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CHEMICAL DECONTAMINATION OF THE
ANL-2 HIGH-PRESSURE WATER LOOP

by

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ABSTRACT

This report describes the chemical decontamination of the ANL-2 High-pressure Water Loop at the MTR. Three separate chemical treatments were employed, each followed by a water flush. A mixture of sodium hydroxide and potassium permanganate was first applied to oxidize partially and loosen the magnetite corrosion film on the loop surfaces. Next, the system was treated with a solution of Versenol 120 to remove and suspend the loosened oxide film. The third chemical treatment was a mixture of sulfamic acid, HEDTA, hydrazine, and Rodine 80. After the first two chemical treatments a brown residue remained, which was presumed to be manganese dioxide. The third solution completely removed all traces of residue from the first two treatments. After a delay of one MTR fuel cycle (three weeks) due to mechanical difficulties, the loop was operated for approximately 300 hours at 420°F and 380 psig with excess hydrogen to passivate the loop surfaces. Approximately 70 per cent of the corrosion film was removed from the loop surfaces as a result of the chemical decontamination.

INTRODUCTION

The ANL-2 High-pressure Water Loop has been in operation at the MTR for six years. The function of this loop, as well as of other similar in-pile loops, is to contain specimens of reactor materials and components for testing the effects of neutron irradiation under controlled conditions of heat transfer. During this period of operation an excessive amount of corrosion products accumulated on the surfaces of the loop. It was noted that, following thermal transients, quantities of this material were released and became suspended in the coolant water. Migration of the material was also observed during steady-state operation. Some of the corrosion products tended to plate out on the surfaces of fuel specimens being irradiated in the facility. A resulting increase in the resistance to heat transfer at the surfaces of the fuel specimen caused the core temperature of some specimens to be higher than that desired.

When irradiated, stainless steel corrosion products become radioactive, and include nuclides such as Fe^{59} , Co^{60} , Co^{58} and Mn^{56} . The radiation hazard imposed by the deposition of this material on the surfaces of the ANL-2 loop components had begun to limit the accessibility of these components. This was particularly undesirable because at the MTR much of the necessary maintenance of loop equipment must be completed during reactor shutdown periods of from three to five days. Chemical decontamination of the ANL-2 loop was therefore undertaken in order to at least remove partially corrosion products which had accumulated in the loop.

DESCRIPTION OF THE ANL-2 LOOP

The ANL-2 high-pressure water loop was constructed to investigate the effects of irradiation upon fuel elements and structural materials under simulated reactor operating conditions. It has been in essentially continuous operation since early 1954. In its present design the loop operates at a maximum pressure of 1500 psi and at a temperature which is specified for each particular experiment being conducted. It is constructed entirely of 300 series stainless steel. Figure 1 is a schematic diagram of the ANL-2 loop. Reference 1 contains a detailed description of the loop. A brief description of the major loop components is presented here.

Pumps: Coolant circulation is maintained with Westinghouse 100A canned rotor pumps. The normal flow rate of 60 gpm is provided with one pump operating and two on stand-by.

Line Heaters: Under normal operating conditions the amount of heat dissipated through the external surfaces of the loop is greater than the heat supplied by gamma heating of the in-pile tube and by fission heating of the fuel specimen being irradiated. The additional heat required to maintain the desired operating temperature is supplied by electrical line heaters of the clamshell type. The total capacity of the line heaters is 60 kw.

Pressurizer-Degassifier: System pressure is maintained by a pressurizer and degassifier unit. A portion of the coolant water may be bypassed through the unit. The total capacity of the unit is 40 gallons.

Heat Exchanger: A water-to-air type of heat exchanger provides for emergency cooling.

In-pile Tube: The in-pile tube is mounted in horizontal beam hole HB-2 of the MTR. The beam hole extends to within two inches of the reactor core face. The tube is eighteen feet in length and has an outside diameter of three and one-half inches. With the exception of its hemispherical tip of 316 stainless steel, the in-pile tube is constructed of 347 stainless steel. Cartridges containing test specimens to be irradiated are positioned at the reactor core end of the in-pile tube. The maximum thermal neutron flux just inside the reactor end of the in-pile tube is 2.5×10^{14} nv.

Figure 1. The ANL-2 Loop

Out-of-pile Tube: The out-of-pile tube is similar to the in-pile tube, but it is shorter in length. Control samples are mounted in this tube.

Purification System: Coolant water quality is maintained with a bypass purification system. The system is composed of a regenerative heat exchanger, a deoxygenating resin column, a demineralizer column, and two micrometallic filter cartridges.

Makeup System: A small positive displacement pump of 3 gallons per hour capacity is used to inject makeup water into the system. Plant demineralized water which has been degassed provides the influent to the makeup pump.

DECONTAMINATION EQUIPMENT AND SYSTEM CHANGES

Two 55-gallon stainless steel drums were used for chemical mixing and storage. The dissolution of chemical reagents was aided by a portable mixer and a 12-kilowatt immersion heater. The chemical solution tanks were manifolded to the intake of a booster pump of 3-gpm capacity. The

effluent line of the booster pump was connected to the system at the normal point of makeup injection. To prevent the possibility of chemical attack at the main coolant pump-bearing surfaces, a tubing line was connected from the makeup pump outlet to the coolant pump vents. During the decontamination operation demineralized water was continuously pumped through the coolant pump vents and over the pump-bearing surfaces at a rate of 3 gallons per hour. The bearing material of the main coolant pumps is Graphitar. Figure 2 is a schematic diagram of the chemical makeup and injection system.

Figure 2. Chemical Injection System

An operating pressure of 350 psi was maintained by applying helium pressure at the top of the pressurizer unit. The minimum safe operating pressure of the main coolant pumps is 200 psi. Figure 3 is a schematic diagram of the auxiliary pressurization system and spent solution transfer system.

SAFETY CONSIDERATIONS

Before beginning the decontamination operation, a thorough investigation was made with regard to the possibility of damage to system components by the chemical reagents. References 2, 3, and 4 contain accounts of decontamination tests performed with similar chemical reagents. From these accounts it was determined that no corrosive attack would result from the contact of the loop surfaces with the chemical decontamination solutions. Auxiliary tubing lines for chemical solution transfer were constructed of 300 series stainless steel for adequate corrosion resistance. Reagent-grade chemicals were used to prevent the possibility of stress corrosion by chloride or fluoride ions.

Figure 3. Chemical Transfer System and Loop Pressurizing System to MTR

The disposal tank, also constructed of 300 series stainless steel, was equipped with a pressure-relief valve. A vent line was connected from the tank to the MTR plant venting system. The tank was also equipped with a vacuum-breaker valve. To decrease the radiation hazard to personnel working in the area, the disposal tank was filled with water to one-half of its volume prior to any solution transfer.

Standard chemical handling precautions were observed. Because the spent solutions were highly radioactive, the disposal tank and transfer lines were monitored frequently.

PREPARATION AND DESCRIPTION OF REAGENTS

Solution 1: Solution 1 was a mixture of ten per cent sodium hydroxide and three per cent potassium permanganate. One-hundred gallons of this solution were prepared. The reaction between anhydrous sodium hydroxide and water is exothermic and the amount of heat released is large. As was expected, the solution temperature increased to near the boiling point. Fumes consisting of the water vapour with entrained potassium permanganate were evolved. Because of the toxicity of these fumes, protective clothing and air respirators were worn by personnel involved in its preparation.

Solution 2: Solution 2 was composed of twenty per cent by weight Versenol 120 (trisodium hexamethylenediamine tetraacetic acid) in water. Versenol 120 is supplied in the liquid form, and since it is chemically mild, no handling difficulties were encountered. Versenol 120 is a chelating reagent.

Solution 3: Solution 3 was a mixture containing the following constituents:

Sulfamic Acid	20% by weight
HEDTA (Hexamethylenediamine tetraacetic acid)	5% by weight
Hydrazine	5% by weight
Rodine 80	1% by weight

In this solution, sulfamic acid acts to neutralize any excess caustic residual remaining from the first treatment. Additional corrosion product removal is also effected by sulfamic acid. HEDTA, here in its acid form, acts as a suspension agent. Hydrazine is a powerful reducing agent. In conjunction with the other constituents of Solution 3, hydrazine effects the removal of the residual film of manganese dioxide remaining after the first treatment. Rodine 80 is an organic inhibitor which retards the corrosion of stainless steels. Reference 3 contains an account of the preparation and use of Solution 3.

The dissolution of the constituents of Solution 3 was difficult. An immersion heater was used to heat the solution to approximately 200°F (93°C). At lower temperatures sulfamic acid was observed to crystallize out of solution.

DECONTAMINATION PROCEDURE

The decontamination operation was completed during the shutdown period for MTR Cycle 132 beginning on January 4, 1960. The operation required three days for completion. The total surface area to be decontaminated was approximately one-hundred square feet. The total volume of the loop is eighty gallons. Before injecting the first solution the loop was flushed with demineralized water. Following this first water flush, radiation levels were monitored at various points of the system.

Step 1: The system was filled with the alkaline permanganate solution (Solution 1) and pressurized at 350 psi. Flow was maintained at 60 gpm with bypass flow through the pressurizer unit. For this and succeeding treatments the purification system was valved out. Solution temperature was increased to 220°F (105°C) by means of the line heaters. The circulating time for this solution was one hour with fifteen minutes at temperature.

Surge tank (pressurizer) level is normally established by filling the system full of liquid and then draining the surge tank to a desired level. Considerable difficulties were encountered here because the normal drain system could not be used. For the same reason it was difficult to properly vent the system. All liquids drained from the loop were pumped to a disposal tank on the main floor.

After the first chemical treatment, the loop was filled with water and pressurized with helium as in Step 1. The circulating time for this and succeeding water flushes was one-half hour.

Step 2: The system was filled with the Versenol 120 solution (Solution 2) and pressurized with helium as in Step 1. The solution temperature was increased to 175°F (80°C) by means of the line heaters. The circulating time for this solution was one hour with approximately one-half hour at temperature. This treatment was followed by a water flush.

Step 3: The third chemical treatment consisted of filling the loop with Solution 3 and again pressurizing with helium. The solution temperature was increased to 200°F (93°C) by means of the line heaters. The circulating time for this solution was one hour with one-half hour at temperature. This treatment was followed by four water flushes. After each flush a sample of the flush water was taken. A determination of the gross beta-gamma activity for each sample was made. Samples taken after the third and fourth flushes were comparatively low in activity.

The chemical treatments would normally have been followed immediately by a conditioning period of 300 hours at normal operating conditions to passivate the loop surfaces. The failure of one of the main coolant pumps due to loss of pump cooling oil flow caused a delay of three weeks (one reactor cycle). The failure of this pump was in no way connected with the decontamination operation. Following this delay, the loop was operated for approximately 300 hours at operating conditions. The dissolved hydrogen concentration of the coolant water was maintained at 25 cc/kg. Purification flow was maintained during the conditioning run.

ACTIVE SOLUTION DISPOSAL

Because of the quantity and chemical nature of the spent reagents, the MTR hot-waste disposal system could not be utilized for solution disposal. All loop equipment with the exception of the in-pile tube is located on the basement floor of the MTR. It was necessary, therefore, to pump the spent chemical solutions from the loop drain to a 1000-gallon disposal tank on a truck on the main floor, a vertical distance of approximately 30 feet. A booster pump of 3-gpm capacity was employed for this operation. An air pressure lift system was installed as a backup for the

normal solution transfer system. By applying air pressure at the top of the pressurizer the spent solution in the loop could have been forced from the loop to the disposal tank.

The spent chemical solutions were transported by truck approximately three miles to the Chemical Processing Plant for concentration by evaporation and subsequent disposal.

RESULTS

Radiation levels at various points of the system were monitored just before the first chemical treatment and just after the last water flush. The gross beta-gamma readings are recorded in Table I. Consecutive readings were taken in exactly the same manner to assure a reasonably accurate estimate of the amount of corrosion product removal. Neglecting the readings taken at points of low flow and at "dead legs," the average decontamination factor was 3.3. Approximately seventy per cent of the corrosion film was therefore removed.

TABLE I

Radiation Levels for Various Locations in the ANL-2 Loop
before and after Chemical Decontamination

Location	Beta-Gamma Level, mr/hr		Decontami- nation Factor	Flow
	Before Decontami- nation	After Decontami- nation		
In-pile Tube Outlet	800	250	3.20	Normal
In-pile Tube Inlet	700	100	7.00	Normal
Auxiliary Line Heaters	280	100	2.80	Normal
No. 1 Line Heaters	250	150	1.67	Normal
No. 2 Line Heaters	235	130	1.80	Normal
Heat Exchanger (Bottom)	450	100	4.50	Normal
Pump Intake Manifold	350	200	1.75	Normal
Pump Outlet Manifold	450	150	3.00	Normal
Surge Tank (Bottom)	800	500	1.60	Low
Pump Inlet Filter	380	380	0.00	Low
Pump Outlet Manifold Filter	2700	3700	-	Low
Particle Accumulator (Before Heat Exchanger)	390	100	3.90	Low
Particle Accumulator (Before Line Heaters)	850	350	2.42	Low

As would be expected, corrosion removal at most of the low-flow areas of the loop was less than at points of normal flow. For example, the radiation level at the bottom of the surge tank decreased by only a factor of 1.6.

Of the primary system filters, only the pump outlet filter contained a filter cartridge. The radiation level at the bottom of this filter assembly increased from 2.7 r/hr to 3.7 r/hr during the decontamination operation. It is intended to mechanically decontaminate this filter assembly at a later date.

Any of several methods for chemical decontamination could have been employed. It is believed that the method used effected satisfactory corrosion product removal, but in view of the limitations encountered at the MTR, a simpler method is recommended. Solution disposal was the most difficult problem of the whole operation. Reference 5 contains a procedure for a potentially simpler two-step method utilizing alkaline permanganate followed by ammonium citrate. Under MTR conditions, where solution transfer and disposal are difficult and where there is a time limitation, a method using a smaller total volume of solution should receive thorough consideration.

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