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Corrosion Degradation of Steam Generators in Korea

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ABSTRACT

Six pull tube examinations from Korean nuclear power plants have been carried out by Korea atomic energy research institute(KAERI) and some foreign laboratories since the first commercial operation of Kori unit 1 in 1978. A total of 15 tubes were extracted that exhibited different types of failures such as pitting, outer diameter stress corrosion cracking (ODSCC), primary water stress corrosion cracking (PWSCC), intergranular attack (IGA), etc. Pitting of plant A was related with the high copper dissolved from condenser material, Cl^- and high dissolved oxygen. Transgranular SCC of plant B seemed to be related to the lead compound. ODSCC and IGA in plant A were connected with caustic environments in the crevices. PWSCC in plant A and plant C originated from the inherent characteristics of the materials, which were not properly thermally treated. After the failure analyses, a performance of nondestructive testing was evaluated based on the destructive metallographic examination, and some counter measures such as material change, inhibitor injection, molar ratio control, and temperature reduction operation were suggested.

KEY WORDS: Steam generator, failure analysis, pitting, stress corrosion cracking, ECT.

INTRODUCTION

Since the commercial operation of Kori unit 1 in 1978, 16 nuclear power plants have been operating in Korea. Various corrosion problems such as pitting, stress corrosion cracking (SCC), and wear have been reported in steam generators; in one case, a plant replaced its steam generators (SGs) due to the severe corrosion problems in 1998 after 20 years of operation. Korea atomic energy research institute(KAERI) and some foreign laboratories have carried out 6 destructive examinations on the pull out tubes from the SGs of Korean nuclear power plants. Reliability of defect sizing with eddy current testing (ECT) during In service inspection (ISI), is of great concern to the utility companies since SG tube repair relies entirely on the defect estimation by the ECT during maintenance periods. Improvement of the reliability of nondestructive examination during ISI is one of the most important objectives of pulled tube examinations.

A shape of the defect, relationship between nondestructive examination signal and destructive sizing on the defect were obtained, and various countermeasures were suggested depending on the water chemistry and material characteristics. Impurities detected on the secondary side of the tube were Na^+, Cl^-, SO_4^{2-} and Fe_3O_4, Fe_2O_3, etc. A cause of the corrosion can be elucidated by analysis of the deposits. Water chemistry guidelines can also be made or modified by doing the deposit analysis, and operation efficiency of a steam generator is improved.

This paper addresses the feature of the failures and countermeasures to suppress the corrosion damage of steam generators of Korean nuclear power plants (NPPs) by analysis of the sludge and defects of the pulled tubes.

EXPERIMENTAL

Defect tubes pulled out from the NPPs during the ISI based on eddy current test (ECT) signals were transferred to the hot laboratory of KAERI. Detailed nondestructive examinations using the eddy current method, and radiography were performed on the tubes in the hot cell, and then destructive metallographic examinations were carried out. The types and sizes of defects were characterized, and collected sludge near the defect tubes were also analyzed. The carbide size and its distribution were analyzed by scanning electron microscopy (SEM), transmission electron microscopy(TEM) and optical microscope.

Like other destructive analyses[1], corrosion products were also analyzed using methods such as X-ray diffractometry (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), Auger electron spectroscopy (AES), Ion chromatography (IC), and Atomic absorption spectroscopy (AA). It is hard to surmise impurity concentration in crevices, which is a main cause of corrosion of the tubes. Therefore information on the corrosion product in the sludge pile or crevices is an important clue to understand the corrosion process at a specific region. The physical properties of the sludge were analyzed mainly by X-ray diffraction (XRD) [2].

RESULTS and DISCUSSION

Pitting

The SG tubing material of plant A, which has been operating commercially since 1978, was low temperature mill annealed alloy 600. During the ISI in 1988, 4 tubes from the SG A and B were extracted and examined by KAERI and B & W (Babcock and Wilcox)[2]. Defect morphology was analyzed by radiography, SEM, and deposits were examined by energy dispersive X-ray spectrometer (EDX), XRD, AA, IC, AES, etc.

Radiography and optical microscope photos showed that pits were formed around the top of the tubesheet (TTS) on the secondary side of the tubes. Maximum penetration depth was 94 % of the tube wall (TW) on a tube of SG B. Fig. 1 is one of the tubes having pitting in plant A. Besides the main alloying elements (nickel, chromium and iron), other impurities such as oxygen, aluminum, silicon, sulfur, calcium, titanium and copper, were detected inside the pit. The band type precipitates were formed at the mouth of the pit, and were mainly composed of copper. The condenser tube material of the plant was copper alloy before it was replaced with titanium alloy in 1988; hence the condenser tubes were considered to be the main source of copper in the pit. Metallic copper and a little copper oxide (Cu_2O) were detected in the hard scale and sludge collected from the tube surface. Iron in the form of magnetite (Fe_3O_4), and metallic nickel were also detected in the sludge. Other relevant information is that occasional condenser leakage had been reported, and hideout return tests showed that the Cl^- concentration in the crevices had been up to $10^3 \sim 10^4$ times higher than in the secondary bulk water. This implies that Cl^- from seawater had been introduced into the secondary side of the SG.

Acceleration factors of the pitting were Cl^-, sulphate, dissolved oxygen, sludge. A Cl^- induced acidic environment in the crevices and oxides like Cu_2O increase corrosion potential of materials in the reducing environment of the secondary water

Following these analyses, some countermeasures were suggested as follows: (1) suppression of impurities from condenser leaks such as Cl^-, sulphate, (2) reduction of dissolved oxygen, (3) deposit removal using chemical cleaning or sludge lancing, (4) installation of a water chemistry control program.

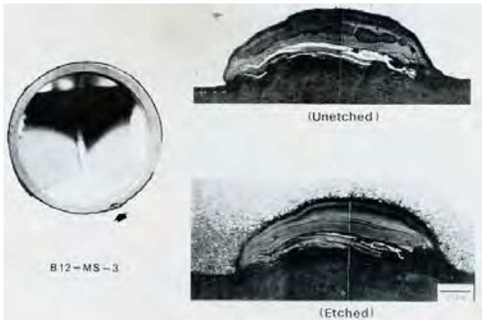


Fig.1 Cu band inside the pit of SG tube from plant A

Another analysis on the pits of plant A was carried out in 1992. A pit of 44 % of TW was found with IGSCC inside the pit formed on the outer surface of the tube. Corrosion products in the pit contained silicon, nickel, aluminum, barium, iron, lead and sulfur, etc. Metallic copper was detected on the outer surface of the tube. Copper and iron were the main elements in the sludge collected from around the tube. Lanced sludge had 22 % copper and 50 % iron, and hard scale, around the pulled tubes, was found to contain 46% copper and 28% iron. The composition of the hard scale of another sampled area is shown in Fig. 2 [3]. The copper concentration at the tube surface was about 80%. This shows that the chemical cleaning solution employed did not remove this scale, totally, and considerable amounts of copper still remained on the outer tube surface.

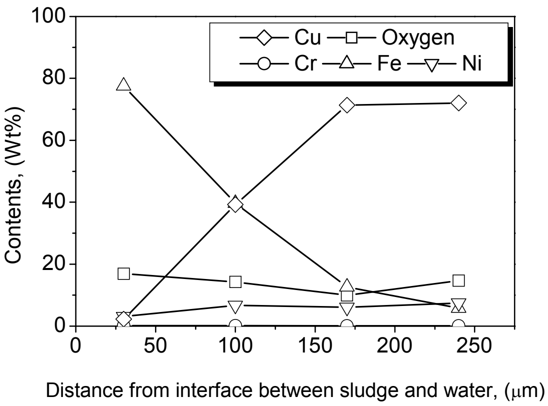


Fig. 2 Analysis of scale collected from plant A

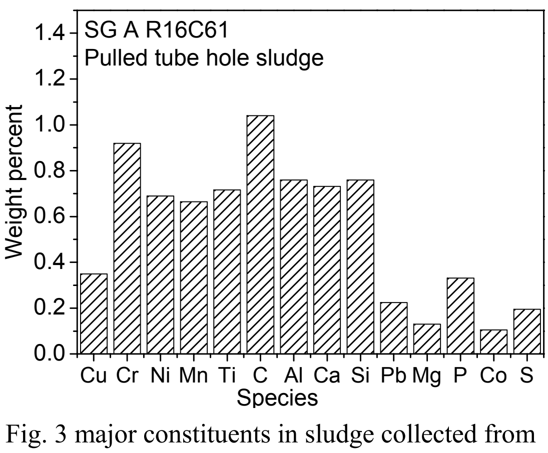


Fig. 3 major constituents in sludge collected from plant B

Secondary-Side Stress Corrosion Cracking

Steam generators of plant B which are equipped with thermally treated alloy 600 tubes have been operating since 1983. Two tubes of the SG B showing defects at the top of tube sheet were extracted in 1990[4]. The criteria in selecting the pulled tubes were penetration depth over 40 %, presence of dent indications and the depth of the sludge pile, etc. Stereomicroscope was used to show the outer surface of the tube, and a 35 mm camera was used to examine the roll transition. Outer diameter of the tubes was measured to determine tube ovality at the transition area. For the destructive examination, SEM/EDX, ICPS, X-ray fluorescence, IC, XRD were used.

Aluminum, silicon, sulfur and chloride ions were detected at the surface of the tube; the sulfur seemed to come from organic compounds such as ion exchange resins. Lead was also detected in the sludge, and its maximum concentration on one specimen was 5.55%. A lead peak was also shown at the crack tip by EDX analysis as shown in Fig. 3. A total lead content of 2250 ppm was detected in the sludge collected from one of the extracted tubes. Silicon and lead were even detected on the fractured surface. The deposit was mainly composed of nimite, magnetite and nickel oxide (NiO) as shown in Table 1[4]. The nimite is a mineral chlorite, which is soluble in acidic water. Thus the fact that nimite was detected in the sludge means that the crevice between the tube and the sludge was alkaline. ESCA revealed that the copper was a form of copper oxide (Cu_2O), and the nickel was a form of nickel oxide (NiO). Metallic iron was also found around the dented tube. (Table 1)

Table 1 Plant B S/G tube OD deposit analysis by XRD[4]

Compound	Wt% of crystalline materials
Nimite*, $(Ni, Mg, Al)_6(Si, Al)_4O_{10}(OH)_8$	65 %
Magnetite, (Fe_3O_4)	17 %
Nickel oxide, (NiO)	9 %
Talc, ($Mg_3Si_4O_{10}(OH)_2$)	9 %
Cu_2O	Trace

The types of defect detected in plant B were a mixture of denting, PWSCC and ODSCC. In the case of ODSCC, the cracks were aligned in the tube axial direction, and penetrated 23 % of the TW. An inner diameter circumferential PWSCC crack penetrated 14 % of the TW. As indicated before, 2250 ppm lead was detected in the sludge around the failed tube, and the crack propagated with a transgranular mode as shown in Fig. 4. This kind of transgranular stress corrosion cracking (TGSCC) has been reported in other plants such as St. Lucie-1, Calvert Cliffs-1, Farley-2, where lead was considered as the root cause of cracking[5]. Therefore the TGSCC in plant B was also concluded to be related with lead pollution.

Countermeasures suggested to reduce the threat of cracking were sludge removal using sludge lancing, pressure pulse cleaning, and suppression of impurities ingress such as oxygen and ionic impurities. An examination of the role of lead on stress corrosion cracking (PbSCC) of alloy 600 was proposed.

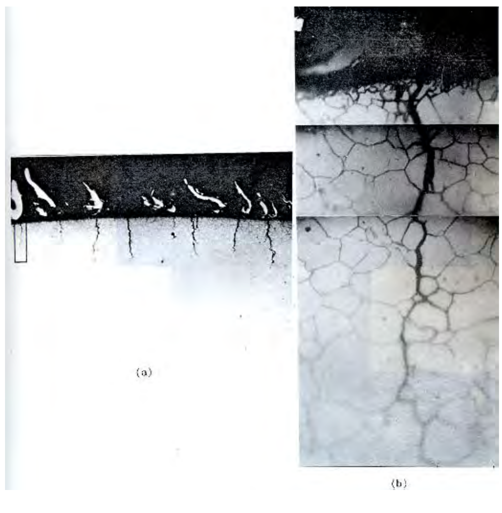


Fig. 4 TGSCC detected in plant B

Pulled tubes from plant A, which were examined in 1988 due to a pitting problem, showed ODSCC and leakage from SG tubes in 1994. According to ECT measurements during the ISI, the pits did not propagate so much but PWSCC was detected on 50 tubes, and 296 significant signals of ODSCC were obtained from two SGs. Two tubes showing ODSCC were extracted and analyzed using SEM, optical microscopy, and Wavelength Dispersive X-ray spectroscopy (WDX) in 1995[6].

Three OD axial cracks were observed between 18 and 23 mm above the top of the tube sheet (TTS+18•23mm), and five other axial cracks at around TTS+50•72mm. The cracks initiated and propagated with an intergranular mode and some intergranular attack (IGA) was also found at the TTS. The deepest crack penetrated through the tube wall. WDX analysis on the sludge collected from around the tube showed that large amounts of copper had accumulated on the surface of the tube; the maximum content was 75 weight percent. The high copper seemed to change into copper oxide during a periodical tube inspection period, which is known to increase the corrosion potential of the tube. Hideout return tests indicated that the cracking environment was probably caustic[6].

As potential countermeasures to this ODSCC, crevice flushing, TiO_2 injection, suppression of dissolved oxygen, power reduction operation, and Na/Cl molar ratio control were suggested[6].

Primary Water Stress Corrosion Cracking

As described above, mill annealed alloy 600 tubes of plant A have suffered from pitting and ODSCC. When the new type of defect, PWSCC, was detected during the ISI after the chemical cleaning in 1990, 22 tubes in SG A, and 26 tubes in SG B had to be sleeved. In order to characterize the behavior of the PWSCC defects and verify the new Motorized Rotating Pancake Coil (MRPC) inspection method, which has been applied since 1992, three tubes were pulled out in 1992[3].

Multiple circumferential cracks, which penetrated up to 56 % of the TW, were found inside the tube. Also, multiple axial cracks up to 6.8 mm long, and 100 % of the TW were observed on the inner wall of the tube.

In alloy 600, the best microstructure resistant to most forms of IGSCC is reported to have a semi-continuous carbide decoration at its grain boundaries[7,8]. In this case, many carbides in the microstructure of the pulled tubes were within the grains and this microstructure seemed to render the tubes susceptible to PWSCC. After this failure analysis, shot peening and a reduction of primary water operating temperature were recommended as countermeasures in order to suppress PWSCC.

The steam generators of plant C have been operating since 1988. The tubing material is thermally treated alloy 600, and the tubes were mechanically full depth rolled to the top of tube sheet and kiss rolled a short distance above it. The kiss roll length of the tubes was shot peened after the 5th cycle of operation in 1994. 793 tubes from the higher temperature region of hot leg side were examined by MRPC in 1993, and a lot of the axial cracks inside the tube were detected at the roll transitions. Two tubes were extracted from SG C in 1994 and examined by EdF[9], The objectives of the examinations were to determine the failure mode and to predict the crack propagation rate. To achieve these goals, the failure behavior was compared with the French experience using similar material. In addition to that, the chemical composition, grain size and mechanical properties were measured based on the heat number of each tube. Finally, the apparent growth of the longest cracks per tube inspected between 1993 and 1994 was calculated. The crack length and depth determined from the MRPC data and destructive analysis data obtained after a burst test were also compared.

The average grain size was consistent with ASTM number 9 for both tubes indicating that the grain is rather small. Others have reported that tubes with small grain size (>ASTM 8) were susceptible to PWSCC[10,11]. High tensile strength (>717 MPa), high carbon (>0.018 %), high silicon and low chromium were other indicators of potentially high cracking susceptibility[11]. Average crack growth rates in plant C were estimated to be 0.5 mm/year to 1.3 mm/year depending on the tubes, which were on the lower boundary of those observed previously for mill annealed tubes.[9]

There was no ODSCC indication by ECT on the outer surface of the two tubes examined. One tube had 2 longitudinal cracks of which the maximum length and depth were 6.86 mm and 99% TW respectively. This tube had a leak pressure of 42.2 MPa and a burst pressure of 65.4 MPa. The other tube had 3 longitudinal cracks of which the maximum length and depth were 5.88 mm and 93% TW respectively, and it showed a leak pressure of 31.5 MPa and a burst pressure of 59.2 MPa. These are large margins of safety compared to the worst-case scenario. The test results are summarized in Table 2.

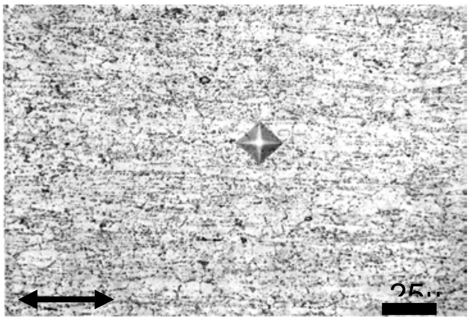
Table 2 Details of cracks in plant C inspected in 1994[9]

Tube	Carbon %	Burst test under water	crack number	length, mm	Angular position, ^{o}	maximum depth, mm	Minimum ligament, mm
L02C45	0.033	Leak at 422bar(6120psi)	1	6.86	274	1.26	0.075
			2	0.39	284	0.11	
L04C33	0.044	leak at 315bar(4565psi)	1	5.88	60	1.18	0.08
			2	2.93	94	0.82	
			3	2.39	322	0.58	

Remedial measures were suggested such as defining plugging criterion based on crack length, nickel plating, preventive sleeving and primary water temperature reduction.

Despite the shot peening carried out in plant C in 1994, the ECT voltage of the tubes continued to increase, and primary to secondary coolant leakage was reported from SG B and SG C in 1997. A total of 2067 defect signals were collected from the three steam generators of this plant in 1998. Of these, 986 tubes were sleeved, and two defected tubes plus a sound tube were extracted and analyzed in 1999[12]. In this analysis, crack lengths and depths were compared with the ECT data. The ECT history on the two defected tubes was studied, and the effect of shot peening was evaluated based on the ECT results of each ISI. The microstructure in terms of carbide morphology was also studied using TEM.

The alloy 600 tubes of unit C were mill annealed for 2 minutes at 960 ^{o}C-1000 ^{o}C, and thermally treated for 12 hours at 700 ^{o}C–730 ^{o}C to develop carbides at the grain boundaries. However, the microstructural analysis showed that many carbides were inside the grains rather than at the grain boundaries, as shown in Fig. 5. This microstructure has been



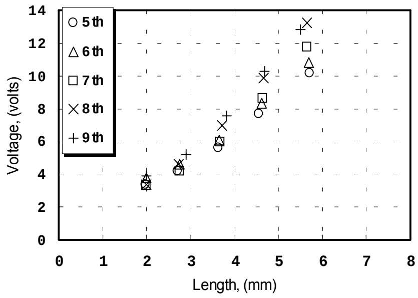


Fig. 7 Crack length saturated around 6 mm in plant C

Fig. 5 Intragranular carbide of the tube(plant C)

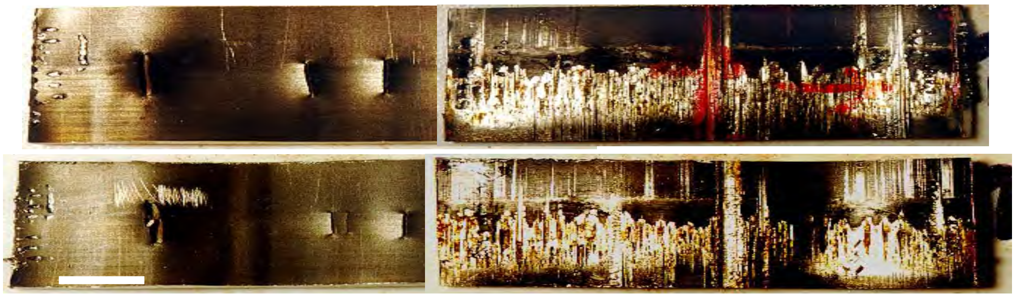


Fig. 6 PWSCC developed at similar axial location at the plant C

classified as type II or type III as suggested by EdF[11], which are rather susceptible to PWSCC. The carbide microstructure seemed to be related with too high a carbon content (0.035%) to show any beneficial effect of the 700 ^{o}C thermal treatment. That is to say, the mill anneal temperature was too low to dissolve the total carbon into the solid solution prior to the thermal treatment.

Inside diameter cracks 2.5mm ~ 6mm long were located at the top of the tube sheet and penetrated 72 % to 100 % of the TW as shown in Fig. 6. Another tube, which was considered as a sound tube from the ISI, had a crack 2.1 mm long and 84 % wall penetration. This means that there were likely to be many undetectable cracks on the tubes of the SG at the Kiss roll transition.

Average crack length and EC voltage variations from whole defective tubes in each ISI are presented in Fig. 7. The crack length was about 4 mm at the 4th ISI, and it increased to 7 mm at the 7th ISI, but it did not increase very much afterwards until the 9th ISI. EC voltage, which is closely related to crack opening and depth, developed steadily from 6 volts at the 4th ISI to 15 volts at the 9th ISI. It was known that crack length tended to saturate around 6 mm regardless of which tube was examined. However, the depth increased continuously, and the crack mouth became wider every year as indicated in Fig. 7. Thus shot peening had a good influence on the suppression of crack length, but it was not so beneficial on the prevention of crack deepening.

It was also observed that there were PWSCC sensitive areas in particular regions of the tube bundle depending on the SG concerned. This distribution was considered to arise not only from the coolant distribution, but also from the material characteristics of the tube heats.

The main cause of the PWSCC in plant C was a susceptible microstructure. Consequently, the recommendations suggested after this analysis were as follows: Tubes having large increases in EC voltage should be repaired. Detailed inspection was required of the PWSCC sensitive regions depending on the particular steam generator. An allowable leak rate limit of 10 l/min for plant C was also recommended.

SUMMARY

One of the important things to elucidate the cause of corrosion in steam generators is to analyze the corrosion product formed during their operation. As of year 2001, a total of 15 tubes were pulled out from three Korea nuclear plants. Soft and hard sludge collected around the defected tubes were analyzed using EDX, ICPS, XRD etc.

Corrosion products in the defect areas were also examined. Hide out return test results were used to determine the cause of the corrosion. ECT reliability was evaluated by comparing defects from destructive analysis with the ISI data.
-Pitting at plant A was related with a high copper amount, which came from the condenser material. Cl^- and high dissolved oxygen ingress were other causes of corrosion.
-TG SCC in plant B seemed to be related to the presence of lead. ODSCC and IGA in plant A appeared to be related to the caustic environments in the crevices.
- PWSCC of plant C originated from the inherent characteristics of the tube materials, which in our opinion were not properly thermally treated.
- Depending on the various corrosion types; impurity reduction, dissolved oxygen reduction, inhibitor addition, molar ratio control, primary water temperature reduction, shot peening, and nickel plating were recommended as remedial measures.

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