MASTER

CORROSION IN NUCLEAR POWER PLANTS

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Operating nuclear power plants are of two quite different types, depending on the type of nuclear reactor utilized. These are boiling water reactors (BWR) or pressurized water reactors (PWR); the corrosion problems are substantially different for the two systems and so we shall consider each separately. Corrosion has not threatened the safety of reactor systems and in no case has corrosion resulted in the release of radioactive material that has posed a hazard to the public. The problems are more operational and their disadvantages are the cost of down time and a potential increase in required excess system capacity.

Boiling Water Reactors

In a boiling water reactor, pure water is boiled at 550°F by the nuclear fuel and, after spray removal, the steam is used to drive a turbine generator. Water purity is maintained by bypass circulation through ion exchange resins and sometimes by a full-flow condensate demineralizer; the fraction of steam void in the nuclear core is maintained at an acceptably low level by recirculation systems that pump water through the core. See Figure 1 for a schematic drawing of a reactor vessel and one of the recirculation loops.

The most persistent nuisance related to corrosion has been the accumulation of transported radioactive corrosion product ("crud") in the piping system external to the reactor vessel. These pipes are checked periodically with eddy current and other gauges to assure the absence of leaks (sometimes in quite cramped quarters), and the crud causes exposure of the workmen to a gamma radiation field that limits the time each workman can perform such operations. When it is necessary to replace a component or a defective piece of pipe, the exposure can be greater and the time in the vicinity of the repair can be so limited that a substantial number of

Figure 1. Schematic of BWR Reactor Coolant System. (1)

skilled workmen can be required for what would otherwise seem to be a simple repair. In one instance, it was reported that all of the nuclear-qualified welders in the eastern part of the United States were "burned out" during a repair at one nuclear plant.

The activity level increases with time of reactor operation both in the cooling water and on non-fuel-rod surfaces. Figure 2 shows similar dose rates at piping surfaces of a number of BWR's. In Figure 3 calculated surface activities for four radionuclides are shown in comparison with measured activities for Co-60 in Nine Mile Point-1. Irregularities correspond to shutdown periods. The oldest BWR's have now reached a condition in which it is believed that the expense and down time required for surface decontamination are justified, and such procedures are being planned.

A second major corrosion problem for boiling water reactors is the stress corrosion cracking of stainless steel pipes in the recirculation systems and (to a lesser extent) in the core spray system, designed to add water rapidly to the reactor core area in the event of accidental loss of coolant. Stress corrosion cracking in BWR's occurred as early as 1965 in Dresden 1 piping. (4-7) Cracks have appeared every few years since then with a major rash of over two dozen through-wall piping cracks occurring in about a dozen BWR's beginning in the fall of 1974 and extending through the present time. Pin-hole or "weeping" leaks developed. Most of these cracks occurred in 4" or 10" diameter type 304 stainless steel seamless piping in the heat affected zone (HAZ) near welds, with the cracks initiating on the inside surface of the pipe and propagating outward intergranularly. An additional 60 or so incidents of stress corrosion have been discovered in which cracks had not penetrated the pipe wall. The overall average occurrence rate for HAZ cracks is in excess of one incident per plant. An example of one of these cracks is shown in Figure 4, in which the weld metal is clearly shown adjacent to the crack. Cross-sections of some of the cracks are sketched in Figure 5.

The location of the cracks in these systems and the inspection of the various reactors are shown in Figure 6 and in Table I. The bypass valve shown in the figure is used to control the water flow at startup and then remains closed during reactor operation. One exception has been

Figure 2. Dose Rates at Exterior Surfaces of BWR Recirculation Piping. (2)

Figure 3. Calculated Activity versus Time on Non-Fuel-Rod Surfaces for Nine Mile Point-1. Points Represent Experimental Data for Co-60. (3)

Figure 4. Cross Section of Crack in Loop A Weld 10K14. The intergranular nature of the crack is shown.

Dresden-2 Core Spray Piping. (2)

Figure 5. Typical Piping Cracks in 4-inch Bypass Lines. (a) Dresden-2 Loop A, (b) Dresden-2 Loop B, and (c) Quad Cities-2 Loop B. ⁽¹⁾

Figure 6. Schematic of 4-inch recirculation Bypass Line in BWR. Note: All shop welds, except at weld-o-lets and joints A; dotted line indicates special design for Monticello. Each circle represents a circumferential cracking incident as detailed in Table I. (1)

TABLE I

Four-inch Recirculation Bypass Line Cracks
at HAZ of Weld Joint⁽¹⁾

Circle No	Location			Inspection Date	Crack Type	Wall Penetration
	Reactor	Loop	Country			
1	Dresden-2	A	US	9/74	Single or Multiple Circumferential ↓	Leaker
2	Dresden-2	B	"	12/74		"
3	Quad Cities-1	A	"	1/75		"
4	Quad Cities-2	A	"	12/74		-
5	Quad Cities-2	B	"	12/74		Leaker
6	Hamaoka-1	A	Japan	9/74		-
7	Millstone-1	B	US	12/74		80%
8	Fukushima-1	A	Japan	9/74		Leaker
9	Dresden-2	B	US	12/74		-
10	Millstone-1	A	"	12/74		Leaker
11	Peach Bottom-3	B	"	12/74		-
12	Millstone-1	A	"	12/74		-
13	Hamaoka-1	A	Japan	9/74		89%
14	Dresden-2	B	US	12/74		Leaker
15	Quad Cities-2	B	"	9/74		92%
16	Peach Bottom-3	B	"	12/74		36%
17	Monticello-1	B	"	1/75		90%

the bypass line of Monticello-1 loop B (dotted line) which was designed to operate with the bypass valve open during reactor operation.

The cost of repairing these lines is very high (~ \$200K/day of outage due to the cost of replacement power) since they must be repaired when the reactor is down. The question remains open as to whether such a crack could occur in one of the larger diameter (e.g. 26") primary coolant lines. In that event the plant outage and therefore the cost would be significantly greater.

The current procedure for dealing with the cracks has been to eliminate the line if possible or to replace it with an alternate material such as type 304L stainless steel, which is less susceptible. In some cases where the type 304 stainless steel piping has simply been replaced with the same material, cracks have recurred within relatively short times.

The location of the cracks in the core spray lines is illustrated in Figure 7; the inspection dates and crack characterization are summarized in Table II. The core spray lines were fabricated from type 304 SS except for the type 316 SS safe ends and dutchmen in Dresden-2. All forged safe ends with or without forged dutchmen were welded to low alloy steel nozzle and then given a post-weld stress release. Subsequently, the remaining pipe sections were welded together.

Measurement of local stresses and analyses of the systems has indicated that the residual stresses in BWR piping are of primary importance. These arrive from several causes. When the pipe is manufactured it is usually straightened after annealing. This straightening process locks in residual stresses. When the loose ends of the piping runs are welded in the field they usually have to be lined up using hydraulic jacks, thus a "fit-up" or "cold-springing" stress is locked into the piping when it is welded. Prior to the actual welding the pipe ends are machined and ground to cut the weld groove, eliminate out of roundness, and to clean the pipe surface. This weld preparation procedure can produce residual stresses on the pipe surface that exceed the initial annealed strength of the material (the material work hardens so that the yield stress rises). Finally, when the weld is made the shrinkage of the weld metal during cooling can cause high bulk residual stresses that can be tensile in the HAZ of the weld. None of these residual stresses is normally accounted for in the

Figure 7. Schematic of 254-mm Core-Spray Line in BWRs. Each circle represents a cracking incident as detailed in Table II. (1)

TABLE II
Core-Spray Line Cracking
at HAZ of Weld Joint⁽¹⁾

Component Name	Figure No	Circle No	Location			Inspection Date	Crack Type	Wall Penetration
			Reactor	Loop	Country			
Safe-end 203 mm-Forging, Furnace Sensitized	5a	1	Fukushima-1	A	Japan	-/75	Single Circ.	-
	"	2	"	B	"	-/75	Multiple Long	Leaker
	"	3	Tsuruga	B	"	3/75	Single Long	"
Safe-end 254-mm Forging Furnace Sensitized	5b	1	Dresden-2	A	US	1/75	Multiple Long	Leaker
	"	2	"	B	"	1/75	Single Long	"
	"	11	"	A	"	2/75	Multiple Long	"
Dutchman 254-mm Forging Furnace Sensitized	5b	10	Dresden-2	B	US	2/75	Multiple Circ.	Leaker
		12	"	A	"	2/75	Multiple Circ. and Long.	32% (MT)
Elbow Section 203-mm Rolled	5a	7	Fukushima-1	A	Japan	-/75	Single Circ.	(UT)
Elbow Section- 254-mm Rolled	5b	5	Dresden-2	A	US	2/75	Long Branded into Y	11% (MT)
	"	6	"	A	"	2/75	Single Long.	67% (MT)
Straight Run 254-mm Mill Ann.	5a	6	Fukushima-1	B	Japan	-/75	Single Circ.	-
Straight Run 254-mm Mill Ann.	5b	3	Dresden-2	A	US	1/75	Circ. Branded into Long.	Leaker
	"	4	"	B	"	1/75	Single Circ.	(PT)
	"	7	"	A	"	2/75	Circ. Branded into U	47% (MT)
	"	8	"	A	"	2/75	Multiple Circ.	Leaker
	"	9	"	A	"	2/75	Single Circ.	(PT)

Notes: Circ. - Circumferential, Long - Longitudinal, UT - Ultrasonic Inspection, PT - Dye Penetrant Inspection
MT - Metallurgical Examination

design of the system since they are highly variable and do not arise from the "design" loads applied to the system, yet they are the major source of the stresses of concern in BWR stress corrosion cracking.

There has been a substantial effort to understand the mechanism of the cracking and to establish satisfactory procedures for its elimination. The lead in this has resided most strongly in the Electric Power Research Institute; the Corrosion Advisory Committee established by that institute has been serving as a panel of experts in establishing the program. There has been funding from EPRI, from NRC, and from ERDA (now DOE), and GE has borne some expense. The three factors that are known to be important include the environment (oxygenated water), a susceptible material (304 SS, evidently requiring sensitization), and high local stresses. There has been some consideration of chemical treatment of the water in BWR's; at the moment this seems unlikely since many changes would be required and the practicability of the use of additives is questioned for a system in which there is boiling and potential local high concentration of non-volatile solutes (or stripping of volatile solutes) at fuel element surfaces. There has been considerable discussion about the use of alternate materials. At the moment choices center around 304L, 316, and 316L stainless steel.

Pressurized Water Reactors

The water in the entire primary loop of a PWR is maintained at a pressure (2250 psi) sufficient to prevent bulk boiling (maximum bulk temperature $\sim 600^{\circ}\text{F}$). This primary water is passed through the tubes of a steam generator from which the steam (800 psi) drives a turbine generator, is condensed in a separate condenser, passes through possible water treatment systems and is preheated prior to return to the steam generator.

In the primary circuit, the crud problem is identical in character to that in the BWR but the levels of crud are substantially lower due to the opportunity to select water chemistry that minimizes the problem. The water is maintained alkaline with lithium hydroxide, and a hydrogen over-pressure is maintained to minimize the oxygen content of the water. Boric acid is often added as an auxiliary control of nuclear reactivity for convenience in adjusting to the reactivity of fuel as it is "burned."

There have been cracking and fracturing of turbine discs; some of these have evidently been caused by corrosion, stress corrosion, or corrosion fatigue. There is nothing in this behavior that is known to be unique to PWR plant turbines as compared to those in other plants.

The point of major concern and the source of maximum inconvenience due to corrosion is in the steam generator. In recent years these generators have been designed specifically for the nuclear plants so there has been no extensive operating experience with them in other systems. They are large, about 60 feet tall and 10-15 feet in diameter, and have been increasing in size, as indicated in Figure 8. Tube wall temperatures have been in the range 503-536°F⁽⁸⁾. Their corrosion problems have been described. (8, 9, 10)

The secondary side of steam generators is particularly sensitive to the water chemistry since the process of boiling concentrates non-volatile solutes and at locations corresponding to sites of regular boiling very strong solutions are often encountered. Based on experience with steam generators in other systems, the most common treatment for initial PWR's involved the addition of phosphates and the removal of impurities primarily through blowdown. There was no extensive continuous purification of the water other than deaeration. Impurities in the secondary coolant used in the condenser tend to leak into the steam system; the phosphorus leads to the production of soft phosphates or iron or calcium that can in principle be removed by blowdown. However, a portion of these phosphates combined with corrosion products tends to accumulate as a sludge deposit in areas of limited access to free flowing coolant, such as on the tube sheet or on tubing supports. Quantities of sludge have been substantial, as indicated in Table III. As a result of this accumulation it appears that there has been reaction between alkali metal salts and corrosion product oxides to produce strong alkali (sodium hydroxide for example). The strong alkaline solution has led to areas of severe wastage and pitting in steam generators. This has sometimes led to perforation and at other times to breaking of tubes.

In addition there have been a number of instances of stress corrosion cracking, a phenomenon that is well known for stainless and inconel in alkali. In fact the transition from stainless steel tubes in early steam generators

Figure 8. Evolution of steam generator size. (8)

TABLE III
SLUDGE REMOVAL FROM PLANTS
AFTER CHANGING FROM PHOSPHATE TO AVT OPERATION^(2A)

Plant	Months on phosphate	Sludge removal date	Sludge removed (lb.)
Beznau 1	33	6/75	Not measured (est 700)
Beznau 2	34	8/75	300
Ginna	60	3/75	Not measured (est 2000)
		2/76	Not measured (est 3000)
Point Beach 1	47	1/75	1200
		3/75	1450
		11/75	600
Point Beach 2	28	2/76	1600
Zion 1	21	3/76	30
Connecticut Yankee	96	6/76	2365
Surry 1	29	11/75	410
Surry 2	23	5/75	Not measured (est 2300)
		5/76	Not lanced
Turkey Point 3	23	11/75	1200
Turkey Point 4	14	6/75	370
		5/76	(est 1200)
Indian Point 2	21	6/76	300

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to inconel 600 tubes in the next generation of heat exchangers was largely occasioned by the incidence of cracking, particularly at the U-bends in the typical PWR steam generators.

A third type of corrosion damage has been observed in the crevice between a tube and tube sheet or a tube support plate (see Figure 9). The carbon steel sheet or plate corrodes extensively to produce a corrosion product of increased volume, leading to "denting" of the tube. Sometimes perforation or cracking occurs, and in all cases there is a reduction of cross-sectional area for the flow of water or steam. In the case of phosphate water treatment, the sludge is believed to have been causative in the denting phenomenon by plugging tube-sheet crevices and allowing the development of acid chloride (e.g. of nickel, copper, and iron) solutions from chloride in leakage.⁽¹⁰⁾ However, a number of PWR's have been run with all volatile treatment (AVT) in which only ammonia and hydrazine are added to the feed water. In these cases too, denting has now been observed rather extensively; the accelerated acid chloride attack apparently does not require the abetting action of phosphate sludges.

As steam generator corrosion became more evident and there was discussion of the relationship of the problem to the water treatment used, the ratio of sodium to phosphate was first changed and then systems were switched from phosphate to AVT. At one time it was hoped that this would eliminate the problems when all of the old sludge had been washed out of the steam generators; however, this has been demonstrated not to be true by an increasing incidence of denting in systems which had never had phosphate treatment.

The prevalence of cracking, pitting, and thinning can be gauged by examination of Figure 10. The recent status of denting in PWR steam generators is indicated in Table IV and V.

Since discontinuance of phosphate water treatment, tube thinning has largely been eliminated and the incidence of tube cracking has been held at manageably low frequency by adherence to the free caustic limitation in the AVT chemistry guidelines. Thus far, tube pitting has not been detected in any of the plants operating with AVT.⁽¹⁰⁾ A number of changes have been considered in resolution of the denting problem; it is a continuing cause of concern.

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Figure 9. A Typical 15 Mil Dent. (2a)

Figure 10. Operating plant chemistry control/inspection history.
Westinghouse steam generator tube examinations as of May 1, 1975. (8)

TABLE IV
OPERATING PLANTS DENTING STATUS⁽¹⁰⁾

Plant	Degree of Denting	Condenser Cooling Water	Condenser Tube Material
Surry 1	Extensive	Brackish	90Cu 10Ni
Surry 2	Extensive	Brackish	90Cu 10Ni
Turkey Point 3	Extensive	Sea	Al Brass
Turkey Point 4	Extensive	Sea	Al Brass
San Onofre	Extensive	Sea	90Cu 10Ni
Indian Point 2	Moderate	Brackish	Admiralty
Ringhals 2	Moderate	Sea	Al Brass
Point Beach 2	Minor	Lake	Admiralty
Robinson 2	Minor	Lake	Admiralty
Beznau 2	Minor	River	Admiralty
Point Beach 1	Minor	Lake	Admiralty
Ginna	Minor	Lake	Admiralty
Conn Yankee	Minor	River	Admiralty

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TABLE V
OPERATING PLANTS FREE FROM DENTING⁽¹⁰⁾

Plant	Condenser Cooling Water	Condenser Tube Material	Accumulated Operation Period (Mo.)
Zorita	River	Admiralty	116
Beznau 1	River	Admiralty	96
Mihama 2	Sea	Al Brass	62
Zion 1	Lake	Stainless steel	49
Zion 2	Lake	Stainless steel	43
Prairie Island 1	River	Stainless steel	43
Prairie Island 2	River	Stainless steel	31
Kewaunee	Lake	Admiralty	40
Takahama 1	Sea	Al Brass	40
Doel 1	Sea (FFCP)	Al Brass	36
Takahama 2	Sea	Al Brass	31
Genkai 1	Sea	Al Brass	30
Cook 1	Lake	Admiralty	30
Tihange 1	River	Admiralty	29
Doel 2	Sea (FFCP)	Al Brass	23
Trojan	River (FFCP)	Admiralty	19
Yankee Rowe	River	Admiralty	200
BR-3	River	Admiralty	178
Ardennes	River	Admiralty	156
Enrico Fermi 1	River	Admiralty	129
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Babcock and Wilcox PWR's have used different water treatment. No additives are used and full flow demineralization of condensate is employed to remove accidental impurities added by condenser leakage. Experience with these reactors has not yet been extensive, but there have been no leaks in steam generator ascribed to corrosion damage.

References

1. C. F. Cheng, W. A. Ellingson, J. Y. Park, "Effect of Residual Stress and Microstructure in Stress-Corrosion Cracking in BWR Piping," submitted for publication to J. Nuclear Materials, 1977.
2. R. W. Weeks, "Metallurgy and Materials," presented at the Faculty Institute in Water Reactor Safety Curriculum Development, conducted by Center for Educational Affairs and Argonne Universities Association's Nuclear Engineering Education Committee at Argonne National Laboratory, December 13-17, 1976.

2a. Douglas Fletcher, W, 1976; cited in Reference 2.
3. J. Blok, J. Younger, "Contribution of Fuel Rod Deposits to the Buildup of Radiation on Out-of-Core Surfaces of the Nine Mile Point-1 BWR", NEDC-13461, Class 1, March 1977, General Electric Company.
4. H. H. Klepfer, et al, "Investigation of Cause of Cracking in Austenitic Stainless Steel Piping," Vols. I and II, G. E. Report NEDO-21000-1 & 2, 75NED35, Class 1, July 1975.
5. NRC Technical Report NUREG - 75/067, "Investigation and Evaluation of Cracking in Austenitic Stainless Steel Piping of Boiling Water Reactor Plants," Pipe Cracking Study Group, October, 1975.
6. C. F. Cheng and E. B. Potter, "Intergranular Stress-Assisted Corrosion Cracking of Type 304 Stainless Steel Piping in Dresden-I BWR Systems," Symposium on Materials Performance in Operating Nuclear Systems, CONF-730801, p. 273-98, (1973).
7. C. F. Cheng, "Intergranular Stress-Assisted Corrosion Cracking of Austenitic Alloys in Water-Cooled Nuclear Reactors," J. Nucl. Mater. 56, p. 11-23, (1975).
8. W. D. Fletcher and D. D. Malinowski, "Operating Experience with Westinghouse Steam Generators," Nuclear Technology, 28, 356-373 (1976).
9. John R. Weeks, "Materials Performance in Operating Pressurized Water Reactor Steam Generators," Nuclear Technology, 28, 348-355 (1976).
10. D. D. Malinowski, W. D. Fletcher, "Update of Operations with Westinghouse Steam Generators," Paper presented at meeting of American Nuclear Society, June 12-16, 1977, New York, N.Y.