STEAM GENERATOR LOCAL WATER CHEMISTRY AND SCC OF AUSTENITIC STEEL

K. Šplíchal, A.Brožová, Vl. Krhounek, M. Ruščák, * K. Pochman

ABSTRACT

The titanium stabilized austenitic steel similar to the type of 321 is sensitive to the stress corrosion cracking under horizontal steam generator operating condition. SCC was observed under crevice corrosion parameters and has resulted in the transgranular or intergranular cracking at the both, components primary collectors and heat exchange tubes. The crevice environment is characterized by aggressive impurities and "non aggressive" compounds. Sulfates and chlorides as aggressive species and silicates and alumino-silicates as "non aggressive" species on the other hand are present in significant amount in the crevice environment under operating condition. Local water chemistry parameters were evaluated with MULTEQ Code. As input data the measured operational values of local and bulk environments have been used. The determined parameters were compared with the results of thread hole environment analyses and tube surface investigations respectively. Results of the hideout return profiles measurement showed an increase of sulfate concentration by one order of magnitude. Increase of the chloride content was not been observed, its value remains at operation levels. Examination of surface layers showed the preferential accumulation of sulfates, silicates and alumino-silicates in the deposit at tube support plates and in thread holes comparing relative to free span surfaces. The content of species in the water and deposits and the crystallographic structure of deposits correspond to MULTEQ results.

Rising displacement tests were carried out with 0.5T CT specimens at a temperature 275 ^{0}C in the model water environment which simulated the crevice conditions. The experimental values are presented for crack growth rate versus stress intensity factor.

Corrosion damage of the titanium stabilized austenitic steel is likely to be determined by the presence of sulfates and chlorides and other aggressive agents, as Cu. It is supposed that other decisive factor is the presence of silicate-base compounds which impacts pH values and take part in the corrosion processes indirectly.

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INTRODUCTION

Corrosion damage of WWER 440 steam generators takes place in secondary circuit regions under crevice conditions. In most cases the stress corrosion cracking (SCC) is initiated on the tube outer surface at tube support plates and in threaded holes of the primary collector flanges. Such damage to the tubes results in the need for tube plugging. This is aimed at reducing the possibility of unstable crack propagation and the consequential release of radioactivity. Excessive damage to threaded holes can lead to the need to replace the upper part of a primary collector.

CORROSION DAMAGE

The WWER 440 steam generators are horizontal structures with two cylindrical primary collectors for primary water inlet and outlet. The heat exchange tubing, tube support plates (TSP) and primary collectors are made of titanium-stabilized austenitic stainless steel, similar to AISI 321.

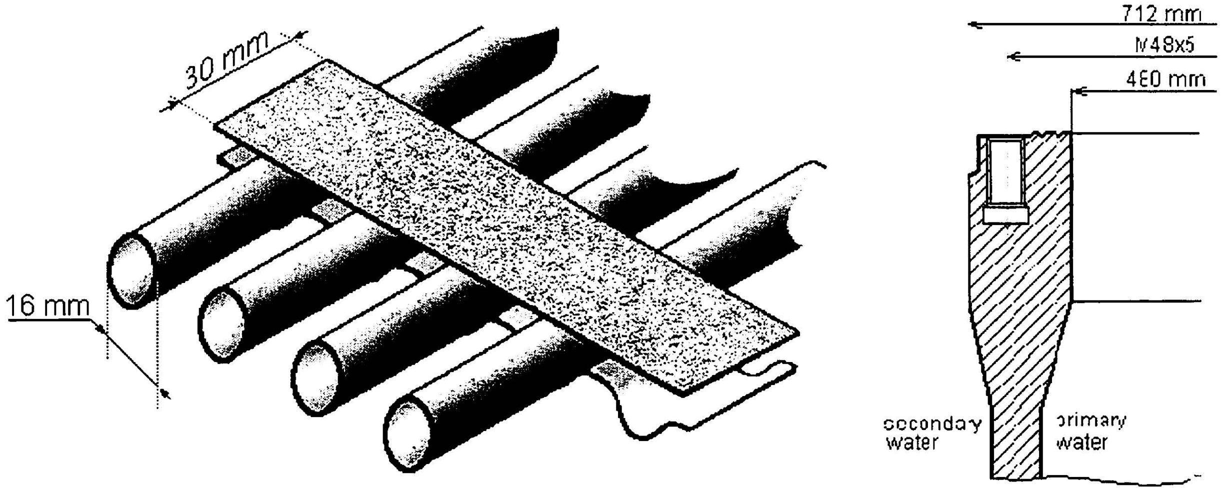

Fig.1. WWER steam generator tube support plate and primary collector thread hole

Corrosion damage of tube outer surfaces indicated on the Fig. 1 and primary collectors thread holes (TH) is affected by the local parameters of the secondary environment, the surface condition, the deposit layers, as well as the thermal and mechanical stresses. Individual steam generators and nuclear power plant (NPP) units exhibit a different extent of SCC of their tubes. About 90 to 95 % of defects indicated by the eddy current method take place at tube support plates, in most cases in hot sections of the tubes (Fig.2). The SCC of tubes results in formation of cracks, preferentially oriented in the longitudinal direction and initiated either directly on the outer surface or in the lower part of corrosion pits. The principal mechanism of crack propagation is intergranular stress corrosion cracking (IGSCC).

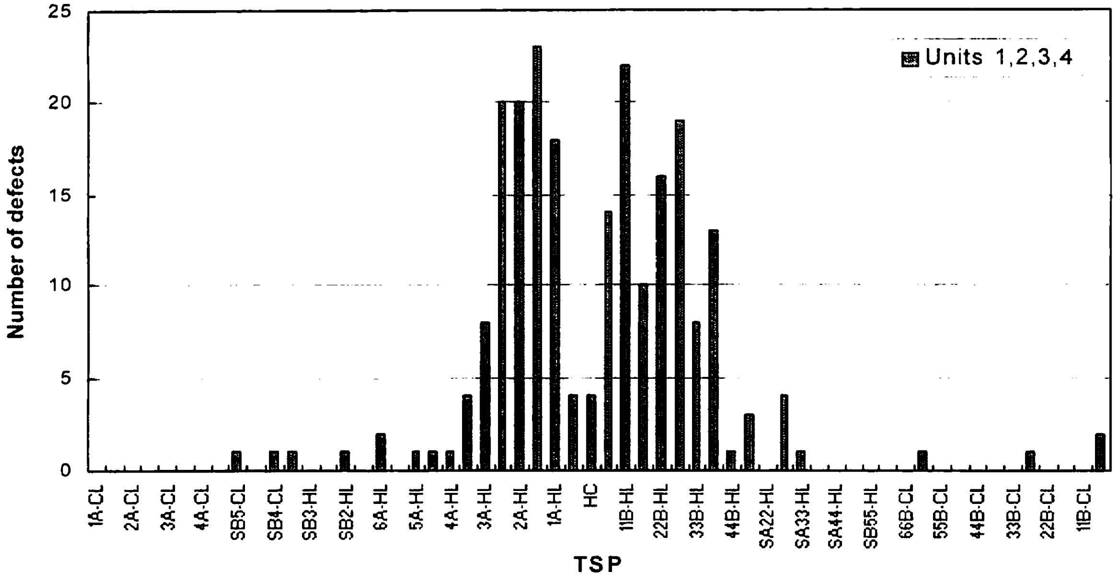

Fig.2. Number of defected tubes of 4 NPP units in dependence on the TSP location.
HL - hot leg, CL-cold leg, HC-hot collector

Corrosion damage of thread holes has been observed only in one of the primary collectors of our NPP steam generators. The main factor influencing the SCC is the effect of mechanical stresses which are determined by the extent of prestresses attained predominantly during tightening of the collector head bolts. The damage was initiated at stress concentrates in the lower part of the thread hole. The crack propagation through the collector wall was largely transgranular with crack branching, and the fracture mechanism was quasi-cleavage of the austenitic matrix. Intergranular cracks were detected only in isolated regions, especially at the tip of a branched crack.

WATER ENVIRONMENT

Evaluation of the bulk parameters is based on measurements carried out on the feedwater as well as on the continuous or periodical blowdowns. The local parameters are determined from measurements on hideout returns (HOR) and from analyses of deposits formed at tube support plates and on the free surface of heat exchange tubes. In the case of primary collectors, analyses of the water environment and of deposits removed from thread holes are employed [1].

Heat exchange tubes

Hideout return profiles for chlorides, sulfates, sodium, calcium and SiO_2 and the equivalent ratio $[Na]/[Cl]+[SO_4]$ are shown in Fig.3, together with a plot of the decreasing primary coolant temperature. As follows from the HOR data, sulfates, SiO_2 and calcium are preferentially released during the steam generator cooldown, their contents changing by one or two orders of magnitude; the change of the sodium content in this case was not as pronounced. However, in some steam generators an increase of sodium content by an order of magnitude has been observed. No increase of the chloride content has been seen, its level remained at operating values below 15 μg/kg.

The composition of the concentrated environment at second tube support plate was evaluated using the MULTEQ Code (Version 2.22, Database V 2.77, Option 4 - remove precipitates true) [2]; in this way the environment of a crevice was determined from the hideout return profiles. A bulk water temperature of 260 °C and maximum temperature in the crevice of 297 °C were used. The value of $5.6x10^8$ was found as the maximum values of the concentration factor. The calculated compositions of the water environment in neutral and alkaline regions are shown in Tab. 1 for concentration factors of $4,8x10^4$ and $1,3x10^8$ respectively together with pH_T values.

Table 1. Calculated composition of TSP environment [mol/kg].

Concentration factor	pH_T	Na	Ca	Mg	Cl	SO4
4.8×10^4	7.7	3.7×10^{-3}	1.0×10^{-6}	1.5×10^{-11}	1.7×10^{-5}	1.5×10^{-5}
1.3×10^8	10.0	1.3	3.9×10^{-10}	6.6×10^{-15}	4.5×10^{-2}	5.0×10^{-1}

Concentration factor	pH_T	$Na SO_4$	Na_2SO_4	H_3SiO_4	H_2SiO_4	$Al(OH)_4$
4.8×10^4	7.7	9.0×10^{-5}	2.0×10^{-5}	5.6×10^{-4}	2.3×10^{-8}	2.9×10^{-5}
1.3×10^8	10.0	2.0×10^{-1}	1.1	4.5×10^{-1}	3.0×10^{-1}	9.5×10^{-7}

It is assumed that TSP with simple crevice geometry and loose deposits in crevices would not enable concentration of solutions whose concentration factor is higher than $1x10^8$. The corresponding calculated $pH_{(T)}$ values would then be lower than 10. As follows from the table, the composition of a concentrated solution is characterized by a higher content of sulfates, chlorides, sodium and silicate based compounds. This is in agreement with the above mentioned HOR results with the exception of chlorides. Other components such as Ca, Mg are present to a considerably lesser extent.

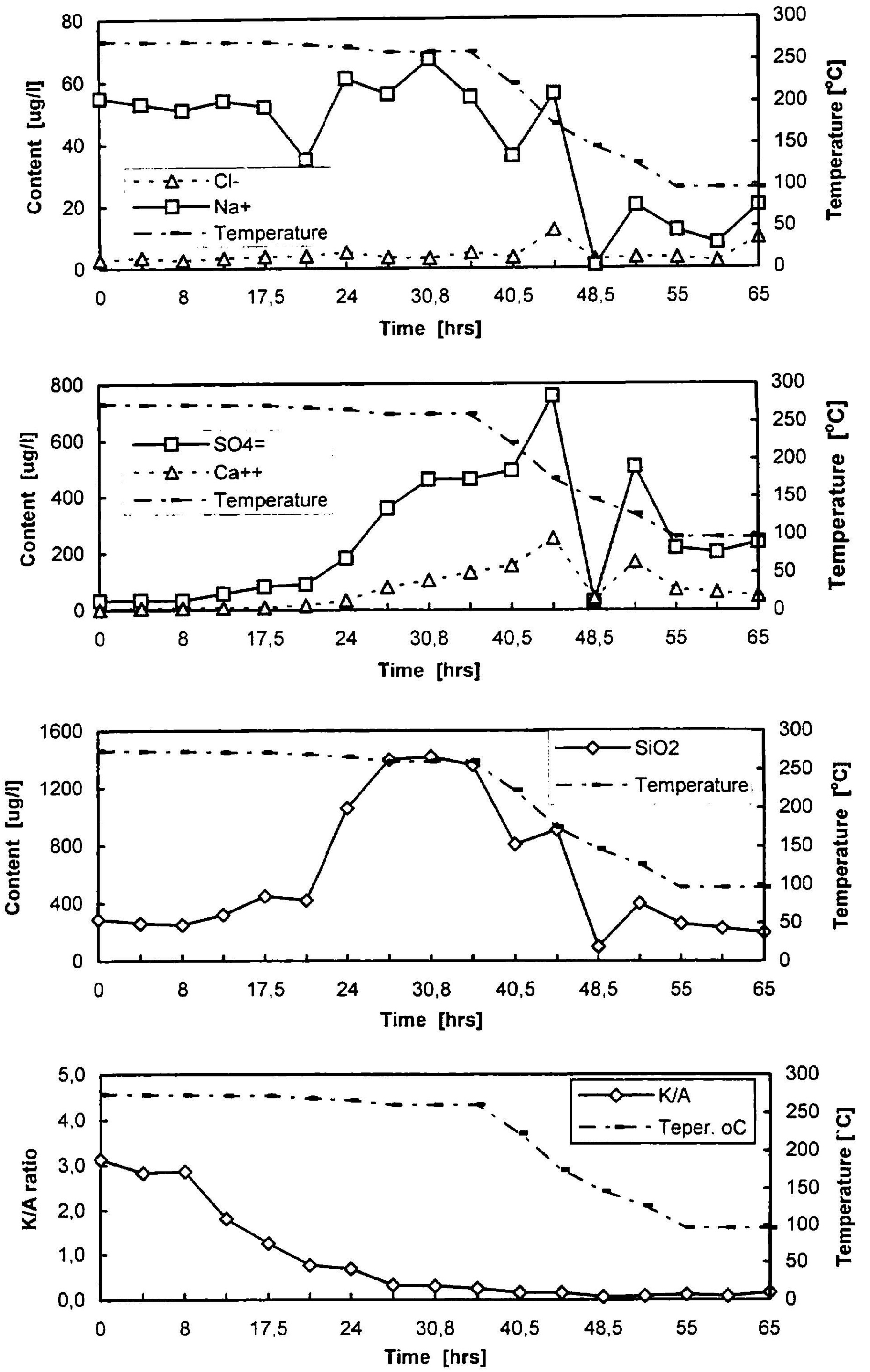

Fig.3. Hideout return profiles of Na, Cl, SO_4 , Ca, SiO_2 and time dependence of the equivalent ratio K/A.

Thread holes

The presence of water environment in thread holes is primarily due to repeated boilover of the bulk water from a region close to the hot collector and or to flooding of steam generators during the unit shutdown or during a hydraulic test. Characterization of the water environment in the former case is based on chemical parameters of the blowdown water during operation and in the latter case on the composition of hideout return at the temperature, when flooding of steam generators takes place. The water samples taken from thread holes after opening of the hot collector head were analyzed and the results obtained are listed in Table 2, together with the hideout return and blowdown data. The table shows the concentrations of species in thread hole environment and blowdowns, the total cumulative hideout return and the equivalent ratio $[Na]/[Cl]+[SO_4]$. The comparison of the species contents in the thread hole water and blowdown (BD) proved the significant difference for compounds of SO_4, SiO_2, and Ca. The ratio $SO_{4(TH)}$ / $SO_{4(BD)}$ is by three or one order of magnitude higher than the ratio $SiO_{2(TH)}$ / $SiO_{2(BD)}$ and ratio $Ca_{(TH)}/Ca_{(BD)}$ respectively. These results indicate different conditions of solute concentration processes and precipitation of compounds.

Table 2. Bulk and local water parameters

SG	Environment	Solute concentration [mg/kg], [g] *					Equivalent ratio
		SO4	Cl	Ca	Na	SiO2	
A2	Thread hole water	25.3	4.9	3.9	12.9	0.42	1.1
A4		9	6.5	2.6	5.8	0.78	0.9
C3,4,6		17.9	2.0	1.3	18.8	0.32	2.1
B2	Total cumulative hideout return*	56.8	1.06	27.9	52.0		3.6
C4		75.0	1.3	21.2	12.1	175.0	0.3
D1		46.3	1.6	20.0	8.1	137.5	0.4
D2		58.9	2.7	31.4	13.0	201.2	0.4
A 1- 6	Blowdown water	0.015	0.013	0.020	0.059	0.086	3.6
B 1- 6							
C 1- 6							
D 1- 6							

The water chemistry parameter in thread holes was evaluated by means of the MULTEQ Code - Option 1. Concentration factor values calculated for the temperature difference between the collector wall (275 °C) and bulk water (259 °C) were determined in the range up to 10^5, corresponding pH values in the range of 6.0 to 10 . As input values for Na, Cl, SO_4 and SiO_2 average contents of species in blowdowns were used. Calculated pH values do not change even if the initial sulfate content attains the value of 0.050 mg/kg which is permissible for blowdown water. The composition of concentrated environment is consistent with the TSP results. However, determination of the amount and concentration of TH medium under operating conditions is difficult in view of the fact that these parameters are affected significantly by the non-uniform boilover, the different bulk water composition in proximity of the hot collector and undefined conditions for water evaporation from thread holes.

DEPOSITS AND SURFACE LAYERS

For investigation deposits were isolated both from the tube surface and the lower part of thread holes. Deposits taken from the thread holes and TSP regions contained preferentially Si, Ca, Mg, Na and Al. In the case of regions at the tube support plates Cu, Pb, Ba and Zn were also established. The deposits on free tube surfaces consisted mainly of magnetite and spinels with varying contents of Ni, Zn, Mn and Cr, as well as Cu and Ti. To a much smaller extent silicates and other impurities such as Ca and sulfates were present. Crystallographic structures of the compounds correlate well with the results of MULTEQ calculations, taking into consideration a relatively large variability in the composition of silicate-based compounds (Tab. 3).

Table 3. SEM-EDS analyses and X-ray diffraction analyses

TH	**Chemical composition [wt. %]**								
	Si	Al	Ca	Mg	Na	Fe	Ni	O	Al/Si
	6.9	18.3	3.1	2.7	2.9	3.8	17.4	47	2 ; 4.5
	X - ray diffraction analysis								
TH	$CaAl_2SiO_6$; $CaAl_2 SiO_8$; $(MgFe)_2Al(SiAl)_2O_5(OH)_4$; $(FeCr)_2O_3FeO$; Al(OOH)								
	MULTEQ Code evaluation								
TH	$CaSiO_3$; $Ca_2Mg_5Si_8O_{22}(OH)_2$; nephelin								
TSP	$CaSiO_3$; SiO_2 ; $Ca_2Mg_5Si_8O_{22}(OH)_2$; $Na_2Si_2O_5$; albit								

The fracture face of samples cut from the collector flange was analyzed after opening of the cracks by the application of a tensile force. Oxide films of 4 to 8 μm in thickness, present on the fracture surface, were subject to an AES analysis carried out at the mouth, middle and tip of a

23,5 mm long crack. The results are summarized in Tab. 4. and an example of Auger in-depth composition profile in the region of the crack middle is presented in Fig.4.

Table 4. AES analysis of oxide layers on the fracture face [A.C. %]

AES location	Fe	Cr	Ni	Zn	S	Si
Crack mouth	deplet.	deplet.	enrich.	< 2	cca 1 *	
Crack middle	deplet.	deplet.	enrich.	< 2	cca 1 *	
Crack tip		deplet.	enrich.	cca 2	cca 1 $^{+}$	7

* up to a maximum depth 1500 Ă ; + up to a maximum depth 300Ă

Oxide layers observed in these three locations exhibited an identical trend, although the processes of depletion and enrichment seem to be more rapid at the mouth and the middle of the crack than at its tip. Oxide layers at the mouth and the middle of the crack were depleted of chromium and iron and enriched with nickel, whereas at the tip the layers were depleted of chromium and enriched with nickel, as observed at the middle and the mouth, but did not exhibit any iron depletion. The chromium depletion could be associated with the presence of a non-acidic environment. Sulfur was determined along the whole length of the crack, silicon only at its mouth.

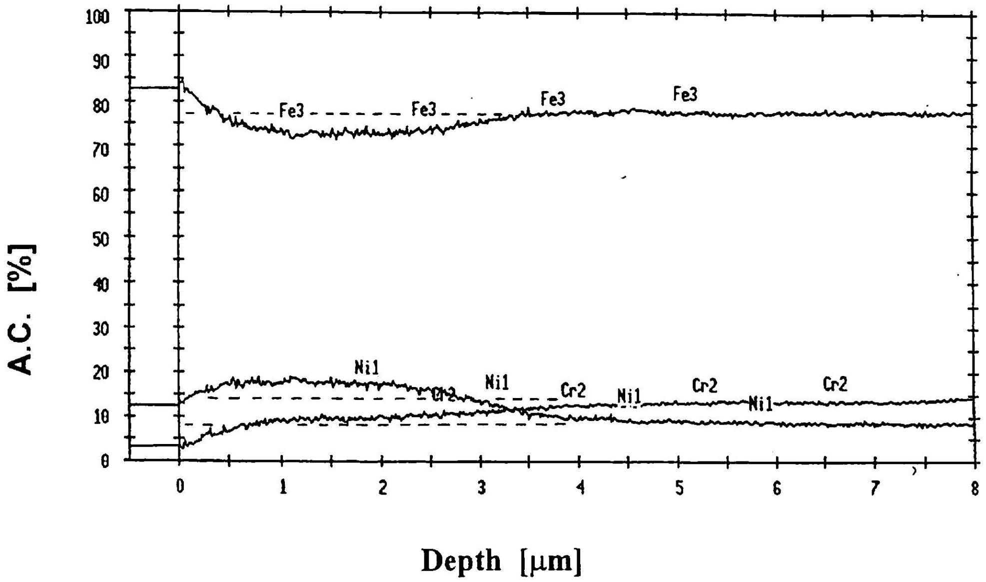

Fig.4. AES depth profile in the crack middle, Ni, Cr, Fe normalized to 100 % .

SCC TESTS

Material from a removed part of a collector was subjected to corrosion-mechanical tests carried out in a model corrosion environment at a temperature of 275 °C. To measure the threshold value K_{ISCC} and the rate of crack propagation by stress corrosion cracking the rising displacement test (RDT) has been chosen. Pre-cracked 0.5T compact tension (CT) test specimens with side grooves were employed. The crack length was measured by reversed dc potential drop method. The specimens were loaded in the corrosion environment with stroke rates ranging from 0,5 to 500 μm/h. During the test the applied force, displacement and potential were recorded, the latter being used to calculate the crack increment. The composition of the model environment was as follows: SO_4 15 mg/l, Cl 5 mg/l, Ca 40 mg/l, SiO2 300 mg/l, Al 40 mg/l.

As a result of the tests J-da curves were obtained for the different stroke rates. The threshold value J_{ISCC} was determined as the minimum value in the plot of the initiating J_i against the stroke rate (see Fig. 5). The calculated K_{ISCC} value then equaled 18 MPa.m$^{1/2}$ [3]. The threshold value K_{ISCC} has been obtained for the state of plane deformation.

As evidenced earlier, the rate of the crack propagation during a RDT test has two additive components a mechanical component $(da/dt)_{MECH}$ and a component resulting from the corrosion environment. The rate of the corrosion crack propagation $(da/dt)_{ENV}$ was determined by subtracting the mechanical component $(da/dt)_{MECH}$ from the measured total rate $(da/dt)_{TOT}$ according to the relation [4]:

$$(da/dt)_{ENV} = (da/dt)_{TOT} - (da/dt)_{MECH}$$

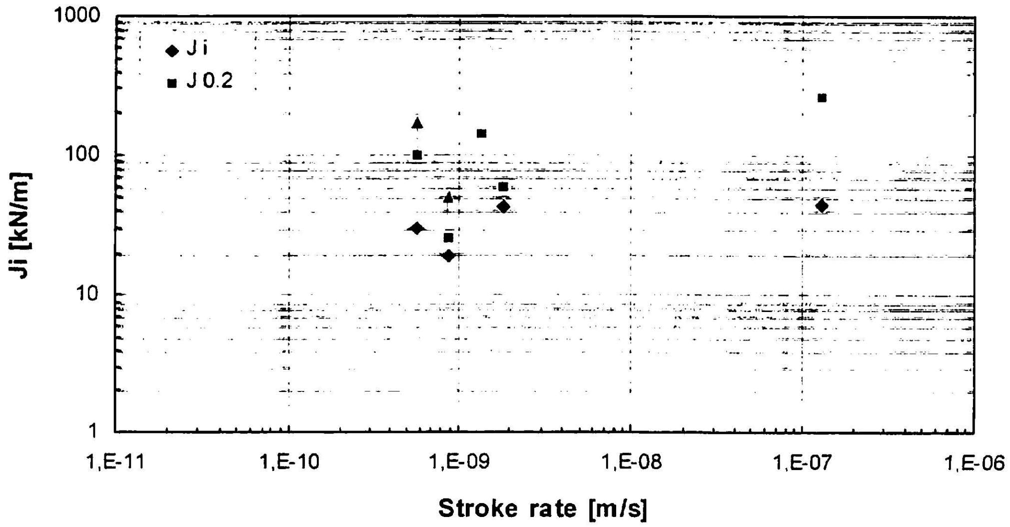

Fig.5. Effect of the stroke rate on the initiating value J_i and the conventional value $J_{0.2}$ of the J-integral

The resulting dependence of $(da/dt)_{ENV}$ values on the stress intensity factor K is shown in Fig. 6. The results of RDT tests on the collector material are in a good agreement with the data obtained by the method of active constant loading for the identical steel of a forged nozzle (Fig.7) [3]. In practice the threshold value K_{ISCC} could be lower by a factor of 3 to 4 for shallow cracks with prevailing plain stress [5].

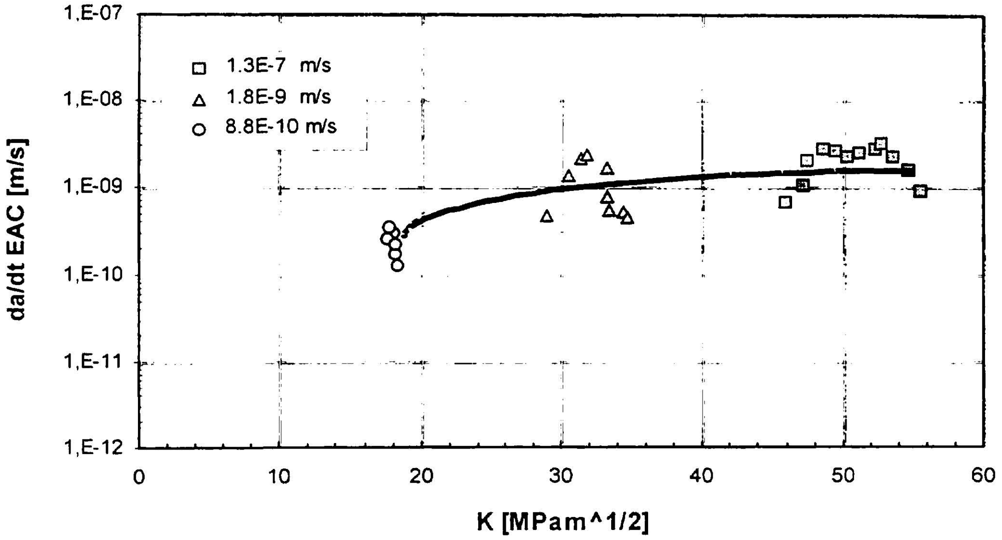

Fig.6. The corrosion crack propagation rate in dependence on the stress intensity factor K

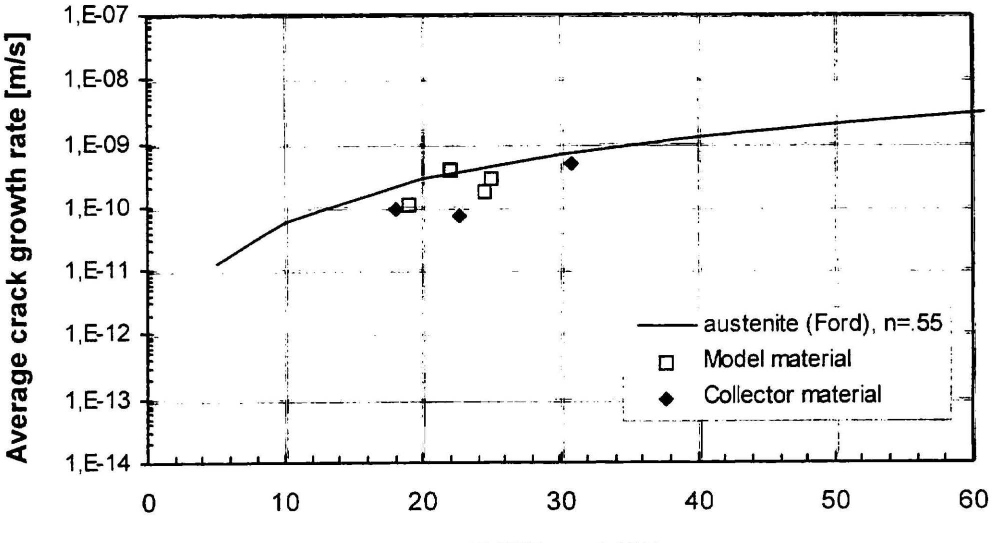

Fig.7. Comparison of the results of tests on the model material and the material of the operated collector [4,6]

DISCUSSION

Corrosion damage of the titanium stabilized austenitic steel is likely to be determined by the presence of sulfates and other aggressive agents, such as Cu, Cl, Na or possibly Pb. The other impurities such as Fe, Mn, Zn, SiO_2, Ca, Mg and Al, can affect the oxidation-reduction processes, the attainment of the resulting pH values and the compactness of the oxide films. It is assumed that one of the significant factors is the presence of silicate-base compounds. These compounds take part in the corrosion processes, indirectly, by their sorption properties and their buffering capacity [7,8]. Results of the hideout return regions show an increase by one or two orders of magnitude in the concentration of sulfates, sodium and silicate based compounds in the blowdown water. No increase has been observed, in the hideout return regions, in the chloride content which remained at the operational levels, of under 15 µg/kg. Average pH values in blowdowns of the 24 NPP steam generators range from 8 to 9. From the results obtained, it can be concluded that the pH_T values in the crevice environment could be lower than 10. This is as suggested by the results of investigation of the deposit compactness and the AEC analysis, and, to a certain degree, by the pH of the water sampled from the thread holes.

Using the MULTEQ Code the water chemistry parameters have been evaluated. Composition and crystallographic orientation of the precipitates are approximately in agreement with the results of analyses of deposits formed at tube support plates and in thread holes. The calculated tube support plate and threaded hole water chemistry parameters indicate enhanced contents of sulfates, chlorides, sodium and silicates. This corresponds well with the composition of water sampled from the thread holes. However, the values are not in agreement with the observed easy release of chlorides from crevices on the tube surface. This is likely to be controlled by uncompacted deposits and the simple geometry of crevices. Another factor influencing the acidity or alkalinity of the environment is calcium. According to the MULTEQ Code, calcium occurs in the form of silicates. The presence of $CaSO_4$ in the thread hole deposits has not been evidenced either experimentally or by calculating the composition of precipitates. Precipitation of $CaSO_4$ predicted by MULTEQ could take place only if the calcium content in the bulk water increased by two orders of magnitude.

The fracture mechanism of the crack propagation is transgranular for collector thread hole conditions characterized by lower value of the concentration factor of cca $8x10^5$ and higher level of mechanical stresses. The crack propagation is intergranular for tube support plate conditions characterized by higher value of the concentration factor of $5x10^8$ and level of mechanical stresses [9].

In the model environment of the thread hole, the collector material was evidently sensitive to stress corrosion cracking. The K_{ISCC} value of 18 $MPa.m^{1/2}$ and the SCC plateau rate of the crack propagation, ranging from 9.10^{-10} to 3.10^{-9} m/s, have been determined. These values have been obtained for an environment corresponding to the water sampled from the thread holes, in terms of chloride and sulfate contents,. That is to the concentration level of 10^2 or 10^3 in comparison to the bulk water.

CONCLUSIONS

The stress corrosion cracking and pitting in steam generators have been predominantly located in the tube support plate and in the primary collector thread hole crevices. Both transgranular and intergranular cracks have been observed. The local water chemistry differs from its bulk parameters, as demonstrated by deposits in the crevice region, hideout return profiles, as well as by chemistry of the water removed from the primary collector thread holes. Experimental investigation of the crack initiation and growth has been carried out to assess the in-service inspection results as well as the life prediction of steam generator components.

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DISCUSSION

Authors: K. Šplichal, A. Brozová, V. Krhounek, M. Ruscák, K. Pochman, Nuclear Research Institute Rez plc. and NPP Dukovany

Paper: Steam Generator Local Water Chemistry and SCC of Austenitic Steel

Questioner: J. Gorman

Question/Comment:

What is the cracking morphology and the postulated causes?

Response:

Fracture morphology of crack propagations is intergranular for heat exchange tubes and transgranular for primary collector thread hole area. That was determined for titanium stabilized austenitic steel. Corrosion damage of this type steel is likely to be determined by the presence mainly of sulfates and other aggressive agents, such as Cu, Cl, Na or possibly Pb.