Nuclear Materials
ENGR2110 Term Paper

Boric Acid Corrosion of Reactor Components

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A pressurized water reactor is a type of nuclear reactor that uses light water as the moderator. Pressurized water reactors utilize a primary and secondary loop to harness the energy released during the nuclear fission process. The purpose of the primary loop is to convert the fission energy to steam while the secondary loop converts steam into electrical power. The primary loop is kept under extremely high pressure (~2250 psi) which allows the reactor coolant to reach high temperatures (~650°F) without boiling. This combination of high pressure and high temperature has a large influence on the types of materials that must be selected for the construction of primary side components. The main equipment of the primary system includes the reactor pressure vessel, primary loop piping, the pressurizer, steam generators and reactor coolant pumps.

Another plant parameter that contributes heavily to the material selection used for construction of primary components is the primary side water chemistry. Ordinary light water is used as a neutron moderator along with other chemical additions to the reactor coolant to help control the fission process. One such additive is boric acid, which is used as a neutron poison in controlling the fission process by readily absorbing neutrons. By varying the amount of boric acid dissolved in the reactor coolant, the reactor operators can control the rate of fission in the core. Primary side water chemistry is highly specialized in order to provide efficient control of the fission process. However, primary side water chemistry can be detrimental to the primary components if it escapes from the primary pressure boundary.

Due to the high pressure, temperature and specialized water chemistry in the primary system, material selection for the construction of primary components is vital to ensure the integrity of the primary pressure boundary. In order to contain the high internal pressures (resulting in high internal stresses) present in the primary loop, primary components are typically constructed from low alloy carbon steel plates or forgings. Forging materials are preferred due to the reduced number of weld seams. Typical materials for the construction of primary components include A333, A533 and A508; these materials provide an economical means to provide the high strength required to withstand such high internal pressures. Due to the presence of boric acid, which can be extremely corrosive to the low alloy steel material, the internal surfaces of the components must be clad with stainless steel overlay such as 304L, 308L or 309L. This combination of low alloy steel and stainless steel cladding allows the primary components to contain the high pressures and corrosive nature of the reactor coolant. However, vessel head penetrations, bolted closures and valves have lead to problems with reactor coolant leaking from the primary pressure boundary resulting in corrosion of primary components.

Boric acid corrosion is the main form of corrosion that results from primary pressure boundary leakage. Boric acid corrosion occurs when there is a crack or some other small primary pressure boundary leak. As the reactor coolant escapes through the crack it moves from the high temperature, high-pressure environment of the reactor coolant system to the containment environment. The sudden drop in pressure causes some of the reactor coolant to flash from liquid to steam which results in a concentrated boric acid solution. This concentrated boric acid solution can corrode the carbon steel primary components if there is no method for detection and mitigation of the problem. This is just a brief description of the mechanism of boric acid, a more detailed description is provided later.

The potential problems that can arise from boric acid corrosion of reactor components has been recognized by the NRC for some time now. On March 17, 1988 the NRC released Generic Letter 88-05, “Boric Acid Corrosion of Carbon Steel Reactor Pressure Boundary Components in PWR Plants”. In this Generic Letter, the NRC requested that all licensees provide information related to their boric acid inspection plans. Five industry events lead to the release of NRC Generic Letter 88-05, they were as follows:

- Turkey Point Unit 4; Corrosion resulting from leaking incore instrumentation tubes resulted in corrosion of reactor vessel head components. Corrosion of up to 0.25 inches was discovered.
- Salem Unit 2; The reactor vessel head experienced corrosion to a maximum depth of 0.36 inches resulting from the weld of an instrumentation penetration leaking on to the bare metal surface of the reactor vessel head.
- San Onofre Unit 2; 18,000 gallons of reactor coolant spilled into containment resulting from a failed valve. The valve failed after a boric acid solution corroded the bolts that held the valve packing in place.
- Arkansas Nuclear One Unit 1; Corrosion through 67 percent of the pressure boundary occurred due to leakage from a high pressure injection valve dripping onto a high pressure injection nozzle.
- Fort Calhoun; Boric acid corrosion reduced seven reactor coolant pump studs to a nominal diameter of 1.0-1.5 inches. Reactor coolant pump studs with no signs of corrosion had a nominal diameter of 3.5 inches.

These industry events highlighted the fact that leakage from the primary pressure boundary, even at rates acceptable from a technical specification standpoint, can result in significant corrosion of reactor components. As a result, the NRC stated its belief that "boric acid leakage potentially affecting the integrity of the reactor coolant pressure boundary should be procedurally controlled to ensure continued compliance with the licensing basis" (NRC Generic Letter 88-05). The NRC requested that all licensees of operating pressurized water reactors and holders of construction permits for pressurized water reactors submit documentation to provide assurance that a systematic program was in place to help prevent further incidences of boric acid corrosion. The NRC requested that the program have a method to determine likely locations where primary pressure boundary leaks that were smaller than technical specification limits could occur. The NRC also requested that licensees provide a means for examining and evaluating the affects of boric acid corrosion where leakage had occurred. Finally, the NRC stated that the plan should include an action plan to ensure that the problem does not occur elsewhere in the plant, which if necessary included modifications to the plant.

Most programs of this type assumed that only a small amount of reactor pressure boundary wastage would occur as a result of leaking primary coolant. The justification for this assumption was that as the primary coolant exits the primary pressure boundary it flashes to steam due to the sudden drop in pressure. This flashing process results in deposits of boric acid crystals, as shown in Figure 1. These crystals were assumed to cause minimal corrosion at reactor operating condition, therefore, significant corrosion was only assumed to occur during outages when the temperature of the equipment falls below 212°F and the boric acid crystals can be in solution.

Figure 1 - Boric Acid Crystals Resulting from Primary Pressure Boundary Leakage (picture taken from lecture 13b)

Many of the events in Generic Letter 88-05 resulted from leaks in reactor vessel penetrations. Penetrations in the reactor vessel and head, such as control rod drive mechanisms (CRDMs) and incore instrumentation (ICI) tubes, are typically fabricated from Alloy 600 material. The NRC released Generic Letter 97-01 titled “Degradation of Control Rod Drive Mechanism Nozzles and Other Vessel Closure Head Penetrations” to address cracking and possible leakage from reactor vessel head penetrations. Generic Letter 97-01 focuses primarily on cracking that may occur at the weld between the CRDM nozzle and the reactor vessel head, known as the J-groove weld. Cracking that occurs at the J-groove weld is typically a result of primary water stress corrosion cracking (PWSCC). Primary water stress corrosion cracking is a type of cracking that occurs from a combination of effects. In order for PWSCC to occur, three elements must be present, a susceptible material, an aggressive environment and high stress. In the case of CRDM J-groove welds Alloy 600 is the susceptible material. It is now a well-recognized fact that Alloy 600 is susceptible to PWSCC. This has lead to development and introduction of Alloy 690, which is more resistant to this type of failure. The aggressive environment present in the reactor coolant system can lead to local chemistry modifications and increased oxygen content near the welds. The required stresses can be the result of several factors such as swelling, residual stresses from the welding process or irradiation-induced stresses.

Based on domestic reactor vessel head inspections, evaluations performed by various owners groups and experience from European utilities, the NRC concluded in 97-01 that it is probable that domestic plants also experienced these cracks in the J-groove welds and CRDM penetrations. However, the NRC determined that these types of reactor vessel head cracking do not pose an immediate safety concern.   The basis for this determination was that cracks would be axial in orientation resulting in detectable leakage prior to failure and that the leakage would be detected during visual examination and walk downs performed prior to any significant damage occurring. The NRC did, however, acknowledge the fact that cracking of CRDMs and other vessel head penetrations is a cause for concern and should be investigated further.

The stance taken by the NRC in Generic Letter 97-01 was challenged in 2000-2001 when inspections lead to the discovery of cracked and leaking Alloy 600 vessel head penetration nozzles at four pressurized water reactors. Nozzle cracking was discovered at Oconee Nuclear Station Unit 1 in November 2000 and at Arkansas Nuclear One Unit 1 in February 2001. The cracking experienced at these two plants was determined to be axial in orientation and deemed by the NRC to be of limited safety concern. However, with the discovery of circumferential cracking at Oconee Nuclear Station Unit 3 and Oconee Nuclear Station Unit 2, which occurred in February 2001 and April 2001 respectively, serious concerns were raised about the potential safety implications resulting from cracks in vessel head penetrations.

At the time, cracking in vessel head penetrations fabricated form Alloy 600 was not a new issue, axial cracking had been initially identified in the late 1980's. However this was the first time that circumferential cracking had been identified in the J-groove weld of a CRDM penetration. This resulted in the NCR reassessing their assertion of Generic Letter 97-01 that cracking of vessel head penetrations was not an immediate safety concern. NRC bulletin 2001-01, Circumferential Cracking of Reactor Vessel Head Penetration Nozzles, expresses the concerns the NRC had with their stance in Generic Letter 97-01. The main issues that the NRC had with their conclusion presented in Generic Letter 97-01 were as follows:

- Circumferential cracking had been identified in the Alloy 600 weld metal in the J-groove weld for the first time. This contradicts the initial conclusion that cracking would be predominately axial in orientation.
- The cracks identified in Arkansas Nuclear One Unit 1 raised concerns about the adequacy of the susceptibility model established in Generic Letter 97-01. Arkansas Nuclear One Unit 1 was predicted to still have over 15 effective full powered years before reaching the conditions of the limiting plant.
- Circumferential cracking outside of the structural welds had been identified for the first time. This raised concerns about the possibility of rapid crack propagation possibly resulting in control rod ejection.
- Circumferential cracking on the CRDM outside diameter and inside diameter raised concerns about the effects of reactor coolant leakage.

- The circumferential cracking was identified due to the presence of small amounts of boric acid residue. This questioned the adequacy of using visual examinations as the primary method for detecting cracks.

Following the discovery of circumferential cracking at Oconee Unit 3, the NRC met with the EPRI Materials Reliability Program to discuss the issue. This resulted in a revised relative susceptibility determination to cracking based on operating time and temperature for each pressurized water reactor. Westinghouse, Babcock & Wilcox and Combustion Engineering first developed this relative susceptibility model during the mind 1990's. The susceptibility of an individual plant was based on factors such as operating temperature, years of operation, fabrication methods for the reactor vessel head and other information gathered by previous inspections. Based on the revised susceptibility model, each pressurized water reactor was ranked according to operating time and temperature and compared to the Oconee Unit 3 at the time the circumferential cracks were identified. Based on this comparison, each operational pressurized water reactor could be divided into one of four groups as follows:

- Plants which have demonstrated that PWSCC had occurred, through detection of boric acid deposits, in vessel head penetrations and can therefore expect other vessel head penetrations to experience cracking.
- Plants determined to have a high susceptibility to PWSCC based on a ranking of less than 5 effective full power years (EFPY) to reach the conditions at Oconee Unit 3.
- Plants determined to have a moderate susceptibility to PWSCC based on a ranking of more than 5 EFPY but less than 30 EFPY to reach the conditions at Oconee Unit 3.
- Plants determined to have a low susceptibility to PWSCC based on a raking of more than 30 EFPY to reach the conditions at Oconee Unit 3.

Based on the ranking of an individual plant, different inspection methods were recommended. For plants that have already determined the presence of PWSCC through the detection of boric acid deposits, a qualified volumetric examination of 100% of the vessel head penetration nozzles may be appropriate. This examination would assess the structural integrity of the vessel head penetrations. For plants determined to have a high susceptibility to PWSCC an effective visual examination of 100% of the vessel head penetrations should be performed at a minimum. This qualified examination should be capable of detecting and accurately categorizing leakage from any vessel head penetration nozzles. For the plants determined to have a moderate susceptibility to PWSCC a visual examination of 100% of the vessel head penetration nozzles should be performed. Finally for those plants determined to have a low susceptibility to PWSCC no additional examination requirements beyond those currently employed at the facility were required. As a result of NRC Bulletin 2001-01 all operating plants were required to submit their plans for inspection of the vessel head penetration nozzles and their process for inspection of the reactor vessel head to determine if any corrosion had occurred. It was inspection activities in response to NRC Bulletin 2001-01 that discovered the worst instances of boric acid corrosion in the nuclear industry.

In February 2002, the Davis-Bessie Nuclear power station went into a planned refueling outage. As part of this outage, inspection of the reactor vessel head was planned to fulfill licensing requirements related to NRC Bulletin 2001-01. The inspection activities resulted in the identification of axial cracks in five of the CRDM nozzles near the J-groove welds. It was determined that the cracks had initiated on the inner diameter of the nozzle and were caused by PWSCC. Additionally, three of these five CRDM nozzles contained through-wall cracks which resulted in pressure boundary leakage. The affected nozzles (nozzles 1, 2 and 3) were all located near the center of the reactor vessel head and it was decided by the licensee that these three nozzles, as well as the other two which had indications but no leakage, should be repaired. During the repair process, nozzle 3 was agitated and fell away from the top of the reactor vessel head until it contacted an adjacent CRDM nozzle. While investigating the reason for the displacement of nozzle 3, workers discovered a cavity in the reactor vessel head between nozzle number 3 and nozzle number 11. Figure 2 shows the location of the cavity on the Davis-Bessie reactor vessel head while Figure 3 shows the approximate dimensions.

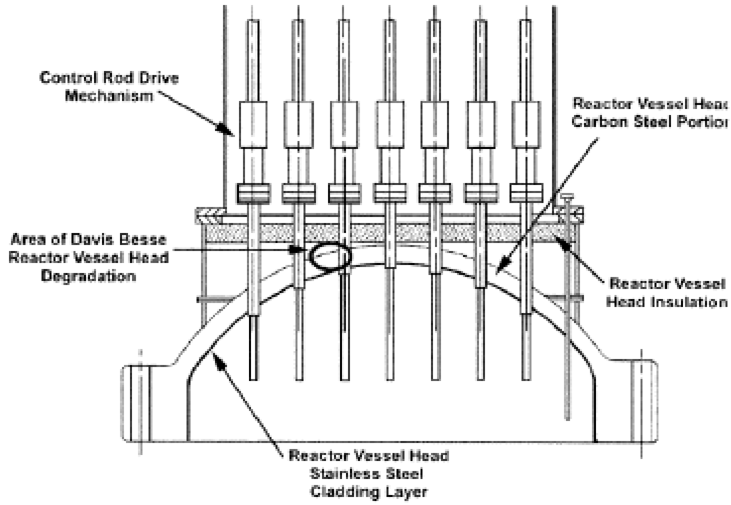

Figure 2 - Location of Davis-Bessie Reactor Vessel Head Degradation (NUREG 6875)

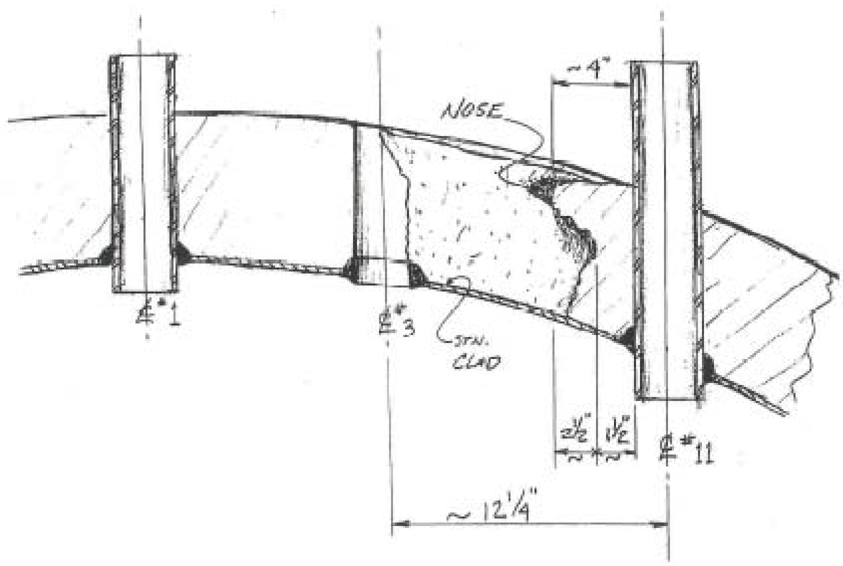

Figure 3 - Approximate Dimensions of Davis-Bessie Reactor Vessel Head Cavity (NRC website)

As a result of the corrosion of the reactor vessel head at Davis-Bessie, only a thin layer, roughly 1/8 of an inch thick, of stainless steel cladding was left to hold back primary side pressure (~2250 psi). During an inspection of the cavity, a crack was noticed in this thin layer of stainless steel cladding, the location of this crack is noted in Figure 4 with a small dot and arrow. It was later discovered that the stainless steel cladding, which had essentially become the primary pressure boundary, had deflected upwards over a small area indicating that the material had yielded.

Primary water stress corrosion cracking of Alloy 600 CRDM nozzles had been observed before, but never had vessel head degradation of this magnitude been experienced. The extent of the damage experienced at Davis-Bessie is shown in Figure 4. In other cases where through wall cracking had lead to reactor coolant leakage, very low leakage rates had occurred. However, the experience at Davis-Bessie showed that this might not always be the case. Since this type of degradation had never been experienced it was important to understand what lead to such an aggressive attack of the reactor pressure vessel head. As a result of the reactor vessel head degradation experienced at Davis-Bessie, an entire generation of reactor vessel closure heads was replaced across the United States. These replacement closure heads used Alloy 690 reactor vessel penetrations as opposed to Alloy 600. As compared to Alloy 600, Alloy 690 has a superior resistance to stress corrosion cracking.

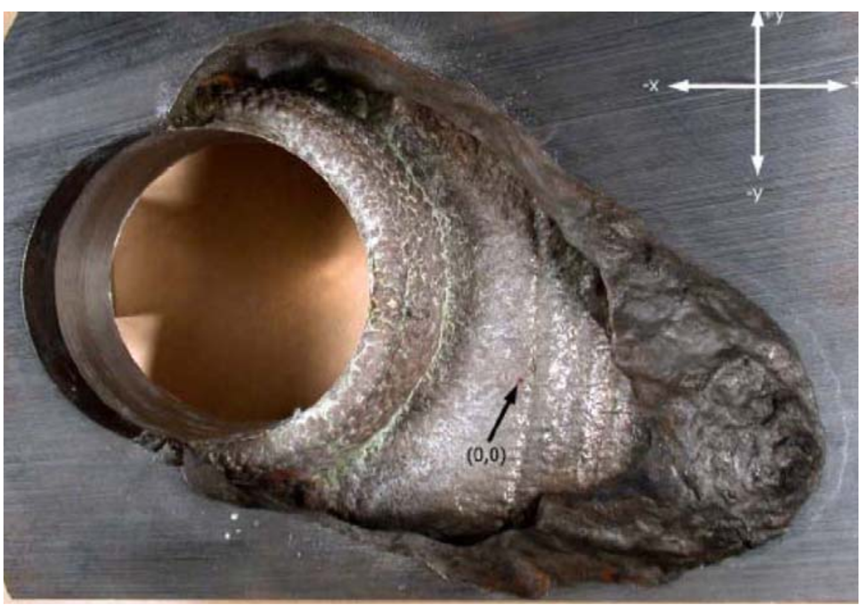

Figure 4 - Davis-Bessie Reactor Vessel Head Cavity (NRC Website)

The root cause report for the Davis-Bessie incident provides a likely scenario, which lead to the severe degradation of the reactor vessel head. The root cause report suggests that the degradation occurred in the following manner:

- Crack initiation and growth to through wall; The root cause report suggests that a crack was initiated as a result of PWSCC around three years after Davis-Bessie began operations in 1987. By 1996 the crack had grown to a through wall crack and penetrated above the J-groove weld. At this stage, primary pressure boundary leakage would have been very low due to the limited extent of through wall cracking.
- Minor weepage and latency period; As the crack grew larger reactor coolant would be allowed to enter the annulus between the Alloy 600 CRDM nozzle and the carbon steel reactor vessel head. It was postulated that his annular gap would be opened as a result of corrosion processes and the presence of a concentrated boric acid solution. At this stage primary pressure boundary leakage would be identifiable as a result of deposits of boric acid crystals.
- Late latency period; As the crack continued to grow the annular gap increased in width resulting in an increased annular flow area. This may have resulted in oxygen entering the annulus accelerating the corrosion process.
- Deep annulus corrosive attack; As the annulus increased in size the velocity of flow as well as the differential pressure would decrease. This would result in increased corrosion rates due to increased oxygen penetration.
- Boric acid corrosion; The leakage would no longer immediately flash to steam due to reduced heat transfer to the surrounding metal. This would result in an increased amount of moist steam in the annular gap. The leakage rate from the crack would increase as the size of the gap increased resulting in a concentrated boric acid solution filling the annular gap.

The information presented in the Davis-Bessie root cause report was only partially complete due to the fact that some of the information necessary to complete the report had not been generated at that time. Corrosion of low alloy steel in the type of environment present in the Davis-Bessie incident was not well known or researched.

In 2004 Argonne National Laboratory performed a series of experiments that were intended to gather data on the electrochemical potential and corrosion rates of reactor components in solutions of varying temperature and boric acid concentration. The experiments were undertaken to provide a better understanding of the severe boric acid corrosion that had occurred at the Davis-Bessie Nuclear Power Station. Based on experimental data gathered over the 15 or so years preceding the Davis-Bessie incident it was common thinking that severe boric acid corrosion could not occur at elevated temperatures. This was due to the fact that the escaping reactor coolant would vaporize as it exited the primary pressure boundary resulting in the formation of boric acid crystals, which were known to cause only minor corrosion. After the Davis-Bessie incident, it was discovered that this was not always the case, so the NRC in conjunction with Argonne National Laboratory undertook a test program to better understand the corrosion characteristics of reactor vessel materials at various temperatures and boric acid concentrations.

The experiments undertaken at Argonne National Laboratory attempted to recreate three possible environments present at Davis-Bessie. The experiments were performed in the following environments:

- A high temperature, high-pressure aqueous environment was intended to mimic a low leakage though a crack with the annulus plugged.
- High temperature boric acid powder at atmospheric pressure with and without the addition of water was intended to simulate low leakage through the crack with the annulus opened.
- A low temperature saturated boric acid solution, both aerated and deaerated, corresponded to significant cooling due to high leakage through the nozzle crack and the nozzle annulus opened.

Based on the experimental data, Argonne National Laboratory was able to conclude that the corrosion rates of the A533, Gr.-B steel of the reactor vessel head experienced a greater amount of corrosion of either the 308 stainless steel cladding material or the Alloy 600 vessel head penetrations. The corrosion rates of the A533, Gr.-B varied depending on the environment to which they were subjected.

The experiments for the high temperature, high-pressure aqueous environment experienced an average corrosion rate of 5 mm per year. The amount of corrosion experienced in this environment decreased as the temperature increased. The low temperature boric acid solution experienced an average corrosion rate of 40 mm per year in the aerated solution and an average corrosion rate of around 25 mm per year in the deaerated solution. The decrease in corrosion rate in the aerated versus deaerated case is most likely due to the lack of oxygen present in the latter case. The greatest corrosion rates were experienced in the high temperature boric acid powder at atmospheric pressure with the addition of water. This test case experienced corrosion rates as high as 150 mm per year. This is most likely due to the fact that this case had the highest concentration of boric acid present. Based on the information gathered at Argonne National Laboratory, the nuclear industry gained a better understanding of the corrosion properties that are present in and around the reactor vessel head.

Corrosion of the reactor vessel as a result of boric acid is not limited to the reactor vessel closure head. Wherever there is a penetration into the reactor vessel, the potential exists for primary pressure boundary leakage and boric acid corrosion. This includes the bottom mounted instrumentation tubes. One such instance of boric acid leakage from bottom mounted instrumentation tubes occurred at South Texas Project Unit 1 (STP-1). In the 2003 spring outage a routine boric acid corrosion inspection of the reactor vessel detected a small amount of boric acid residue on two of the 58 bottom mounted instrumentation tubes. Subsequent non-destructive examinations revealed small axial cracks and through wall cracks in both of the bottom mounted instrumentation tubes. The types of non-destructive examinations employed included dye penetrant, eddy current, magnetic particle, profilometry and ultrasonic examinations. Although all of these types of non-destructive examinations had been performed elsewhere, some had to be substantially modified in order to be applied to the bottom of the reactor vessel. One of technological innovations that were used for the first time at STP-1 was phased array ultrasonic examination of the bottom mounted instrumentation tubes. Another innovative technique employed at STP-1 was a specially designed remotely operated probe used to perform eddy current inspections of the J-groove welds. These techniques were devised specially for this project and had to be completed under enormous time pressure.

After the non-destructive examination was finished, the conclusion was made that the nozzles were to be replaced by new, more corrosion resistant Alloy 690 penetrations. In order to ensure better workmanship and lower radiation dose to workers, a full-scale mockup was used. This full scale mock up, shown in Figure 5, allowed workers to practice the repairs in a dose free environment so the work could be performed more quickly in the field.

Figure 5 – Full Scale Mockup Used at STP-1 (Nuclear News, October 2004)

Due to the innovations employed during this incident, STP-1 was back online and producing electricity within four months of the initial discover of boric acid residue. The events at STP-1 show the dedication of the nuclear industry to quickly and effectively mitigate problems related to primary pressure boundary leakage that could result in boric acid corrosion of reactor components.

In order to prevent the types of catastrophic events that could happen as a result of boric acid corrosion of the primary pressure boundary it is critical that each plant have a boric acid inspection plan. These inspection plans help to reduce the risk of boric acid degradation by employing a well thought-out approach for the inspection, assessment and mitigation of boric acid leakage. The first step in an effective boric acid inspection program is inspection. The inspection plan should clearly lay out the type of inspection and the frequency of inspection. Various types of non-destructive examinations that may be employed include visual exams, eddy current, dye penetrant, magnetic particle and ultrasonic testing. Any findings during the inspections should be immediately documented and brought to the attention of the proper authorities. Should boric acid leakage and subsequently degradation be identified, the damage must be promptly and accurately evaluated. Based on the results of the evaluations an engineering decision needs to be made as to whether the component can be returned to service or if the component needs repaired/replaced. Primary pressure boundary leakage resulting in boric acid corrosion of reactor components is a real problem that the nuclear industry faces everyday. Effective control and mitigation of this leakage and degradation is essential to ensure the safe operation of each and every nuclear power station.

References

"Boric Acid Corrosion of Light Water Reactor Pressure Vessel Materials" – J.H. Park et. al, NUREG/CR 6875 Nuclear Regulatory Commission 2005.

Conaway, Edward. "STP's First-of-a-Kind Leakage Repair." Nuclear News October 2004: 32-34.

Cramer, Stephen D., et al. ASM Handbook. Volume 13C: Corrosion: Environments and Industries. Pages 362-385. Materials Park, Ohio: ASM International, 2006.

Nuclear Regulatory Commission (U.S.), Generic Letter 88-05, "Boric Acid Corrosion of Carbon Steel Reactor Pressure Boundary Components in PWR Plants," March 17, 1988.

Nuclear Regulatory Commission (U.S.), Bulletin 2001-01, "Circumferential Cracking of Reactor Pressure Vessel Head Penetration Nozzles," August 03, 2001.

Nuclear Regulatory Commission (U.S.), Bulletin 2002-01, "Reactor Pressure Vessel Head Degradation and Reactor Coolant Pressure Boundary Integrity," March 18, 2002.

Nuclear Regulatory Commission (U.S.), Bulletin 2002-02, "Reactor Pressure Vessel Head and Vessel Head Penetration Nozzle Inspection Programs," August 09, 2002.

Nuclear Regulatory Commission (U.S.), Information Notice 2002-11, "Recent Experience with Degradation of Reactor Pressure Vessel Head," March 12, 2002.

Nuclear Regulatory Commission (U.S.), Bulletin 2003-02, "Leakage from Reactor Pressure Vessel Lower Head Penetrations and Reactor Coolant Pressure Boundary Integrity," August 21, 2003.