

## ADVANCED LIQUID WASTE PROCESSING TECHNOLOGIES: THEORETICAL VERSUS ACTUAL APPLICATION

Tracy A. Barker  
Chem-Nuclear Systems, Inc.

### ABSTRACT

This paper provides an overview of Chem-Nuclear Systems, Inc. (CNSI) experience with turn-key chromate removal at the Maine Yankee Nuclear Plant. Theoretical and actual experiences are addressed on topics such as processing duration, laboratory testing, equipment requirements, chromate removal, waste generation, and waste processing.

Chromate salts are used in industrial recirculation cooling water systems as a corrosion inhibitor. However, chromates are toxic at concentrations necessary for surface inhibition. As a result, Chem-Nuclear was contracted to perform turn-key chromate removal and waste disposal by demineralization.

This project was unique in that prior to on-site mobilization, a composite sample of chromated waste was shipped to CNSI laboratories for treatment through a laboratory scale system. Removal efficiency, process media requirements, and waste processing methodology were determined from this laboratory testing. Samples of the waste resulting from this testing were processed by dewatering and solidification, respectively. TCLP tests were performed on the actual processed waste, and based on the TCLP results, pre-approval for media waste disposal was obtained.

### INTRODUCTION

Proper selection of equipment and materials for any project at a nuclear power plant is imperative to ensure that costs, schedule, and desired results are maintained. This paper leads the reader step-by-step through the process used for planning and executing the turn-key removal of chromates in the Maine Yankee Component Cooling System (CCS). This paper is also designed to contrast the theoretical accuracy of derived data used during the planning stages of the project with the actual data gathered from the chromate removal.

Chromates are probably the most effective cooling system corrosion inhibitor available today. The anionic inhibitor forms a highly passive film of ferric and chromic oxides, similar to those naturally found on stainless steel. The primary problem is that chromium, like other heavy metals, is known to be toxic to aquatic life and is listed by OSHA as a carcinogen. Hence, many industrial sites are replacing chromate addition processes to comply with EPA regulatory guidelines.

The complexity of Maine Yankee's chromate removal process was compounded by the presence of radioactive contamination in the CCS. Once the solution was removed from the CCS, the toxicity of the chromates (EPA regulated), and the hazards of the radioactivity (NRC regulated) combined for a mixed waste form. Maine Yankee chose to perform the chromate removal with the plant at full power, prior to their refueling outage, to reduce the number of outage projects. Therefore, CCS flow and temperatures had to be maintained within plant operating specifications. To minimize impact on plant operations, Chem-Nuclear chose to treat the CCS with a slip stream created by connecting the process system between the CCS heat exchanger influent and effluent drains. A Chem-Nuclear Advanced Liquid Processing System (ALPS<sup>®</sup>) ion exchange based system was applied for the removal of the chromates.

### COMPONENT COOLING SYSTEM (CCS) OPERATING PARAMETERS

Maine Yankee has used Sodium Chromate for inhibiting corrosion in their Primary and Secondary Component Cool-

ing Systems for over ten years. The Component Cooling System (CCS) is a recirculating water system that provides cooling water to critical plant components. In doing so it forms a buffer between the radioactive reactor coolant systems and the non-radioactive Service Water System, thereby reducing the possibility of discharging radioactivity to the environment. The CCS is divided into two independent trains called the Primary Component Cooling (PCC) water system (volume approximately 14,000 gallons) and the Secondary Component Cooling (SCC) water system (volume approximately 16,000 gallons). The PCC and SCC systems have redundant flow loops.

### CCS Liquid Characteristics

Operating specifications for the CCS require a pH between 7.0 and 9.5, and chromate (as  $\text{Na}_2\text{CrO}_4$ ) concentrations between 500 and 1,000 ppm. Chromium concentrations of less than 5.0 ppm are considered to be non-hazardous. But due to conservatism and the concern of chromates leaching from the interior surfaces of the CCS, Maine Yankee targeted 50 ppb as the residual chromate concentration at the completion of the project.

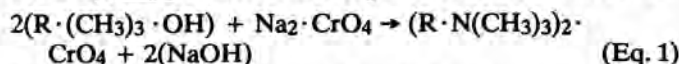
### EQUIPMENT AND MEDIA REQUIREMENTS

A unique factor in this project was that the CCS was on-line with the reactor at full power. As a result, Chem-Nuclear had to take every precaution to minimize chemical and physical impact on the operation of the CCS. Based on the information provided, Chem-Nuclear chose ion exchange over reverse osmosis and other treatment processes as the optimum method. The following reasons are given:

- Capital Equipment Costs are Minimized
- A Difficult to Process Concentrate Stream is Not Produced
- Positive Control is Maintained Over the Hazardous Chromates (Once the chromate is attached to the resin bead it is not easily displaced)

Maine Yankee's request for proposal focused on the removal of the chromates and did not specify the presence or

removal of any other ionic materials present in the CCS. However, sodium had to be present in ionically equivalent concentrations to the chromate. The sodium must be removed to prevent the generation of sodium hydroxide by the reaction of the sodium chromate with the anion resin (as shown in Eq. 1 below): Note: R is the basic organic structure of the resin.



The sodium hydroxide formed would have increased the pH and caused excessive corrosion to CCS materials.

There are large numbers of commercially available organic ion exchange resins. For standard ion exchange processes these can be categorized into four basic types; strong and weak acid cation, and strong and weak base anion. The weak resins were not chosen for the following reasons:

- Weak acid and weak base resin have a high selectivity for hydrogen and hydroxide ions, respectively. At a near neutral pH, both hydrogen and hydroxide ions will be present which reduces the weak resin capacity.
- The advantage of weak resin exists in its ability to be regenerated with an almost chemically equivalent amount of regenerant. However, in this case regeneration was not feasible due to the radioactivity present.
- It was theorized that the strong base resin, due to its high affinity for chromate, would hold the chromate ion even during the acetic acid leach portion of the TCLP when high concentrations of acetate ions are present.

Chem-Nuclear proposed the use of strong base anion resin due to its high selectivity for chromates and strong acid cation resin for the removal of the sodium. A two-bed cation/anion processing scenario was chosen over that of purely mixed bed, due to the uncertainty of other ionic materials present in the CCS. Mixed bed resin is usually composed of chemically equivalent amounts of cation and anion resin. If the cation chemical equivalency of the liquid to be treated is greater than that of the anion; then the cation resin in the mixed bed would deplete prematurely leaving good anion resin in a no longer useful bed, and vice versa.

#### Theoretical Media Requirements

To estimate the volume of resin needed for the project the volume of liquid and ionic concentration were required. Maine Yankee provided the estimate shown in Table I.

The volume of anion resin required for the project can be determined by using Eq. 2, and assuming an ion exchange capacity for the anion resin of 1.2 meq/cc. The concentration of chromate ion ( $C_1$  in Eq. 2) can be determined by multiplying the sodium chromate concentration by the fraction of the molecular weight of chromate divided by the molecular weight of sodium chromate. This fraction is 0.72.

$$V_A = \frac{C_1 V_L}{W_I R_A} \times 133.67 E-06 \quad (\text{Eq. 2})$$

- $C_1$  = Conc of Chromate Ion (mg/L)
- $V_L$  = Volume of Liquid (gal)
- $V_A$  = Vol of Anion Resin (Ft<sup>3</sup>)
- $W_I$  = Equivalent Ion Wt (mg/meq)

$$R_A = \text{Resin Capacity (meq/cc)}$$

Inserting Table I data into Eq. 2 provides an anion resin volume of approximately 25 ft<sup>3</sup> required for chromate removal. Due to inherent inefficiencies in the processing system (dead spots, leakage, etc.) the theoretical volume of resin must be increased. Based on previous processing knowledge, the theoretical volume of resin considered an 85% utilization of the resin capacity. This yields a 30 ft<sup>3</sup> volume of resin required for chromate removal. If a chemically equivalent concentration of cations are present in the CCS, cation resin volumes can easily be calculated by multiplying the volume of anion resin required by the capacity of the anion resin divided by the capacity of the cation resin as shown in Eq. 3.

$$V_c = \frac{R_A}{R_c} \times V_A \quad (\text{Eq. 3})$$

A cation resin capacity of 1.8 meq/cc would yield a required cation volume of 20 ft<sup>3</sup>. This cation resin volume is deceiving, because sodium unlike chromate is a weakly held ion. Due to this fact sodium is easily displaced from the cation resin by other cations present in the process stream. As ionic compensation, an additional 25% of cation resin should be used. This would bring the total volume of resin for the project to 30 ft<sup>3</sup> of anion resin and 25 ft<sup>3</sup> of cation.

Chem-Nuclear's standard 30 ft<sup>3</sup> ALPS<sup>®</sup> vessels conform well to each of the projected media requirements. Chem-Nuclear synthetic resins are provided in 7 ft<sup>3</sup> containers; therefore, 28 ft<sup>3</sup> of Cation and Anion resin can be loaded into two vessels, respectively. This volume of resin should be sufficient for lowering ion concentrations in the CCS to levels that would be suitable for polishing by mixed bed resin. A vessel loaded with mixed bed resin will likely be required near project end to obtain the target chromate concentration of 50 ppb. Recommended flow rate through the selected vessels is 50 gpm, this correlates to a surface flow velocity through the vessel of just over 7 gpm/ft<sup>2</sup>.

TABLE I

Component Cooling System Characteristics

Cooling System	Primary (PCC)	Secondary (SCC)
Volume (gal)	14,000	16,000
Sodium Chromate (ppm)	600	600

#### Theoretical Schedule Requirements

The time required for removing the chromates from the CCS was determined by substituting the above data into Eq. 4.

$$t = \frac{V}{kF} \times \ln \frac{C_o}{C_t} \quad (\text{Eq. 4})$$

- $t$  = time to obtain concentration  $C_t$  (min)
- $V$  = Volume of Liquid (gal)
- $k$  = Removal efficiency (%)
- $F$  = Flow Rate (gpm)



$C_0$  = Concentration at  $t = 0$

$C_t$  = Concentration at  $t$

This equation is based upon a system containing a contaminant equally dispersed within a liquid, and a slip stream cleanup system which directs its effluent back to the system. From Eq. 4, a processing time of 1.8 and 2.1 days for the PCC and SCC, respectively (or 9.25 turnovers per system) was required.

At this point, equipment, media, and schedule requirements had been determined. All of which were useful for developing project costs, tasks, and duration.

### LABORATORY SCALE STUDY

Chem-Nuclear acquired a composite sample of the chromated wastewater and processed it through a laboratory scale system similar to that used at Maine Yankee. Wastewater to resin volume ratios and surface flow velocities on the laboratory and full scale system were equal to simulate on-site processing. The purpose of the testing was to ensure that no mixed waste would be generated.

#### Laboratory Analysis and Results

Two small ion exchange columns were set up and filled with 75 g and 100 g of cation and anion resin, respectively. The column was operated at a flow rate of approximately 0.34 L/min which correlates to a surface velocity of approximately 7 gpm/ft<sup>2</sup>. The 12 L composite sample had an initial chromate concentration of approximately 360 ppm. The sample was transferred through the laboratory system until the chromate concentration was reduced to 0.2 ppm. The effluent from the laboratory column was monitored on timed intervals to verify that ionic break-through of the chromate did not take place. The laboratory column contained an amount of resin proportional that in the full scale system; therefore, no chromate break-through confirmed the theoretically calculated amount of resin to be accurate.

At this point the resins were transferred into a common container and then split into two waste samples. One sample was solidified with a cement binder and the other was dewatered. The samples were then tested in accordance with the EPA Toxicity Characteristic Leaching Procedure (TCLP). The results of the TCLP testing, showed that 0.17 ppm of chromium leached from the dewatered sample and 0.08 ppm leached from the solidified sample. This confirmed that the acetate ion introduced by the TCLP test would not displace the chromate ion from the anion resin. No absorption of chromium onto the cation resin was expected or identified.

The EPA limit for leachable chromium is 5 ppm; therefore, the waste resin was not considered a mixed waste and received pre-approval for disposal before the on-site phase of the project started. Processing of waste resin for disposal by dewatering is more cost effective than solidification. Hence, dewatering was selected as the preferred method for waste processing. The laboratory scale testing proved the chromate removal and waste processing methodology chosen for the project to be effective and efficient before mobilization of equipment and personnel. Since the process parameters were known and verified, only required materials were mobilized to the site.

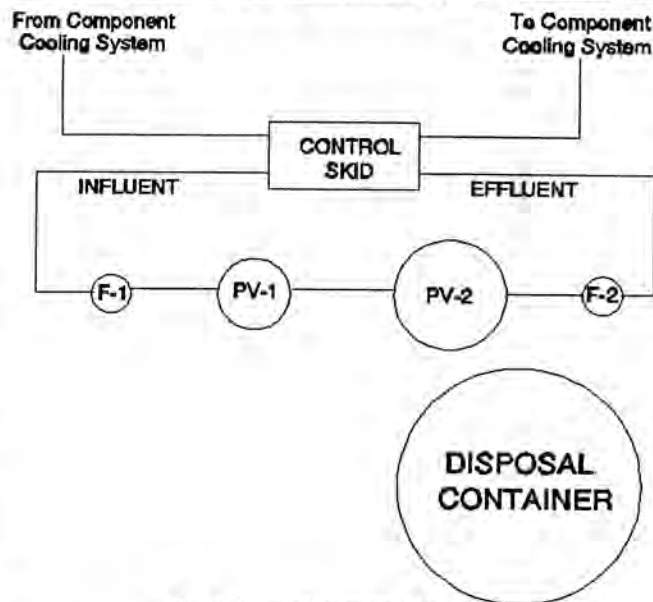


Fig. 1. Typical system flowpath.

### FULL SCALE PROCESSING

The equipment utilized for full scale processing is shown in Fig. 1. It consisted of a pump/control module, two filtration vessels, and two pressurized ion exchange vessels. High concentrations of particulates were not expected, because the CCS continually flowed through the CCS filtration system and the sodium chromate inhibitor kept corrosion to a minimum. Hence, pre and post filters on the Chem-Nuclear system were in place to protect the resin beds and CCS from unusual process disturbances such as transient sludge movement and resin breakdown.

As planned, the system was operated at a flow rate of approximately 50 gpm, which provided a surface velocity of 7 gpm/ft<sup>2</sup> and a spacial velocity of 1.8 gpm/ft<sup>3</sup>. Typical operating ranges for surface and spacial velocities are 4 - 10 gpm/ft<sup>2</sup> and 0.25 - 5 gpm/ft<sup>3</sup>, respectively for optimum results.

The results from an ionic analysis performed after on-site mobilization are given in Table II. A significant concentration of nitrate remained in the system from a previous period when nitrite inhibitors were used in the CCS. From the analysis it was obvious that a nitrite/nitrate removal process, liken to the chromate removal, had not been performed. The nitrites had oxidized to the more stable nitrates in the period since they were injected into the CCS. The presence of acetate and formate ions is likely due to the injection of a scale inhibitor. Many scale inhibitors contain carboxyl groups which upon decomposition form acetate and formate. The calcium, sulfate, and other common ions probably entered the system through heat exchanger leakage between the service water and component cooling systems.

Theoretical chromate concentrations can be developed by rearranging Eq. 4 and solving for  $C_t$  as shown in Eq. 5.

$$C_t = C_0 \times 1 / \{e [(F \cdot t \cdot k) / v]\} \quad (\text{Eq. 5})$$

Sodium chromate concentrations were monitored throughout the project with a portable colorimeter. The initial chromate concentration from this monitoring was used in Eq. 5, with  $k$  normalized to 1, to contrast theoretical values with those actually obtained from the full scale process in Fig. 2. The theoretical and actual values conformed initially but the

TABLE II  
Component Cooling System Water Analysis

Ion	PCC (ppm)	SCC (ppm)
Fluoride	<1	<1
Chloride	1.9	1.4
Acetate	2	<2
Formate	11.5	12.9
Bromide	<1	<1
Nitrite	<1	<1
Nitrate	320	272
Phosphate	<1	<1
Sulfate	8.3	7.9
Chromate	335	335
Sodium	148	140
Calcium	1.1	0.7
Magnesium	0.3	0.4
Aluminum	<0.1	0.1
Iron +3	<0.1	<0.1
Copper +2	<0.1	<0.1

degree of deviation increased as the chromate concentrations decreased. Factors influencing the deviation of the actual results from those predicted by Eq. 5 are listed as follows: 1) The CCS is composed of multiple mini-systems which are not always on-line and flowing through the CCS heat exchanger where the Chem-Nuclear ALPS<sup>®</sup> equipment was connected. The flushing of these systems continually re-contaminated the CCS with Chromates; 2) The chromates, over ten years, had built up a protective film in the CCS. The slow dissolution of this film continually added chromate; 3) Porous materials such as gaskets, valve packing, filters, and sludge continuously introduce chromate; 4) The ion exchange system does not have a perfect removal efficiency. Effluent chromate concentrations ranged from 0.002 to 0.14 ppm depending on system conditions. This contributes to the increased processing times at low chromate concentrations. All these factors combine to allow the theoretical estimates to obtain desired values much quicker than those actually obtained by the full scale system.

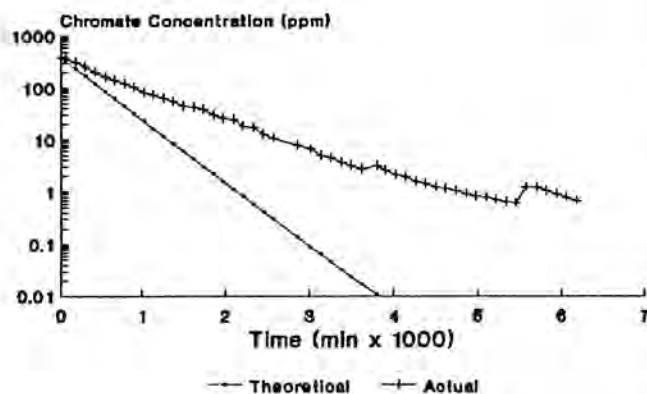
The key factor for prolonging the project was the leaching and dissolution of chromates from the interior surfaces of the CCS. Systems processed to chromate concentrations of less than 0.1 ppm would quickly leach back to a concentration greater than 1 ppm within 24 hours or less. Figure 3 is an example of the chromate leaching and dissolution.

The secondary component cooling CCS was initially processed from a chromate concentrations of 430 ppm to 0.7 ppm as shown in the upper portion of the figure. The CCS was then disconnected from the ALPS<sup>®</sup> for six days. During this period the chromate concentration increased to over 3 ppm. The ALPS was then re-connected to the CCS and the chromate concentration was reduced to 0.6 ppm.

The chromate film was very tenacious and effective for protecting the CCS surfaces. This was evidenced by the small amount of corrosion products in the system. The 25 micron pre- and post- filters for the ALPS<sup>®</sup> never built up a substantial differential pressure and did not require a change out for the duration of the project.

Also plotted on Fig. 3 is the result of Eq. 5 with the removal efficiency constant  $k$  set equal to 48 percent. Even though the modified theoretical results from Eq. 5 closely correlate with actual full scale operation, it would be a misnomer to say that the system had a 48% removal efficiency. The ALPS<sup>®</sup> continuously produced water with a chromate concentration of less than 50 ppb. The poor removal efficiency was actually caused by the continuous injection of chromates by CCS sub-systems and piping surfaces. The lowered removal efficiency significantly increased processing times because these factors were not initially considered. On closed processing systems, such as tanks, the actual results should compare much more closely to theoretical values.

On several occasions, the PCC and SCC chromate concentrations were taken below 1 ppm. At this point both anion and cation resin beds were sluiced out to the dewatering/disposal container and one of the ion exchange vessels was reloaded with mixed bed resin. This was done to maximize the systems water purity at low ionic concentrations for dissolving the chromate film. The CCS was in full operation to support cooling of reactor components. This meant that chemical and physical conditions of the CCS could not be changed to support removal of the chromate film on the inside of the piping, i.e., a chemical cleaning at elevated temperatures. The only approved method for dissolving the chromate film was to



### Theoretical Vs. Actual Secondary Component Cooling

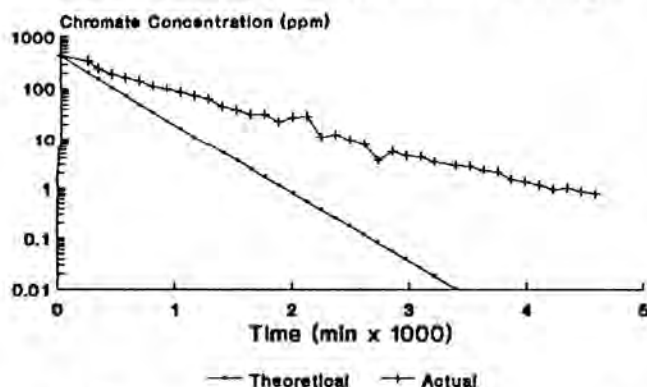


Fig. 2. Theoretical vs. actual primary component cooling.

continue operation of the Chem-Nuclear ALPS<sup>®</sup> to maintain high purity water in the CCS. The ALPS<sup>®</sup> was rotated between the PCC and SCC to maintain water purity in both systems.

#### SUMMARY AND CONCLUSIONS

Based on the results from this project, theoretically developed estimates for ion exchange volume requirements and removal efficiencies can be accurately determined. It was originally estimated that 55 ft<sup>3</sup> of media would be required to reduce chromate concentrations to less than 1 ppm and this was actually experienced in the full scale application. The final 28 ft<sup>3</sup> of mixed bed resin was used primarily in a polishing capacity.

The primary departure from theoretical estimates was in the area of scheduling. The Chem-Nuclear ALPS<sup>®</sup> was operated for approximately two months after the CCS chromate concentration had been reduced to less than 1 ppm. The objective was to elutriate the chromates from the interior surfaces of the CCS. Approximately 130 system turnovers (3.8E + 06 gal) was processed through the ALPS<sup>®</sup>. And CCS

chromate concentrations below 50 ppb were often achieved, but the chromate persisted to leach back to over 100 ppb when the ALPS<sup>®</sup> was not in service. Since there was a 5 ppm chromate limit, Maine Yankee decided that a sufficient amount of chromate had been removed from the CCS and the project was concluded.

This project provided the following conclusions:

1. Laboratory scale testing assists in the planning of a properly planned chromate removal campaign. It permits efficient on-site operations and mitigates the potential of unknown problems.
2. Caution must be taken with removal of EPA characteristic materials from a radioactive stream to avoid the formation of a mixed waste - which will greatly increase disposal costs.
3. Chem-Nuclear was able to effectively process, on-line, using a slip stream filtration and ion exchange system.
4. Processing duration was increased due to recontamination of the CCS by sub-system flushing and leaching of chromates from the interior piping surfaces.