A Review of a Molybdate-Based Corrosion Control Program in Closed Cooling Water Systems at a Nuclear-Powered Electrical Generating Station

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By

Kenneth Soeder
Jamestown Chemical Company, Inc.
West Haven, Connecticut

James Mockridge
GPU Nuclear Corporation
Forked River, New Jersey

Charles Goldey
Jamestown Chemical Company, Inc.
West Haven, Connecticut

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SINCE THEIR INTRODUCTION in the early 1970s, molybdate-based cooling water treatment programs have been used to control the corrosion of steel and its alloys in many different types of open and closed recirculating systems. Today, the use of molybdate programs has become widespread in both industrial and commercial applications. In many situations, the technology offers specific benefits over alternative treatments, including low environmental impact, proven perfomance, limited nutrient loading, thermal and hydrolytic stability and cost competitiveness[1,2,3]. Recent studies have also demonstrated that molybdate works well in anaerobic conditions and is particularly effective against pitting-type corrosion[4]. Moreover, most molybdate-based products offered in the marketplace today incorporate aromatic azoles for the protection of copper and copper-bearing alloys and dispersants to control fouling by hardness salts and metal oxides, further expanding areas of application for the technology.

The primary objective of this paper is to review, in a case history format, the use of a molybdate-based treatment program to control corrosion in the critical closed cooling water systems associated with a nuclear-powered electrical generating station. Working in close cooperation with both the Chemical Engineering and Plant Operating Departments of GPU Nuclear Corporation, Jamestown Chemical Company was able to develop a proprietary, molybdate-based corrosion control program for use in the aggressive environment inherent to their closed recirculating cooling water systems. In the studied application, which included systems subject to radioactive contamination, the product provided excellent corrosion results for a wide variety of metals, including carbon steel, 90/10 copper-nickel, stainless steel, aluminum/bronze, monel, titanium and aluminum/brass. In addition, use of the molybdate product enabled the plant to avoid discharge, operating, plant safety and microbiological problems previously associated with alternative treatment programs.

BACKGROUND INFORMATION:

GPU Nuclear Corporation operates a 650 megawatt, nuclear-powered electrical generating station in Forked River, New Jersey. In operation since 1969, the facility uses Boiling Water Reactor Technology (see Figure 1 on following page) to provide steam and electrical power for customers located throughout the New Jersey, Pennsylvania and Maryland power grid. The plant currently uses four separate closed recirculating water loops, each operating in conjunction with a carbon steel, shell and tube heat exchanger and a brackish service water system, to provide cooling for a wide variety of process and comfort cooling equipment. Included in these systems are items such as turbine lube oil coolers, air compressors, package air-conditioning units and recirculating pump coolers, some of which are subject to radioactive contamination. Brief descriptions of some of the components of the individual systems are outlined below:

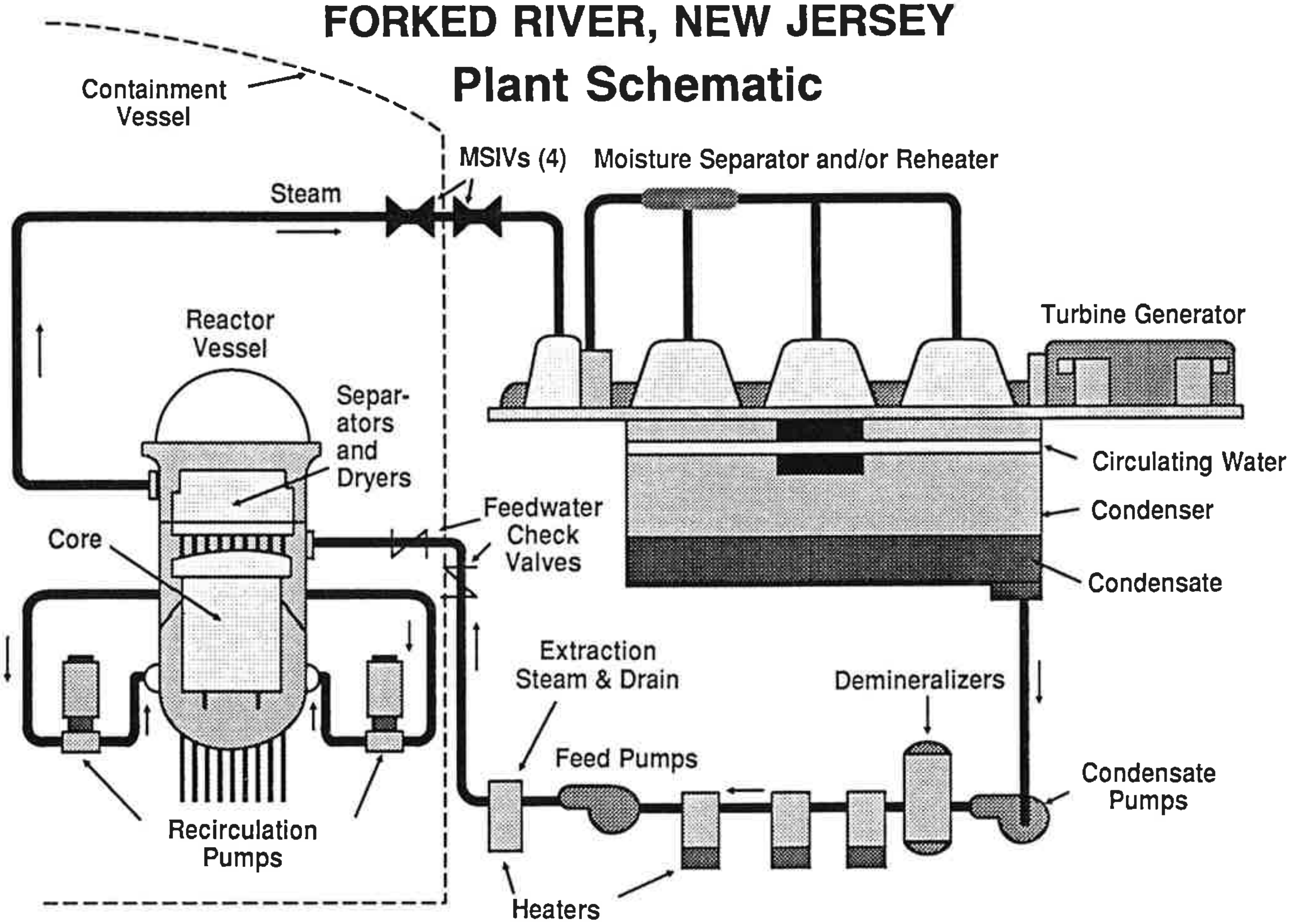
Augmented Office Building (AUGCCW) - The AUGCCW system has a total volume of 1,000 gallons and cools refrigeration units for the water removal subsystem, condenser (recombiners) and the refrigeration unit for the charcoal vault coolers. Materials of construction include carbon steel, monel, 90/10 copper-nickel and stainless steel.

New Radwaste Building (NRWCCW) - The NRWCCW system has a total volume of 1,500 gallons and cools the evaporator condenser, condensate cooler, vent condenser, waste pumps and sample coolers. Materials of construction include carbon steel, 90/10 copper-nickel, aluminum/brass and monel.

FIGURE 1

GPU NUCLEAR CORPORATION
OYSTER CREEK GENERATING STATION
FORKED RIVER, NEW JERSEY

Plant Schematic



Reactor Building (RBCCW) - The RBCWW system has a total volume of 12,000 gallons and cools reactor building equipment that is subject to radioactive contamination, including recirculating pumps, auxiliary pumps and the reactor recirculating pumps. Materials of construction in the system include carbon steel, monel, stainless steel and titanium.

Turbine Building (TBCCW) - The TBCCW system has a total volume of 10,500 gallons and cools components not subject to radioactive contamination, including condensate pump motor coolers, turbine lube oil coolers, air compressors and after coolers and the control room air conditioning system. Materials of construction include carbon steel, aluminum/bronze, monel and aluminum/brass.

The closed systems typically operate within the 75° to 100°F temperature range and use a demineralized water with the following characteristics as the makeup source:

Demineralized Makeup Water Characteristics:

Parameter:	**Value:**
pH:	5.7 – 6.6
Conductivity:	0.058 microsiemens
Chlorides, (as Cl):	Less than 5 ppb
Sulfates, (as SO_4):	Less than 20 ppb

With very low hardness levels, and an estimated Langelier's Saturation Index (LSI) of –3.0, the makeup water is characterized as being aggressive to most metal surfaces. Suspended solids levels within each system were also maintained below 50 ppb through the use of 5 micron bag filtration devices.

PREVIOUS CHEMICAL TREATMENT HISTORY AND RESULTS:

Recognizing the need to provide corrosion protection in the aggressive environment of these multi-metal systems, the plant first used a corrosion inhibitor based upon sodium chromate. With increased emphasis upon environmental compliance and plant safety, especially when one considers that even closed systems must be periodically drained to perform routine maintenance, the chromate-based program was soon discontinued. The plant next used a nitrite-borate inhibitor as its treatment program. After operating the program for two years, however, several problems arose. First, as a neutron absorber, the boron component of the program had the potential to interfere with nuclear reaction if the product ever contaminated the primary closed cooling water system. In addition, the sodium nitrite included in the product supported microbiological growth and caused impingement and erosion problems within the system. And finally, the boron component of the product was not readily removed from the system by the ion exchange resins used in the waste water treatment program, thereby potentially compromising the plant's zero discharge permit. Unfortunately, corrosion coupon studies were not conducted by the previous vendor while the plant was operating on either the chromate or nitrite-based treatment programs.

MOLYBDATE PROGRAM RESULTS:

Working closely with GPU Nuclear Corporation's Chemical Engineering and Plant Operating Departments, Jamestown Chemical Company developed a proprietary, molybdate-based treatment program designed to inhibit corrosion throughout the multi-metal closed cooling water systems at the plant. Using analytical-grade raw materials to prevent system contamination by aggressive fluoride and chloride ions, the product was initially dosed to each system via a chemical metering pump at a rate of 2,000 ppm (as product) to provide a molybdate residual of 100 ppm (as MoO_4) in the recirculating water. The pH of the system water was also maintained by the use of the product between the values of 8.0 and 10.5.

FIELD STUDY RESULTS:

Program results were monitored in each of the individual systems using four-station corrosion coupon racks. Corrosion coupons were selected to duplicate materials of construction within the individual closed systems, and were evaluated using the analytical procedure outlined in Figure 2.

FIGURE 2
PROCEDURE FOR EVALUATION OF COUPONS

1. After removing the corrosion coupon from the system, perform a visual inspection, noting any apparent corrosion or deposition.
2. Clean the coupon with distilled water and acetone.
3. Dry and desicate the coupon for 6 hours.
4. Weigh the coupons to the fourth decimal place.
5. Record data in the log book.
6. Perform the folowing corrosion rate calculation:

$$\text{Corrosion Rate} = \frac{(K)\ (W)}{(A)\ (T)\ (D)}$$

Where: K = 3.45 x E6
W = Mass Lost
A = Area = 21.806 cm^2
T = Exposure Time (hours)
D = Density (g/cm^2)

During the course of the 32-month field study, corrosion rates for the various metals used in the closed cooling water systems averaged as follows:

Corrosion Coupon Studies
Averaged Study Results

Material of Construction:	Results (mils per year):
Aluminum/Brass	0.002
Aluminum/Bronze	0.001
Carbon Steel	0.055
90/10 Cu-Ni	0.001
Monel	0.001
Stainless Steel	0.005
Titanium	0.008

Results from the individual corrosion coupon studies are outlined in Tables 1 - 4 (following page). Visual inspections were also conducted on each coupon as it was removed from the system to detect any problems caused by either corrosion or deposition. These visual inspections indicated that clean conditions were being

TABLE 1
Augmented Offgas Building Closed Cooling System
Corrosion Coupon Results
(all results expressed in mils per year)

	Study Dates		
Material of Construction:	**12/10/91 to 5/13/92**	**5/15/92 to 12/3/92**	**12/12/92 to 6/4/93**
Carbon Steel	0.106	0.046	0.014
Stainless Steel	0.014	0.001	0.000
90/10 Cu-Ni	0.004	0.001	0.000
Monel	0.007	0.001	0.000

TABLE 2
New Radwaste Building Closed Cooling System
Corrosion Coupon Results
(all results expressed in mils per year)

	Study Dates			
Material of Construction:	**9/26/90 to 3/27/91**	**5/15/91 to 8/26/91**	**9/1/91 to 12/3/92**	**12/12/92 to 6/4/93**
Carbon Steel	0.017	0.001	0.002	0.014
Aluminum/Brass	0.002	0.005	0.000	0.000
90/10 Cu-Ni	0.001	0.000	0.000	0.000
Monel -	0.001	0.000	0.000	0.000

TABLE 3
Reactor Building Closed Cooling System
Corrosion Coupon Results
(all results expressed in mils per year)

	Study Dates		
Material of Construction:	**11/12/91 to 5/13/92**	**5/15/92 to 12/2/92**	**12/10/92 to 6/4/93**
Carbon Steel	0.059	0.042	0.044
Stainless Steel	0.011	0.000	0.001
Titanium	0.020	0.002	0.001
Monel	0.006	0.001	0.000

TABLE 4
Turbine Building – Closed Cooling System
Corrosion Coupon Results
(all results expressed in mils per year)

	Study Dates		
Material of Construction:	**11/8/91 to 5/13/92**	**5/15/92 to 12/2/92**	**12/10/92 to 6/4/93**
Carbon Steel	0.220	0.087	0.061
Aluminum/ Bronze	0.001	0.001	0.000
Aluminum/ Brass	0.004	0.003	0.000
Monel	0.006	0.001	0.000

maintained in the systems, as little or no indication of corrosive attack, iron deposition or microbiological contamination was noted. These observations were further supported by data generated from the coupon studies, as the test results were all deemed excellent by the quidelines established by the National Association of Corrosion Engineers (NACE)[5] and the standards established by GPU Nuclear Corporation. Also of interest was the fact that in most instances, corrosion rates for all types of metals actually improved over the course of the study, perhaps suggesting that, over time, enhanced system cleanliness resulting from improved corrosion control was contributing to better program performance.

SUMMARY:

By taking advantage of the environmental, performance and safety advantages associated with molybdate-based treatment programs, Jamestown Chemical Company was able to develop for GPU Nuclear Corporation a proprietary formulation that provided its nuclear-powered electrical generating station with excellent corrosion control throughout the the plant's multi-metal closed recirculating cooling water systems.

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