Investigation of Corrosion and Stress Corrosion Cracking in Bolting Materials on Light Water Reactors

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Abstract

Laboratory experiments performed at BNL have shown that the concentration of boric acid to a moist paste at approximately the boiling point of water can produce corrosion rates of the order of several tenths of an inch per year on bolting and piping materials, which values are consistent with service experience. Other failure evaluation experience has shown that primary coolant/lubricant interaction may lead to stress corrosion cracking (SCC) of steam generator manway studs. An investigation was also performed on eleven lubricants and their effects on A193 B7 and A540 B24 bolting materials. H_2S generation by the lubricants, coefficient of friction results and transgranular SCC of the bolting materials in steam are discussed.

1. Introduction

Brookhaven National Laboratory (BNL) was requested by the U. S. Nuclear Regulatory Commission (NRC) to evaluate two different instances of bolting degradation at nuclear power plants. The two modes of degradation investigated were:

1) General corrosion adjacent to leaking gaskets.
2) SCC of steam generator manway studs.

The purpose of this paper is to present the results of these two investigations and an additional laboratory test program which evaluated the effects of various lubricants on common bolting materials.

2. Wastage Corrosion of Bolts

In a number of pressurized water reactors (PWR), gaskets around pumps have sometimes allowed seepage of small amounts of the primary coolant. The water flashes to steam, leaving behind a sludge or paste consisting of the dissolved boric acid and lithium hydroxide from the primary coolant. The most notable incident of this type of degradation occurred at the Fort Calhoun plant in May 1980 [1-5]. At that time during a visual inspection, dripping insulation was noticed on one of the reactor coolant pumps. Inspection of the affected pumps revealed that 6 of 16 studs on one pump and 3 of 16 studs on a second pump had sustained significant corrosion damage; the worst case being one stud which had its diameter reduced to approximately 2.8 cm from its original diameter of 8.9 cm (Figure 1).

Weight loss experiments and a literature review [6-8] were performed at BNL on the corrosion rates of low alloy steel materials in H_3BO_3 and H_3BO_3 + (LiOH or KOH) solutions.

This investigation led to the following general conclusions regarding corrosion of ferritic components by leaking PWR primary coolants containing boric acid.

1) Ferritic material is susceptible to corrosion attack by H_3BO_3 + LiOH solutions up to at least 178°C with the rate of corrosion rapidly increasing up to 100°C, then declining as water is boiled off.

2) A corrosion rate of at least 3 mm/year can be attained at 100°C. This rate is entirely consistent with field experience.

3. Stress Corrosion Cracking of Steam Generator Manway Studs

When steam leaks through a gasket in a PWR, it can also react with any lubricants used to assemble the bolted joint. An occurrence of this type occurred in March 1982 at a maintenance outage of the Maine Yankee Power Plant, where 5 of 20 primary manway studs failed during removal of the (cold leg) primary manway cover from steam generator No. 2.

Figure 2 is a photograph of a "through cracked" stud. The crack was approximately 6.35 cm into the thread area "inserted end" of the stud. The fracture face of the stud was relatively flat and had a black oxide appearance.

A longitudinal section was made of the small end of the cracked stud, perpendicular to the main fracture face (Figure 3). It can be seen in the photomicrograph that numerous secondary cracks are present, initiating at the main fracture (areas A-F). These cracks had some branching associated with them. The major secondary cracks appeared to be generally transgranular in nature. This microstructure was typical for the ASTM A540-B24 steel.

An observed area (on the threaded area) of the bolt had such a high peak in sulfur that a wavelength dispersive spectrographic scan was accomplished to determine if molybdenum was present with the sulfur. It was seen that this particular area was concentrated in Mo which was indicative that a molybdenum disulfide type lubricant was probably used sometime in the service history of the stud.

Previous work performed at BNL on turbine disk steels [9] has shown that reductions of greater than a factor of three on the notched tensile strengths of a low alloy steel in a steam environment can occur when molybdenum disulfide lubricants are present. Bolt cracking incidents attributable to molybdenum disulfide and the products of its hydrolysis have occurred at Arkansas 1, Oconee [10], as well as at Maine Yankee. The analysis concludes that the cracking was environmentally assisted and typical of a SCC phenomenon induced by the lubricant/coolant interaction.

4. Testing of Lubricants and Their Effect on A540 B24 and A193 B7 Bolting Materials

In the first quarter of 1983, the NRC reported [11] 44 distinct instances of bolting degradation at nuclear power plants between October 1964 to March 1982. It was evident from this report that the largest single casue of bolting degradation was SCC. At least two [10, 12] analyses involving SCC of fasteners attributed the failure to a lubricant/moisture interaction which resulted in a corrosive environment.

It was this lubricant/moisture interaction which was of sufficient concern to the Office of Nuclear Regulatory Research (ONRR) of the NRC to provide funding to BNL for an investigation into the effects of lubricants on fastener degradation. This investigation was performed on eleven commonly used lubricants by the nuclear power industry. The investigation included energy dispersive spectroscopy analysis (EDS) of the lubricants, notched-tensile constant extension rate testing (CERT) of bolting materials with the lubricants, frictional testing of the lubricants and weight loss testing of a bonded solid film lubricant.

4.1 EDS Analysis of Lubricants

The lubricants tested were numbered one thru 11 and were classified as follows:

1 Chemically pure MoS_2
2 Commercially available MoS_2 spray
3 Commercially MoS_2 spray (different manufacturer)
4 Commercially MoS_2 spray (3rd manufacturer)
5 Graphite in isopropanol
6 Graphite in ammonia
7 Nickel + graphite lubricant
8 Copper + graphite lubricant
9 Anti-seizing lubricant
10 Nickel based never seizing lubricant
11 Never seizing lubricant

Each of these lubricants was either sprayed or smeared onto carbon blocks and then loaded into a scanning electron microscope (SEM) and subjected to EDS for constituent analysis.

It was observed from the different EDS scans that there is a significant variance in the chemical constituents of even similar type lubricants. The appearance of possibly detrimental elements in lubricant #2 (antimony) and #5 (sulfur) plus the total absence of molybdenum in the moly-lube type lubricant #4 give evidence that independent chemical analysis of lubricants prior to their general use in critical applications would be a prudent course of action.

4.2 Steaming Tests of MoS_2

Three steaming tests were performed in order to determine if a gaseous sulfide could be produced by steaming MoS_2. The tests involved steaming (boiling demineralized H_2O) in a glass dissicator with chemically pure MoS_2 suspended above (no physical contact) the boiling water. The water was boiled for 5 hours during which time any gas produced was vented into cadmium acetate. At the end of the test, the amount of sulfur produced was measured in both the gaseous effluent and the liquid which remained in the dissicator. Each of these tests showed that the steaming of MoS_2 produces hydrogen sulfide (H_2S). The amount of gas produced appears to increase with exposure time as Southwest Research Inc. experiments [13] showed increased yields of H_2S with increased exposure times.

4.3 Frictional Testing of Lubricants

In trying to prevent SCC of bolts, the material and the environment may not be able to be altered, in which case the applied tensile stress (preload) may have to be altered (if design conditions allow) to keep the applied tensile stress below a critical level. Since preload is dependent on the coefficient of friction for a given lubricant, a factor of 2-3 (some lubricants have ranges given) in this frictional coefficient, may throw the applied stress into the critical range of SCC susceptibility.

The coefficient of friction for these lubricants were measured by the "sled and bed" technique (similar to ASTM D 1894-75). Both static and kinetic measurements were made and the lubricants tested both wet and dry, if possible.

The results show that the coefficients of friction, for even similar types of lubricants, vary widely. For example, the static values for lubricants 1-4, (all purportedly molybdenum disulfide-based lubricants), ranged from 0.026 to 0.273 dependent upon manufacturer and condition (wet or dry).

4.4 Notched Tensile CERT

In order to ascertain if bolting materials (specifically A193-B7 and A540 B24 Class 2) would have an environmental interaction with any of the lubricants and steam, constant extension rate tests (CERT) were performed at 100°C and 280°C on 50% notched specimens.

This investigation involved a total of 62 notched tensile CERT. In addition to 44 tests on A193 B7 and A540 B24 materials; 18 tests were conducted on both A193 B7 and A540 B24 C1.2 material coated with a bonded solid film lubricant.

All of the tests were conducted in a stainless steel autoclave. Approximately 1000 ml of demineralized H_2O was added to the autoclave and then the specimen loaded above the water. The temperature of the solution was raised to test temperature (either 100°C or 280°C) through the use of resistance heating coils. After the required temperature was stabilized (approximately 30 minutes) the test pull was commenced. When the lubricant tests were conducted, the lubricants were either sprayed on or brushed onto the notched area of the specimen. All specimens were tested at a strain rate of approximately 5-9 x 10^{-7} sec^{-1}.

The notched tensile tests of the bolting materials showed that both A540 B24 Class 2 and A193 B7 materials are susceptible to a SCC failure in steam at 280°C (Figure 4). The use of MoS_2 or a copper + graphite lubricant appear to enhance this susceptibility to SCC, although these test results are inconclusive.

4.5 Weight Loss Testing of Bonded Film Lubricant

Previously discussed data were accumulated by BNL on an AISI 4135 steel in H_3BO_3 and H_3BO_3 - KOH solutions at 21°C and 60°C. In addition, BNL work on A193-B7 and AISI 4130 material at higher temperatures was plotted to determine if extrapolations were valid. The temperature dependence of the graph (Figure 5) is evident.

A total of nine specimens coated with the bonded solid film lubricant were subjected to the same tests as the bare metal specimens. Five specimens were tested at 100°C (3 for 132.5 hours and 2 for 77 hours). Two specimens were also tested at 178°C for 120 hours and two specimens at 315°C for 130 hours.

It is evident that the corrosion rate at 178°C and 100°C for the solid bonded film lubricant is almost an order of magnitude less than for the bare metal alone, while no additional protection is offered by the lubricant at 315°C.

5. Conclusions

a. The appearance of potentially detrimental elements in the chemical analysis (EDS scans) of the various lubricants clearly shows a marked difference in composition between supposedly similar (e.g. MoS_2 based) lubricants.

b. The steaming tests of the chemically pure MoS_2 show that in the presence of steam (100°C), MoS_2 will hydrolize to form detrimental gaseous sulfides (H_2S).

c. The wide variation of measured coefficients of friction for similar lubricants shows that generalizations of this value for "same type" should not be made.

d. The notched tensile tests of the bolting materials showed that both A540 B24 Class 2 and A193 B7 materials are susceptible to a SCC failure in steam at 280°C. The use of MoS_2 or a copper + graphite lubricant appear to enhance this susceptibility to SCC, although these test results are inconclusive. However, literature references and prior work done at BNL do show that molybdenum disulfide can have a significant material effect on low alloy steels in the presence of moisture.

e. The solid bonded film lubricant weight loss specimens show a marked decrease in metal loss at 100°C and 178°C when compared to previously reported bare metal data. This lubricant protection disappears at 315°C, where the results on previously coated specimens differed little from results on bare metal specimens.

6. Acknowledgements

The author wishes to especially thank Dr. J. Woodward for her helpful discussions and contributions to this research. The author also wishes to thank R. Sabatini for the SEM/EDS work, L. Gerlach for the testing, A. Cendrowski and D. Horne for the hardness testing, O. Betancourt for her typing skills. The author also wishes to thank E. Woolridge (ONRR-USNRC) for his patience and support and Dr. J. Weeks for his constant support.

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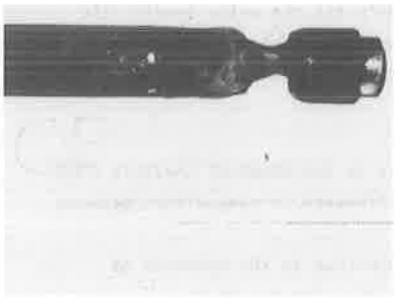

Figure 1 Photograph of the worst case bolt at Ft. Calhoun (Boric Acid Wastage).

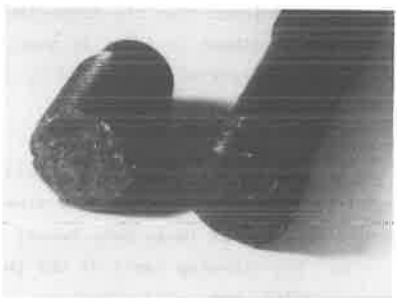

Figure 2 Photograph of "through cracked" stud from Maine Yankee Plant (Lubricant SCC).

Figure 3 Photomicrograph of cracking exhibited by the Maine Yankee Stud (Lubricant SCC).

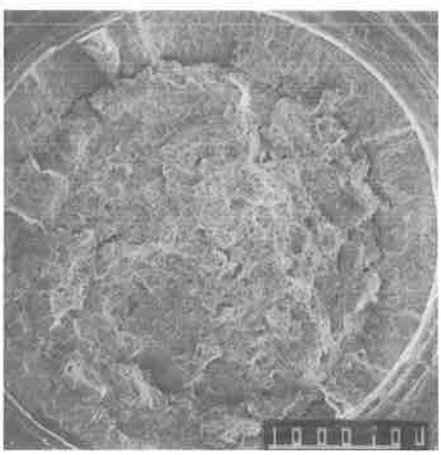

Figure 4 SEM photo of transgranular SCC evident on a A540 B24 bolt CERT in H_2O at 280°C.

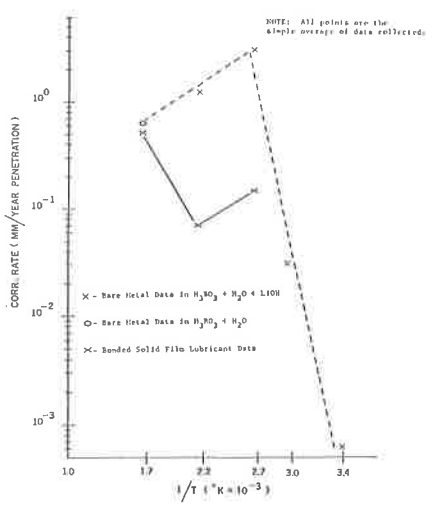

Figure 5 Graphical representation of weight loss experiments for the low alloy steels tested.