ENVIRONMENTAL EFFECTS ON MATERIALS IN OPERATING NUCLEAR POWER REACTORS*

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(OUTLINE OF TALK GIVEN IN BRUSSELS, BELGIUM, 9/24/84)

NUCLEAR PLANTS HAVE BEEN GENERATING COMMERCIAL POWER IN THE U. S. FOR APPROXIMATELY TWENTY YEARS. DURING THIS TIME, CORROSION PROBLEMS HAVE DEVELOPED, AND AS WITH ANY NEW TECHNOLOGY, NOT ALL WERE ANTICIPATED. IN SOME INSTANCES, CORRECTIVE MEASURES TAKEN FOR ONE PROBLEM HAVE PRECIPITATED ANOTHER. THUS WE'VE SEEN TOO OFTEN A "FIRE TO THE FRYING PAN" SYNDROME.

MASTER

WHAT I'D LIKE TO DO IN THIS TALK IS REVIEW SEVERAL AREAS IN WHICH CORROSION PROBLEMS HAVE OCCURRED, AND HOW WHAT WE HAVE LEARNED CAN HELP IMPROVE FUTURE PERFORMANCE. METALLURGISTS TOO OFTEN TALK ONLY ABOUT THE BAD THINGS THAT HAPPEN, AND SO SHALL I. MATERIALS IN THE VAST NUMBER OF INSTANCES BEHAVE JUST FINE. BUT, AS IN THE NEWSPAPERS, IT IS THE PROBLEMS THAT DRAW OUR ATTENTION.

SLIDE 1 - SUBJECTS TO BE DISCUSSED.

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NONE OF THESE TOPICS HAS ANYTHING TO DO WITH THE NUCLEAR PORTION OF THE PLANTS. YET ALL OF THEM, AND OURS AND THE PUBLIC'S INTEREST IN THEM, HAVE EVERYTHING TO DO WITH THE FACT THAT THEY ARE OCCURRING IN NUCLEAR PLANTS. THE NEED FOR ZERO LEAKAGE PUT DEMANDS ON CORROSION LIMITS THAT WERE PREVIOUSLY UNKNOWN IN UTILITY INDUSTRY.

ALL THESE SUBJECT AREAS HAVE RECEIVED MUCH PUBLIC ATTENTION. THE BOILING WATER REACTOR (BWR) CRACKING PROBLEM HIT ALL THE FRONT PAGES WHEN THE FLEDGLING NUCLEAR REGULATORY COMMISSION (NRC) ORDERED ALL OPERATING UNITS SHUT DOWN FOR INSPECTION IN 1974-5. "STEAM GENERATOR TUBES MAY BE THE ACHILLES' HEEL OF THE NUCLEAR INDUSTRY" SAID NEWSWEEK ON APRIL 19TH 1983. "THERE HAVE BEEN A SIGNIFICANT NUMBER OF INCIDENTS OF FAILED OR SEVERELY DEGRADED BOLTS AND STUDS" SAID THE NEW YORK TIMES ON APRIL 18, 1983. WHILE THESE CORROSION PROBLEMS HAVE CAUSED CONSIDERABLE ADVERSE PUBLICITY AND OPERATIONAL HEADACHES FOR THE INDUSTRY, THE SAFETY OF THE NUCLEAR PLANTS HAS NOT BEEN JEOPARDIZED. RESEARCH IS IMPROVING OUR UNDERSTANDING THEM SO THAT I BELIEVE FUTURE PERFORMANCE CAN BE SIGNIFICANTLY IMPROVED, AND SAFETY MAINTAINED.

BWR PIPE CRACKING

SLIDE 2 - BWR CIRCUIT. NOTE: INTERPLAY OF COMPONENTS.
NOTE: CONDENSER IS UNDER VACUUM. MUST CONTROL AND MONITOR IMPURITY INLEAKAGE.

SLIDE 3 - BWR RECIRCULATION PIPING.

SLIDE 4 - 3 RING CIRCUS CAUSES OF SCC: STRESS, ENVIRONMENT,
SUSCEPTIBLE MATERIAL.

SLIDE 5 - STRESS: PRIMARILY RESIDUAL.

SLIDE 6 - RESIDUAL STRESS PATTERNS.

SLIDE 7 - ENVIRONMENT PRIMARILY OXYGEN

NOTE: LITTLE EFFECT AT HIGH OXYGEN LEVELS.

SLIDE 8 - MATERIAL: SENSITIZATION OF STAINLESS STEEL.

OCCURS IN WELD HEAT AFFECTED ZONES IN SAME AREA AS
PEAK RESIDUAL STRESSES.

SLIDE 9 & 10 - HAZ & CRACKING IN WELDS - DRESDEN-2; NOTE:
WITH 4" (SLIDE 9) AND 10" LARGER DIA. PIPE,
CRACK IS CLOSER TO WELD IN LARGER PIPE.

SLIDE 11 - BWR H₂O CHEM. DESIGN LIMITS.

SLIDE 12 - RG 1.56: LIMITS

IMPURITY EFFECTS: WHAT CAN ENTER COOLANT.

SLIDE 13 - MILLSTONE SEAWATER INTRUSION.

SLIDE 14 - DUANE ARNOLD DEMINERALIZER BREAKUP.

SLIDE 15 - CRACK PROPAGATION RATES VERSUS STRAIN RATES -
SENSITIZED STAINLESS STEEL IN OXYGENATED WATER.

SLIDE 16 - CPR_{MAX} VS. $1/T$. NOTE: MAXIMUM IN RATE AND
MAXIMUM IN STRAIN-RATE RANGE OF SUSCEPTIBILITY AT
200°C LOW ACTIVATION ENERGY -- SUGGESTS LIQUID
PHASE RATE CONTROLLING STEP.

SLIDE 17 - FE SOLUB. (FROM Fe_3O_4).

SLIDE 18 - CPR VS. FE SOLUB. (FROM Fe_3O_4 IN ACID
ENVIRONMENT).

SLIDE 19 - MECHANISM SKETCH. SUGGEST MIGRATION OF Fe^{++} IN
CRACK IS RATE CONTROLLING STEP.

ROLE OF S. BOTH IN STEEL AND IN SOLUTION:
INCREASE ACIDITY, Fe^{++} SOLUBILITY, CONDUCTIVITY
OF SOLUTION IN CRACK. DISCUSS INITIATION AND
PROPAGATION OF CRACKS.

SOLUTIONS: MATERIAL: USE LOW-C OR STABILIZED STAINLESS STEEL.

SLIDE 20 - IHSI - JAPANESE - USED ON SUSQUEHANNA, SHOREHAM,
AND MOST JAPANESE BWR'S. (STRESS).

SLIDE 21 - H₂O CHEM. KEEP IMPURITIES LOW AND O₂ LOW WITH
USE OF H₂.

PWR STEAM GENERATORS - THE ACHILLES HEEL?

SLIDE 22 - SCHEMATIC OF WESTINGHOUSE STEAM GENERATOR.

PRIMARY SIDE STRESS CORROSION CRACKING

SLIDE 23 STEAM GENERATOR MATERIALS

TUBING IS INCONEL - NICKEL CR, FE BASE ALLOY.

REVERSE SENSITIZATION

O₂ IN BWR CAN CAUSE CRACKING WHEN SENSITIZED.

H₂ IN PWR CAN CAUSE CRACKING WHEN NOT SENSITIZED.

SLIDE 24 - WHERE OCCURRING - TUBE-TUBE SHEET CREVICE
(OBRIGHEIM).

SLIDE 25 - WHERE OCCURRING - U-BENDS, RADIOGRAPHS

- BNL PROGRAM (SEE ENCLOSED REPRINT BY BANDY AND
VAN ROOYEN

- DISCUSS IN TERMS OF MECHANISMS - STRESS (RESIDUAL
FROM COLD WORK), MATERIAL, ENVIRONMENT.

- WHAT TO DO? PLUG TUBES, STRESS RELIEF, H_2O
CHEM. CHANGE, MATERIAL CHANGE.

THREE MILE ISLAND - THIOSULFATE CONTAMINATION -

SLIDE 26 - NEWMAN AND BANDY - CRACK PROPAGATION RATES.
DESCRIBE CLASSIC RATHER THAN REVERSE
SENSITIZATION.

- SOLUTIONS - ALL ENVIRONMENTAL -
RAISE PH - COMPETING ION EFFECT - ELIMINATE
SULFUR - THEN OXYGEN.

SECONDARY SIDE PROBLEMS

SLIDE 27 - NATURE OF TUBE-TUBE-SHEET INTERACTION.

- DESCRIBE CONCENTRATING MECHANISMS. (HEATED
CREVICES).

SLIDE 28 - PHOSPHATE WASTAGE.

SLIDE 29 - BEZNAU - IGA & SCC

SLIDE 30 - BANDY AND VAN ROOYEN'S WORK SHOWING POTENTIAL
RANGES FOR IGA AND SCC.

SLIDE 31 - DENTING SCHEMATIC

- RUNAWAY Fe_3O_4 PRODUCTION BY TUBE SUPPORT PLATE CORROSION. OXIDIZING POTENTIAL, Cl^- TRIGGER IT IN CREVICES.

SLIDE 32 - DENTING INDIAN POINT. DISTORTION OF INCONEL 600 TUBES LED TO IGSCC FROM PRIMARY SIDE.

SLIDE 33 - PALISADES - PITTING. ROLE OF CU IONS.

SLIDE 34 - PALISADES - IGA.

SLIDE 35 - IGA VS. CAUSTIC STRESS CORROSION.
SAME AS SLIDE #30.

- THE SOLUTIONS ARE ALL ENVIRONMENTAL FOR AN OPERATING PLANT, AND CONSIST PRIMARILY OF TIGHTER CONTROLS ON CONDENSER LEAKAGE AND ON OXYGEN LEVELS IN THE SECONDARY COOLANT.

MECHANICAL DAMAGE - THE GINNA SYNDROME (SEE ATTACHED PAPER BY CZAJKOWSKI).

SLIDE 36 - TUBES IN TUBE SHEET.

SLIDE 37 - SKETCH OF TUBE SHEET - SHELL - WRAPPER.

- IMPORTANT TO KNOW ROLE OF FOREIGN OBJECTS AND THE SUBSEQUENT CONDITION OF PREVIOUSLY PLUGGED TUBES.

PIPING AND VESSEL CRACKING

SLIDE 38 - TYPES OF CRACKS IN FEEDWATER NOZZLES.

- SOLUTION - ELIMINATE THERMAL STRESSES
- ROLE OF CORROSION. NOTE: CRACKS ARE FILLED WITH
OXIDE. $CL + O_2$ S IN STEEL?

SLIDE 39 - STEAM GENERATOR VESSEL, SHOWING LOCATION OF
CLOSURE WELD.

SLIDE 40 - INDIAN POINT-3 VESSEL CRACK (THROUGH-WALL)
STRESSES - RESIDUAL - INCREASE IN HARDNESS NEAR
WELDS. ENVIRONMENT - $CL^- O_2 Cu^{++}$

SLIDE 41 - INDIAN POINT-3 - PART THROUGH-WALL CRACK.
MATERIAL UNLIKELY TO CHANGE. WE'RE SETTING UP
NOW TO INVESTIGATE SOME OF THESE PAST VARIABLES
IN OUR LABORATORIES.

SLIDE 42 - NINE MILE POINT - STAINLESS STEEL PIPING - 2ND
SIDE CRACKING - CL^- CONTAMINATION.

TURBINE CRACKING

SLIDE 43 - DISC FRAGMENTS.

SLIDE 44 - PIECE RECEIVED AT BNL. NOTE: CRACKS, MoS_2 .

SLIDE 45 - MoS_2 EXPERIMENT. DESCRIBE CRACKING MODEL.

BOLTING

SLIDE 46 - CRACKED MAINE-YANKEE BOLT.

MoS_2 - NOTE: BRANCHING CRACKS.

SLIDE 47 - BORIC ACID WASTAGE - OUR LAB. DATA REPRODUCED
RATE AT CALVERT CLIFFS. 0.2-0.3 INCHES/YR.
CURRENTLY HELPING NRC DRAFT POSITION.

IN CONCLUSION, I WOULD LIKE TO TACKLE THE THORNY ISSUE OF
OPERATIONAL NUISANCE VERSUS PUBLIC HEALTH AND SAFETY PROBLEMS.
REMEMBER, MOST MATERIALS ARE BEHAVING WELL, AS DESIGNED.

SLIDE 48 - SAFETY & OPERATIONAL ISSUES

I THINK WE ARE LEARNING, PROCEEDING WITH CAUTION, AND THAT
FUTURE PERFORMANCE AND EXPERIENCE WILL BE MUCH IMPROVED.

EXTENSIVE RESEARCH IN WHICH WE ARE ONLY ONE OF MANY
LABORATORIES INVOLVED, HAS SHOWN CAUSES AND SOLUTIONS TO
PROBLEMS. IMPLEMENTATION CAN BE DIFFICULT AND EXPENSIVE IN AN
OPERATING UNIT, HOWEVER, AND RESEARCH ON SOLUTIONS MUST BE
THOROUGH IF WE ARE TO AVOID REPEATING THE "FIRE TO THE FRYING

PAN" SYNDROME. FOR, ALTHOUGH WE THINK WE'RE SMART, THERE'S ALWAYS THE POSSIBILITY THAT, LURKING IN THE CREVICES AND STRESS CORROSION CRACKS IS THE UNKNOWN DEVIL.

THANK YOU FOR LISTENING

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CORROSION IN LWR NUCLEAR PLANTS

BWR PRIMARY PIPE CRACKING

SENSITIZED STAINLESS STEELS

CONDENSER CORROSION (BWR & PWR)

PWR STEAM GENERATORS

FEEDWATER NOZZLE CRACKING

TUBING/SUPPORT PLATE DEGRADATION

TURBINE CRACKING (BWR & PWR)

AUXILIARY PIPE CRACKING (PWR)

the direct cycle bwr system

Figure 2-1. Basic Configuration of BWR Recirculation System with Respect to Reactor Pressure Vessel

SOURCES OF HIGH STRESS LEVELS

1. APPLIED STRESSES (STATIC AND ALTERNATING)
2. THERMAL STRESSES, THERMAL TRANSIENTS
3. RESIDUAL STRESSES FROM
 - a) WELDING
 - b) FITUP
 - c) SURFACE PREPARATION

X-RAY AXIAL RESIDUAL STRESS
ID SURFACE
4 in (10cm) DIAMETER PIPE
TYPE 304 SS
CONVENTIONAL WELD

Effect of oxygen concentration on the intergranular stress corrosion of sensitized Type 304 stainless steel (from only one heat) in 550°F water at two stress levels. (After Clarke and Gordon, Ref. 104.)

FIG. 9. (a) Cross Section Showing Metallography of "Circumferential" Rad in Direction of
Loop 3. Map. 610X. Neg. No. VSC-181011.

SLIDE 10

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INTERGRANULAR CRACKS IN HAZ D-II LOOP A 10K14 MAG 50

Table 4-3
BWR WATER CHEMISTRY

	Concentrations — Parts Per Billion (ppb)				Conductivity (μ mho/cm at 25°C)	pH at 25°C
	Iron	Copper	Chloride	Oxygen		
Condensate (1)*.....	15-30	3-5	≤ 20	20-50	~ 0.1	~ 7
Condensate Treatment Effluent (2)	5-15	< 1	~ 0.2	20-50	< 0.1	~ 7
Feedwater (3)	5-15	< 1	~ 0.2	20-50	< 0.1	~ 7
Reactor Water (4)						
(a) Normal Operation	10-50	< 20	< 20	100-300	0.2-0.5	~ 7
(b) Shutdown	—	—	< 20		< 1	~ 7
(c) Hot Standby.....	—	—	< 20	See Outline	< 1	~ 7
(d) Depressurized	—	—	< 20	8,000	< 2	6-6.5
Steam (5).....	0	0	0	10,000-30,000	~ 0.1	—
Control Rod Drive† Cooling Water (6) ..	50-500	—	< 20	$\leq 8,000$	~ 1	~ 6

*Numbers and letters in parentheses are keyed to Figure 4-1.

†This water may be close to air saturated demineralized water, in which the conductivity and pH is primarily due to absorbed carbon dioxide gas from the air.

ACCEPTABLE WATER CHEMISTRY LIMITS FOR POWER OPERATION
(U. S. NRC - REGULATORY GUIDE 1.56)

	LIMIT ¹	MAXIMUM ²
SPECIFIC CONDUCTANCE AT 25°C (μ S)	1	10
CHLORIDE (PPM)	0.2	0.5
PH AT 25°C	5.6-8.6	-

SLIDE 12

¹CAN BE EXCEEDED UP TO 72 HOURS PER INCIDENT, BUT NOT MORE THAN 2 WEEKS PER YEAR.

²AN IMMEDIATE ORDERLY SHUTDOWN IS REQUIRED.

SLIDE 13

Figure 1 Crack propagation rates in furnace-sensitized Type 304 stainless steel, estimated from slow strain rate tests (from 15)

Figure 2 Effect of temperature on maximum crack propagation rates, taken from data in Figure 1 (from 15).

Figure 3 Solubility of Fe_3O_4 in solutions saturated with H_2 at 1. atm at 25°C (from 16).

Figure 4 Comparison of curves from Figure 2 with solubility of Fe in 10⁻⁵ m HCl, from Figure 3.

Figure 5 Schematic model of crack propagation mechanisms (from 15).

SLIDE 20

CERT EXPERIMENTS ON SENSITIZED TYPE 304SS IN SIMULATED BWR - QUALITY WATER AT 289° C

(DATA FROM ARGONNE NATIONAL LABORATORY)

STEAM OUTLET TO
TURBINE GENERATOR

MOISTURE SEPARATOR

UPPER SHELL

SWIRL VANE
MOISTURE SEPARATOR

TUBE BUNDLE

LOWER SHELL

FEEDWATER
INLET NOZZLE

PREHEATER SECTION

PARTITION

TUBE PLATE

PRIMARY
COOLANT OUTLET

PRIMARY
COOLANT INLET

Westinghouse

NUCLEAR PLANT
STEAM GENERATOR

SLIDE 22

STEAM GENERATOR MATERIALS

SECONDARY SIDE

Vessel

Carbon Steel

Tube Sheet

Carbon Steel

Tubes

Stainless Steel

Inconel-600

Incoloy-800

(Tube Support Plates)

Carbon Steel

Ferritic Stainless Steel

PRIMARY SIDE

Inconel-600

Stainless Steel

Figure 5 Print of double wall x-ray radiograph of R1-C6. Solid lines show approximate locations of major cuts; sections are identified; surfaces polished for metallography are designated by ▲. Underlined sections were flattened and their ID surfaces examined at 5X. Further cuts of E6C are given in next figure.

Fig. 10. Tube-tubesheet crevice.

SLIDE 28

Micrographs of Stress Corrosion Cracks. Beznau Nuclear Power Plant

Figure 3-12 Superimposition of the potential areas for IGA and SCC on the polarization curve in 10% NaOH + 1% Na_2CO_3 solution at 300 C at a scan rate of 20 mV/min.

Figure 1. Crosssectional view of denting at tube support plates.

SLIDE 32

SLIDE 33

SLIDE 34

Figure 3-12 Superimposition of the potential areas for IGA and SCC on the polarization curve in 10% NaOH + 1% Na_2CO_3 solution at 300 C at a scan rate of 20 mV/min.

SLIDE 36

GIDNA STATION
STEAM GENERATOR EVALUATION
NRC MEETING
APRIL 30, 1982

ACCESS HOLE LOCATION

D.C. COOK
H.B. ROBINSON
BEAVER VALLEY

(a) SINGLE LARGE CRACK AT ROOT OF THE NOTCH

SALEM
GINNA
SURREY
KEWANEE
POINT BEACH

(b) SEVERAL SMALL CRACKS IN COUNTERBORE REGION

SAN ONOFRE

(c) SHALLOW CRACKS IN WELD AND COUNTERBORE REGION

Figure 1. Schematic depicting the closure weld of Steam Generator # 32 where the leak occurred.

SLIDE 40

ID

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LUCIUS PITKIN INC

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SLIDE 41

SLIDE 42

SLIDE 43

SLIDE 44

TABLE 5
RESULTS OF NOTCHED TENSILE TESTS

PLANE OF MAIN FRACTURE SURFACE

Micrograph of bolt section depicting extensive secondary fracture. The fracture surface is highly irregular and shows signs of fatigue crack growth.

SAFETY ISSUES

1. Any deterioration of reactor coolant pressure boundary has a potential effect on reactor safety.
2. Stress corrosion cracks have always leaked detectably or been found by inservice inspection before pipes have ruptured.
3. Pipe and tubing ruptures were anticipated in the design of nuclear plants, and safety circuits provided to protect the nuclear core from meltdown.
4. Solutions must be found for both operating nuclear units and new units to prevent continued widespread deterioration.

OPERATIONAL ISSUES

1. Shutdowns to repair or replace corroded parts can cost \$500,000. or more per day to the utility
2. Radiation exposure to workers