oxide film in this area and results in little or no resistance to corrosion of the metal under the deposit. The rate of corrosion is then governed by the cathodic reaction; therefore, the factors initiating the pit formation are no longer essential for its growth.

Pitting corrosion is strongly initiated by chlorides and the ions of heavy metals such as Cu, Cr, Hg, and Ag. The quantity[2] of these ions in the water must be reduced below a critical concentration to prevent pitting, because these metals will deposit electrochemically and have potentials that are noble (cathodic) to the potential of the aluminum. The potential on the aluminum surface varies from point to point; at highly anodic points the deposition potential is greatest and a more noble metal is most likely to be deposited.

Reduction of the thickness of the protective layer, or complete removal in localized areas, can result from improper handling of the slugs during charging or discharging operations. Minor breaks in the protective layer produce ideal locations for pit formation. The utmost care should therefore be used in handling uranium slugs.

Galvanic Corrosion

Galvanic corrosion of aluminum is related to pitting corrosion; however, it is normally associated with the contact of aluminum and dissimilar metals. When dissimilar metals[3] in electrical contact are exposed to an electrolyte, a galvanic current flows from one to the other; corrosion of the anodic member of the couple is directly related to the galvanic current by Faraday's law.

- 4 -
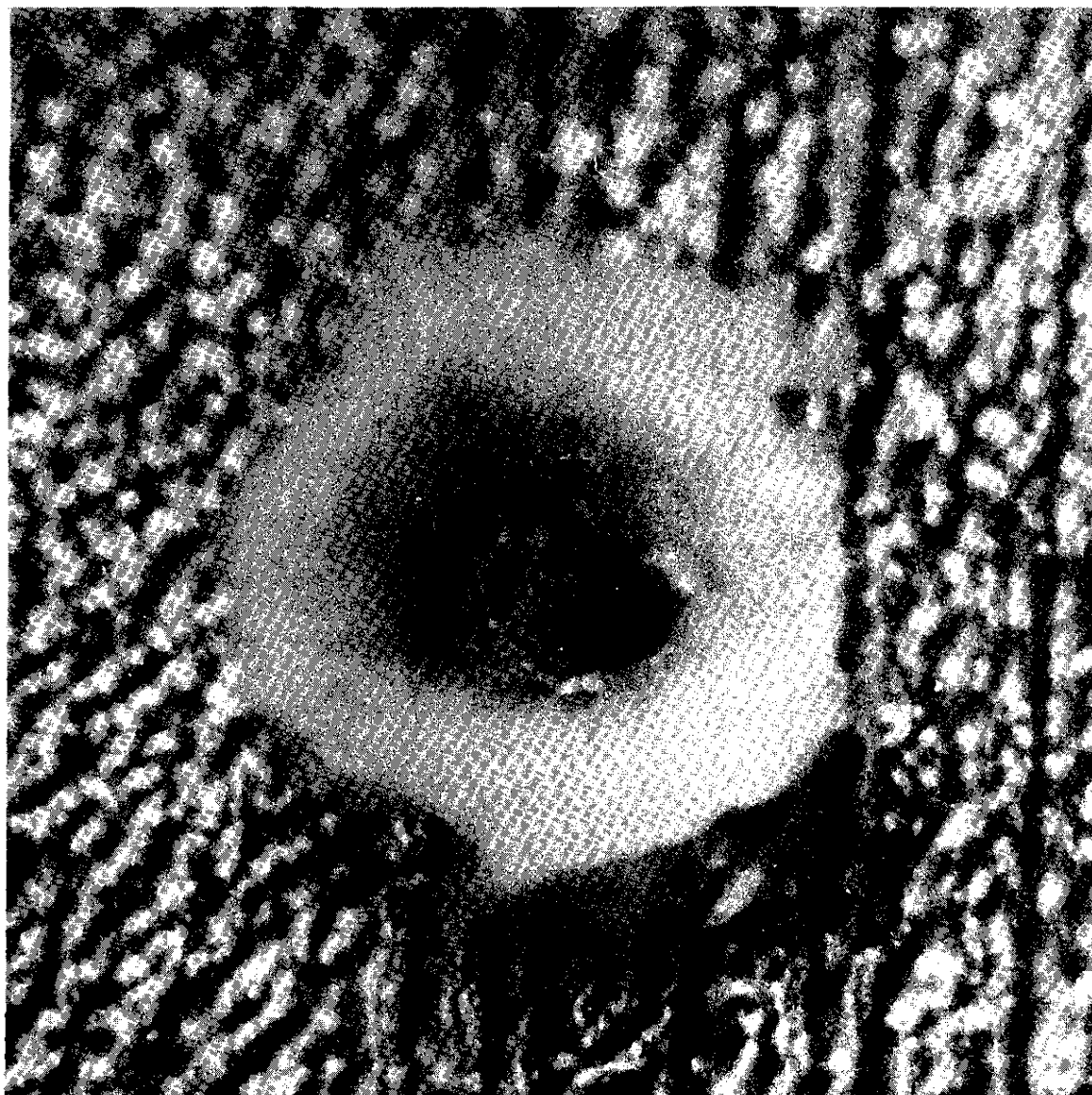
FIG. 2 PITTING CORROSION ATTACK ON TYPE 1100 ALUMINUM
The Al(OH)$_3$ deposit around the periphery of the pit
is in the gelatinous state

Couples between aluminum-clad slugs and supports of dissimilar metals should be avoided. In addition, reduction of the conductivity of the electrolyte will reduce the current flow.

Corrosion Medium

Tests[1] have shown that no pitting corrosion will occur on aluminum, even when in contact with stainless steel, as long as the water is sufficiently pure. Water becomes more corrosive to aluminum with increasing content of corrosion products. Failure to remove or prevent the formation of corrosion products eventually makes the water so corrosive that pitting develops.

The H_2O and D_2O used in aluminum corrosion tests[1] turned milky (bluish-white) after about 60 days, probably due to colloidal $Al(OH)_3$. Such dissolved corrosion products increase the conductivity of the water and increase the probability of pitting or galvanic corrosion.

Chloride ion concentrations as low as 7 ppm can cause corrosion attack on aluminum. Chlorides break down the passivity of the protective oxide layer and increase the conductivity of the water.

Methods of Preventing Corrosion

High Purity Water

High purity water with very low conductivity is an effective means of controlling the corrosion of aluminum. Tests[4,5] with various ion exchange resins at the Savannah River Laboratory showed that ions are effectively removed from effluent D_2O with the strong acid - strong base mixed bed resin "Amberlite"* XE-150. D_2O conductivity was maintained at 0.02 μmho/cm, which demonstrated that the columns deionized D_2O effectively and that few ionic impurities passed through the columns. Light water effluent can be reduced to a conductivity of 0.1-0.05 μmho/cm; bulk water conductivity can be maintained at approximately 0.1-0.2 μmho/cm.

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* Trademark of Rohm and Haas Company, Philadelphia, Pennsylvania.

- 6 -

The construction and operation of an ion exchange resin column is relatively easy; minimum design requirements for a column suitable for a small research reactor are shown in Figure 1.

Continuous operation of the ion exchange column is desirable; however, it can be used intermittently. The effectiveness and exhaustion point of the resin column are determined by the use of in-line conductivity cells with a cell constant of <0.1.

Industrial Instruments, Inc, Cedar Grove, N. J. can supply suitable conductivity cells. Conductivity values can be read directly from a conductivity bridge (eg, Industrial Instruments Model RC16B1) or recorded on a Brown ElectroniK Conductivity Recorder supplied by Minneapolis-Honeywell Regulator Co., Brown Instrument Division, Philadelphia, Pennsylvania.

Inhibitors

The addition of small amounts of inhibitors to H_2O or D_2O effectively decreases the corrosion rate of aluminum. Tests[6] have shown that chromates are specific corrosion inhibitors for aluminum in water; $MgCrO_4$ at 0.03M concentration is the most effective. In addition, 0.03M concentrations of $CaCrO_4$ or Na_2CrO_4-$MgCrO_4$ can be used. Experience with inhibitors is limited, but no difficulty is anticipated.

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