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SUBJECT: Secondary-Side Water Treatment for Corrosion Control in
Aluminum Heat Exchangers: Practices and Results at the
Oak Ridge Research Reactor

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ABSTRACT

Standard water treatment practices have proven adequate for scale and corrosion control on the secondary side of the ORR pool-cooling heat exchanger. Corrosion rates measured on specimens exposed to secondary water showed maximum corrosion rates of approximately 1 mpy during the first exposure period and these rates decreased during subsequent exposure. Examination of the heat exchanger tube bundle after 6 months and 13 months of operation showed only minor film formation and very little evidence of corrosion. The corrosion testing program will be continued and an automatic pH control system will be installed in the secondary water system.

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Secondary-Side Water Treatment for Corrosion

Control in Aluminum Heat Exchangers:

Practices and Results at the

Oak Ridge Research Reactor

INTRODUCTION

The Oak Ridge Research Reactor (ORR) is an MTR-type reactor fueled with enriched uranium in the form of aluminum-clad fuel elements. Most of the heat generated in the core of the reactor is removed in the core-cooling loop which consists of the core tank, decay tank, and air-cooled radiators with the appropriate pumps and piping. At 20 Mw total power approximately 0.7 Mw of heat is generated in the pool in which the reactor core tank is submerged. The pool water is cooled by passing it through an aluminum alloy heat exchanger which is served by a conventional redwood cooling tower. This report is concerned with the pool cooling system.

The development of high-strength, corrosion-resistant aluminum alloys during recent years has made the use of aluminum alloys, even for such items as heat exchangers, increasingly practical. Many aluminum alloys have been accepted into pressure code specifications¹ for use in unfired pressure vessels at temperatures up to 400°F.

The excellent corrosion resistance of aluminum alloys helps prevent the accumulation of corrosion products on heat-exchange surfaces and the smooth finish resists the deposition of solids from other parts of the system, thus maintaining high heat-transfer rates.²

Nevertheless, when water is used as a coolant, careful attention must be paid to water quality and corrosion control to insure long life and satisfactory performance. Fortunately, many of the water-treatment systems developed for use with steel systems can be applied to aluminum or mixed aluminum-steel systems. The same standards of cleanliness and the control of dissolved and suspended solids considered necessary in steel systems apply also to aluminum or mixed aluminum-steel systems.

The purpose of this report is to discuss generally the most important factors in water-treatment programs and to present the practices currently in use at the ORR. The final section is concerned with the effectiveness of the water-treatment practice at the ORR as determined by a corrosion test program conducted in the cooling system and by examination of parts of the system.

GENERAL WATER-TREATMENT CONSIDERATIONS

Corrosion Inhibitors.--Sodium chromate in the range of 300-500 ppm of chromate can be used effectively as a corrosion inhibitor for aluminum and aluminum-steel systems. However, the "dianodic" system using chromate-polyphosphate is effective at much lower inhibitor concentrations and is preferable to the straight chromate system. Chromate concentrations of 10 to 30 ppm with polyphosphate concentrations of 2 to 10 ppm at pH 6.5 to 7.5 give excellent inhibition in oxygenated dynamic systems. Care must be exercised in designing aluminum systems to prevent the formation of static areas, and provisions should be made for flushing dead-end piping.

pH Control.--Many natural waters, particularly those suitable for domestic use, contain varying amounts of alkalinity. Upon concentration by evaporation

from a cooling tower, the pH of these waters increases. At sufficiently high pH values, delignification of cooling-tower wood occurs and alkaline corrosion of aluminum alloys may also become a problem. Since the dianodic chemical treatment gives optimum corrosion inhibition on aluminum and steel in the pH range 6.5 to 7.5, waters which become highly alkaline when concentrated must be controlled through additions of nitric or sulfuric acid. Best results are obtained by continuous pH monitoring and continuous automatic acid additions. Where pH increases slowly, intermittent slug feeding of acid may suffice.

Microbiological Control.--The uncontrolled growth of microorganisms in a cooling-water system results in deterioration of tower wood and localized corrosion on metal surfaces under colonies of organisms.

Whether the source of the organisms is a contaminated water supply or airborne contamination, the first step in their control is to identify the classes of organisms present, since the treatment is more or less specific for many types. Once the organism has been identified, the type and quantity of toxicant necessary for a lethal dosage can be prescribed.

Most commonly used organic toxicants are compatible with aluminum systems. Examples of such toxicants are: soluble salts of saturated and unsaturated chlorophenols or mixtures of these; dialkyl dimethylammonium chlorides and alkyl trimethylammonium chlorides in which the alkyl chains range from 6 to 18 carbon atoms; chloramine; and rarely, chlorine. Toxicants containing copper, mercury, or salts of other heavy metals are to be avoided in aluminum systems since they can produce severe pitting.^{2,4,5,6,7}

General Housekeeping.--All materials, organic or inorganic, which will not remain in a fine, well-dispersed suspension should be removed from the cooling water before it enters the heat exchanger. Once formed, the heavier, larger particles make maintenance of clean metal surfaces very difficult. Suspended particles settle out in areas of low velocity or impinge on tube and tube-sheet surfaces at extremely high velocities with sufficient force to adhere to the surface.³ Corrosion cells resulting from the deposition of solids on the metal surface can cause severe localized pitting and tuberculation. Flow velocities throughout the circulating system above some minimum value, usually in the range of 3 fps, will minimize the tendency of these solids to settle out on heat transfer surfaces and improve the over-all corrosion picture by eliminating stagnant areas which are undesirable in aluminum systems.

Most of the insoluble material in cooling waters originates as airborne dust, dirt, fly-ash, etc., scrubbed from the air by the cooling tower. Much of this material will accumulate in the relatively quiescent waters of the cooling-tower basin and the circulating-pump sump. Frequent and thorough cleaning of these areas will greatly aid in keeping the accumulated foreign materials from entering the circulating stream.

Control of Dissolved Solids.--Most natural waters, especially those suitable for industrial cooling, contain varying amounts and kinds of dissolved solids. Excessive amounts of some of these can lead to difficulties in cooling systems. For example, waters which contain substantial quantities of calcium salts, especially carbonates and bicarbonates, tend to become scale-forming as they are concentrated in cooling towers and subsequently

heated (see Appendix I). Likewise, excessive concentrations of alkaline or neutral sodium salts are known to accelerate the delignification of wooden parts of cooling towers. Other difficulties may also arise.

As a result, it is necessary to limit the amount of concentration which takes place in most cooling towers unless high-quality water is used and wind-drift losses are high enough to compensate for the evaporation. This rarely occurs. Thus, blowdown and/or chemical treatments must be resorted to in order to prevent the damages resulting from accumulation of dissolved solids. Sequestering agents and acidification are used to extend the limit of the concentration of calcium salts that can be tolerated, whereas ion exchange or dilution with water of low solids content are the only methods which can reduce the concentration of sodium salts. Fortunately most natural waters other than sea water do not contain large quantities of sodium salts.

OAK RIDGE RESEARCH REACTOR WATER TREATMENT

The ORR pool-cooling heat exchanger is a standard shell and U-tube type, baffled on the shell side to produce counter-current flow. The shell is welded 5154 aluminum; the tubes are 3003 aluminum clad on the outside with 7072 aluminum for increased resistance to corrosion by cooling tower water. The tube sheet is 6061-T6 aluminum for maximum strength. The designed tube-inlet temperature is 101°F, and the outlet temperature, 90°F. On the shell side, the inlet and outlet design temperatures are 81 and 92°F, respectively. Maximum design flow rates of 900 gpm are specified for both sides.

The primary side of the heat exchanger sees only high-purity deionized water. No corrosion problems are anticipated here as long as the water quality is maintained. The secondary-side water treatment program practiced

in the ORR was recommended by the National Aluminate Corporation and consists of the following:

Corrosion Control.--Corrosion inhibition is obtained by feeding a proprietary mixture of sodium chromate and sodium polyphosphate glass. This material is fed to the make-up water merely by passing the water over balls of the chemical held in a bypass feeder. Because of the low solubility of the glass, the make-up water dissolves only a few ppm of the chemicals.

Control of the inhibitor concentration is achieved by analyzing the tower water for chromate. The recommended chromate concentration is 20 to 25 ppm, which results in a phosphate concentration of 4 to 5 ppm. Varying the bypass volume through the feeder provides concentration control over a narrow range.

pH Control.--The high blowdown rate used at the ORR virtually eliminates the necessity of additional pH control. Occasionally, when the pH rises above the upper limit (pH 7.5), small additions of sulfuric acid are made manually to decrease the pH to the lower control point (pH 6.5).

Microbiological Control.--Two patented organic toxicants are used to control microorganisms. Once weekly an "amine type" toxicant (probably a quaternary ammonium salt) is fed to the cooling tower to produce a concentration of 100 ppm. Once every three weeks a water soluble, unsaturated chlorophenate is fed to the system to produce a concentration of 300 ppm. This combination treatment has held biological growth in the cooling water to an insignificant amount.

General Housekeeping.--The ORR operates on a 4-week cycle. Three weeks of operations are followed by one week of down-time. During the shutdown period, the cooling-tower basin is drained and any large amounts of debris,

leaves, etc., are removed. No special attempt has been made to remove fine sand, clay, etc., by washing. This fact has probably contributed somewhat to the deposits found in the heat-exchanger shell when it was inspected (see later section).

Control of Dissolved Solids.--For water having the composition of Oak Ridge municipal water (Table I) five cycles of concentration are considered the upper limit. Design data were based on an 11°F temperature drop, in which case the number of cycles of concentration that would occur with no blowdown is 12 cycles (Appendix II).

Table I. Oak Ridge Municipal Water

Chemical Analysis

1955-1958

Ion	Cl	SO ₄	CO ₃	Ca	Mg	TDS*	pH
Parts per Million							
Average	3	18	64.3	21	7.2	77	7.2
Maximum	6	28	101	34	13	890	6.6-7.7

* Total dissolved solids.

Since it is desirable to maintain 5 or less cycles of concentration, the blowdown rate must then be 0.17% (Appendix II) at the maximum recirculation rate of 900 gpm. This requires a 1.6-gpm blowdown. In actual practice the heat generated in the pool is less than expected and the evaporation loss considerably lower. The temperature differential across the heat exchanger averages around 5°F, and the evaporation losses from the tower average 3 to

4 gpm with 4 to 5-gpm blowdown. Replacement of evaporated water and blow-down requires a total of approximately 9 gpm make-up.

OBSERVATIONS AND CORROSION MEASUREMENTS IN THE ORR

Observed Corrosion Rates.--Coupons of four of the aluminum alloys used in the ORR have been exposed in the cooling-tower sump to permit measurement of the actual corrosion rate. Three sets of coupons have been exposed for periods of 190, 2180, and 5568 hr, respectively. In all cases, the observed corrosion rates have been 1 mpy or less. Some minor pitting was observed, but only one pit as deep as 6 mils was observed. Figure 1 shows the weight losses observed for these alloys for the three periods of testing. Photographs in Fig. 2 to 5 show the appearance of the corrosion test coupons before and after the 5568-hr test period.

Figure 6 is a photomicrograph of a pit found in one 3003-H14 coupon after 2180 hr. Figure 7 also shows a pit found in 5154-F after the same period. In both figures the metal in the upper part of the photograph was unexposed metal used to protect the surface of the specimen during polishing. These two pits are the only two significant pits found in examining over 160 square centimeters of aluminum alloy surfaces exposed to cooling tower water for periods up to 2180 hr.

Corrosion tests are still in progress in the pool-cooling system.

Examination of the ORR Heat Exchanger.--Since its installation, the pool-cooling-water heat exchanger has been disassembled twice and examined for evidence of corrosion. Both examinations took place during scheduled ORR shutdowns; the first occurred during the week of November 3, 1958, and

Fig. 1. Corrosion Rates of Aluminum Alloys in ORR Cooling Tower Water (5-27-58 to 1-22-59).

Before Testing

After 5568 hr
in Test

After Defilming

Fig. 2. 1100-H14 Aluminum Exposed in the ORR Cooling-Tower Sump

Before Testing

After 5568 hr
in Test

After Defilming

Fig. 3. 3003-H14 Aluminum Exposed in the ORR Cooling-Tower Sump

Before Testing

After 5568 hr
in Test

After Defilming

Fig. 4. 5154 Aluminum Exposed in the ORR Cooling-Tower Sump

Before Testing

After 5568 hr
in Test

After Defilming

Fig. 5. 6061-T6 Aluminum Exposed in the ORR Cooling-Tower Sump

Fig. 6. Photomicrograph of Pit Found in 3003-H14 Aluminum Alloy After 2180 hr in ORR Cooling-Tower Sump (250X)

Fig. 7. Photomicrograph of Pit in 5154-F Aluminum Alloy After 2180 hr in ORR Cooling-Tower Sump

the second was made on July 13, 1959. The latter date represented approximately 13 months of water circulation in the secondary system. At the first examination, very light general corrosion was observed. One deep pit (10 to 15 mils) was found after the first examination which was repaired by welding. There was however, evidence of very minor localized attack over large areas of the tubes (Fig. 8). The attack may have been associated with the thin layer of deposit found over the entire tube bundle. Chemical analysis of the deposit showed the major constituents to be silicon, aluminum, iron, zinc, and calcium. This would indicate that the system had been operated for at least a part of the time with insufficient chemical treatment. In addition, small amounts of lead and copper were found. Although the film would not, per se, be cause for great concern, the presence of the latter two elements in the film indicates that pitting may be expected after prolonged use unless the source of these metals is removed. None of the components of the secondary system is known to contain lead or copper; thus some further investigation must be carried out to locate the source of these metals in the system.

The second examination was made seven months after the initial inspection. No significant change in the appearance or the condition of the tube bundle was observed. All tubes were covered with a very uniform, adherent, light gray-colored film. No pitting was found. There were, however, fairly voluminous accumulations of small pebbles, mud, and silt on various portions of the bundle. Presumably, the source of the accumulations was the sump from the cooling tower.

Planned Improvements.--A continuous pH recorder-controller is to be installed in the secondary water system to meter acid to the cooling tower.

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Fig. 8. ORR Pool-Cooling Heat Exchanger Tube Bundle
After Six Months of Service

This will improve pH control and should prevent any further accumulation of calcium salts in the system. It should also improve the performance of the corrosion inhibitors.

In addition, a screen or strainer is to be put into the pump discharge line to prevent the larger insolubles from reaching the heat exchanger.

SUMMARY

An aluminum alloy heat exchanger in the pool cooling system of the ORR has given satisfactory service with a moderate amount of care taken to control chemical treatments on the secondary side and to maintain a clean system. More careful attention to these considerations would undoubtedly reduce the moderate corrosion rates observed. The appearance of the secondary side of the heat exchanger and the results obtained in the corrosion test program indicate that aluminum heat exchangers in research reactors can be expected to give long, efficient service with standard, routine water-treatment practices. However, continuous vigilance must be exercised to prevent the entrance of heavy metal ions into the system and to control the chemical treatment of the water to assure long and satisfactory performance from this system.

APPENDIX I

For any water of known composition, a pH value called the stability point ($\text{pH}_{(s)}$) can be calculated which indicates the pH at which this water will be neither corrosive nor scale-forming. This index, based on a modified Langelier Index calculation,^{8,9} shows that for Oak Ridge water the $\text{pH}_{(s)}$ is 8.2 to 8.6. The observed pH of these waters is 6.6 to 7.7, indicating that this water is corrosive at all observed compositions. At 5 cycles of concentration, however, the $\text{pH}_{(s)}$ becomes 7.2 to 7.4, whereas the observed pH is 7.9 to 8.4. Thus concentrating this water causes it to become scale-forming in behavior. Note, however, that the recommended pH range for the ORR cooling tower is 6.5 to 7.5 (with corrosion inhibitors) resulting in a water having little tendency to deposit scale.

Maintaining the pH below 7.5 for water concentrated to 5 cycles or blowing down to maintain less than 5 cycles of concentration also keeps the alkalinity below 300 ppm, which is the maximum recommended for a system of this type.

APPENDIX II

In a cooling tower, cooling is accomplished mainly by the evaporation of water. Cooling water through 10°F requires approximately 1% evaporation. Thus for 11°F the evaporation is 1.1% of the total circulation.

Wind drift from the tower has the same effect on water composition as blowdown (removes water and solids). For a well-designed, induced-draft tower the wind loss averages 0.1%. Thus the equilibrium concentration of this tower with no blowdown would be $\frac{1.1 + 0.1}{0.1} = 12$ cycles of concentration. That is, the concentration of dissolved solids in the circulating system would be 12 times that of the make-up water.

To maintain 5 cycles of concentration the blowdown must be

$$\frac{\text{evaporation loss}}{\text{cycles desired}-1} - \frac{\text{evaporation loss}}{\text{cycles occurring}-1} = \frac{1.1}{4} - \frac{1.1}{11} = 0.17\% \text{ of total circulation}$$

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