EX SITU PASSIVATION OF STEAM GENERATOR MATERIALS

Ron Morris, Rick Reid,
Westinghouse Electric Company

1. INTRODUCTION

This paper describes a chemical process that has been developed to form a chromium-rich passive oxide film on primary side surfaces in steam generators prior to installation (i.e., pre-service passivation). The process uses an oxidizing agent to accelerate the formation of the same type of chromium-rich inner layer that would normally develop on the steam generator tube surfaces during operation. Based on past experience with use of oxidants, this process would have no deleterious material effects on the Inconel 690 steam generator tubes. This paper provides the basis for this statement and goes further to provide the benefits for its use and insight to a practical application.

2. BACKGROUND

Corrosion resistance in alloys such as Inconel 690 is imparted by formation of a thin (50 Å or less), chemically inert, chromium-rich oxide layer on the base metal surface. Once developed, the chromium-rich layer protects the base metal from further corrosion (oxidation). Base metal in this condition is considered to be *passive*[1,2].

Under typical operating conditions in a Pressurized Water Reactor (PWR) nuclear power plant, development of the passivation layer on Inconel 690 proceeds in a step-wise fashion, ultimately resulting in a dual oxidation film comprising the passive chromium-rich inner layer and an active nickel-rich oxide outer layer. Oxide development is initially rapid (about 50 percent complete in 50 days); however complete development of the film may take 500 days or longer.

Nickel, and to a lesser extent iron, is released from the outer active layer during the oxidation film development phase. This phenomenon occurs over the first three operating cycles following steam generator replacement. A significant fraction of these corrosion products precipitate or deposit on fuel surfaces, and eventually be activated by the neutron flux during plant operation (i.e., CRUD formation). The primary radionuclide of concern is cobalt-58 that results from activation of nickel-58. Corrosion product release, activation and redistribution may lead to several operational problems, the most significant of which include:

- The corrosion product burden on fuel surfaces may lead to CRUD-induced problems such as CRUD-Induced Power Shifts (CIPS) or localized fuel damage.

- CRUD will eventually be released from fuel surfaces and be incorporated in active oxide layers on out-of-core surfaces, including the steam generator tubes. By a similar mechanism, activated corrosion products from non-steam generator surfaces are also incorporated into the active nickel-rich outer layer on the steam generator tubes. This condition ultimately results in elevated out-of-core dose rates. This was a significant problem for South Texas Project Unit 1[3].

To mitigate problems associated with the initially dynamic oxide film formation on fresh Inconel, many utilities have performed some type of pre-service passivation during initial plant start-up after steam generator replacement. These techniques generally include some period of operation under essentially normal operating coolant conditions prior to core load. The duration of these passivation periods ranges from several days to weeks. A summary of passivation methodologies employed at select sites is provided in Reference[4].

To-date, pre-service passivation has been largely ineffective in mitigating corrosion product-related problems following steam generator replacement. This is partially due to the time required for full oxide development on Inconel. However, the problems are primarily due to the active nickel-rich layer that naturally develops as part of the passivation process, rather than the fact that the metal is not passive.

Deactivation of the film by removal of the nickel-rich oxide using a standard reducing chemical decontamination process has been recommended[5,6]. However, this approach would only be beneficial after significant development of the normal oxide film, and cannot be considered a stand-alone solution.

3. MATERIAL STUDIES AND TESTING

Oxidizing agents have been used for more than 20 years for chemical decontamination of nuclear plant primary systems. Numerous corrosion studies have been performed to qualify these solutions for use in such applications. Corrosion studies have shown that exposure to a decontamination process that includes these oxidizing agents results in a worst-case general corrosion of no more than 0.3 µm/hr to Inconel and austenitic stainless steel base metals, as well as associated weldments. Typical values are 0.01 µm/hr or less. The studies have also shown that exposure does not result in localized attack such as pitting, intergranular attack (IGA) or stress corrosion cracking (SCC), and does not increase the growth rate of existing cracks. Corrosion studies have included examination of:

- general corrosion and localized effects using flat specimens;
- the potential for IGA/cracking effects in highly stressed materials using U-bend, reverse U-bend, bent-beam and simulated roll-transition specimens;
- potential effects on crack growth rates using pre-cracked C-ring and wedge-open loaded specimens;
- and potential crevice corrosion using simulated crevice specimens.

These studies ultimately resulted in qualification for use in fuel-in full reactor coolant system decontaminations. The concentrations used in these studies were four to five times higher than that used for the passivation process. Additionally, the corrosion studies were generally performed on Inconel Alloy 600 in the mill annealed condition, which is much less resistant to corrosion effects than thermally treated Inconel Alloy 690 material.

Laboratory testing conducted to develop the passivation process was performed on actual lot samples of Alloy 690 steam generator tubing obtained from Sandvik. Post-exposure examination of these specimens showed only very minor general corrosion (0.025 μm or less after 72 hours of exposure), and no evidence of localized corrosion.

These results, combined with the results of previous studies on the effects on Inconel alloys, clearly show that no deleterious effects are expected to occur as a result of a field *ex situ* application of the pre-service passivation process.

4. EX SITU APPLICATION DISCUSSION

To be fully effective, pre-service passivation of fresh Inconel 690 surfaces must include development of the thin chromium-rich passive layer as well as deactivation or elimination of the active nickel-rich outer layer. Methods of deactivation include chemical modification (e.g., through zinc addition) or removal (e.g., by chemical dissolution). Deactivation by removal would only be effective after nearly complete development of both layers of the oxide film, while chemical modification may be effective as the film develops.

Since effective deactivation of the outer layer by chemical removal may proceed only after the oxide film has significantly developed, and significant development takes 50 days or longer under typical operating conditions, it is not economically practical to complete pre-service passivation after steam generator installation using this approach. Further, this approach is not economically attractive even if applied *ex situ* unless the duration of the oxide development phase can be shortened.

Development of the oxide film may be accelerated by changing the environment under which the film develops, and this can only practicably be done in an *ex situ* application. Possible environmental changes include increasing the oxidation temperature and/or establishing more aggressive oxidizing conditions. Accelerating the rate of oxide film formation by establishing more aggressive oxidizing conditions is the favored approach.

An approach to pre-service passivation involves circulation of an oxidizing solution through the steam generator tubes in an *ex situ* application. Laboratory testing has demonstrated that the desirable single chromium-rich passive oxide film is successfully created using this method.

Application of the passivation process requires approximately four days, including three days for passivation and one day for system heat up, cool down and clean up. The process is applied at 200ºF using a temporary circulation and clean up system. After application of the chemical process, all chemicals are removed on ion exchange resin, and the steam generator surfaces are completely rinsed with demineralized water.

5. BENEFITS OF EX SITU PRE-SERVICE PASSIVATION

The following key benefits result from application of the *ex situ* Pre-Service Passivation Process:

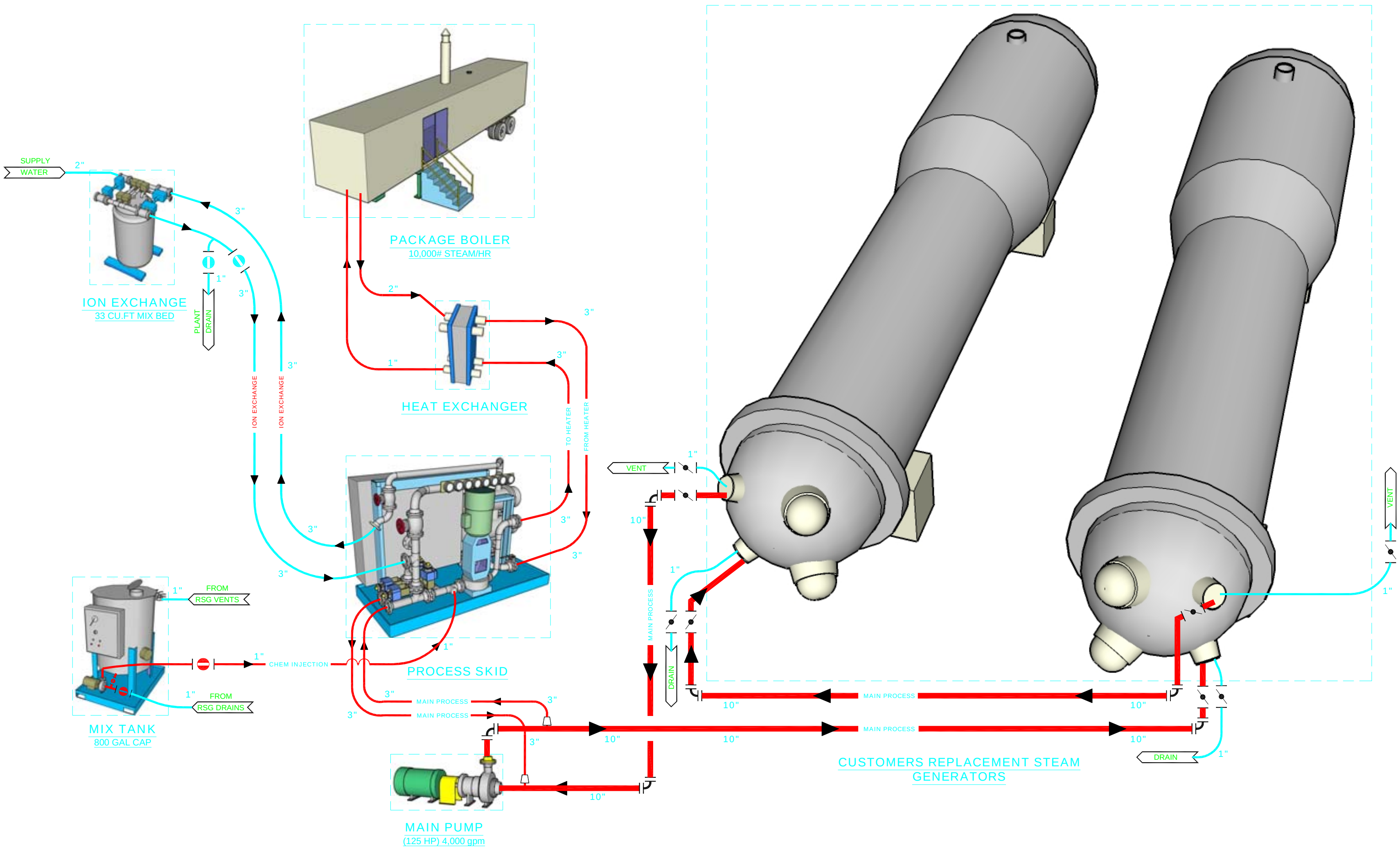
- Reduces corrosion product release associated with development of the active nickel-rich oxide film, which in turn:
    - Mitigates CRUD-induced fuel problems (e.g., AOA/CIPS);
    - Reduces Co-58 levels;
    - Reduces shutdown chemistry control problems typically experienced for several operating cycles following steam generator replacement;
- Provides immediate protection of Inconel tubes, which are otherwise only marginally protected during the first several weeks of operation following replacement until a passive film develops;
- Reduces activity buildup in SG tubes, and associated dose rates in the SG bowls;
- Eliminates the need for a Pre-Startup hold, which provides a direct critical path savings.

6. INSIGHT TO AN EX SITU APPLICATION

Two sites were visited to appreciate the complexities of an *ex situ* application. At the time, the first site was in the process of pre-service activities on four replacement steam generators and the second site was expecting delivery. In both cases it was determined that the passivation process could be applied to the generators in pairs or four at one time due to the similar staging of the generators prior to final installation. One of the main areas of concern was the time needed to perform the passivation process. Between the delivery of the steam generators and their installation various on-site activities were to take place, such as visual inspections and eddy current examinations, and scheduling the passivation process was a challenge.

The equipment needed to perform the passivation of the RSGs includes a circulation pump, process monitoring, and associated instrumentation and controls in the main flowpath. Additional pumping, heating, sampling, corrosion monitoring, and instrumentation and controls would be on a side stream to the main flowpath generated by the main circulation pump. The main circulation pump produces flowrates up to 2,500gpm which is necessary to ensure that flow is through all of the steam generator tubes. Other equipment to support the project includes ion exchange capability for the cleanup of chemicals, a chemical mixing tank, flow reversal equipment and steam heat exchanger which provides heat for the process. The equipment is located inside a berm in case of any leakage or spills and the hoses, piping and to some degree the generators themselves are insulated for heat conservation. Hold-up and rinse tanks would be provided for the passivation of the generators in pairs. A process summary and process flow diagram is given below.

PASSIVATION PROCESS SUMMARY		
DESCRIPTION	**TEMP ^{O}F**	**DURATION (Hrs)**
System Fill, Heat-up and Check-out	75 –195	12
Chemical Application	195	72
On-Line Clean-up by Ion Exchange	195 – 160	4
Sluice Resins	75	8*
TOTAL DURATIONS		96


SUPPLY WATER
2"
ION EXCHANGE
33 CU.FT MIX BED
PLANT DRAIN
PACKAGE BOILER
10,000# STEAM/HR
HEAT EXCHANGER
TO HEATER
FROM HEATER
ION EXCHANGE
PROCESS SKID
MIX TANK
800 GAL CAP
FROM RSG VENTS
FROM RSG DRAINS
CHEM INJECTION
MAIN PROCESS
MAIN PUMP
(125 HP) 4,000 gpm
VENT
DRAIN
CUSTOMERS REPLACEMENT STEAM GENERATORS

7. REFERENCES

1. Smith, G. D., "The Role of Protective Scales in Enhancing Oxidation Resistance," INCO Alloys Publication.

2. Stott, F. H., *Materials Science and Technology, Volume 5*, August 1989.

3. OE21112, "Unexpectedly Large Corrosion Product Release during Cool Down (South Texas project)," July 21, 2005.

4. Riddle, J., "Effect of Steam Generator Replacement on PWR Primary Corrosion Product Transport," EPRI Report 1003601, August 2002.

5. "Siemens Concept for Preconditioning of Replacement Steam Generators," Siemens Presentation to U. S. Utilities, April 1999.

6. Ocken, H. L., "Surface Treatments to Reduce Radiation Fields." EPRI Report NP-5209-SR, April 1988.