THREE MILE ISLAND UNIT 1 STEAM GENERATOR DEGRADATION AND REPAIR

TECHNICAL EVALUATION REPORT

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INTRODUCTION

In November 1981, primary to secondary side leaks were discovered in both of the once-through steam generators (OTSG) at Three Mile Island Unit 1 (TMI-1). Subsequent inspections and failure analysis performed by the utility and their consultants revealed widespread circumferential intergranular stress corrosion cracking (SCC) on the Inconel 600 tubes in the upper portions of both OTSG's. In January 1982, Brookhaven National Laboratory (BNL) was requested to participate in the NRC task force evaluating the causes of this incident and the effectiveness of the remedial actions. An extensive SCC test program was carried out in order to understand the SCC behavior of Inconel 600 in the metallurgical condition in which it is present in the TMI-1 OTSG's. Both laboratory work and theoretical evaluations contributed to our understanding of the water chemistry environment that caused the incident.

The present TER is based on our review of two GPUNC Topical Reports and a final Third Party Review Report on the problem(1). It takes into account the insights gained as a result of our own related investigations. Further information was obtained during several meetings attended by some or all of the authors, especially the one at NRC Headquarters on April 5, 1983.

Much of the experimental work performed at BNL has already been documented in the form of technical papers for research journals. Copies of these papers are attached in Appendix A.

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DISCUSSION

All of the evidence provided in the GPUNC reports, combined with our own laboratory investigations, confirms that the intergranular SCC occurred on heavily sensitized Inconel 600 at temperatures below 100°C, and resulted from the presence in TMI-1 coolant of both oxygen and metastable sulfur compounds. The sulfur species are believed to have originated from leakage of sodium thiosulfate from the reactor building spray system into the primary coolant. In September 1981, hot functional testing was performed, at which time there was no primary-to-secondary leakage. Following cooldown from this testing, sodium thiosulfate entered the reactor coolant, possibly at levels of 4 to 5 ppm. Additional thiosulfate contamination may have resulted from injections of the borated water storage tank (BWST) contents, since the water in the BWST had been previously mixed with water from the reactor building spray piping. The reactor coolant system was vented to the atmosphere through a control rod drive mechanism vent in October 1981, and oxygen entered the primary side of the OTSG's at the hot leg or upper end.

Previous Occurrences of Low Temperature SCC at TMI-1

In the summer of 1979, in-service inspections showed a significant number of defects in the heat-affected zones of stainless steel piping at TMI-1, especially where the borated water was stagnant and had access to the air. In 1979, the U.S. Nuclear Regulatory Commission put out I&E Bulletin 79-17, "Pipe Cracks in Stagnated Borated Water Systems at PWR Plants."(3) In reviewing the data in this bulletin, it became evident that this phenomenon occurred most frequently in those units that had thiosulfate in their building spray systems, especially TMI-1 and ANO-1. In October 1979, BNL transmitted this conclusion to the NRC, along with preliminary recommendations regarding control of the use of thiosulfate solutions in PWR's.(4)

Portions of the TMI-1 spent fuel pool piping containing a through-wall stress corrosion crack were received at BNL in the fall of 1979. A failure analysis was performed,(5) which provided evidence of sulfur contamination on the fracture surfaces. Under a research program for the Department of Energy,

H. S. Isaacs, B. Vyas, and M. W. Kendig began investigating the SCC of sensitized stainless steels at ambient temperature by thiosulfate solutions. Their first observations (6) clearly showed that thiosulfate solutions corresponding to less than 1 ppm sulfur were sufficient to cause intergranular SCC of sensitized Type 304 stainless steel. These results were transmitted to the NRC in the spring of 1980 with a suggestion that the NRC recommend removal of thiosulfate solutions from PWR containment sprays. NUREG-0691 (7) recommended on page 2-49 that contamination of the external and internal surfaces of piping by caustic, chloride or thiosulfate ions be carefully controlled.

In the OTSG fabrication, the Inconel 600 tubes are already in place when the vessel is given a post-weld heat treatment equivalent to approximately 18 hours at 621°C. This situation automatically produces a sensitized condition in the Inconel tubing. The TMI-1 steam generator failures are therefore probably due to SCC of the sensitized Inconel 600 tubing.

Experimental Work at BNL Related to the Mechanism of TMI-1 Steam Generator Failures

Based on the above considerations, SCC tests were performed on sensitized Inconel 600 to determine the effects of thiosulfate or similar sulfur compounds. These experiments demonstrated for the first time that very low levels of sulfur compounds in borated water could cause SCC in sensitized Inconel 600 at ambient temperatures. The objective of these tests was to assess the influence of a variety of metallurgical and environmental factors on the initiation and growth of the cracks. The results have clarified the differences between various metastable sulfur compounds, the behavior of the alloy at different degrees of sensitization, and the mechanism of SCC inhibition by lithium hydroxide. Sensitized Inconel 600 behaves very similarly to sensitized Type 304 stainless steel in sulfur environments.(8,9,10)

The results of this investigation are summarized:

(i) Using the best available information on the water chemistry prevailing at the time of the cracking, SCC of severely sensitized material was reproduced in the laboratory at temperatures from 22 to 95°C, and at rates varying from 0.1 to 2.5 mm/day. Dissolved oxygen is required at these temperatures.

(ii) Mill-annealed or thermally stabilized material is immune to low temperature SCC by sulfur compounds.

(iii) In the absence of lithium hydroxide additions, the threshold sulfur concentration for SCC (as $Na_2S_2O_3$ added to aerated 1.3% boric acid at 40°C) is less than 75 ppb.

(iv) Initiation of SCC is often slow under static loading, but a brief period of dynamic straining is sufficient to initiate cracks which then require low stresses for propagation. Initiation under static load is particularly difficult in marginally sensitized material, which is therefore not suitable for tests aimed at generating conservative water chemistry criteria.

(v) Sodium tetrathionate is much more effective than sodium thiosulfate in the initiation stage of SCC, especially on marginally sensitized material. However, very little difference was noted between the sulfur compounds on their effects on crack growth under static or dynamic loading.

(vi) Lithium hydroxide additions inhibit SCC; as a general guide, the ratio of Li to S concentrations should be maintained greater than 10/1, expressed in ppm. This is thought to be related to the necessity for concentration of the thiosulfate ion in the cracks by electromigration; lithium hydroxide inhibits SCC by partial neutralization of the boric acid and formation of the competing anion, $HB_4O_7^-$.

(vii) Under certain conditions of long exposure, dilute solutions of the metastable sulfur compounds can cause pitting or intergranular corrosion of sensitized Inconel 600 without applied stress.

Based on these results, we believe that a residual sulfur concentration of about 0.1 ppm is harmless, provided that the lithium ion concentration is maintained at approximately 1 ppm. Control of the oxygen concentration will provide a further measure of protection.

Removal of Sulfur from the Surface Films on the Inconel Tubing

The licensee's failure analyses have shown that the tubing removed from TMI-1 has significant sulfur contamination on the surface. There has been concern that this residual sulfur could become aggressive and cause a recurrence of the SCC phenomenon. From our research, it is apparent that the SCC occurs rapidly and at low stress intensities. Since eddy current inspection has shown no further cracking, we are therefore confident that the cracks are currently inactive. The utility has described (1) a technique which they are implementing to remove the residual sulfur from the surface films on the Inconel tubing. The technique involves conversion of the low oxidation state sulfur species to sulfate, using an alkaline solution of hydrogen peroxide. In an attempt to ascertain the non-aggressive nature of dilute sulfate solutions, an exploratory test was performed at BNL in which a U-bend specimen of sensitized Inconel 600 was immersed in a borated solution obtained by (a) heating about 10 ppm thiosulfate with excess hydrogen peroxide at 60°C and pH 10 for one hour, (b) destroying the remaining hydrogen peroxide, and (c) bringing the pH down to 5 (the natural pH of boric acid solutions). No SCC was observed in this sulfate-containing medium after a 42-day exposure, in contrast with a parallel test in which a similar specimen was exposed to 10 ppm thiosulfate at pH 5, without hydrogen peroxide treatment. In addition, experiments are in progress at BNL on the course and rate of the reaction between thiosulfate and hydrogen peroxide in an alkaline medium prepared by

appropriate neutralization of simulated primary coolant. Ion chromatography and colorimetry are used as the analytical techniques for thiosulfate and hydrogen peroxide, respectively. A report on this work will be transmitted to NRC within about a month. Our observations tend to confirm the boundaries of the licensee's procedure.

Balance of Plant

The TMI-1 plant undoubtedly contains sensitized stainless steel components with residual stresses from welding. Based on the literature on susceptibility of sensitized stainless steel to SCC in the presence of oxygen and small amounts of sodium thiosulfate (6,8,9) SCC is expected in any sensitized stainless steel components that saw the same primary coolant environment as the cracked steam generator tubes. However, the licensee describes no evidence of SCC throughout the plant other than that which occurred in the steam generator. Furthermore, the most recent Topical Report (1a), along with information provided at the April 5, 1983 meeting, indicates that the licensee has addressed the relevant issues.| The most probable reason for the lack of SCC in the balance of the plant is that oxygen was not present at high enough concentration.

Why Did SCC Occur Only at the Upper Ends of the Steam Generator Tubes?

The licensee has mentioned oxygen access and alternate wetting and drying as possible reasons for the predominance of cracking at the upper ends of the steam generators. We calculate that, if the water is truly stagnant, oxidation of the sulfur in the surface films could have removed oxygen. This would restrict high oxygen levels to the vicinity of the water-air interface. This hypothesis, however, remains to be demonstrated, as the GPU topical report does not give analyses of oxygen levels throughout the plant during the period from September through November 1981. Following the reducing conditions during operation (and the hot functional testing), the sulfur in the film is likely to have been in a state highly active towards oxygen (i.e., sulfide, polysulfide, etc.), as indicated by the X-ray photoelectron spectroscopy (XPS) analysis performed by GPU's consultants.(11) In order to remove 6 ppm oxygen

from a tube 3/4" i.d., approximately 10^{-7} mole of sulfide per cm^2 must be oxidized to sulfate. This amount is equivalent to a NiS film approximately 10 nm thick, or only 2% of a NiO film 10 μm thick which contains 5% NiS. Some oxygen gettering can also be expected from corrosion processes or from oxidation of metal ions in highly reduced surface films, (e.g., $Fe^{2+} \rightarrow Fe^{3+}$); also from reactions with residual hydrazine, and from reactions involving free radicals produced by the radiation field.

EVALUATION

The repairs to the steam generators proposed by the licensee consist of both mechanical and chemical modifications. Both of these appear acceptable, as discussed below.

Mechanical Modifications

The proposed mechanical modifications consist of either tube expansions to produce a minimum of six inches of fully expanded tube below the lowest known serious defect, or of expansion and removal from service of the tubes where defects are known to exist below the upper tube sheet surface. The plugged tubes will be stabilized to prevent excessive motion of these tubes, in case the defects propagate, by some mechanism, to the point that the tube would break. The criteria established by the licensee for these repairs appear prudent, and we recommend their acceptance by the NRC. Because crack propagation rates are anticipated to have been high during the period between September and November 1981 when a corrosive environment existed in the TMI-1 steam generator, we believe that most stress corrosion cracks that would have propagated through-wall have already done so. Based upon considerations from our previous review of the concept of a leak limiting sleeve for use in Westinghouse steam generators (12), we concur that the criterion of a six inch minimum expansion below the lowest known defect on each tube is acceptable to ensure leak tightness should the defects propagate through-wall.

Chemical Remedies

The licensee has already removed most of the residual sulfur from the primary coolant and is instituting steps to increase the lithium ion concentration. Both of these actions should minimize any further damage by the proposed stress corrosion mechanism. Controls to be implemented by the utility should either prevent or greatly reduce any subsequent intrusion of sulfur compounds into the primary coolant at TMI-1. The sodium thiosulfate tank has been removed.

Considerable sulfur does remain in the surface oxides, however, and it has not been shown conclusively whether this can cause SCC of the Inconel tubing during future operation of the units. Although sulfur compounds have probably been present in the TMI-1 steam generators throughout most of the life of the plant, it took the combination of thiosulfate in solution at low temperature with a low pH (low lithium) and high oxygen concentration to cause the observed cracking. Leaving the residual sulfur in the oxide films is not likely to cause subsequent SCC, except in the event that this combination of circumstances recurs. However, since the remedial procedure proposed by the licensee for removal of this residual sulfur does not appear to pose a safety issue, we recommend its acceptance, especially in view of the fact that the remaining questions regarding its effectiveness are currently being addressed by the licensee.

Likelihood of Cracking Recurring

Given the chemical changes proposed by the licensee, and assuming these are rigidly followed, there will be little opportunity for continued degradation of the steam generator tubes by the same mechanism. The proposed changes in the primary coolant technical specifications are therefore in our opinion satisfactory.

Balance of Plant

The licensee's recent Topical Reports (1a,b) described extensive testing and inspection of components in the reactor coolant and suppoting systems other than the OTSG's. In addition, as reported at the April 3, 1983 meeting, some 304 stainless steel components of the supporting systems were replaced with 304L. We believe that potential problem areas in the balance of the plant have been addressed in satisfactory fashion.

CONCLUSIONS

From our evaluation of the information provided by the licensee and the other consultants, and from the results of our own experimental program, we have reached the following conclusions regarding the return of TMI-1 to service following steam generator repair:

1. The intergranular SCC that occurred in the upper end of the OTSG tubes was due to a combination of high oxygen levels in this portion of the steam generator coolant and the presence in solution of one or more low oxidation state sulfur compounds.

2. The low oxidation state sulfur compounds were probably sodium thiosulfate or its decomposition products.

3. Evidence available to date suggests that the chemical treatment proposed by the licensee does not pose a safety issue. Implementation of this treatment, combined with maintenance of minimal sulfur levels and increased ($\gtrsim$1 ppm) lithium concentrations in the primary coolant, should prevent recurrence of the phenomenon during future operation of the plant.

4. The water chemistry controls to be placed on the primary coolant following return to service are satisfactory.

5. The mechanical tube expansion and the plugging and stabilization criteria proposed by the licensee are satisfactory, and the likelihood of further degradation or leakage occurring as a result of these actions is small.

6. Given the high SCC rates of sensitized stainless steel in oxygen containing thiosulfate environments, it would appear that sensitized stainless steel components in the reactor coolant pressure boundary did not experience as aggressive an environment as did the upper end of the steam generators.
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7. A reinspection of selected areas of the primary coolant pressure boundary, including steam generator tubes, should be made after approximately six months of full power operation following return to service, to confirm that the degradation processes have not continued. This inspection should include all steam generator tubes containing less than 40% through-wall defects which were not previously plugged.

REFERENCES

1. a) T. M. Moran, "Assessment of TMI-1 Plant Safety for Return to Service after Steam Generator Repair," GPUNC Topical Report 008, Rev. 2, 3/30/82;

   b) M. J. Graham and W. Greenaway, "Safety Evaluation of TMI-1 Reactor Coolant System Cleaning," GPUNC Topical Report 010, Rev. 0, 3/3/83;

   c) Report of Third Party Review of TMI-1 Steam Generator Repair, 2/18/83.

2. See Appendix A.

3. U.S. NRC I&E Bulletin 79-17, "Pipe Cracks in Stagnated Borated Water Systems at PWR Plants," Rev. 1, 10/29/79.

4. J. R. Weeks, Letter to H. F. Conrad (CMEB-NRR) 10/30/79.

5. C. J. Czajkowski, "Intergranular SCC of Type 304 SS in the Spent Fuel Pool Piping of TMI-1," BNL-NUREG-28879, October 1980.

6. H. S. Isaacs, B. Vyas, and M. W. Kendig, "The Stress Corrosion Cracking of Sensitized Stainless Steel in Thiosulfate Solutions," BNL-28816, 1980.

7. NUREG-0691, "Investigation and Evaluation of Cracking Incidents in Piping in Pressurized Water Reactors," May 1980.

REFERENCES (Cont'd)

8. R. C. Newman, K. Sieradzki, and H. S. Isaacs, Metall. Trans. 13A, 2015 (1982).

9. K. Sieradzki, H. S. Isaacs, and R. C. Newman, "Ambient Temperature SCC of Sensitized Stainless Steels," CORROSION 82, Preprint 224.

10. R. C. Newman and R. Bandy, "Ranking of Environments in Stress Corrosion Cracking," CORROSION 83, Preprint 9.

11. Final Report on Failure Analysis of Inconel 600 Tubes from OTSG A and B of TMI-1, Battelle-Columbus Laboratories, 6/30/82.

12. J. R. Weeks, "Return to Service of the San Onofre Unit 1 Steam Generators Following the Tube Sleeving Program," Letter Report to S. S. Pawlicki of U.S. NRC, 3/27/81.

APPENDIX A

List of papers by BNL staff originating from laboratory investigations supported (at least partially) by this project. Copies are attached.

1. R. Bandy, R. Roberge, and R. C. Newman, "Low Temperature Stress Corrosion Cracking of Sensitized Inconel 600 in Tetrathionate and Thiosulfate Solutions," Corrosion, in press.

2. R. Bandy, R. Roberge, and R. C. Newman, "Low Temperature Stress Corrosion Cracking of Inconel 600 under Two Different Conditions of Sensitization," Corrosion Science, in press.

3. R. C. Newman and R. Bandy, "Ranking of Environments in Stress Corrosion Cracking," NACE-83 preprints #9.

4. R. C. Newman, R. Roberge, and R. Bandy, "Environmental Variables in the Low Temperature Stress Corrosion Cracking of Inconel 600," CORROSION, in press.

5. R. C. Newman, R. Bandy, and R. Roberge, "Mechanisms of TMI-1 Steam Generator Failures," abstract submitted to ANS-NACE-AIME International Conference on Environmental Degradation of Reactor Materials, Myrtle Beach, SC, August 1983.

6. R. C. Newman, R. Roberge, and R. Bandy in, "Evaluation of SCC Test Methods for Inconel 600 in Low Temperature Aqueous Solutions," paper submitted to Conference on Environment-Sensitive Fracture: Evaluation & Comparison of Test Methods, Washington, DC April 1982, ASTM-STP, in press.