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TECHNICAL BASIS FOR HYDROGEN-WATER CHEMISTRY--LABORATORY STUDIES OF WATER CHEMISTRY EFFECTS ON SCC*

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TECHNICAL BASIS FOR HYDROGEN-WATER CHEMISTRY--LABORATORY STUDIES OF WATER CHEMISTRY EFFECTS ON SCC*

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SUMMARY

The influence of different impurities, viz., oxyacids and several chloride salts, on the stress-corrosion-cracking (SCC) of sensitized Type 304 stainless steel (SS) was investigated in constant-extension-rate-tensile (CERT) tests in 289°C water at a low dissolved-oxygen concentration (<5 ppb). Cyclic loading experiments on fatigue precracked fracture-mechanics-type specimens of this material and Type 316NG were also performed at 289°C in low-oxygen environments with and without sulfate at low concentrations. In these experiments, the crack growth behavior of the materials was correlated with the type and concentration of the impurities and the electrochemical potentials of Type 304 SS and platinum electrodes in the simulated hydrogen-water chemistry environments.

CERT results indicate that the crack growth rate of these steels is largely controlled by the rate of cathodic reduction of oxyanions [e.g., SO_4^{2-}, NO_3^-, PO_4^{3-}, ClO_4^-, AsO_4^{3-}, which have a central atom (S, N, P, Cl, and As) that can assume different oxidation states] as well as by cations (e.g., Cu^{2+}, Cu^+) that can undergo similar reduction (to metallic Cu). The observation that BO_3^{3-} or Zn^{2+}, Mg^{2+}, or Na^+ (added as chloride salts), which cannot undergo cathodic reduction like the other species, does not promote SCC in the low-oxygen environments provides further evidence in support of this mechanism. As in the case of dissolved oxygen, the reduction of these species couples with anodic dissolution or oxidation at the crack tip following film rupture. Since cathodic reduction of the various species occurs simultaneously, these impurities contribute to crack growth in a manner determined by their concentrations and the relative rates of the reduction reactions. The CERT results also indicate different threshold concentrations for each of the species; that is, when their concentrations are below a specific level, which may depend on the strain rate, neither transgranular nor intergranular cracking occurs in high-temperature water.

Long-term fracture-mechanics crack growth experiments on Types 304 and 316NG SS specimens were performed within the range of simulated normal and hydrogen-water chemistries at 289°C under low-frequency, high-R loading at moderate stress intensities. The results of these experiments show that crack growth in both materials ceases after a transition from the normal BWR environment with impurities (200-300 ppb dissolved oxygen plus 100 ppb sulfate) to low-oxygen water (~5 ppb) at this impurity concentration. Crack growth resumes after a transition to the normal environment (with sulfate), or when the sulfate level increases from 100 ppb to 1 ppm in the low-oxygen environment containing 1.4 ppm dissolved hydrogen.

The information suggests that better characterization of water quality, through measurement of the concentrations of individual species (SO_4^{2-}, NO_3^-, Cu^{2+}, etc.) coupled with measurements of the corrosion and redox potentials at high temperatures will provide a viable means to monitor and ultimately improve the performance of BWR system materials.

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CERT AND CYCLIC LOADING EXPERIMENTS IN SIMULATED HWC ENVIRONMENTS

- Feedwater Chemistry Control (O_2, H_2, Impurity Conc., pH, Cond.)
- Monitor Influent and Effluent O_2, Cu
- Monitor ECP of Type 304 SS and Pt
- Crack Growth by Compliance Method
- Fracture Morphology by SEM

INFLUENCE OF IMPURITIES ON SCC OF SENSITIZED TYPE 304 SS IN 289°C WATER AT A LOW DISSOLVED-OXYGEN CONCENTRATION

OXYACIDS

Acid[A] $XO_N(OH)_M$	Conc. (ppm)	Cond. (μS/cm)	pH at 25°C
H_2SO_4	0.1 - 100	0.9 - 800	5.8 - 2.7
HNO_3	0.7 - 63	4.5 - 390	5.1 - 3.0
H_3AsO_4	1.0 - 70	14.0 - 410	4.5 - 3.0
$HClO_4$	0.1 - 80	0.6 - 315	6.3 - 3.1
H_3PO_4	0.5 - 180	2.1 - 610	5.7 - 2.9
H_3BO_3	1.0 - 10,000	0.1 - 7.4	6.4 - 4.9

[A] General Formula Where X Denotes the Central Atom, e.g., S, N, As, Cl, P, and B.

CATIONS

Salt[B]	Me^{Z+} Conc. (ppm)	Cond. (μS/cm)	pH at 25°C
$CuCl_2$	0.5-10.0[C]	2.4-42	6.0-5.7
$CuSO_4$	0.1-5.0[C]	0.8-22	6.0-5.7
NaCl	7.1	42	6.3
$ZnCl_2$	9.2	38	5.9
$MgCl_2$	3.4	37	6.2

[B] Anion Concentrations Range From ~0.1 to 10 ppm.

[C] Feedwater Copper Concentrations; Effluent Values Were Lower by a Factor of 5.

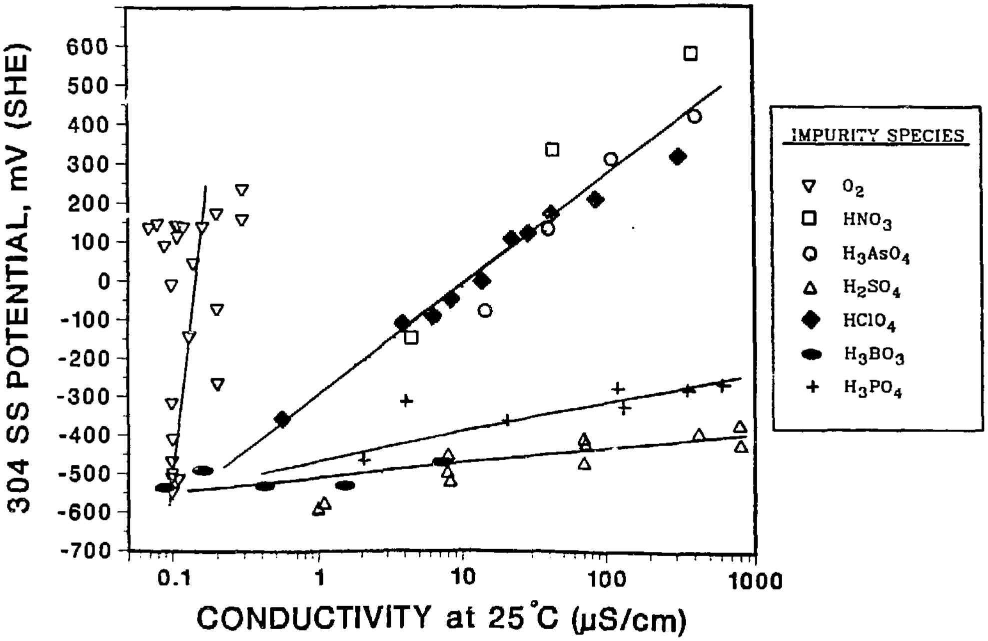

Fig. 3 Effect of Dissolved Oxygen and Several Oxyacids at a Low Dissolved-Oxygen Concentration (< 5 ppb) on the Electrochemical Potential of Type 304 SS in CERT Experiments at 289°C.

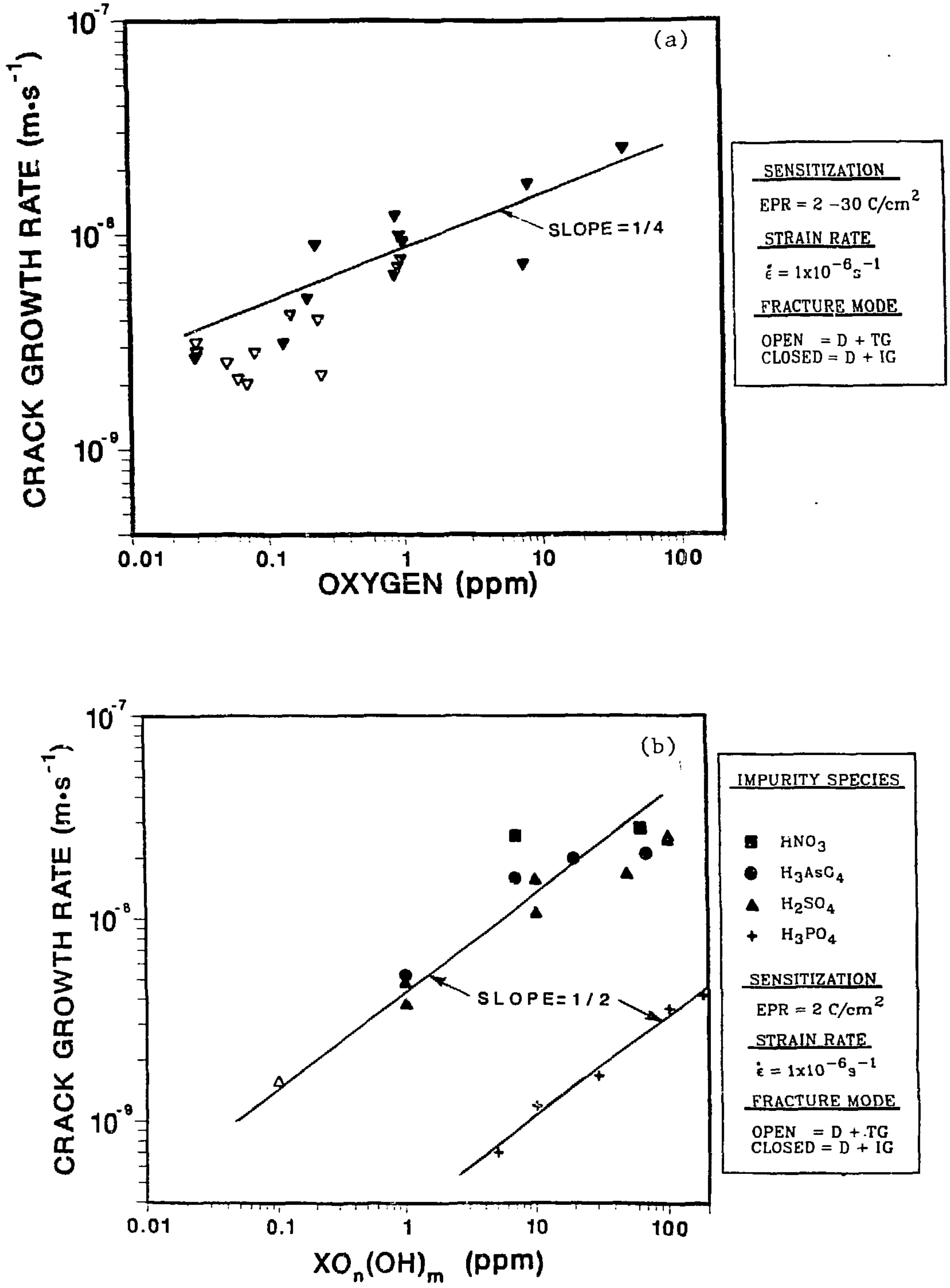

Fig. 4 Dependence of the Crack Growth Rate of Sensitized Type 304 SS CERT Specimens on the Concentration of (a) Dissolved Oxygen, and (b) and (c) Several Oxyacids at a Low Dissolved-Oxygen Concentration in 289°C Water.

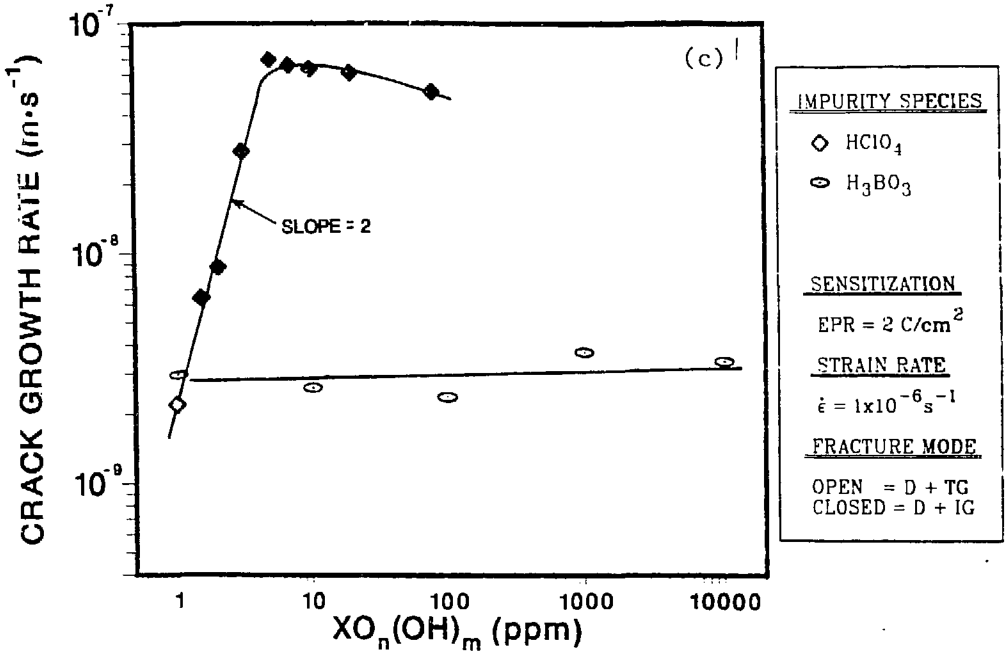

Fig. 4. (Contd.)

CRACK TIP PROCESSES

Anodic Dissolution: $Fe \rightarrow Fe^{z+} + ze^-$

Hydrolysis: $Fe^{z+} + zH_2O \rightarrow Fe(OH)_z^{z-1} + zH^+$

CATHODIC REACTIONS

Dissolved Oxygen: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Proton Reduction: $2H^+ + 2e^- \rightarrow H_2$

Impurity Anions:

$SO_4^{2-} + H_2O + 2e^- = SO_3^{2-} + 2OH^-$

$NO_3^- + H_2O + 2e^- = NO_2^- + 2OH^-$

$AsO_4^{3-} + 2H_2O + 2e^- = AsO_2^- + 4OH^-$

$PO_4^{3-} + H_2O + 2e^- = PO_3^{3-} + 2OH^-$

$8ClO_4^- + 2H_2O + 4e^- = 8ClO_3^- + 4OH^- + 3O_2$

Fig. 5 Anodic and Cathodic Processes Involved in SCC.

ANODIC DISSOLUTION

$$CGR(m\cdot s^{-1}) = \frac{MI_A}{z\rho F} \approx 3.7 \times 10^{-7}\ I_A(amp/cm^2) \qquad \text{(Faraday Law)}$$

$$CGR \approx [Fe^{z+}] = \frac{K_{EQ}}{[e^-]^z} \qquad \text{(Mass Transport)}$$

CATHODIC REACTIONS

SPECIES	EQUILIBRIA	CONCENTRATION DEPENDENCE
O_2	$K_{EQ} = \frac{[OH^-]^4}{[e^-]^4[O_2]}$	$\frac{1}{[e^-]} = \frac{K_1\ [O_2]^{1/4}}{[OH^-]}$
SO_4^{2-}	$K_{EQ} = \frac{[OH^-]^2}{[e^-]^2}\left[\frac{SO_3^{2-}}{SO_4^{2-}}\right]$	$\frac{1}{[e^-]} = \frac{K_2}{[OH^-]}\left[\frac{SO_4^{2-}}{SO_3^{2-}}\right]^{1/2}$
NO_3^-	$K_{EQ} = \frac{[OH^-]^2}{[e^-]^2}\left[\frac{NO_2^-}{NO_3^-}\right]$	$\frac{1}{[e^-]} = \frac{K_3}{[OH^-]}\left[\frac{NO_3^-}{NO_2^-}\right]^{1/2}$
AsO_4^{3-}	$K_{EQ} = \frac{[OH^-]^4}{[e^-]^2}\left[\frac{AsO_2^-}{AsO_4^{3-}}\right]$	$\frac{1}{[e^-]} = \frac{K_4}{[OH^-]^2}\left[\frac{AsO_4^{3-}}{AsO_2^-}\right]^{1/2}$
PO_3^{3-}	$K_{EQ} = \frac{[OH^-]^2}{[e^-]^2}\left[\frac{PO_3^{3-}}{PO_4^{3-}}\right]$	$\frac{1}{[e^-]} = \frac{K_5}{[OH^-]}\left[\frac{PO_4^{3-}}{PO_3^{3-}}\right]^{1/2}$
ClO_4^-	$K_{EQ} = \frac{[OH^-]^4[O_2]^3}{[e^-]^4}\left[\frac{ClO_3^-}{ClO_4^-}\right]^8$	$\frac{1}{[e^-]} = \frac{K_6}{[OH^-][O_2]^{3/4}}\left[\frac{ClO_4^-}{ClO_3^-}\right]^2$

Fig. 6 Dependence of Stress Corrosion Crack Growth on the Concentration of Species Involved in Cathodic Reduction Reactions.

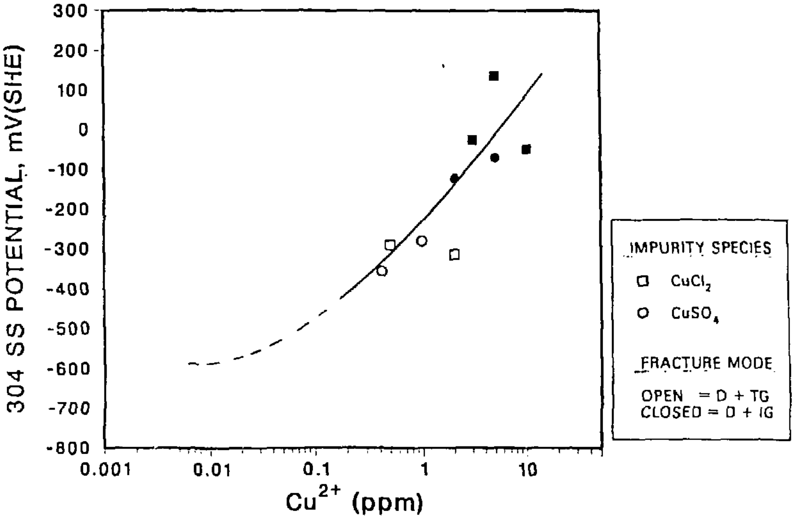

Fig. 7 Effect of Cupric-Ion Concentration in Low-Oxygen Feedwater on the Electrochemical Potential of Type 304 SS in CERT Experiments at 289°C.

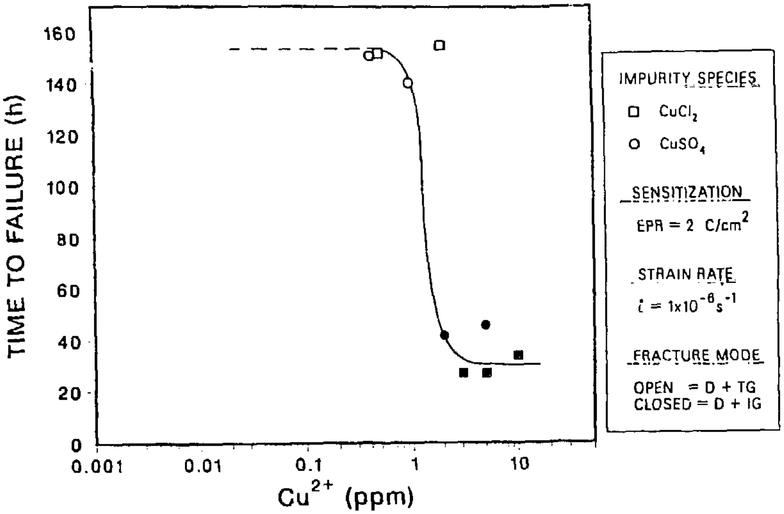

Fig. 8 Effect of Cupric-Ion Concentration in Low-Oxygen Feedwater on the Time to Failure of Sensitized Type 304 SS Specimens in CERT Experiments at 289°C and a Strain Rate of 1 x 10^{-6} s^{-1}.

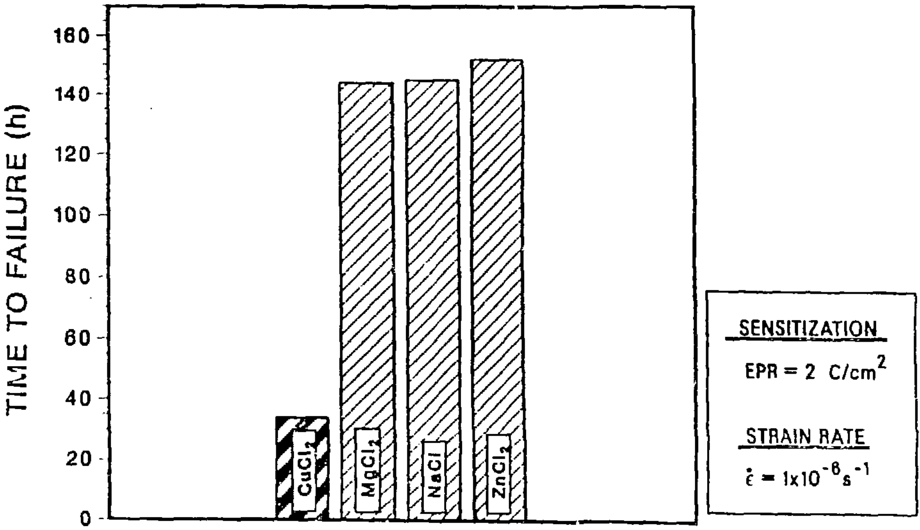

Fig. 9 Effect of Several Salts at a Chloride Conc. of 10 ppm in Low-Oxygen (<5 ppb) Water on the Time to Failure of Sensitized Type 304 SS CERT Specimens at 289°C.

THRESHOLD IMPURITY CONCENTRATIONS FOR SCC OF
SENSITIZED TYPE 304 SS IN CERT EXPERIMENTS[A]
AT 289°C IN LOW-OXYGEN (<5 PPB) WATER

IMPURITY SPECIES	FRACTURE MODE TRANSITIONS		
	DUCTILE	TGSCC	IGSCC
	ANION CONCS. (PPM)		
H_2SO_4	<0.1	<1.0	>1.0
HNO_3	<1.0	-	>5.0
H_3AsO_4	-	-	>1.0
$HClO_4$	-	<1.0	>1.5
H_3PO_4	<1.0	<100	>200
H_3BO_3	-	<10,000	-
	CATION CONCS. (PPM)[B]		
$CuCl_2$	<2.0	-	>3.0
$CuSO_4$	<0.1	<1.0	>2.0
NaCl	-	<7[C]	
$ZnCl_2$	<10[C]		
$MgCl_2$	-	<4[C]	

[A] CERT EXPERIMENTS AT A STRAIN RATE OF 1×10^{-6} s^{-1}.

[B] FEEDWATER COPPER CONCENTRATIONS; EFFLUENT VALUES WERE LOWER BY A FACTOR OF 5.

[C] CHLORIDE CONCENTRATION OF 10 PPM.

LABORATORY STUDIES ON SCC IN SIMULATED HWC ENVIRONMENTS

SUMMARY

CERT EXPERIMENTS

- Oxyacids with Central Atoms That Assume Different Oxidation States Can Cause SCC of Stainless Steels in 289°C Water at Low-Oxygen Concentrations

- Threshold Concentrations for IGSCC Differ for Various Species; Sulfate Is Deleterious at Low Levels (<1 ppm) and Low ECP Values

- ECP of Type 304 SS Increases Significantly with Concentration of Cu and Various Oxyanions in Low-Oxygen Water, with the Exception of SO_4, PO_4, and BO_3

- Cupric or Cuprous Ions in 289°C Water, above a Threshold Concentration, undergo Cathodic Reduction to Metallic Copper and Promote IGSCC of Sensitized Type 304 SS; Other Cations at a High Chloride Level Do Not

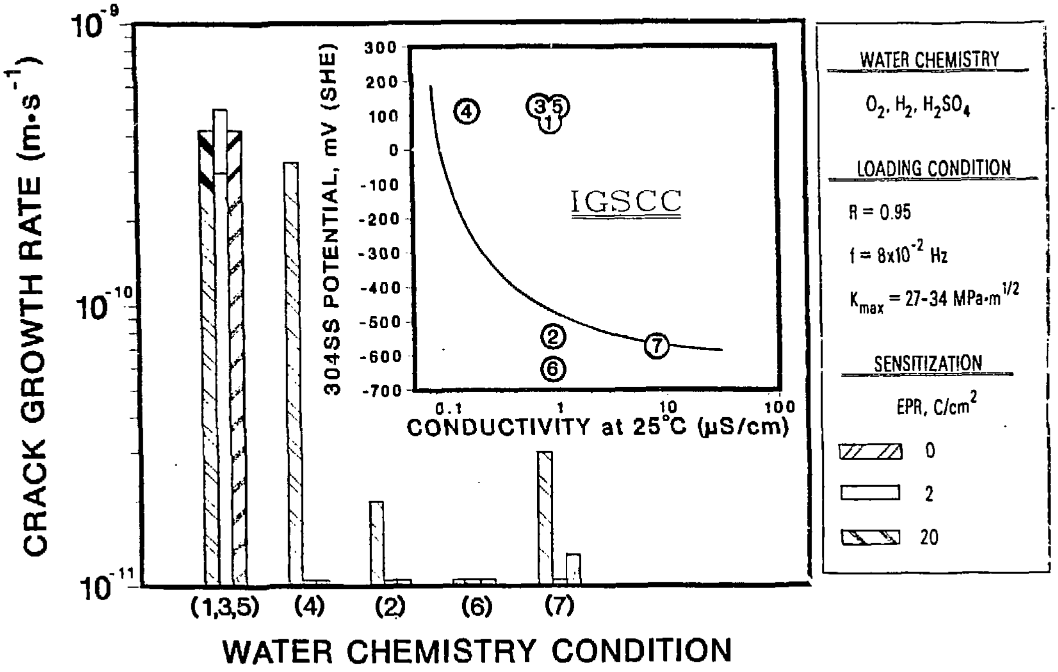

Fig. 10 Effect of Several Simulated BWR Chemistries on Crack Growth Rates of Compact-Tension Specimens of Type 304 SS with Different Levels of Sensitization under Low-Frequency, Moderate-Stress-Intensity, High-R Loading at 289°C. Conditions (2), (6), and (7) simulate hydrogen-water chemistries with low oxygen and sulfate impurity.

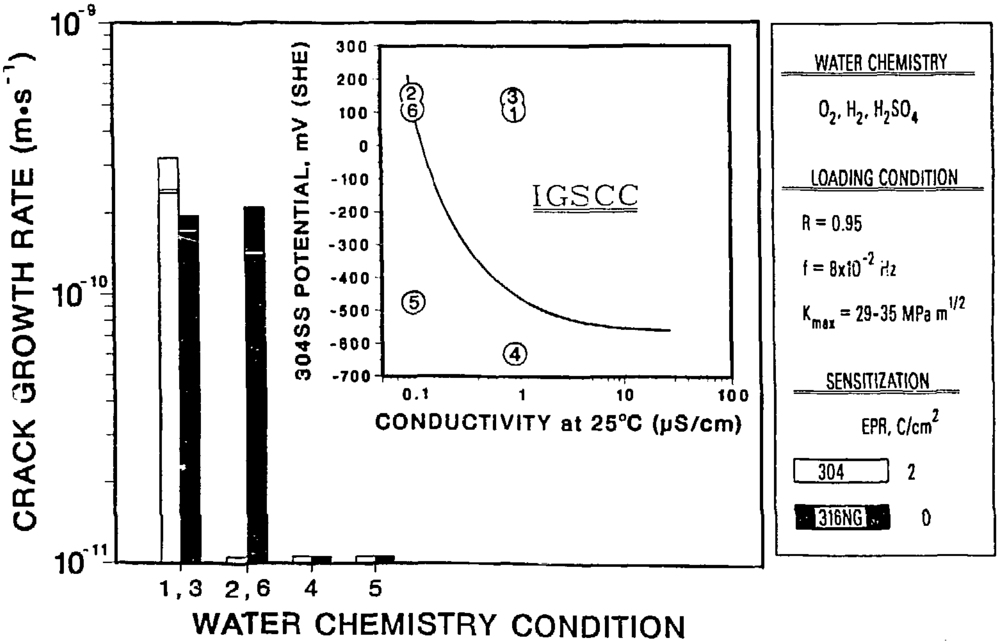

Fig.11 Effect of Several Simulated BWR Chemistries on Crack Growth Rates of Compact-Tension Specimens of Sensitized Type 304 and 316NG SS under Low-Frequency, Moderate-Stress-Intensity, High-R Loading at 289°C. Conditions (4) and (5) simulate hydrogen-water chemistries with and without sulfate impurity at a low-oxygen concentration, respectively.

LABORATORY STUDIES ON SCC IN SIMULATED HWC ENVIRONMENTS

SUMMARY

CRACK GROWTH EXPERIMENTS

- Crack Growth in Sensitized Type 304 and 316NG SS Specimens Ceased under Low-Freq., High-R Loading When Oxygen Was Removed (~ 5 ppb) from Feedwater Containing 100 ppb Sulfate
- Crack Growth in Solution-Annealed and Moderately Sensitized Type 304 SS Specimens Resumed at a Relatively Low Rate When Sulfate in the Feedwater Was Increased from 0.1 to 1 ppm in the Low-Oxygen Environment with 1.4 ppm H_2
- Crack Growth Behavior Is Consistent with the IGSCC Regime Based on CERT Data in Terms of the ECP of Type 304 SS and Conductivity of the Feedwater Containing Sulfate

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LABORATORY STUDIES ON SCC IN SIMULATED HWC ENVIRONMENTS

CONCLUSIONS

- Impurity Species That Participate in Cathodic Reduction Reactions, Similar to Dissolved Oxygen, Promote SCC of Sensitized Type 304 SS
- Ingress of Oxyanions (e.g., SO_4) from Demineralizer Systems and Certain Cations (viz., Cu from Corrosion of Cu-Alloy Condenser Tubes) Can Contribute to SCC of BWR Piping
- ECP of the Steel and Conductivity of the Reactor Water Are Useful in Implementation of HWC; However, Monitoring of the Concentration of Various Species Can Form the Basis for Remedial Actions if the Parameters Exceed Nominal Values