# B&W/FTI HIGH TEMPERATURE CHEMICAL CLEANING PROCESS

J. Jevec, McDermott Technology, Inc
J. Remark, Framatome Technologies, Inc
W. Schneider, B&W Canada

Alliance Research Center
1562 Beeson Street
Alliance, OH (USA) 44601

## ABSTRACT

The B&W/ FTI Chemical Cleaning program has a long history marked by many successful field applications. These include development of a magnetite dissolution solvent in the early 1970's, participation in the EPRI/SGOG chemical cleaning process development program, and participation in numerous applications of the EPRI process in PWR reactor units. The B&W/FTI chemical cleaning program also includes the development and qualification of the Bruce and Pickering chemical cleaning processes, and execution of that process on four reactor units at Pickering. The Pickering application included both the EPRI low temperature process and a modified version of the EPRI elevated temperature crevice process. A high temperature cleaning process has also been developed by B&W/FTI for iron-based deposit removal from CANDU and PWR reactor units. It has been successfully applied at two PWR plants. Application of the high temperature iron process is based on plant heat using a reduced process equipment configuration. The paper describes the high temperature B&W/FTI chemical cleaning process, with emphasis on the testing of steam generator tubing materials, and includes a summary of the results of one field application.

## INTRODUCTION

Corrosion products and other feedwater contaminants from the preboiler cycle of the nuclear steam plant will be transported, during operation, to the secondary side of the steam generator where deposition will occur. As the deposits increase in thickness and loading, they can produce detrimental effects on the steam generator operation. The danger of tubing failures due to corrosion also increases as deposits accumulate . As deposition increases, chemical cleaning becomes an indispensable tool to establish steam generator reliability and availability.

The B&W/FTI chemical cleaning program has a long history dating back to work on fossil boilers in the early 1950's. Building on this fossil experience, Babcock & Wilcox (B&W) presented data (1) in 1971 showing that a solvent composition of 10% EDTA, 1% hydrazine at an initial room temperature pH of 7.0 will satisfactorily and safely remove magnetite from nuclear steam generators. In 1978, the Electric Power Research Institute (EPRI) initiated a program to further the development of a nuclear steam generator chemical cleaning process. The B&W solvent became the basis for the current EPRI low temperature magnetite dissolution solvent. In addition B&W was one of the major contractors in the EPRI chemical cleaning program (References 2, 3, 4).

The B&W/FTI chemical cleaning program includes the development and qualification of the Bruce and Pickering chemical cleaning processes, and execution of that process on four reactor units at Pickering (Reference 5). The Pickering application included both the EPRI low temperature process and a modified version of the EPRI elevated temperature crevice process.

Through joint research and development, B&W and Framatome have developed a high temperature process that can be used to remove deposits from the secondary side of CANDU and PWR steam generators. This R&D was funded by B&W and Framatome but was overseen and guided by U.S. and Canadian utilities pursuing chemical cleaning. Through a series of customer review meetings, utilities provided their input, expressed their concerns, witnessed testing, reviewed raw data and even

contributed their materials and deposits for testing and evaluation.

The goal of the high temperature chemical cleaning (HTCC) process is to improve the overall dissolution rate and the effectiveness of the process. The higher temperature promotes more rapid dissolution and is also effective at dissolution of the hard to dissolve deposit constituents, such as Trevorite (a nickel based deposit). Because of the increased dissolution rate and the fact that the HTCC uses plant heat to maintain temperature, there is less support equipment and the process itself minimizes the overall outage impact. When properly applied, the HTCC will also reduce overall corrosion of the steam generator materials due to the reduced solvent contact time.

The new process relies strongly on the large foundation of research data produced during the development of the EPRI/SGOG processes. The subject process is a higher temperature EDTA process that is more aggressive and can significantly reduce application times (when compared to the standard EPRI processes).

## HTCC PROCESS CORROSION TESTING

The development and testing of the HTCC has been presented elsewhere (Reference 6) and will not be discussed in detail in this paper. A brief description of the testing and the results of a typical application test will be presented. Qualification of the HTCC process for exposure to the steam generator tubing material will also be presented in detail.

Generic and site specific testing was performed in a 10-liter autoclave. Corrosion monitoring was provided by means of coupons, for weight loss and metallurgical examination. On-line free and galvanic corrosion were monitored during the test using the FTI Corrosion Monitoring System (CMS). The CMS used the EPRI recommended approach to corrosion monitoring during chemical cleaning (Reference 3 - linear polarization, and zero resistance ammeters). Some testing included actual steam generator tubing, heated to temperature on the inside to simulate the heat flux across the tubes that would be experienced in actual application. Early testing was performed with the solvent initially in the autoclave. Heating of the solvent occurred in the autoclave from ambient up to the final test temperature. Later tests simulated the actual application, with the solvent heated externally to 93°C (200°F) and injected into a preheated autoclave. The HTCC includes a number of vent cycles to cause boiling and to promote mixing of the solvent. After venting, temperature was restored to the test temperature as soon as possible (typically less than 5 minutes). During venting the vented gas passes through a cooling coil. The condensables are captured in a sealed dry trap. The noncondensable gas then is vented under about 3 liters of water to ensure that no particulate escapes to the atmosphere. Figure 1 is a picture of the autoclave assembly used for testing, with the head removed.

### Corrosion Test Results

Results of a typical test utilizing 10 hours of exposure follow. The solvent used for this test was the typical HTCC solvent:

200 grams/liter EDTA
5 grams/liter hydrazine ($N_2H_4$)
20 mL/liter CCI-801 Inhibitor
pH of 8 (adjusted with ammonium hydroxide ($NH_4OH$)
Application Temperature - 143°C (290°F)

Table 1 summarizes the materials tested, the general location of these materials in a steam generator, and the specimen identification. All of the coupons were galvanically coupled to the system. As previously mentioned, on-line free and galvanic corrosion were monitored during the test using the FTI Corrosion Monitoring System (CMS). The carbon steel surface area to solvent volume ratio (S/V) used for this test was 115 $cm^2$/liter. The total metal surface area to solvent volume ratio was maintained as close as possible to 1145 ± 10 $cm^2$/liter. A loading of 11 g/L Fe (as magnetite) was used in this test. This test included nine (9) vents during the course of solvent exposure.

Table 2 summarizes the results of the chemistry analyses performed during the test. The chemistry results followed the expected trends, based on the other testing in the HTCC program. The EDTA and hydrazine concentration decreased while the iron concentration rapidly increased during the exposure. Essentially all of the deposit was

Table 1
Summary of Tested Materials

| Material | Generic Steam Generator Part | Specimen Type | Specimen Identification |
|---|---|---|---|
| SA-106 GrB | Pressure Boundary and Piping | Coupon | RC106-9 |
| AISI-1018 | Internals | Coupon | C1018-16 |
| E7018 SMAW* | Pressure Boundary and Internal Welds | Coupon | RC7018-8 |
| SA533 GrA | Pressure Boundary | Coupon | RC533-8 |
| SA533/8018 SMAW/HAZ | Pressure Boundary and Internal Welds | Coupon | RH533-1 |
| ERNiCr-3 GTAW/HAZ | Carbon Steel To Inconel Internal Welds | Coupon | RHGTA-1 |
| SA-240 Type 405 | Flow Distribution Plate | Coupon | RC405-4 |
| SA-176 Type 409 | Lattice Support Plate | Coupon | RC409-4 |
| E7018 SMAW | Pressure Boundary and Internal Welds | ZRA Electrode | ZSMW-25 |
| AISI-1018 | Internals | ZRA Electrode | Z1018-4 |
| SA533 GrA | Pressure Boundary | ZRA Electrode | Z533-18 |
| SA533 GrA | Pressure Boundary | LP Electrode | L533-17 |
| Alloy 600 | Tubing | LP Electrode | L600-50 |
| E7018 SMAW** | Pressure Boundary and Internal Welds | LP Electrode | LSMW-19 |

* Key for welds: SMAW = Shielded Metal Arc Weld: GTAW = Gas Tungsten Arc Weld: HAZ = Coupon in test to examine potential for increased heat affected zone attack

** Electrode monitored by linear polarization during the test

dissolved within the first hour of exposure. Also as expected when dissolving magnetite with the HTCC solvent, the pH elevates and buffers at about 8.7. At the completion of testing, the autoclave was inspected and essentially no deposit remained.

The corrosion results, based on weight loss for the coupons are presented in Table 3. The corrosion results, based on weight loss, of the electrodes are presented in Table 4. Included in Table 4 are the CMS predicted values for the various electrodes. Predicted CMS values for ZRA electrodes requires the addition of a free corrosion correction factor (References 3 and 7). For the Table 4 CMS indicated galvanic values, the free corrosion correction was made using the on-line LSMAW data for ZSMAW-25 and Z1018-4. The free corrosion correction for Z533-18 used the final weight loss corrosion value from the L533-17 electrode. The CMS indicated versus weight loss values are considered to be in very good agreement. The CMS also showed the correct order of susceptibility to attack in the HTCC when compared to the coupons. Note from Table 3 that all materials experienced a corrosion loss of 51 $\mu$m (2 mils) or less, with the AISI-1018 material being the most susceptible to corrosion attack during application of the HTCC. Also note the minimal corrosion experienced by the tube support structures (RC405-4 and RC409-4).

Table 2
Summary of Chemistry Results
HTCC Solvent Testing

| Time (Hours) | $N_2H_4$ (g/L) | EDTA (g/L) | Fe (g/L) |
|---|---|---|---|
| Initial | 5.1 | 195 | 0 |
| 0* | 4.0 | 132 | 11.1 |
| 1 | 2.9 | 129 | 11.5 |
| 2 | 2.5 | 124 | 11.6 |
| 5 | 1.4 | 122 | 12.4 |
| 10 | 0.9 | 107 | 12.7 |

* - Time 0 = time at test temperature (143°C for this test)

Table 3
Summary of Coupon Corrosion
HTCC Solvent Testing

| Specimen Identification | Corrosion (μm) | Corrosion (mils) |
|---|---|---|
| RC106-9 | 27.5 | 1.08 |
| RC405-4 | 0.4 | 0.02 |
| RC409-4 | 0.9 | 0.04 |
| RC7018-8 | 14.5 | 0.57 |
| C1018-16 | 51.0 | 2.00 |
| RH533-1 | 13.6 | 0.54 |
| RC533-8 | 15.9 | 0.63 |
| RHGTA-1 | 16.6 | 0.66 |

The CMS output for the ZRA electrodes is shown in Figure 2. There was a sharp increase in corrosion rate on the 1018 carbon steel during the first vent. This is apparently due to a disruption of the inhibitor film that has not yet fully stabilized at the onset of the first vent. Corrosion rates fell with time. When the autoclave was cooled for the termination of the test, the corrosion rate dropped very quickly. This is typical with the HTCC applications.

No pitting or localized attack was observed on the coupons exposed during this test. There was no accelerated galvanic heat affected zone (HAZ) attack in the ERNiCr-3 GTAW coupon (RHGTA-1) or the SA-533 GrA/8018 SMAW coupon (RH533-1). This is typical for a 10-hour exposure to the HTCC. Longer exposure times or utilizing the HTCC to dissolve deposits with elevated levels of copper, have led to pitting type attack in some carbon steels.

HTCC Solvent Velocity Testing

The HTCC solvent was also tested under various flow conditions to verify that, in the presence of magnetite, it would not cause erosion corrosion. Concentrated HTCC solvent was pumped through a test loop containing standard piping materials (SA-106 piping and a SA-105 elbow) at 93°C (200°F) for one hour. This configuration simulated injection of concentrated chemicals impinging on a common base metal, SA-515 Gr70, and an Alloy 600 tube specimen at 5.5 m/s (18 ft/s). The solvent was then diluted to the normal application conditions and circulated through the loop at 149°C (300°F) for an additional 30 hours at 5.5 m/s. The corrosion experienced by the specimens in the test loop was not significantly higher than specimens tested in static autoclaves.

Table 4
Summary of Electrode Corrosion

| Specimen Identification | Weight Loss Corrosion in μm (Mils) | CMS Indicated Corrosion in μm (Mils) |
|---|---|---|
| ZSMW-25 | 6.7 (0.26) | 10.4 (0.41) |
| Z1018-4 | 28.4 (1.12) | 36.3 (1.43) |
| Z533-18 | 8.0 (0.32) | 14.0 (0.55) |
| LSMW-19 | 8.5 (0.34) | 6.6 (0.26) |
| L533-17 | 5.9 (0.23) | Not Applicable |
| L600-50 | 0.00 (0.00) | Not Applicable |

Table 5
Tubing Material Corrosion In the HTCC Solvent

| Specimen | Synthetic Deposits | Plant Deposits |
|---|---|---|
| | Corrosion - μm (mils) | Corrosion - μm (mils) |
| Alloy 400 | 1.37 (0.054) | 1.42 (0.056) |
| Alloy 600 | 0.03 (0.001) | 0.03 (0.001) |
| Alloy 690 | 0.00 (0.000) | 0.03 (0.001) |
| Alloy 800 | 0.00 (0.000) | 0.00 (0.000) |

Testing Of Tubing Materials

The high alloy tubing materials were evaluated in the HTCC by two methods. The first was exposure of samples of tubing during autoclave testing. Total exposure time was 30-hours. The tests evaluating the tubing materials consisted of a deposit loading of 20 g/L magnetite. Both synthetic and actual plant deposits were used during the testing. Results of the tubing exposures are shown in Table 5.

As can be seen from Table 5, the tubing material showed negligible corrosion loss after the 30 hours of exposure to the HTCC.

In addition to the potential for general corrosion attack it is important to ensure that no localized attack should occur on the tubing material, such as stress corrosion cracking (SCC) or pitting. In order to address this issue slow rate anodic scans on Alloy 600 and Alloy 800 were performed.

The objective of the slow rate anodic scan testing was to determine the susceptibility of select tubing materials to localized corrosion mechanisms under the HTCC environment. The concept is to expose a stressed strip of the tubing material to the HTCC solvent environment. The specimen is then polarized at a very slow rate (0.025 mV/sec) from rest potential through to the break away potential. If the material is susceptible to damage in the chemical environment, the slow rate anodic scan will cause pitting or cracking at the apex of the bend.

One of the criteria used for selecting specimen configuration was the ability for comparing the results from this test program with those results from previous chemical cleaning and corrosion testing. The configuration chosen has been used extensively at B&W in past corrosion evaluations, including chemical cleaning corrosion evaluations (References 8 and 9). The specimen is bent to constant deflection as follows:

- Bend specimen in a fixture to a 2.5 cm radius
- Compress the specimen then remove from the fixture
- Compress the specimen in a holder to a span (constant deflection) of 3.65 cm, plastically deforming the specimen in the bent configuration

By nature of their configuration, these specimens are in a highly-stressed state with a degree of cold work. The actual stresses that result from this configuration were not specifically measured in this program. However, in past programs with Alloy 600, x-ray diffraction was performed to determine stress levels. As reported in Reference 4, the stress at the apex of these types of specimens is in the range of 120 ksi. This value is considered sufficient to cause stress corrosion cracking should local breakdown of the passive film occur in the test.

The test strips were polished to a 600 grit finish and cleaned in acetone, followed by a methanol rinse. Nickel wires were attached to the strips, which were then bent, placed into fixtures, and placed into a 1-liter Alloy 600 autoclave. The autoclave was filled with test solution so that the specimen was covered up to the region of the spot weld. The autoclave was then heated to 150°C (302°F) before the poteniodynamic scans were made. A schematic of the test system is shown in Figure 3.

The specimens were allowed to soak for one hour at temperature in the test solution, in order to arrive at a stable open circuit corrosion potential, before the potentiodynamic scan was run. The initial scan was started -0.050 V below the open circuit potential and scanned in an anodic direction to +0.500V, with respect to open circuit potential.

Test results showing the polarization scans on Alloy 600 and Alloy 800 in the HTCC solvent at 150°C

are given in Figure 4. These are fairly typical polarization curves for materials exhibiting passive behavior. The corrosion rates corresponding to the measured open circuit current are quite low and, based on the polarization curves, there are no indications of pitting or localized attack.

There was no visual evidence (at magnifications up to 40X) of pitting or stress corrosion cracking observed on either the Alloy 600 or Alloy 800 specimen following the test exposures. Lack of localized attack was confirmed by SEM examination at up to 5,000X. Overall the surfaces of both specimens were shiny and bright. The Alloy 600 specimen had a slight darkening of the surface. The results of this study indicate that Alloy 600 or Alloy 800 tubing should not suffer localized corrosion damage in the HTCC process.

## PLANT APPLICATION

The HTCC has been applied at the Byron-1 and Palo Verde 1 plants. This section of the paper presents a summary of the application of the HTCC at Palo Verde Unit 1. Details of the application at Byron-1 were presented previously (Reference 10). The sister units at Palo Verde (Units 2 and 3) had been previously cleaned using the EPRI process (Reference 11). Although, these cleanings were overall successful, some ridge deposit remained undissolved in the batwing region of the tube bundle after application of the low temperature process. The high temperature process was applied to Unit 1 in an effort to more completely dissolve these ridge deposits along with removal of the bulk deposits that were in the steam generator.

The HTCC was applied for a total of 10 hours exposure at temperature. The process included eight (8) vents with the solvent covering the tube bundle. Application temperature for this cleaning was 143°C (290°F). For this particular application, the HTCC was followed by a low level application of the EPRI 121°C (250°F) crevice process. This step was the same as employed during the Palo Verde Units 2 and 3 chemical cleanings, maintaining the solvent level approximately 74 cm above the flow distribution plate with the objective to clean out the blocked drilled holes in the flow distribution plate. The crevice step was also applied for 10 hours and included five (5) vents. The cleaning was completed with three rinses (2-low volume rinses followed by a full volume rinse) and a passivation step. The passivation step was the eight (8) hour EPRI hydrazine based passivation.

For the Palo Verde application, all of the solvents were pre-formulated and heated off-line to 93°C (200°F) prior to the plant starting down. As the unit was being brought down off-line, the cold leg temperature was monitored until it reached 143°C. At this time, the temperature on the primary side was held constant and the steam generators were drained to the tubesheet. Solvent was then injected simultaneously into the steam generators. A simplified schematic of the Palo Verde Unit 1 chemical cleaning system is shown in Figure 5.

The dissolved iron versus time for the Palo Verde Unit 1 chemical cleaning is shown in Figure 6. The first reliable sample was not obtained until the 4-hour point of the cycle. By that time the dissolution reactions were essentially complete. This 10-hour application can be compared to the 60 to 80 hour magnetite steps utilized in the successful Palo Verde Units 2 and 3 chemical cleanings.

The total deposit removed per steam generator from Palo Verde Unit 1 is presented in Table 6. Included in Table 6 is the amount of deposit removed per steam generator for Palo Verde Units 2 and 3. Based on the operating time of the units, the amount of deposit removed from each unit was comparable. Of interest is the fact that Units 2 and 3 also included a crevice step after the magnetite step. At the Unit 2 and 3 chemical cleanings the crevice step removed an additional 180 kilograms (400 pounds) of deposit, while at Unit 1 the crevice step removed essentially no additional deposit. Based on the overall dissolution, the crevice step was not a necessary follow on to the HTCC at Palo Verde Unit 1.

Table 6
Summary of Deposits Removed
Palo Verde Chemical Cleanings

| Unit | Kilograms (Pounds) Deposit Removed Per Steam Generator |
|---|---|
| 1 | 2628 (5788) |
| 2 | 2411 (5311) |
| 3 | 2210 (4868) |

The post cleaning inspection indicated that the Unit 1 steam generators were generally cleaner than seen during the post cleaning inspection at Palo Verde Units 2 and 3. Eddy current examination also indicated an effective cleaning. Overall corrosion at Palo Verde Unit 1 was considered as well below the predetermined allowances based on the qualification data (see Table 3 for typical corrosion during a 10 hour application of the HTCC).

In summary, all of the objectives of the cleaning were met. The HTCC was successfully applied as the plant was coming down in power. The 10-hour HTCC application minimized the overall outage impact and the target dissolution was achieved.

## CONCLUSIONS

The B&W/FTI high temperature chemical cleaning process is the result of a long history of chemical cleaning developments. The HTCC process has been developed and qualified for application to PWR and CANDU steam generators. It has been successfully applied in two full scale applications. In the two applications, solvent was applied in a concentrated form (Reference 10) and mixed in the steam generators, and in the final concentration, pre-mixed external to the steam generators. Both approaches are considered as fully qualified. Deposit removal rates and overall deposit removal effectiveness were high in both applications.

Corrosion tests have been performed on materials representative of CANDU and PWR steam generators. The overall corrosion experienced by these materials was confirmed by these test to be low. In addition, localized pitting and stress corrosion cracking was confirmed to not be a problem for steam generator tubing materials during application of the HTCC process.

The process provides the advantages of short cleaning times, crevice cleaning capability, and reduced equipment requirements, when compared to the traditional EPRI/SGOG processes. The process is considered as qualified and field proven for application to the cleaning of CANDU or PWR steam generators that have a variety of iron based deposits.

## REFERENCES:


1. W.S. Leedy and F.J. Pocock, "Chemical Cleaning Of Nuclear Steam Generators," Proceedings of the 32nd International Water Conference p. 67, 1971.

2. J.M. Jevec and W.S. Leedy, "Chemical Cleaning Solvent and Process Testing," Electric Power Research Institute (EPRI) Report NP-2976, April 1983.

3. P.C. Hildebrandt, et. al., "Weld Region Corrosion During Chemical Cleaning of PWR Steam Generators," EPRI Report NP-5267, July 1987.

4. J.L. Barna, et. al., "Assessment of Sulfur in Chemical Cleaning of PWR Steam Generators," EPRI Report NP-5026, February 1987.

5. C.M. Daniel et al., "Recent Experience with Chemical Cleaning of Ontario Hydro CANDU Steam Generators," Proceedings of the 1994 Steam Generator and Heat Exchanger Conference sponsored by the Canadian Nuclear Society, p 3.57, 1994.

6. P. Knollmeyer, "B&W NT/Framatome High Temperature Chemical Cleaning Process Development," Proceedings of EPRI The Steam Generator Sludge Management Workshop, Norfolk, Virginia, p.40-1, 1994.

7. B.P Miglin, et. al., "Galvanic Corrosion Monitoring During Chemical Cleaning,' CORROSION/87 Paper Number 384, NACE International, 1987.

8. J.M. Jevec and W. S. Leedy, "ANO-1/Oconee-1 Chemical Cleaning Qualification Program - Final Report," Babcock & Wilcox R&D Division Report RDD:83:5260-18-01:01, December 1983.

9. R.P. Dow, "Final Report - PNGS-B Chemical Cleaning Qualification Program," BWNS Report 51-1213799-00 prepared for Ontario Hydro, November 1992.

10. W.A. Scheffler et. al. "Byron Unit 1 High Temperature Chemical Cleaning," Proceedings of the Seventh International Symposium of Environmental Degradation of Materials in Nuclear Power Systems, NACE International, p.435, 1995..

11. J.M. Jevec, et. al. "Steam Generator Chemical Cleaning at the Palo Verde Nuclear Generating Station," CORROSION/95, Paper Number 443, NACE International, 1995.

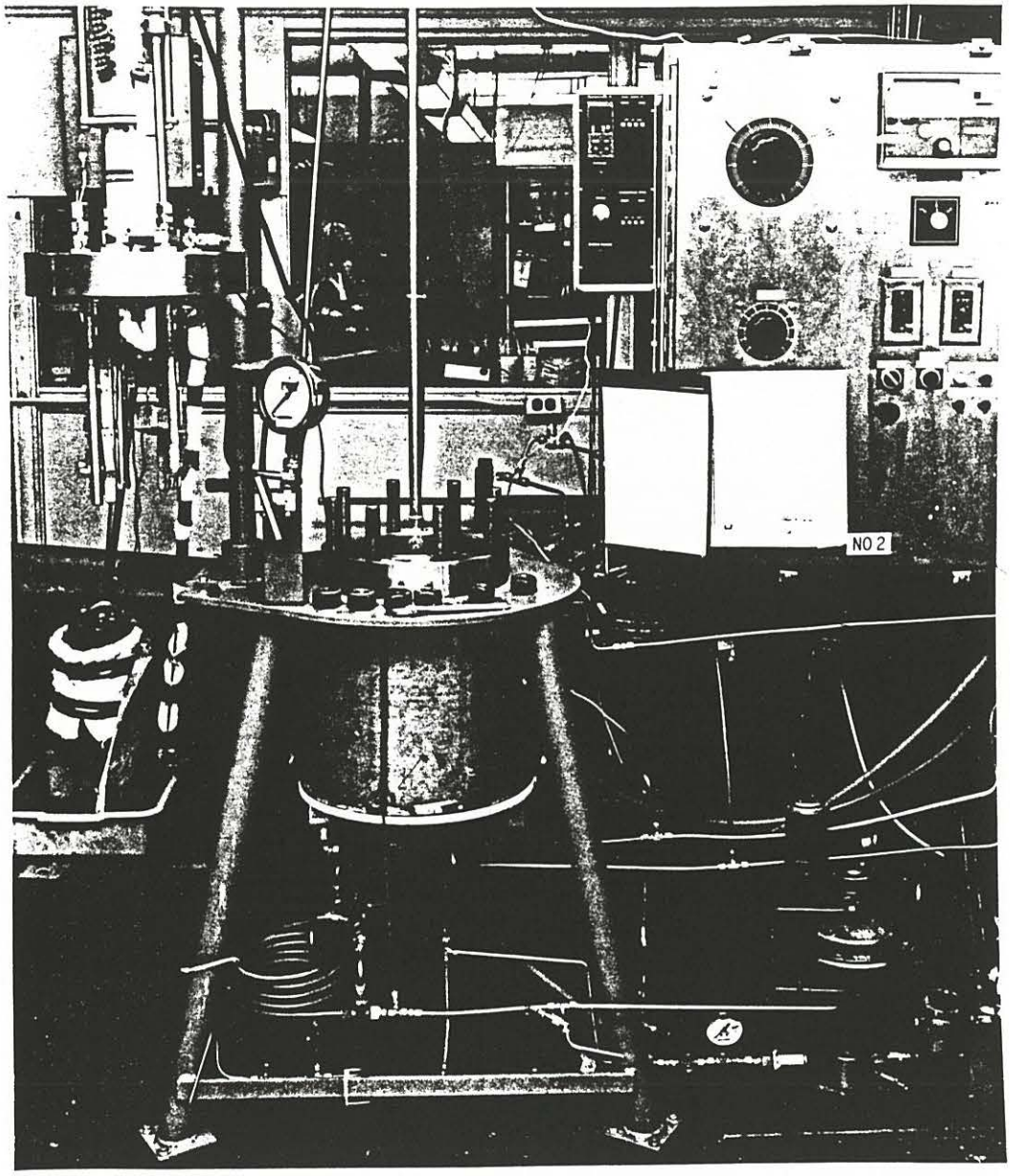


Figure 1 - Autoclave assembly used for HTCC process testing

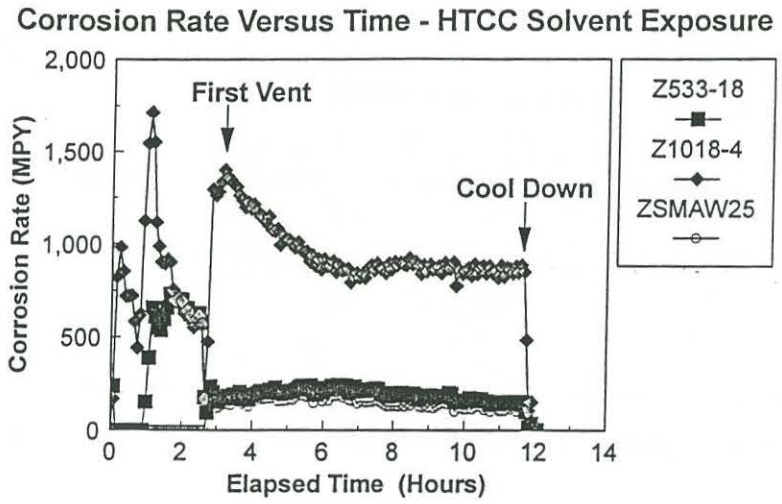


Figure 2 - ZRA corrosion rate versus time for a typical HTCC solvent exposure test

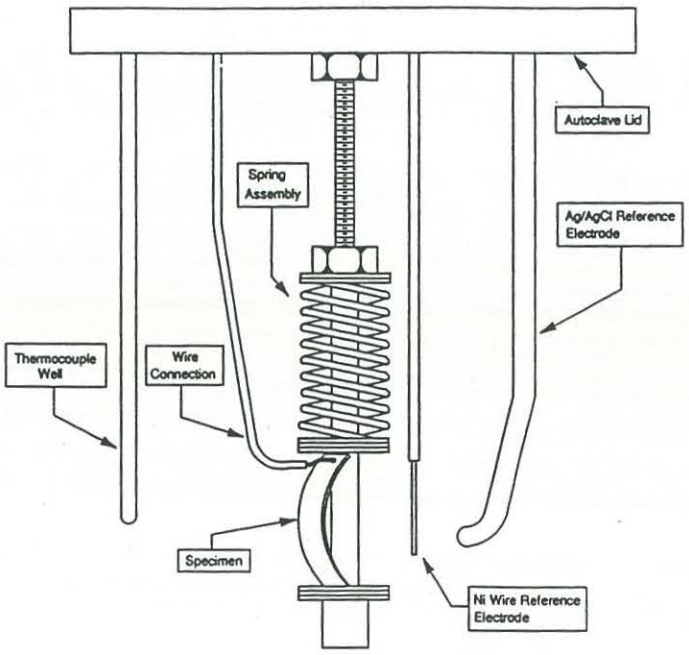


Figure 3 - Schematic of slow rate anodic scan test system

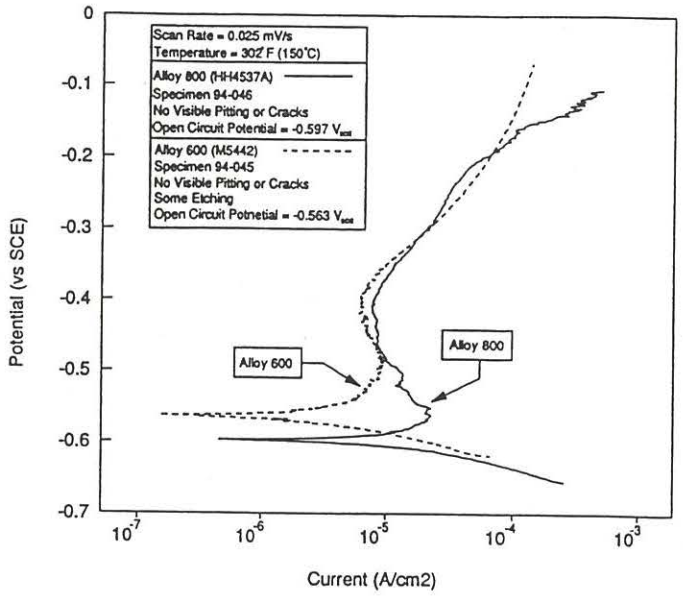


Figure 4 - Slow rate anodic scan of Alloy 600 and Alloy 800 in the HTCC at 150°C

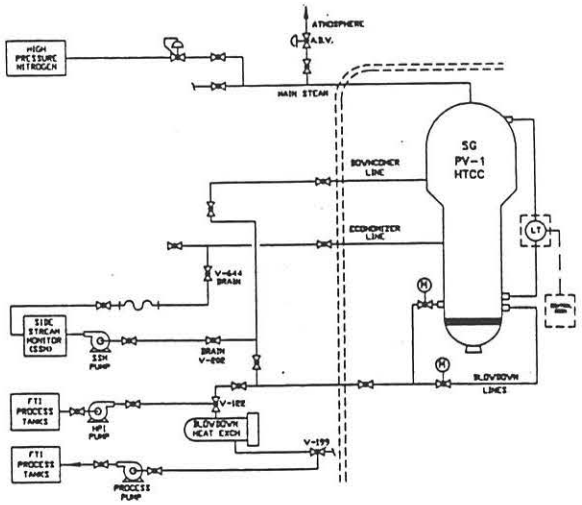


Figure 5 - Simplified schematic of the Palo Verde-1 chemical cleaning system

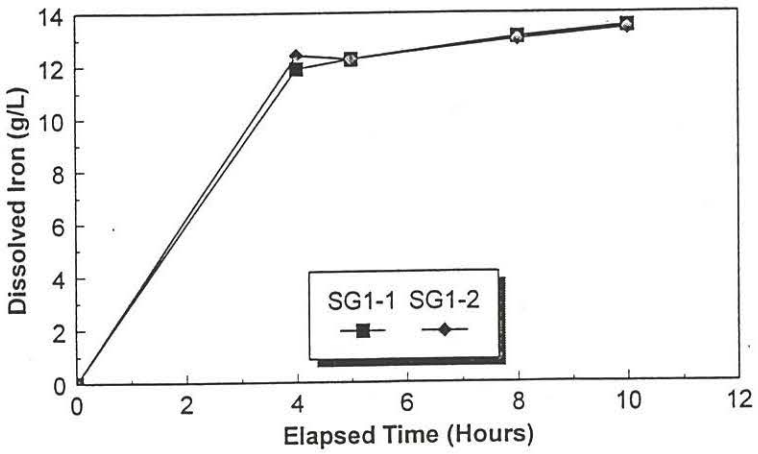


Figure 6 - Dissolved iron versus time for the Palo Verde-1 HTCC step