

NEDO-23631
77NED106
Class I
June 1977

BWR COOLANT OXYGEN CONTROL

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ABSTRACT

This report presents data and evaluates benefits of maintaining low oxygen concentrations in the primary coolant and other water systems of the boiling water reactor. There appear to be substantial technical benefits in terms of reduced materials corrosion, particularly stress-corrosion cracking, and in reduced plant contamination. However, it is difficult to quantify these benefits, due to inadequate field failure data, and lack of material test data at ambient and intermediate temperatures. Control of oxygen during shutdown, startup, and other plant transients appears feasible, and a system for controlling oxygen during these plant modes is described.

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1. INTRODUCTION

The Nuclear Regulatory Commission's (NRC) report on cracking of stainless steel pipe in Boiling Water Reactors (BWRs)¹ recommended investigation of better oxygen control along with recommended use of alternate materials, better welding procedures and joint design to reduce residual stresses, and design and operating modifications to reduce cyclic thermal and vibration stresses. The General Electric report on cracking of stainless steel pipe in BWRs² noted a strong correlation between cracks and the number of plant shutdowns whose duration was greater than 24 hours (rather than total hours of service). High oxygen concentration in the primary coolant during shutdown and restart is one characteristic of such a shutdown cycle. During a restart, oxygen can be trapped in crevices and low flow lines, such as core spray pipes, and high concentrations of oxygen may exist in such places for a significant period of time after the bulk coolant oxygen concentrations have decreased.

A number of programs have already been initiated by General Electric to deal with materials problems such as stainless steel pipe cracking, control rod drive (CRD) materials defects, and feedwater nozzle and sparger cracking. These include removal of the recirculation system bypass line, changes to the CRD return and suction lines, replacement of core spray lines, materials changeout of CRD parts, and recommendations for primary system venting.³ Welding procedure improvements and other improved process and quality control requirements, as well as special design stress rules to prevent stress-corrosion cracking, are being implemented. Other improvements to enhance BWR reliability and performance are being investigated and evaluated. Many of these solutions, however, may not be possible or feasible for operating BWRs, or BWRs now under construction. On the other hand, oxygen control appears feasible for these and future plants.

Oxidizing agents, such as oxygen, in combination with susceptible (sensitized) materials stressed above yield, can cause stress-corrosion cracking. Residual stresses from welding may be present at all times, and during plant startup, high thermal stresses are superimposed. These stresses and a corrosive chemical environment can be sufficient to cause stress-corrosion cracking. The effect of temperature, however, has not been well quantified, and an extensive test program is in progress to evaluate more exactly the magnitude of stress-corrosion and corrosion fatigue cracking in environments simulating current BWR shutdown and start-up conditions.

A verifiable cost-benefit analysis of BWR oxygen control cannot readily be made at this time. Available data is insufficient to accurately determine field failure rates of various materials and components, or the extent and impact on plant availability and operating costs. However, the test results at hand indicate that the benefits could be substantial, particularly for those plants where retrofitability of materials and parts fixes is limited.

A general discussion of material and plant radiation problems associated with oxygen, and a description of typical BWR water chemistry during various plant modes is presented in Section 2. Results of materials tests and evaluations of the effects of oxygen are presented in Section 3. Effects of oxygen on electrochemistry, and the significance of electrochemistry relative to corrosion are discussed in Section 4. Section 5 summarizes the results of the study and presents the General Electric recommendations; while Section 6 lists the main conclusions derived from the study. Appendix A describes a deaeration system for a typical BWR and outlines oxygen control procedures.

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2. GENERAL DISCUSSION

The following discusses results from past and present studies in the areas of materials performance, plant tests, design improvements and plant chemistry relevant to BWR materials problems and improvements.

2.1 MATERIALS PROBLEMS

A summary of major BWR materials problems, which coolant oxygen control (deaeration) may reduce, thereby improving plant availability and reliability, is as follows:

1. Stress-corrosion cracking of weld sensitized 304 stainless steel in piping components.
2. Stress-corrosion cracking of sensitized 304 stainless steel in the CRD system and reactor internal parts.
3. Pitting and corrosion fatigue of carbon steel piping systems including the core spray.
4. Corrosion fatigue crack propagation of A508 steel in feedwater and CRD hydraulic return nozzles.
5. Plant radiation buildup on out-of-core piping and equipment surfaces and operator radiation exposure.

Other potential problem areas of concern where oxygen control may provide added margins include: crevice-corrosion-induced stress-corrosion cracking in Inconel-600 components such as safe ends, and in Inconel-X750 and 304 stainless steel bolting and springs; and stress-corrosion cracking of 304 stainless steel feedwater sparger components; neutron flux monitor tubes; and corrosion of certain hardfacing surfaces.

A critical fact established² from the limited field failure statistical analysis done to date, is that the frequency of stress-corrosion crack failures observed in certain BWR piping correlates with the number of plant startups following plant shutdowns exceeding 24 hours. This suggests that transients in the materials environment and stress cycles are crucial factors. The key mechanisms of failure identified in these cases include stress-corrosion cracking, corrosion fatigue, and crevice corrosion initiated stress-corrosion cracking. Three variables (see Figure 2-1) can be altered, in principle, to reduce such material failures, i.e., (1) Metallurgical condition (sensitization), (2) stress intensity and/or strain-time profiles, and (3) chemical environment.

It is possible to alter the metallurgical condition by selective parts replacement. This is being done, to the extent practical, for a limited number of high failure rate components, including some pipes and some control rod drive components. It is also possible and technically feasible to alter the thermal-plus-pressure cyclic stresses on some components in existing plants. Such retrofits, however, are difficult and expensive. Altering the chemical environment by controlling oxygen appears to be more practical and effective, particularly for existing plants.

High cycle thermal fatigue induced by hot and cold water turbulence initiates the cracking observed in the feedwater nozzle and control rod drive hydraulic return nozzle blend radii. Propagation of these cracks through the nozzle cladding and into the A508 base metal is due to high pressure and thermal stresses encountered during each reactor startup.⁴ Since the cracking is propagated by a corrosion fatigue mechanism, lower oxygen content in the water during startup should reduce the amount of propagation during each cycle. Furthermore, the higher pH resulting from coolant deaeration will tend to lengthen the time-to-failure by stress-corrosion cracking. Results of constant extension rate test (CERT) in inert (argon) atmosphere, low oxygen water and air-saturated (6 to 8 ppm oxygen) water demonstrate the very significant influence of oxygen on the strain-to-failure for stainless (Type-304) as well as low carbon (A508) steels (see Figures 2-2, 2-3 and 2-4).

Crevice corrosion risks in both Inconel and stainless steel can be reduced by design of components, but may not be eliminated. Oxygen control by deaeration will minimize crevice corrosion since the electrochemical driving force between the surface and the crevice tip will be significantly reduced, and the pH will be beneficially higher, because of less air dissolved in the water.

The general corrosion and pitting of materials of construction, particularly carbon and low alloy steels, is a marked function of the oxygen concentration in the water. The low temperature, high oxygen, stagnant water which now exists during shutdown and system layup, provides conditions that promote accelerated general and pitting corrosion of carbon and low alloy steels (see Figure 2-5). Some effects of general corrosion include higher loads on the radioactive waste treatment system, reduced visibility for refueling and in-vessel servicing, and increased fouling of heat transfer surfaces (including fuel). The effect of pitting corrosion is a reduction in fatigue life, since fatigue cracks are known to initiate at pitting sites.

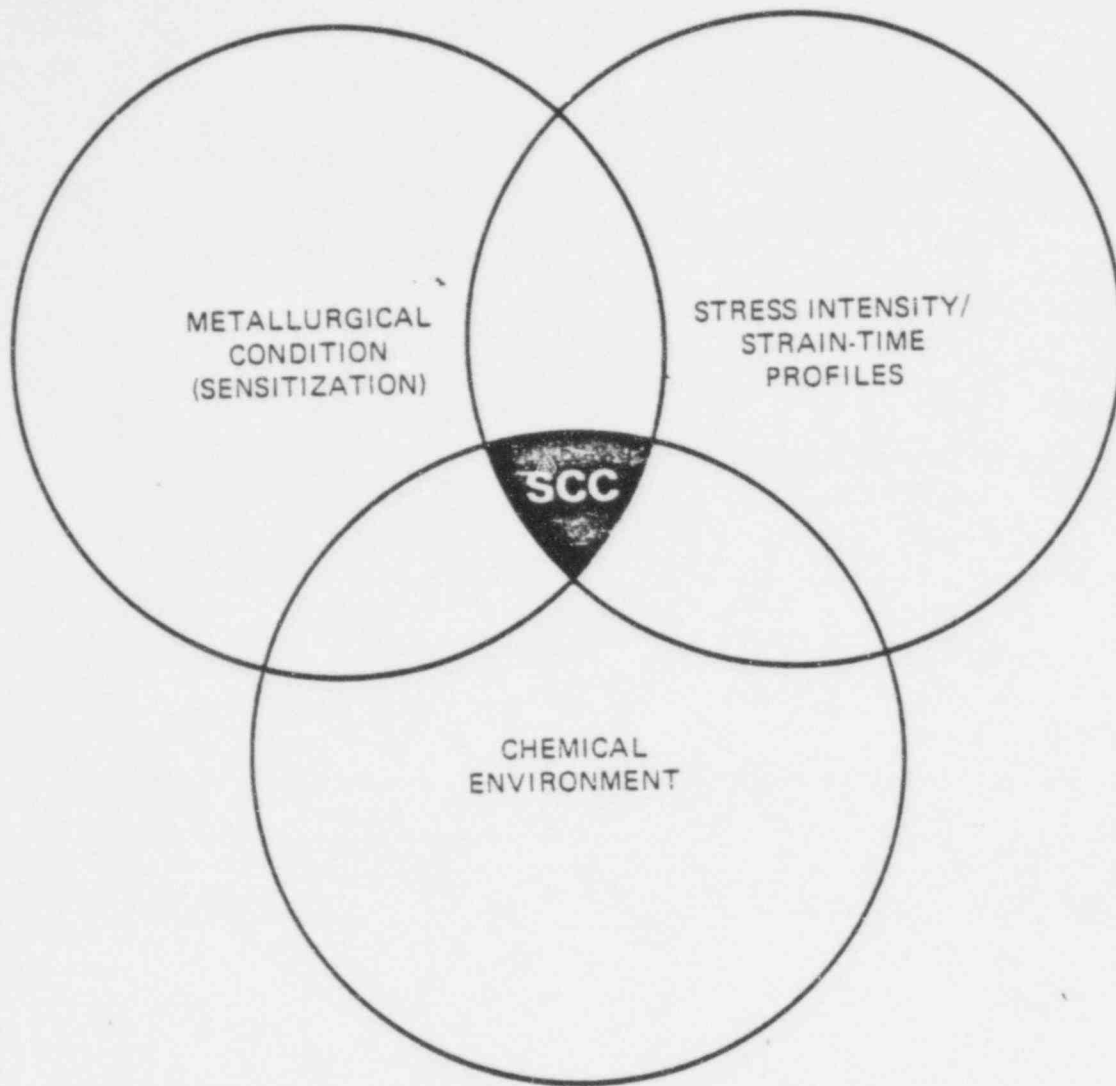


Figure 2-1. Variables Affecting Materials Performance

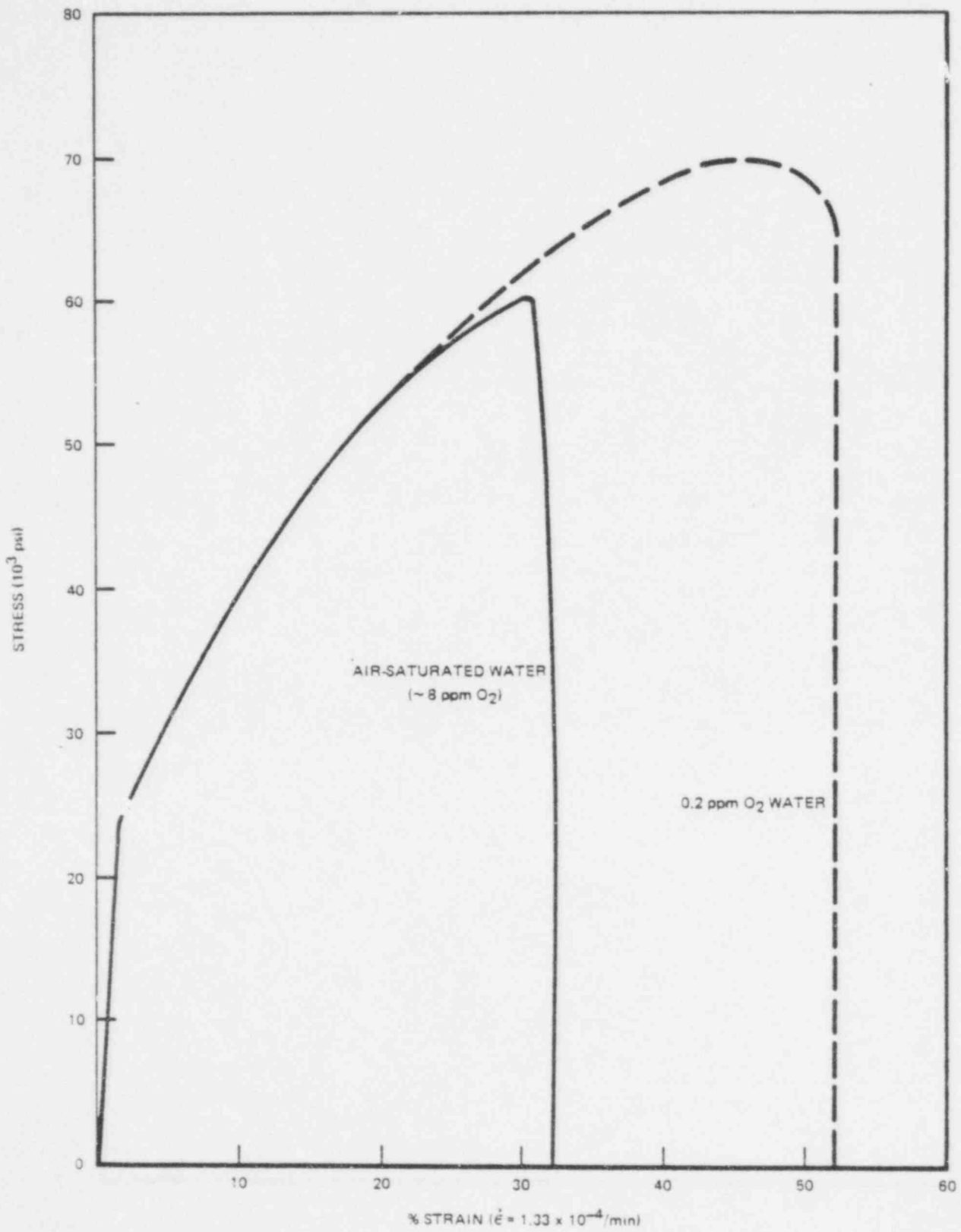


Figure 2-2. Constant Extension Rate Tests on Furnace Sensitized (834264C) Steel⁵

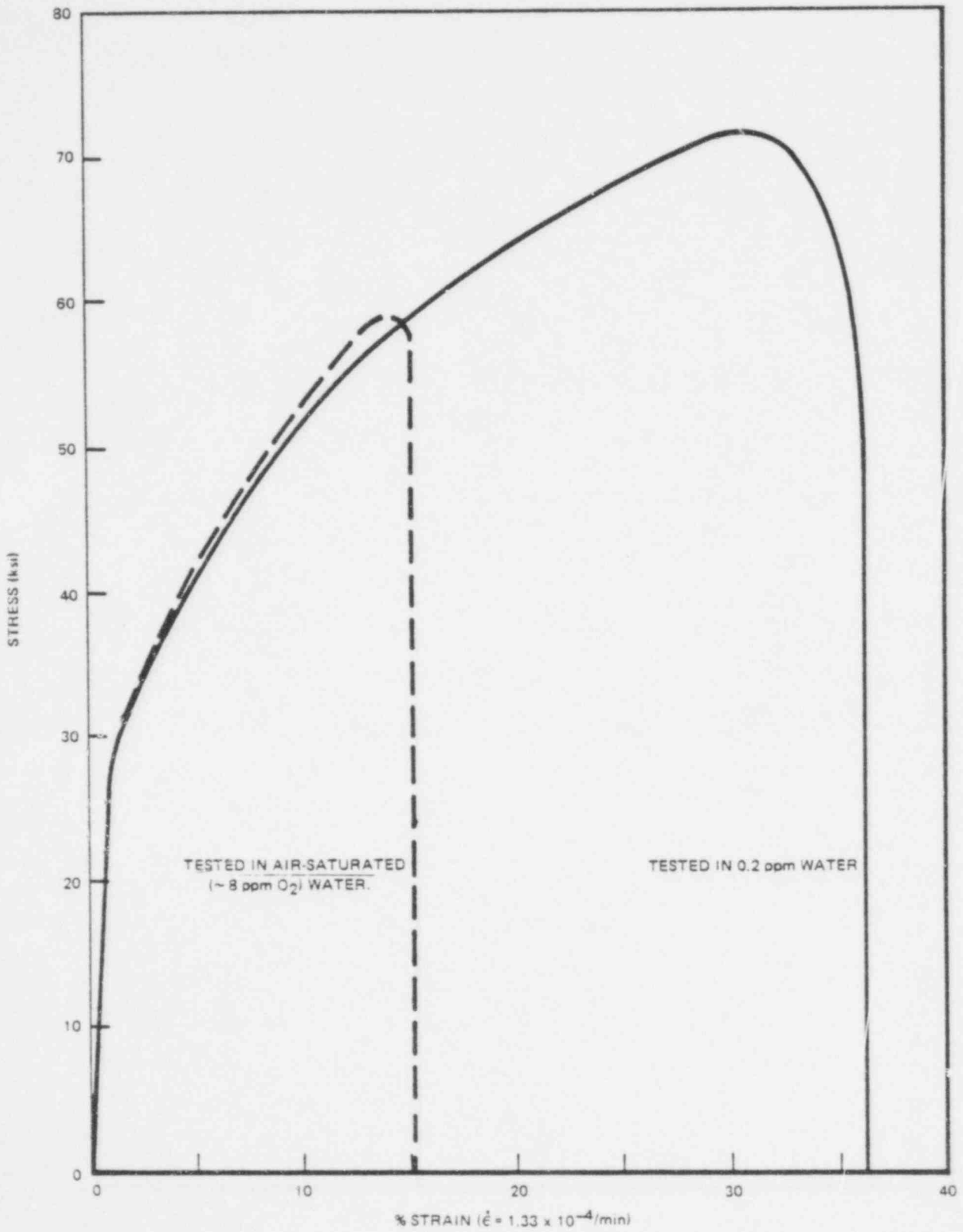


Figure 2-3. Constant Extension Rate Tests on 26-in. Diameter Stainless Steel Pipe Weld Aged at 400°C¹

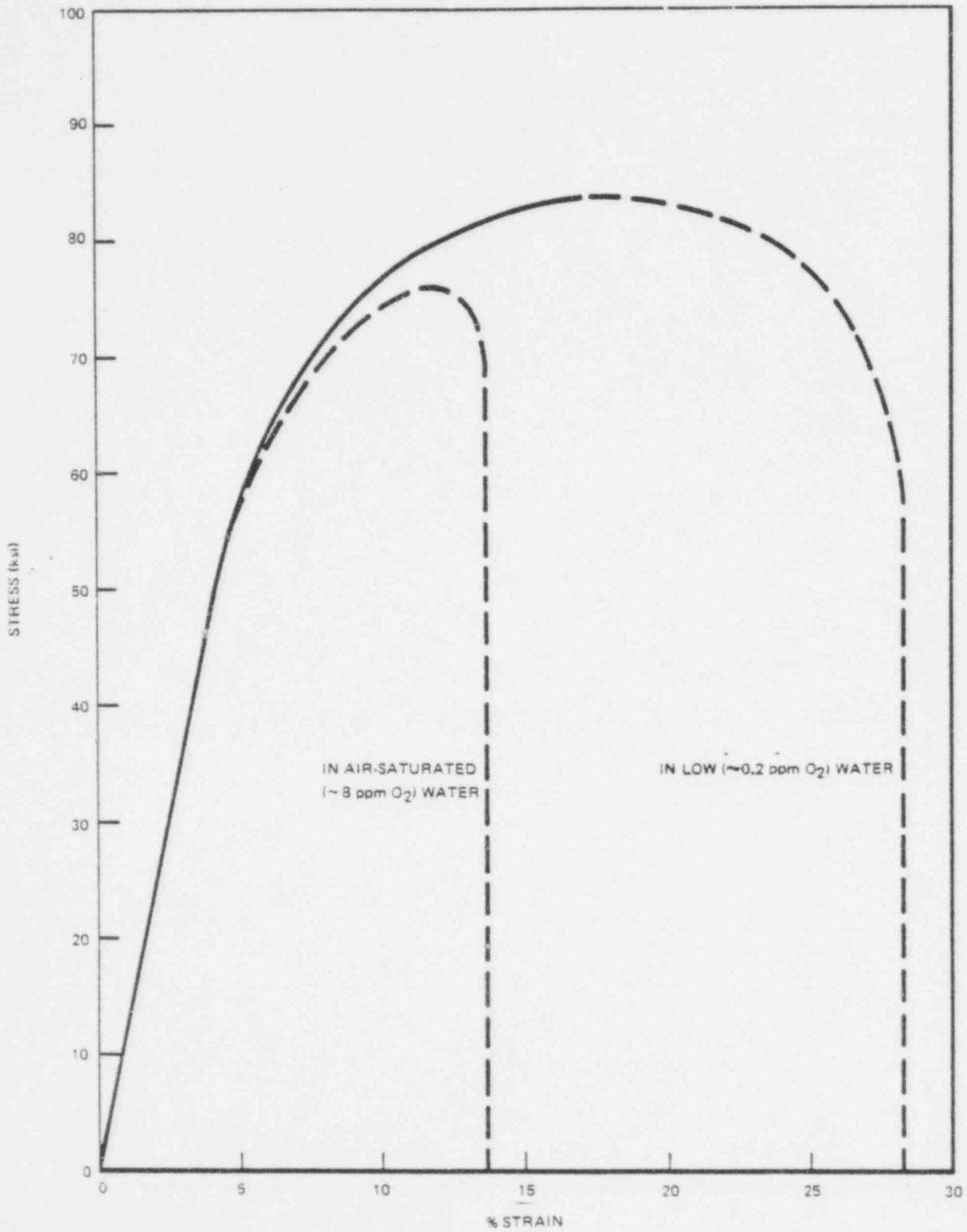


Figure 2-4. Constant Extension Rate Tests on A508 Pressure Vessel Steel[®]

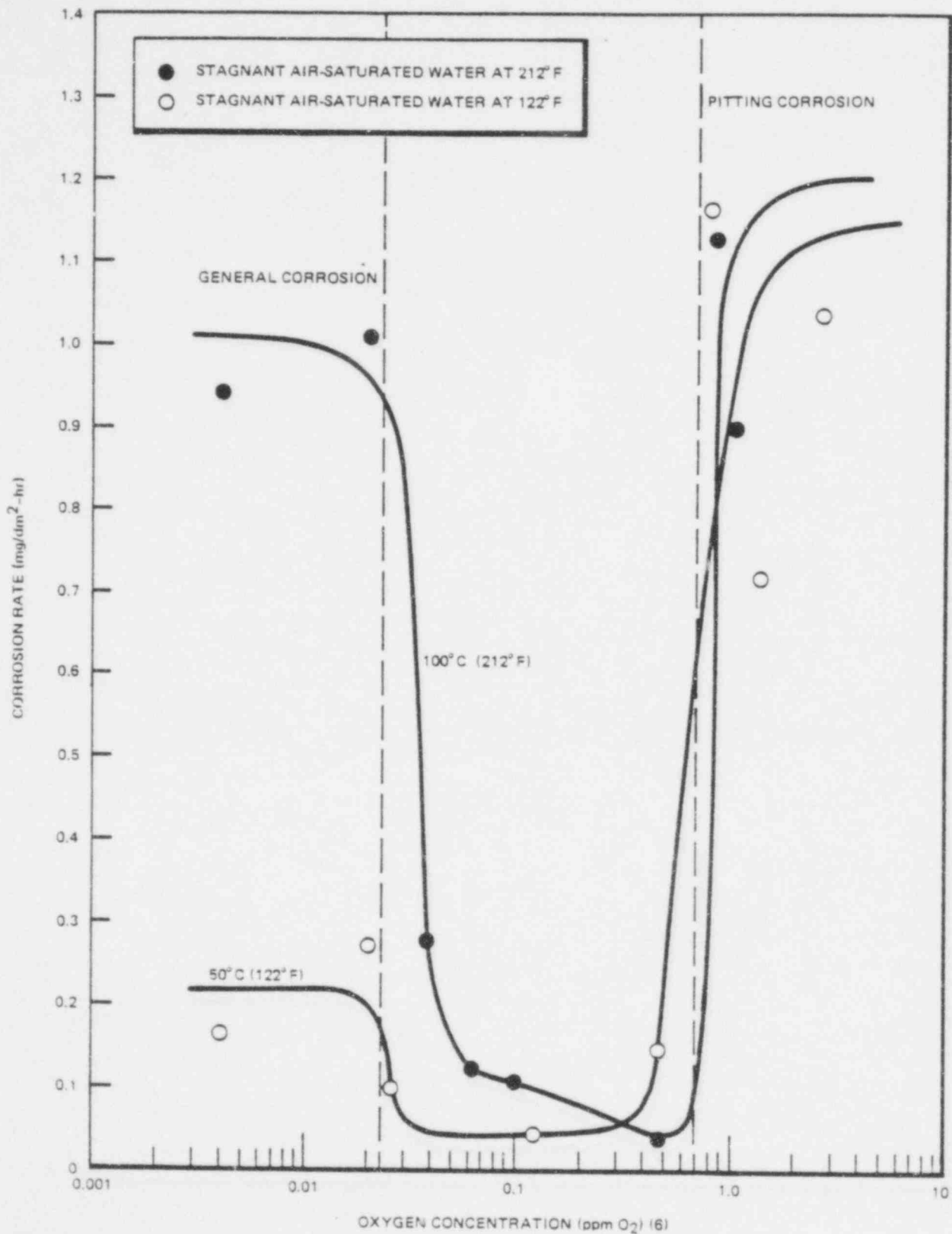


Figure 2-5. Corrosion of Low Carbon Steels versus Oxygen Concentration*

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2.2 PLANT RADIATION

Other important beneficial effects of oxygen/hydrogen peroxide control in the BWR coolant are associated with radiological aspects. Radioactive iodines in water containing high oxygen and hydrogen peroxide can be oxidized to chemical forms which are more volatile and less amenable to removal by ion-exchange methods commonly employed. In addition, carbon dioxide in aerated water taxes the ion-exchange capacity of the filter-demineralizer resins used in the reactor water cleanup system. The overall effect is to increase radioactive contamination and operator radiation exposure levels. Shutdown deaeration for oxygen control is expected to reduce airborne contamination levels, and thus improve plant refueling and maintenance *outage critical path periods*.

Activated cobalt (Co-60) resulting from corrosion of plant structural and wear materials has been identified as a major source of in-plant operator radiation exposure, and a contributor to waste activity. The high intensity radiation that can result from deposition of activated cobalt on certain reactor system piping and equipment surfaces causes difficulty in performing maintenance work and may, therefore, extend plant outages or result in the need for larger maintenance staffs to perform critical jobs.

The beneficial effect on radiation buildup by oxygen/hydrogen peroxide removal may be twofold: (a) reduced availability of source material for activation due to reduced corrosion of materials, and (b) reduced transport/deposition from the core region, where activation takes place, to out-of-core surfaces where the activity deposits. The amount of corrosion of BWR structural or wear materials which contain cobalt as an impurity, or as an alloying element, depends on the oxidative nature of the coolant.

Thus, steellites, which contain as much as 50 to 60% cobalt, corrode and wear more in high oxygen water than in degassed water. These corrosion products are subsequently subject to activation in the core region, or may already have been activated in-place (viz., CRD pins and rollers, and Inconel fuel clips and springs), depending on the location of the material in the plant.

The mechanisms involved in the transport and deposition of activated cobalt are complex; however, the coolant chemistry appears to play a key role. Although not fully understood at this time, it is believed that high concentrations of oxygen and hydrogen peroxide during shutdown may be a significant factor. The coolant concentration of soluble Co-60 is known to increase by orders of magnitude during shutdown. It is postulated that Co-60 is dissolved from in-core surfaces by a combination of high oxygen and hydrogen peroxide concentrations, and thermal solubility effects, and is later transported to, and deposited on primary system surfaces.

2.3 BWR MATERIALS ENVIRONMENT

To better understand the BWR environment and its influence on materials, it is useful to briefly describe the chemical characteristics of the BWR coolant during various plant conditions.

During normal plant operation, the bulk primary coolant is maintained at a near neutral pH, with oxygen and hydrogen present in stoichiometric quantities at nominal levels of 0.2 ppm oxygen and 0.025 ppm hydrogen. These conditions are maintained by inherent mechanisms of radiolysis, steam stripping and water-steam partitioning. During shutdown, when natural oxygen removal processes cease, oxygen concentration increases to a saturation value of 3 to 6 ppm from radiolysis, absorption of air, and input of aerated water from the CRD system.

In addition to differences in oxygen levels, there are a number of other significant differences in coolant chemistry between normal operation and shutdown. Hydrogen is not present in stoichiometric quantities with oxygen, which increases the materials corrosion effect of oxygen. Radiolysis of water at low temperature ($\leq 200^\circ\text{F}$) with excess oxygen⁷ produces hydrogen peroxide, a strongly oxidizing agent which further increases the corrosion potential. Carbon dioxide from air is absorbed in the coolant, forming carbonic acid which increases acidity and corrosion. During plant restarts, nitric acid may be produced locally from the interaction between neutrons and dissolved nitrogen, further increasing acidity and accelerating corrosion, particularly in crevices.

The proposed oxygen control (deaeration) system, as described in Appendix A, would minimize the concentrations of all dissolved gases and hydrogen peroxide, and thus would materially reduce the corrosive effects resulting from shutdown water chemistry.

To determine the need for deaeration of the primary coolant during plant transients, such as starting up and shutting down, calculations and plant measurements were made to characterize these transients with respect to oxygen, nitrogen, carbon dioxide, pH and other water chemistry parameters. It was found that operational procedures can be implemented that will eliminate high oxygen when the plants are in hot standby or being shut down. These procedures mainly include venting of the reactor to maintain saturated water conditions with low solubility for oxygen.³

During plant startup without shutdown deaeration, the coolant oxygen level is normally high during most of the startup even with proper venting. With shutdown deaeration and proper venting procedures, oxygen concentrations would remain low in all parts of the system, including stagnant lines. This is especially important because of high stresses that exist during startup.

2.4 BWR PLANT CHEMISTRY TRANSIENTS

In addition to normally expected chemistry changes caused by variations in plant conditions, i.e., startup, shutdown, normal operation and hot standby, there are several other types of chemical transients that may affect the BWR coolant chemistry. Such transients include ion-exchange resin intrusions, main turbine condenser tube leakages and residual heat removal (RHR) heat exchanger failures. The magnitude of these transients varies in duration and severity, ranging from a few hours to weeks at low pH, high chloride, high sulfate and other chemical species.

Intrusion of ion-exchange resins has occurred on a number of occasions at several BWR plants. Chemical degradation of resins by neutron flux and temperature produces sulfuric acid in the reactor, resulting in low pH and a very corrosive material environment, particularly when high oxygen concentrations are present.

Condenser tube failures occur periodically and, depending on the source of the condenser cooling water and its chemical composition, the impurities (species) and amount that enter the reactor can vary between high (several ppm) chloride to a mixture of hydrochloric acid, sulfuric acid, sodium sulfate, carbonates, fluorides, and other chemical compounds.

In the case of RHR system heat exchanger tube failures, the cooling water can enter the reactor directly without the filtration or partial demineralization which affords some protection against main turbine condenser tube leaks. Thus, high sodium chloride levels in the reactor have resulted from RHR heat exchanger failures in plants utilizing seawater or brackish water for plant cooling.

The above types of transients typically occur during, or as a result of, startup operations. For example, the introduction of resins into the reactor may occur when the reactor is shut down, but degradation only takes place after a significant core neutron flux is established, and/or when the temperature increases. If, during this time period, the coolant also has a high oxygen content, all the aggressive "ingredients" for stress-corrosion crack initiation and propagation are present, and can cause significant damage. In the case of condenser tube leakage, the situation is similar, and plant operating reports show that plants have experienced such problems with several parts per million chloride in the reactor water. In one such incident, significant damage occurred to several stainless steel reactor internal components, including the neutron monitoring system.

No direct correlation has been made, however, between pipe cracking and significant plant chemical transients because the available reports on such occurrences are scarce and incomplete, and the effects on the materials may be contributive to cracking rather than the primary cause. Deaeration during shutdown would significantly reduce the aggressive combination of high oxygen and chlorides (and other chemical species) that have been shown to affect stress-corrosion cracking.

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3. MATERIALS TESTS AND STUDY RESULTS

3.1 INTERGRANULAR STRESS-CORROSION OF STAINLESS STEELS

Four independent studies^{5,8,9,10} have shown that the intergranular stress-corrosion cracking (IGSCC) of austenitic stainless steel under a constant or increasing load is a strong function of dissolved oxygen content at reactor temperatures (550°F). Intergranular failures have been reported in as little as 0.2 ppm oxygen, but never in degassed systems.^{11,12} References 8 and 9 both show that decreasing the dissolved oxygen content from 10 ppm to 0.2 ppm results in an increase in sample lifetime under constant load by a factor of about 40 to 60, as shown in Figure 3-1. This increase is essentially independent of stress level.

Tests under constant displacement rates¹⁰ at three oxygen levels (all other conditions constant: 550°F high purity flowing water, same heat of material sensitized at 1150°F for 24 hours) show that the reduction of area and percent elongations are an inverse function of the oxygen content of the water (i.e., the more oxygen dissolved in the water, the more "brittle" the sensitized stainless steel). The sample appearance also shows a direct dependence of oxygen content, with the amount and severity of cracks increasing with increasing oxygen content. (The constant extension rate test shows environmental interaction with mechanical behavior with a reduction in strain to failure and a change in the failure mode between environmental and air control samples.) These results are summarized in Table 3-1. An independent series of tests with two different heats of stainless steel confirm these results. Figure 2-2 shows the results for furnace sensitized material in air saturated versus 0.2 ppm oxygen water at 550°F. The reduction in failure strain between the two cases is large. Figure 2-3 shows the results from tests with the same material in the "as welded" condition and a mild "aging" condition. Again, the same trend is followed with air-saturated water causing a marked decrease in strain to failure.

Table 3-1
CONSTANT STRAIN RATE TESTS¹⁰ ON
SENSITIZED STAINLESS STEEL IN 550°F HIGH PURITY WATER
WITH VARYING OXYGEN CONTENT

Oxygen Content (ppm O ₂)	RA* (%)	EI* (%)	Comments
Argon Control	60	27.4	1. Completely ductile.
<0.1 (steam)	55	31.5	2. The lower the RA and
<0.1	50	29.7	EI, the more brittle the
0.2	27.4	39.5	fracture behavior.
35 to 40	13.6	21.0	

All tests were run on the same heat (No. 8-1658), annealed for 1 hour at 1950°F and sensitized at 1150°F for 24 hours, and tested at a strain rate of 1.3×10^{-4} in./in./min.

* RA = Reduction in cross-sectional area of test specimen.
** EI = Elongation of test specimen.

The effect of oxygen content on the cracking susceptibility is probably twofold. First, at lower oxygen levels, the oxygen reduction kinetics are probably strongly dependent on the dissolved oxygen content. At higher levels, the rate of oxygen arrival to the crack site is limited to the oxygen diffusion rate, thus failure times are insensitive to oxygen levels above the range of ~1 to 3 ppm oxygen. Secondly, the initiation step is probably a strong function of oxygen content. As reported in Reference 8, initiation begins at the second phase particles located at grain boundaries (e.g., titanium carbides, manganese sulfides). By either mechanical strain, partial dissolution or a combination of both, a crevice develops between the particle

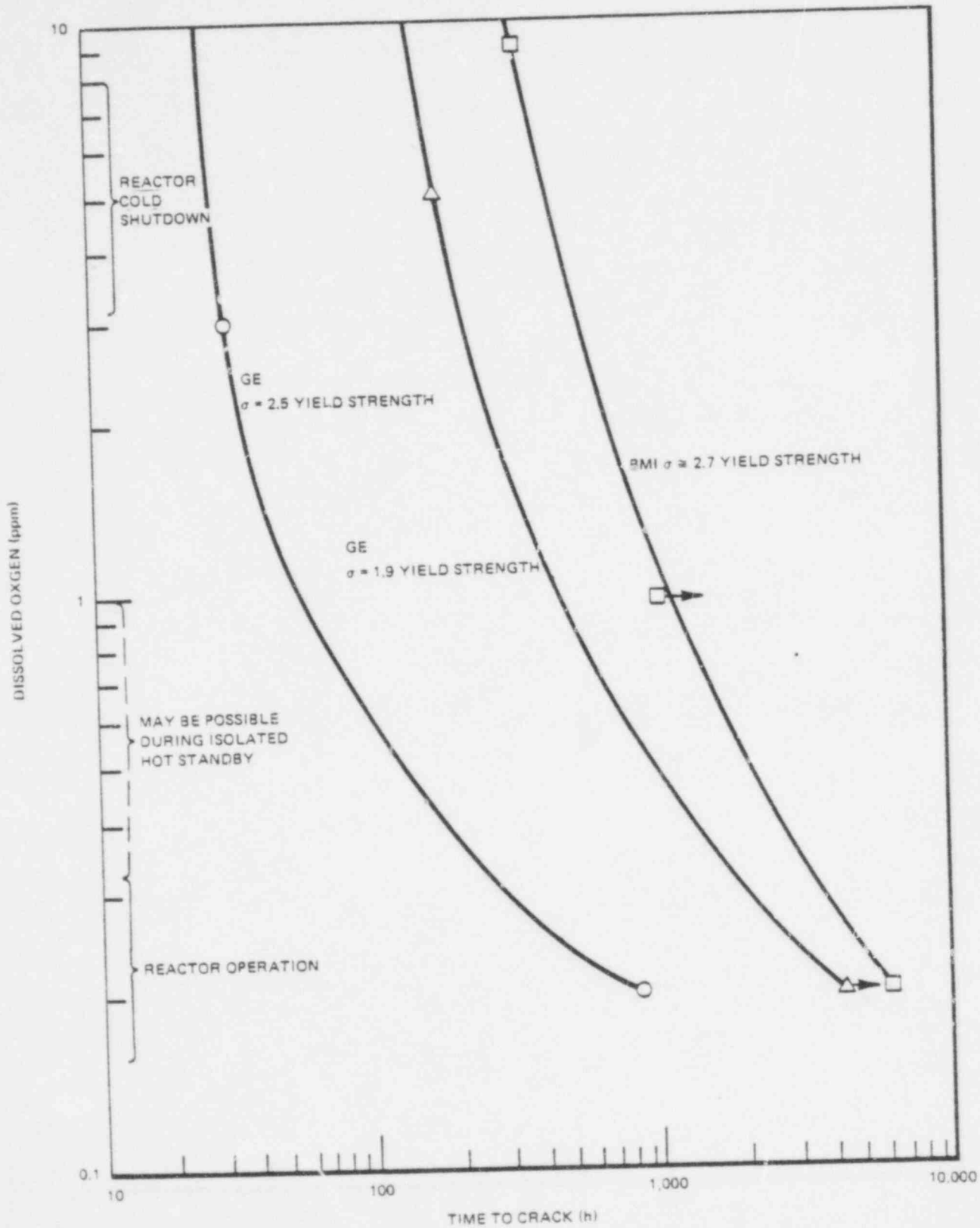


Figure 3-1. Intergranular Stress-Corrosion Cracking of Furnace Sensitized Type-304 Stainless Steel in 550°F Water^{4,5}

and the material or in the region previously occupied by the particle. The oxygen content has a strong effect on both the dissolution rate of the second phase particles and the chemical kinetics of the crack formation. An order of magnitude increase in oxygen content would greatly increase the kinetics and the severity of the crevice chemistry.

After initiation, a propagating crack establishes a crevice chemistry. The rate of propagation is a function of the severity of the crevice chemistry. As can be seen in Figures 3-2 and 3-3, both the time to initiate a crack in a crevice and the propagation rate of a crack is strongly influenced by the oxygen level. The higher the oxygen, the lower the initiation time and the faster the propagation rate.

3.2 INCONEL-600 STRESS CORROSION

The stress-corrosion cracking susceptibility of Inconel-600 is a strong function of oxygen content, as shown in Figures 3-2 and 3-3 from Reference 11. Figure 3-2 shows that for the creviced condition, both sensitized and annealed Inconel-600 have crack "nucleation" times that are very strong functions of oxygen content. Figure 3-3 shows the same is true for propagation rates on Inconel-600.

3.3 CARBON STEEL CORROSION

Tests at General Electric using a constant displacement rate in both 0.2 ppm and 100 ppm oxygen water at 550°F in both plain carbon steel and A508 Class II pressure vessel steel showed that dissolved oxygen plays an important role in crack initiation. In the high oxygen case, a larger number of cracks initiated and the cracks were deeper than for the low oxygen case. These results are summarized in Table 3-2. They show that the probability of stress corrosion of carbon steel and pressure vessel steel is much lower in low oxygen water. These results also imply that the fatigue crack propagation rates in high temperature water are most likely a function of the oxygen content, as the damage done during each strain event appears to be a function of the oxygen content. The results of these tests have recently been confirmed independently⁵ by comparing 0.2 ppm oxygen versus air-saturated water at 550°F for A508 Class II pressure vessel steel as shown in Figure 2-4.

Table 3-2
SUMMARY OF CONSTANT DISPLACEMENT RATE TESTS
ON CARBON AND PRESSURE VESSEL STEELS

Material	Environment	Elongation (%)	Area Reduction (%)	Rupture Stress (ksi)	Comments
Carbon steel	Argon at 550°F	—	36.8	73.5	Ductile failure
Carbon steel	0.2 ppm O ₂ in H ₂ O at 550°F	—	34.4	73.0	Low density transgranular cracks
Carbon steel	100 ppm O ₂ in H ₂ O at 550°F	—	18.4	68.5	High density transgranular cracks
A508 Pressure vessel steel	Argon at 550°F	11.3	57.9	87.5	Ductile failure
A508 Pressure vessel steel	0.2 ppm O ₂ in H ₂ O at 550°F	10.2	57.3	90.0	Low density transgranular cracks
A508 Pressure vessel steel	100 ppm O ₂ in H ₂ O at 550°F	9.9	48.2	86.5	High density transgranular cracks

Displacement rate was such that pure mechanical failure in argon for both steels occurred between 7.6 and 9 hours.

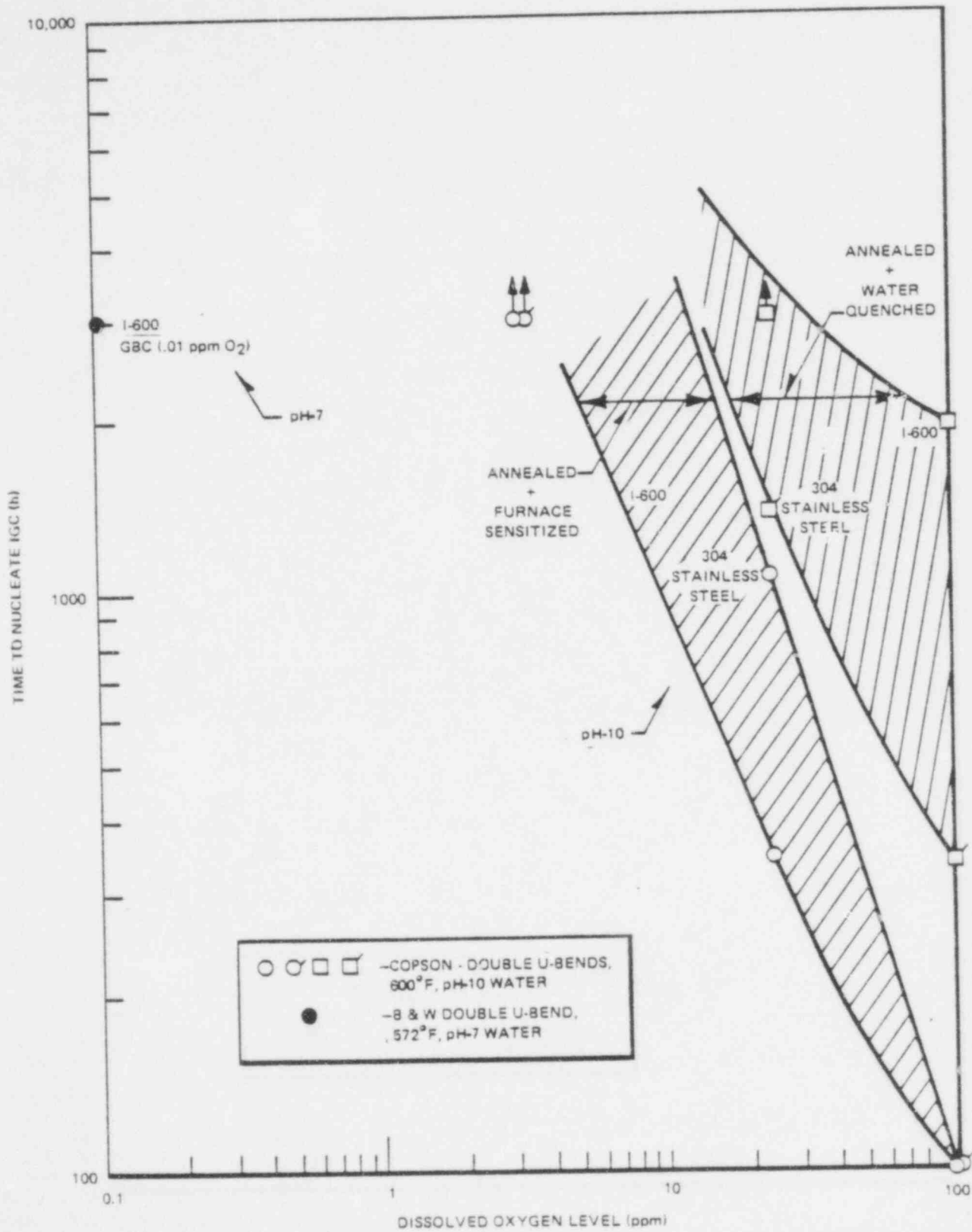


Figure 3-2. Time to Nucleate Intergranular Cracking versus Dissolved Oxygen Content in Double U-Bend Samples of Inconel-600 and Type-304 (creviced) Exposed to 550 to 600°F Water¹¹

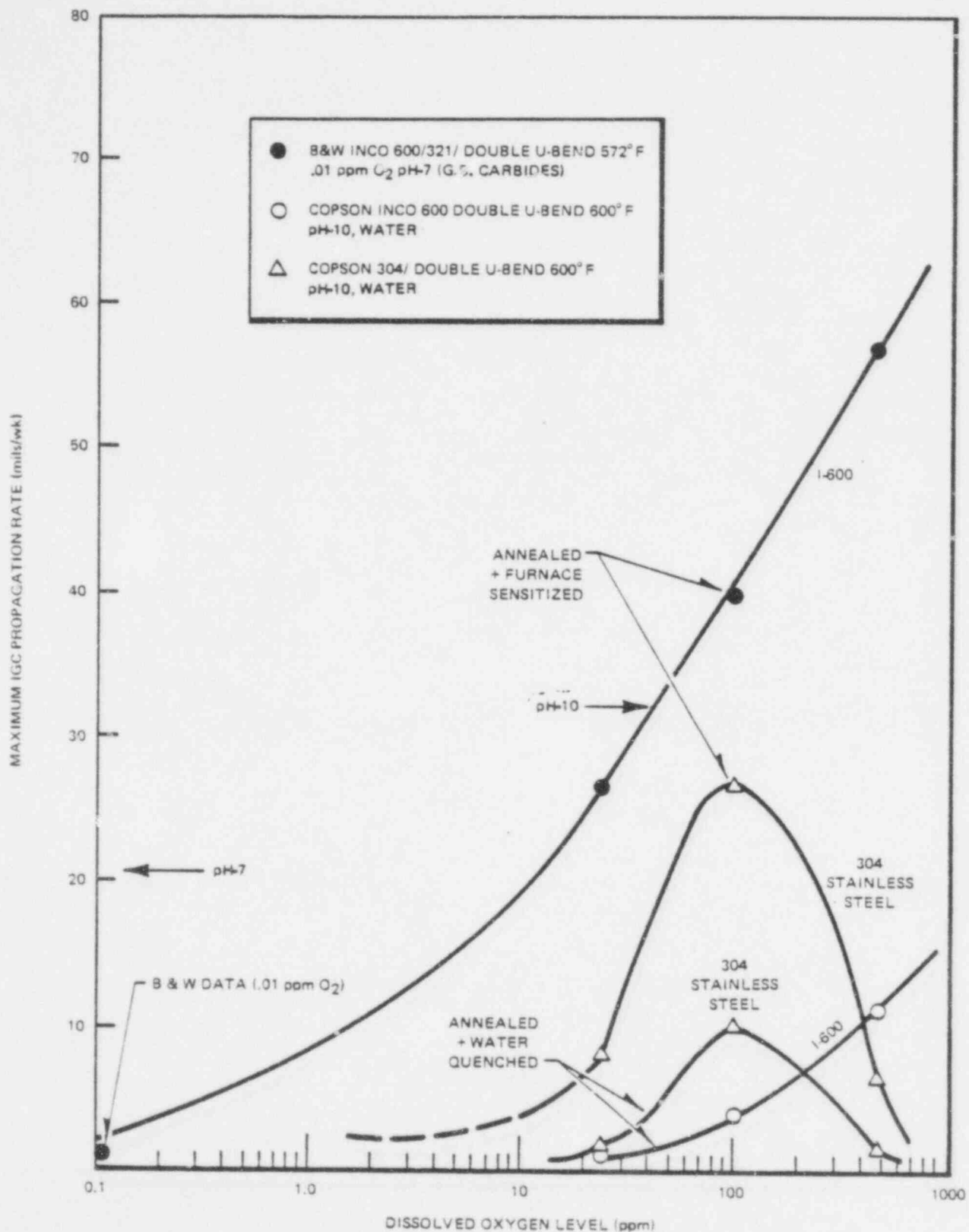


Figure 3-3. Maximum Propagation Rate for Double U-Bend Samples of Inconel-600 and Type-304 (both annealed and sensitized) as a Function of Dissolved Oxygen Content¹¹

There have been no systematic investigations of the effect of dissolved oxygen content on the kinetics of *fatigue* crack initiation and/or propagation rates. However, one can assess the effect of oxygen content during layup on the fatigue behavior of carbon steel. In Reference 13, the fatigue cracks were observed to initiate at pits in the carbon steel samples. At low temperatures, dissolved oxygen plays an important role in the pitting behavior of carbon steels.¹⁴ Under stagnant conditions, the lower the oxygen the less the pitting, and some tests⁸ have shown that below a certain (≤ 0.6 ppm O_2) oxygen level pitting appears to be avoided. Air-saturated stagnant water at 125°F provides for aggressive pitting of carbon or low alloy steel, as shown in Figure 2-5.

Since fatigue cracking initiates easily at pits, one can assume that low temperature exposure to air-saturated water will significantly reduce the initiation time for fatigue cracking over carbon steel layed up in low oxygen water. The fact that oxygenated water accelerates crack growth is in line with the constant extension rate data presented above for carbon and low alloy steels. One would predict that the oxygen level of the water would also affect the growth rate, i.e., higher rates at higher oxygen contents.

3.4 EFFECT OF TEMPERATURE

3.4.1 Stainless Steel

One test program has addressed the effect of temperature on the intergranular stress-corrosion response of sensitized stainless steel in high purity water.¹⁵ Sensitized samples (1085 °F/20h/furnace cooled) of wrought Type-304 were tested under constant extension rate (0.03 mils/min) at six temperatures in air-saturated high purity water. The results of these tests are shown in Table 3-3. From these results, one would conclude that stress-corrosion cracking could initiate during a stress event at temperatures as low as 250°F and possibly as low as 200°F. Confirming data on the effect of temperatures are shown in Figure 3-4 produced in an accelerated test under constant load conditions in oxygenated high purity water.

Table 3-3
RESULTS OF CONSTANT DISPLACEMENT RATE TEST
ON SENSITIZED STAINLESS STEEL¹⁵

Test Temperature (°F)	Mean Stress (ksi)	RA (%)	Failure Time (hr)	IGSCC by Fractography
200	76.5	76.5	120	No*
225	73.0	73.0	159	No*
250	71.4	53.4	116	Yes
300	69.0	53.4	118	Yes
350	68.0	27.8	79	Yes
550	39.5	27.1	74	Yes

Test Conditions

- Samples from 6-in. Schedule 80 Type-304 Seamless Pipe (Heat No. 27388).
- Displacement Rate = 0.03 mils/hr.
- High purity, air-saturated water (~ 8 ppm O_2).
- Samples examined by metallography and scanning electron microscopy (SEM).

* Grain separation in one location of fracture surface, by scanning electron microscopy (SEM)

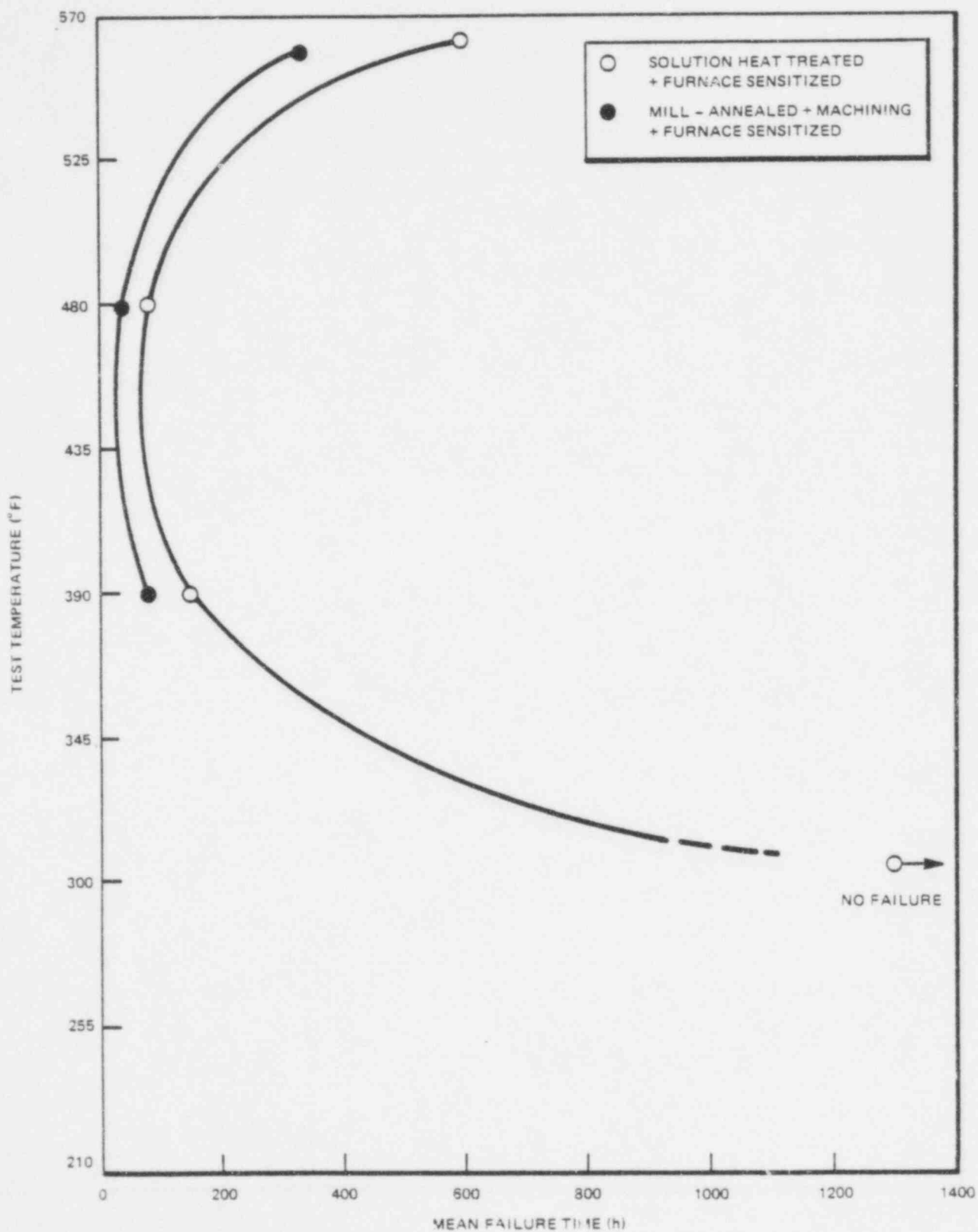


Figure 3-4 Effect of Test Temperature on Mean Failure Time to IGSCC of Sensitized Type-304 Stainless Steel in Oxygenated High Temperature Water¹⁶

One known BWR 304 stainless steel component has suffered stress-corrosion cracking at a temperature far below 550°F in at least two separate plants. The threaded portion of the index tube of the CRD mechanism in some reactors is exposed to aerated water at temperatures in the range of 150 to 250°F. The component is severely sensitized because it is subjected to a nitriding (cracks occurred in unnitrided areas) process during manufacturing and, thus, is expected to be susceptible to stress-corrosion cracking.

There has been another reported failure¹⁷ of a reactor component of welded 304 stainless steel which *never saw temperatures above 145°F*. This failure occurred in a 20-in. Schedule 10 line of the high flux beam reactor (HFBR). The failure mode was intergranular and occurred in the heat affected zone of a weld. The environmental conditions are listed in Table 3-4. The chemistry conditions are somewhat more aggressive than those typical for a BWR because of the nitric acid additions to control corrosion of the aluminum core components. However, the pH of the BWR water can be as low as 5.3 during layup and startup and certain transients, so the conditions of the HFBR are not drastically different from those that may be present in a BWR. The dilute nitric acid content may also resemble somewhat the nitric acid potentially produced by radiolysis of dissolved nitrogen in a BWR during shutdown and startup conditions. The stresses in the weld area were calculated to be as high as 16.8 ksi applied tensile load (not counting the welding residual stresses), so the part was probably loaded on the plastic flow curve during operation, a condition thought to be necessary before IGSCC can occur in the BWR environment. Both the experimental data and the service data clearly indicate that IGSCC of stainless steel can occur at low temperatures in oxygenated environments. Considering the effect of oxygen on crack initiation and propagation at 550°F, it is obvious that lower oxygen during startup, shutdown and layup should reduce significantly the probability of IGSCC in stainless steels.

Table 3-4
SUMMARY OF WATER CHEMISTRY CONDITIONS
OF HIGH FLUX BEAM REACTOR FAILURE AREA¹⁷

Item	Concentration
D ₂ O	99.37
Conductivity	4.6 to 3.0 μmho/cm
pH	5.0 to 5.2
Chloride	<10 ppb
Nitrate	330 to 550 ppb
Turbidity	None through 20 feet
Pressure	200 to 250 psi
Flow velocity	37 ft/sec to 10 ft/sec
Oxygen (dissolved)	15 to 20 ppm

3.4.2 Inconel-600

No experimental data exists on the effect of temperature on the stress-corrosion cracking or corrosion fatigue behavior of Inconel-600 between room temperature and 550°F. One reactor component failure did occur in an Inconel-600 component operating at 420°F in a Swedish reactor.¹⁸ The material was highly stressed (over 0.2% yield), had residual cold work and was heavily sensitized. The reason for the failure was not well defined, and caustic cracking rather than BWR water chemistry effects may have been the attributable cause.

3.4.3 Carbon Steel

General Electric results show that self-loaded, wedged-opening-loading (WOL) samples of A508 and A533 at a stress intensity of $K = 50 \text{ ksi (in.)}^{1/2}$ showed crack extension after combined exposure to simulated BWR conditions plus stagnant water conditions. The fractography showed branching transgranular cracks. The test samples were exposed to flowing simulated BWR water for 209 days at 550°F and ambient temperature 14 times. The test loop was then layed up with

air-saturated water for 301 days. The samples were removed and transgranular crack extensions were observed. Analysis of the layup water at the end of the test duration showed that the water contained about 20 ppm chlorides. Thus, the test conditions were severe both in terms of stress intensity and environment during the wet layup period, but the results do indicate that layup under air-saturated conditions should be avoided.

3.5 STRESS-CORROSION AND PLANT CHEMISTRY TRANSIENTS (STAINLESS STEEL)

Extensive test work has been done to correlate effects of aggressive anionic species, such as chloride-ions, on intergranular stress-corrosion cracking of stainless steels. A summary of results from such tests¹⁸ is represented in Figure 3-5 which correlates stress-corrosion cracking as a function of dissolved oxygen and chloride concentrations under operating BWR coolant conditions. This figure shows that very little chloride content is required to produce stress-corrosion cracking when oxygen is present in quantities greater than that corresponding to steady-state plant operation (0.1 to 0.3 ppm).

Figure 3-6 shows results from tests and correlations¹⁹ that demonstrate the stress-corrosion cracking effect of aerated versus deaerated water as a function of chloride content of the test water. The effect is expressed as the "cracking index" (I_{CSR}) which increases as the propensity for intergranular stress-corrosion cracking increases. As shown in the figure, the effect of oxygen becomes obvious when the material is sensitized, and particularly dramatic at the higher chloride concentrations. This consideration becomes particularly important in connection with condenser/heat exchanger tube leakages and associated cooling water intrusions to the reactor. Because condenser tube leakage is difficult to determine during plant shutdown and startup, the probability for cooling water intrusions to the reactor during these conditions is higher than normal and at a time when the coolant oxygen content is typically high. Therefore, the risk of stress-corrosion cracking from the chloride-oxygen combination is also higher, and deaeration for oxygen control during shutdown and startup conditions would minimize this risk.

Deaeration during startup would also play an important role in reducing the materials damage from demineralizer resin breakthrough and intrusions to the reactor. General Electric data and reactor experience shows that the pH of the reactor water after such a transient can go as low as 3 to 4, and perhaps even lower in localized areas. When these breakthroughs occur during startup, the combination of acidic conditions and high oxygen can nucleate intergranular attack (IGA). This IGA can then serve as a pre-nucleator for IGSCC during steady-state operation and subsequent startup cycles.

The initiation of stress-corrosion cracking in sensitized stainless steel is the "hard step" in establishing a growing stress-corrosion crack as the required stress intensity (K_{ISCC}) value is quite low.² Deaeration during startup would reduce the oxidizing power of the coolant and thus retard or inhibit the formation of intergranular attack in areas of sensitization in stainless steel components.

3.6 SUPPORTIVE TEST PROGRAMS

To better define and quantify the effects of BWR coolant chemistry on plant materials behavior, extensive test work is currently being done in General Electric's and others' laboratories. These test programs include quantitative correlations between oxygen/hydrogen peroxide and materials corrosion propensity, and materials behavior during simulated transient BWR chemical conditions. In addition, in-plant measurements and correlations of chemistry with radiation chemistry and electrochemical corrosion potential are being performed. Preliminary results from these programs are included in this report; and remaining parts of the programs are expected to help quantify the benefits of BWR coolant oxygen control.

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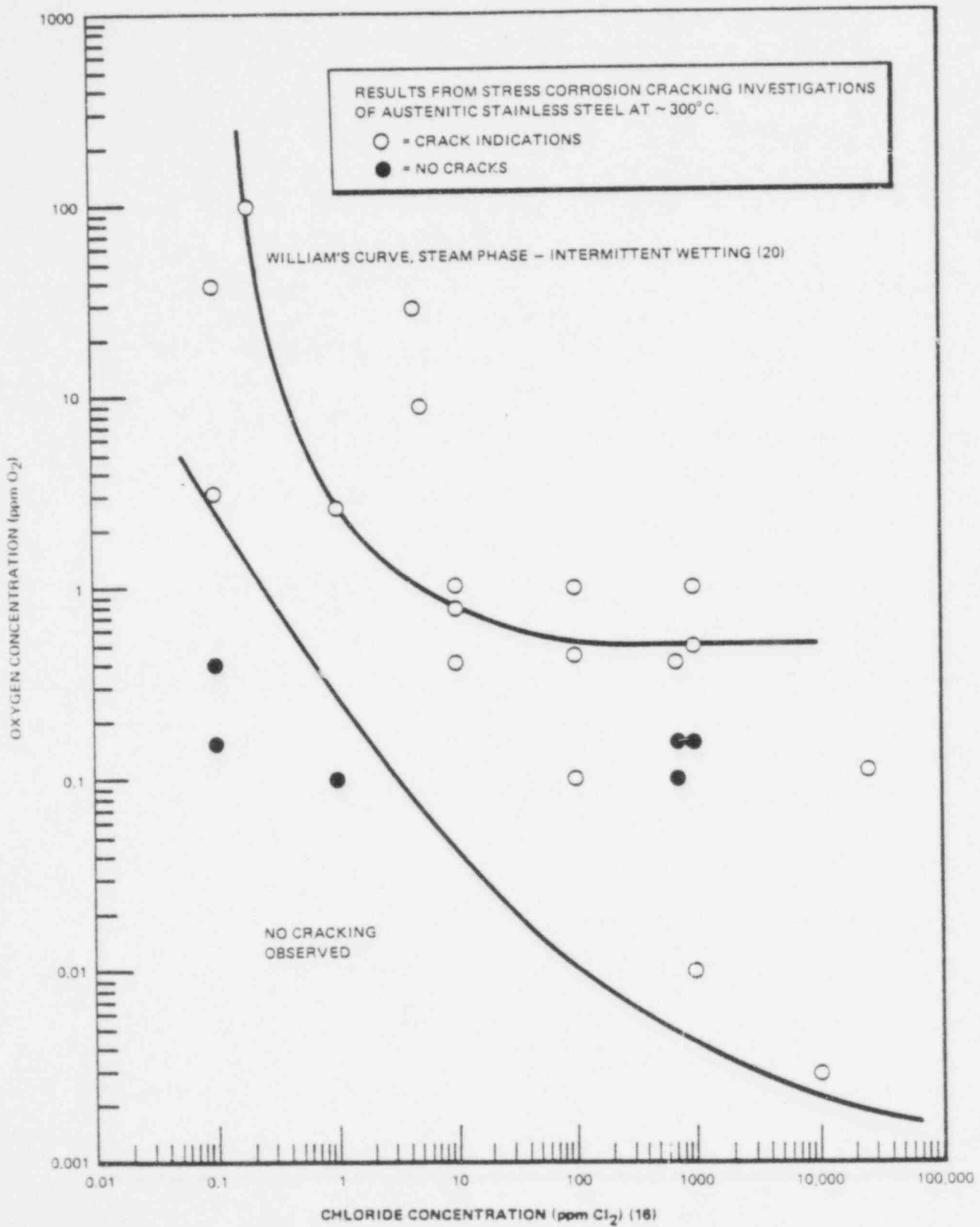


Figure 3-5. Stress Corrosion of Stainless Steel — Oxygen versus Chloride Concentration

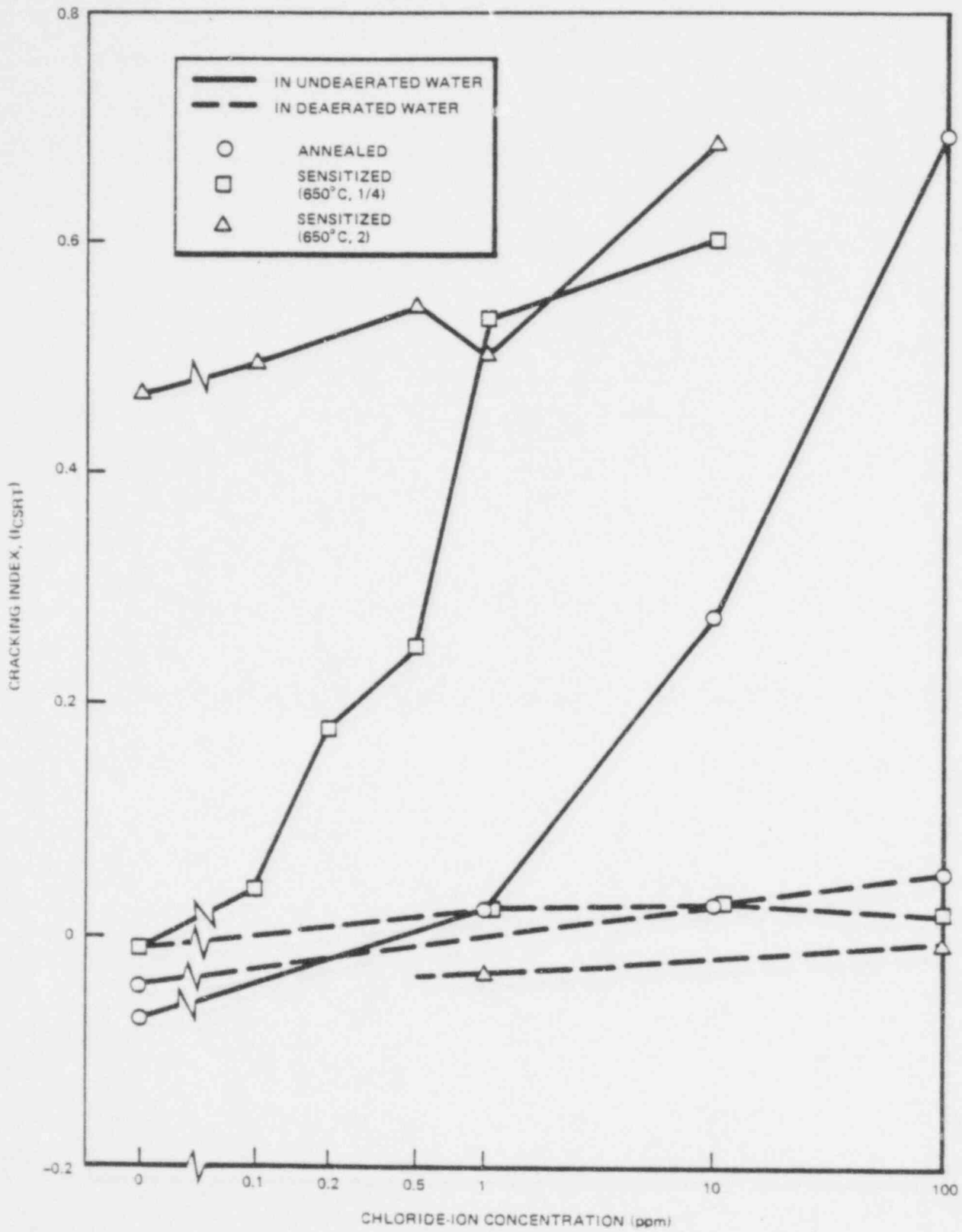


Figure 3-6. Change of Cracking Indices I_{CSRT} with Chloride-Ion Concentration¹³

4. ELECTROCHEMICAL CONSIDERATIONS

The potential benefits of oxygen control during startup have recently been shown by measurements at an operating BWR plant.²¹ The reactor was brought to 200°F and was partially deaerated by a vacuum degassing technique. Continuous electrochemical and chemical measurements were made during the 7-hour degassing cycle. The data are summarized in Figures 4-1 and 4-2, and show that as the degassing process continues at 200°F, oxygen is reduced from 1.5 ppm to 0.045 ppm, hydrogen peroxide (H₂O₂) is reduced from 2 ppm to 0.130 ppm, and the corrosion potential of stainless steel is reduced by 300 mV. This reduction in oxidizing power of the environment greatly reduces the driving force for corrosion processes, including corrosion fatigue and pitting of carbon steel and stress corrosion of stainless steel.

Deaeration during startup is important in reducing high concentrations of H₂O₂ produced by radiolysis from oxygen and water at lower temperatures. Figure 4-3 shows how potent 1 ppm of H₂O₂ is in providing an oxidizing environment. Without H₂O₂ present, the corrosion potential at 77°F increases from +0.1 to +0.25 volts when oxygen increases from 0.1 to 8 ppm. With H₂O₂ present at 1 ppm, the corrosion potential is much more oxidizing, i.e., +0.4V. From this data,²² the benefits of continuous oxygen control by deaerating during shutdown and startup are shown. The reduced concentration of H₂O₂ at lower temperatures will result in a much less severe oxidizing environment (more negative potentials), which will reduce environmentally associated damage due to stress/strain cycles concurrent with these transient events. The fact that H₂O₂ can be reduced by the deaeration process is evidenced by the data presented in Figure 4-1. Also, by removing the oxygen during plant shutdown, little hydrogen peroxide is formed to contribute to the oxidizing power of the coolant.

The electrochemical approach has been useful to show that the laboratory tests in simulated BWR water (0.2 ppm O₂ + 0.025 ppm H₂) at 550°F are representative of the coolant chemistry in the BWR. Measurements at two operating BWRs^{21, 23} show that the corrosion potential of stainless steel in a BWR is reproducible from reactor to reactor during operation and encompasses the range of -0.120 to -0.160V, standard hydrogen electrode (SHE). Equivalent measurements in a simulated BWR environment in the laboratory give similar values, -0.13 to -0.160V, SHE. This data confirms that the laboratory studies presented earlier on the effect of oxygen content on the IGSCC behavior of stainless steel are valid.

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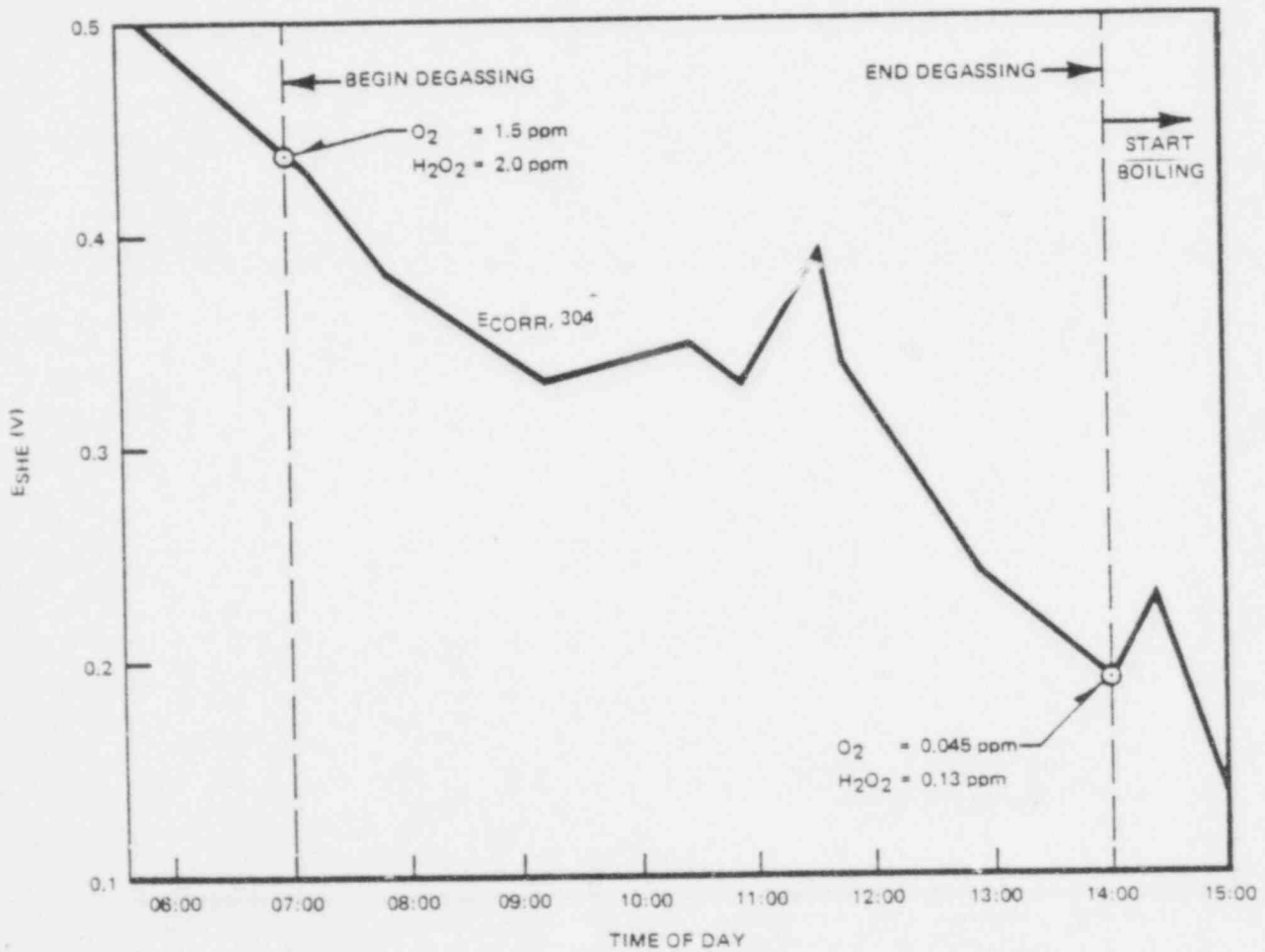
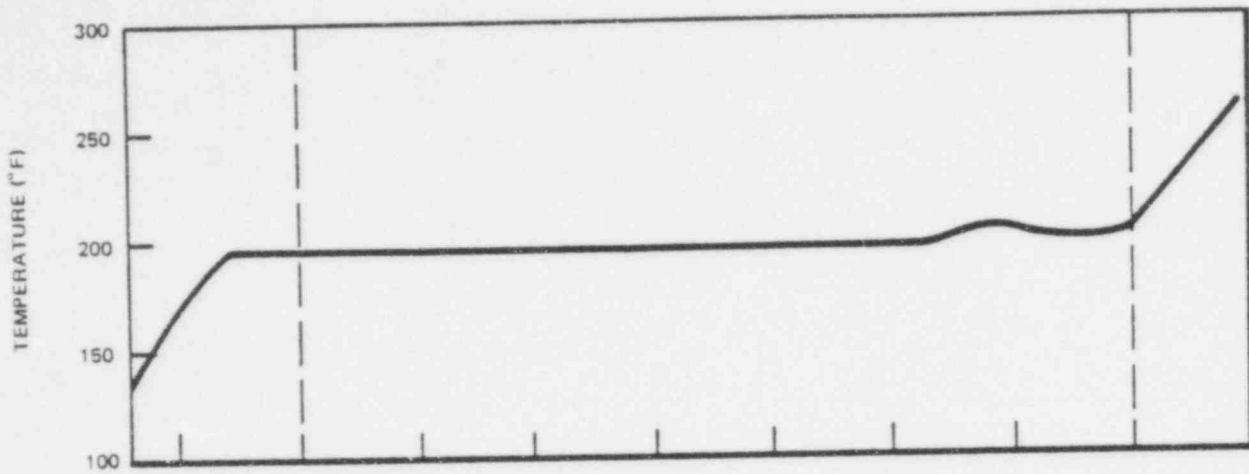


Figure 4-1. Primary Coolant Degassing Results During a BWR Startup²¹

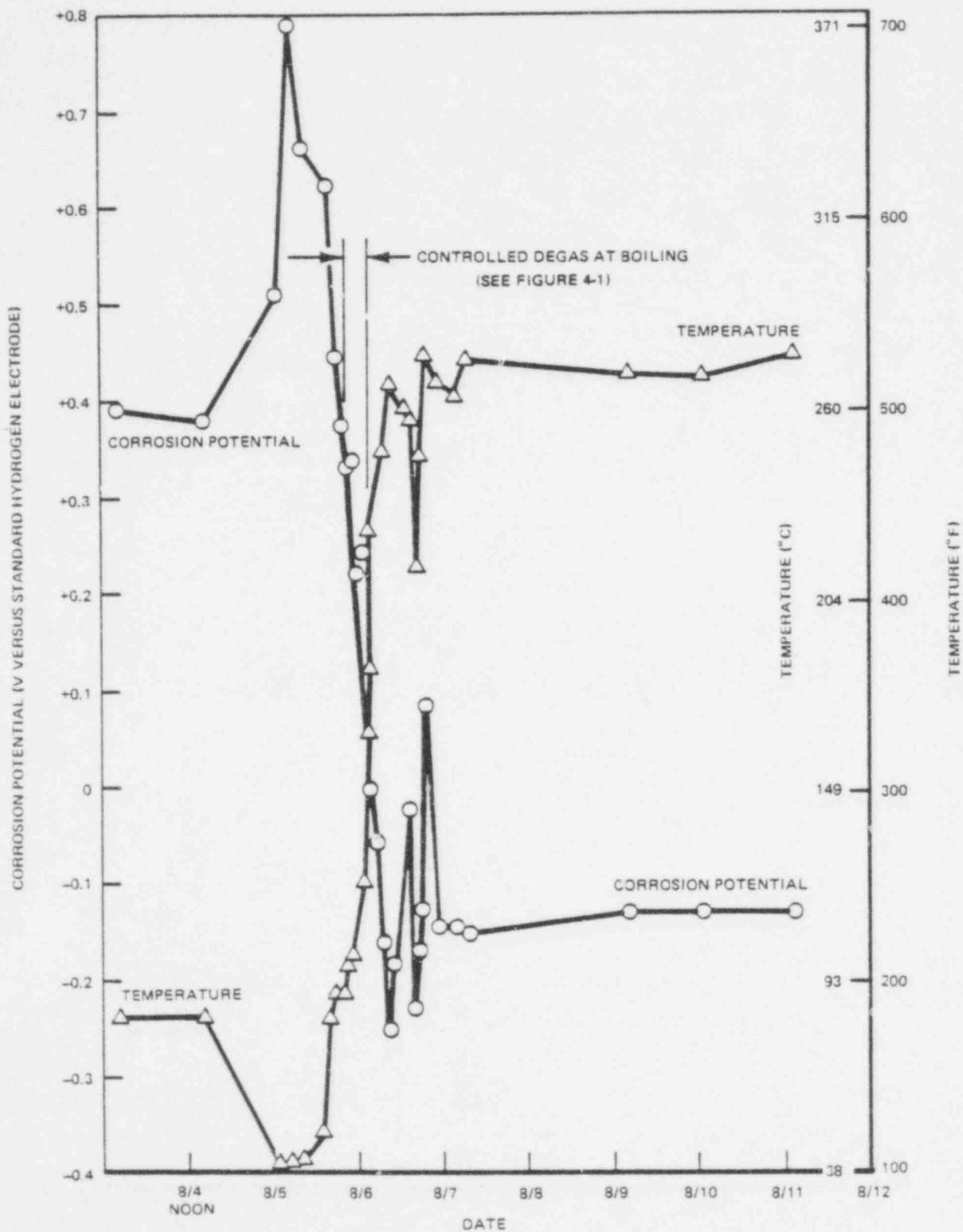


Figure 4-2. Corrosion Potential of Type-304 Stainless Steel During Reactor Startup²¹

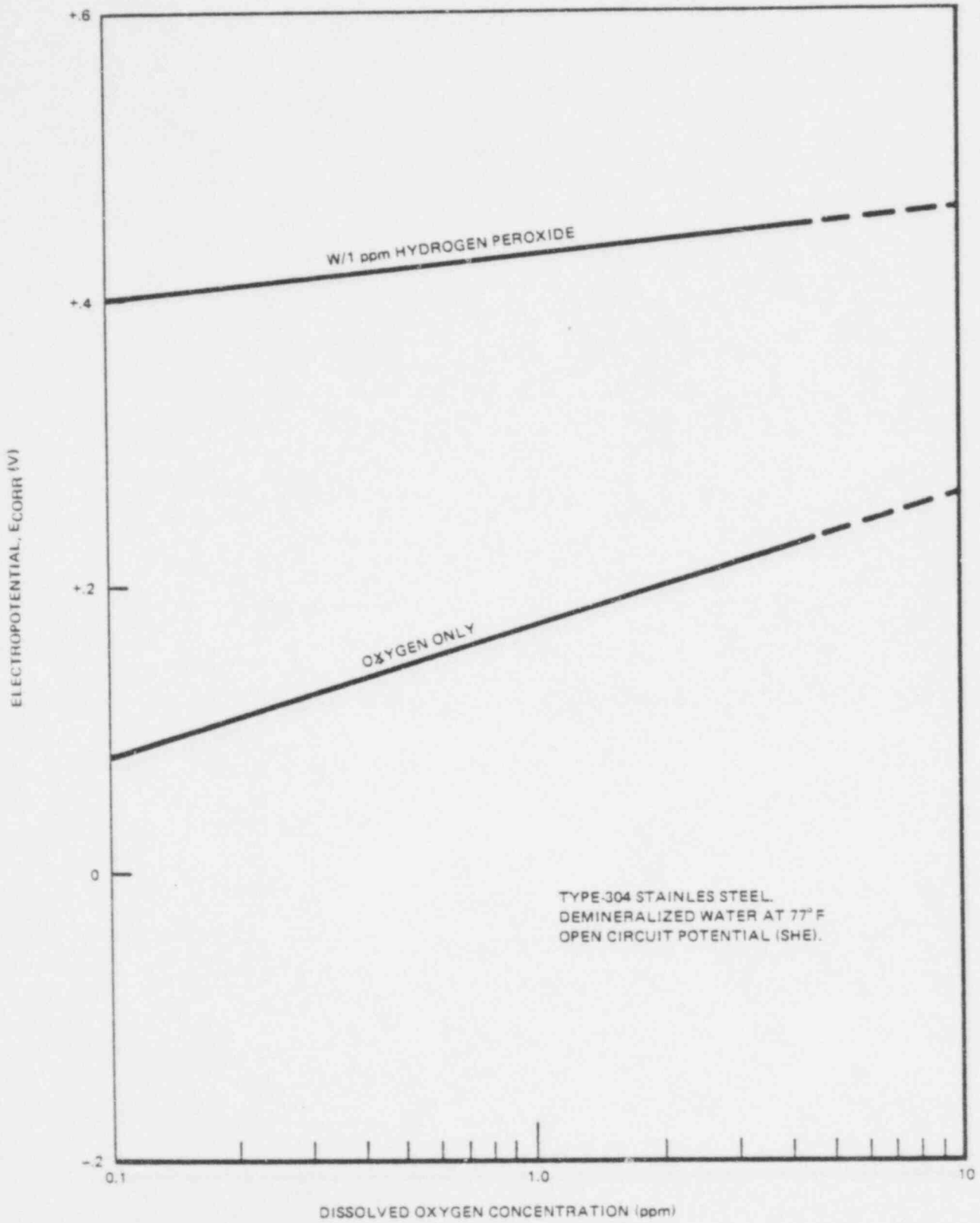


Figure 4-3. Corrosion Potential versus Oxygen Concentration and Hydrogen Peroxide at 77°F²²

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5. SUMMARY AND RECOMMENDATIONS

This study has brought together available material test data and previous studies by General Electric and others, regarding the material effects and radiological aspects of oxygen in BWR water chemistry. Educated benefits estimates indicate improvements in materials performance and associated plant availability and operating costs on the order of millions of dollars per year by implementation of BWR coolant oxygen control during shutdown, layup and startup conditions. A supportive test program is presently underway, and preliminary results confirm that significant beneficial effects on materials performance can be gained by improved coolant oxygen and chemistry control.

A relatively simple deaeration system design to accomplish BWR coolant oxygen control has been developed, utilizing commercially available equipment. This design requires minimal changes to existing operating plant systems, and can be implemented without impact on plant availability and reliability. Therefore, the following recommendations can be made.

- A. Systems should be provided and operating procedures instituted at all BWRs to control oxygen in BWR water systems. Specific objectives of a shutdown oxygen control system should be as follows:
1. During shutdown, maintain oxygen levels in the reactor vessel, recirculation system, reactor water cleanup system, and shutdown cooling portion of the RHR system at the nominal level of 0.2 to 0.3 ppm or less.
 2. Provide continuous low flow flushing of the portion of emergency core cooling (ECC) systems extending from the normally-closed injection valve to the reactor with deaerated water during plant shutdown. This is to prevent any possible buildup or entrapment of oxygen in these lines from radiolysis or other sources.
 3. Provide a supply of deaerated water (≤ 0.05 ppm oxygen) to the CRD system during plant shutdown. This change, combined with recommendations in Reference 24 will result in CRD water being deaerated at all times.
 4. Provide a source of deaerated water to lay up that portion of the RHR system and other ECC systems extending from the normally closed injection valve to the pump check valve. Oxygen in these systems is to be controlled during standby conditions by filling them initially, and after each flow test, with deaerated water, sampling periodically and flushing with deaerated water as necessary to maintain less than 0.6 ppm oxygen.
- B. The oxygen control system and operating procedures described in Appendix A should be studied and evaluated by utilities and architect engineers for adaptation to BWR plants under their control.

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6. CONCLUSIONS

- A. Control of oxygen in a BWR by deaeration as described will result in a significant reduction in the rates of the following material corrosion mechanisms:
1. stress-corrosion cracking initiation and propagation in sensitized stainless steel, low alloy steel, and Inconel;
 2. pitting and corrosion fatigue cracking of carbon and low alloy steel;
 3. crevice corrosion of stainless steel and Inconel;
 4. general corrosion of all materials.
- B. Shutdown deaeration of water in the reactor vessel will reduce the severity of off-normal transients such as resin and chloride intrusions.
- C. Control of oxygen will provide additional margin for other solutions to materials problems, and will reduce the probability of failure of susceptible materials in operating or in-construction plants.
- D. Shutdown deaeration will improve reactor water clarity during refueling and for in-reactor maintenance.
- E. Shutdown deaeration will reduce primary system radiation buildup, and airborne contamination during refueling.
- F. Control of oxygen in a BWR as described will result in substantial economic gains due to improved plant reliability and availability.
- G. An oxygen control system as described in Appendix A is feasible and should be implemented in all BWRs.

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**APPENDIX
BWR COOLANT OXYGEN CONTROL SYSTEM**

Design Criteria
Oxygen Control Techniques
System Description
Oxygen Control Procedures
Oxygen Sources
Sizing Considerations

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The following describes a system and operating procedures for controlling oxygen in BWRs during various plant operating modes. This system was selected on the basis of its being the most economical to install and operate for the majority of plants, including those in operation or under construction.

1. DESIGN CRITERIA

1.1 Systems in Which Oxygen Control is Maintained

1.1.1 Reactor vessel, reactor recirculation system, reactor water cleanup (RWCU) system, and the shutdown cooling portion of residual heat removal (RHR) system during plant shutdown.

1.1.2 Emergency core cooling system (ECCS) and head spray lines from the normally-closed injection valve to the reactor during shutdown (continuous flushing at low rate).

1.1.3 Control rod drive (CRD) at all times.

1.1.4 RHR system and other ECC systems during layup conditions from normally-closed injection valve to pump check valve.

1.2 Oxygen Limits

1.2.1 Design Basis

Deaerator Effluent	≤0.05 ppm
All Other Systems	≤0.25 ppm

1.2.2 Normal limit during shutdown ≤0.30 ppm

1.2.3 Maximum limit during shutdown ≤0.6 ppm

1.2.4 Normal limit for feedwater during startup ≤0.2 ppm

1.2.5 Maximum limit for systems in layup (Item 1.1.4) ≤0.6 ppm

1.2.6 Maximum allowable time for exceeding normal limit

Each Occurrence	≤8 hours
Per Year	≤2 weeks

1.2.7 Other limitations — water from the reactor, or other systems containing water of comparable radioactivity or a high level of corrosion products should be processed through a filter-demineralizer before entering deaeration equipment.

1.3 Material Selection for New Deaeration Systems

1.3.1 Assure compatibility with piping or equipment in connecting systems.

1.3.2 Limit carbon steel to small areas.

1.3.3 Eliminate or restrict to small areas, materials containing cobalt, such as stellite.

1.3.4 Avoid use of copper alloys.

1.3.5 Use no organic coatings on surfaces in contact with process liquid. Other coatings should be fully qualified before use is considered.

2. OXYGEN CONTROL TECHNIQUES

Various techniques have been considered in developing a BWR oxygen control system concept. The following techniques are judged to be the most feasible and practical for the majority of BWR plants. The recommended oxygen control scheme includes a combination of these techniques.

2.1 Vacuum Deaeration

Some understanding of deaeration processes may be gained by briefly reviewing two pertinent gas laws. Dalton's Law states that the pressure of a gas mixture is the sum of partial pressures of the individual components, and that the partial pressure of each component is equal to the total pressure times its mole fraction. Henry's Law states that a quantity of gas dissolved in a given quantity of solution is directly proportional to its partial pressure over the solution, with the exception of those gases which chemically unite with the solvent. Thus, by reducing the partial pressure of a given gas over a solvent, the solubility of that gas in the solvent can be reduced accordingly.

In vacuum deaeration, the total pressure within a tank is reduced to nearly the vapor pressure of the process water. Partial pressures of all gases are reduced to nearly zero. Solubilities of these gases are likewise reduced. A lower water temperature requires a lower deaerator pressure in order to produce water with the same oxygen concentration. With the same water temperature, a deaerator pressure must be lower to supply a lower concentration of oxygen. A characteristic of a vacuum deaerator operated in its design flow range, is that the effluent oxygen concentration is relatively insensitive to the inlet concentration.

A vacuum deaerator, as shown schematically in Figure A-1, is used to provide deaerated water during plant shutdown. This equipment consists of a tall cylindrical tank containing stacks of elements called packing. Pressure in the tank is reduced by means of a mechanical vacuum pump or steam jet air ejector. Water is sprayed into the tank and flows down over the packing. The packing provides a large surface area which allows absorbed gases to escape and be drawn out through the vacuum system. In order to produce lower effluent concentrations of oxygen, it is more economical to use several stages of deaeration. The stages are contained within the same shell, but operate at slightly different pressures.

The major disadvantage with vacuum deaeration is the bulky size of the equipment. A two-stage deaerator, which is necessary to process water at 50°F and produce effluent oxygen concentrations of less than 50 ppb, requires about 55 feet of headroom. A two-stage, 1,000 gpm deaerator is 40 feet high and 6 feet in diameter. A 200 gpm deaerator is the same height and 4 feet in diameter. However, since this system will be located outside, the size should not be a major problem. The main advantages are that there is no adverse effect to water chemistry, and only electrical power is necessary to operate the system.

2.2 Prevention of Aeration

Transport of oxygen into a quiet pool of water is a very slow process controlled by diffusion of oxygen molecules into the water. This process is rapidly accelerated by any action which results in mixing of the surface layer with the bulk liquid, or increases the effective water surface area. Therefore, to minimize aerating water in a tank, all input streams should enter below the water surface such that minimum agitation of the surface is achieved. Recirculation flow rates through open tanks should be minimized.

2.3 Venting

When water in the reactor vessel is greater than 212°F, it can be deaerated by venting to maintain saturated conditions and low solubility for gases. Deaeration can be enhanced by operating the head spray (in those plants where head spray is part of the RHR system). Venting can be done through the head vent, through the turbine bypass valves to the main condenser, or by supplying steam to the turbine gland seal system or steam jet air ejector (SJAE).

Proper venting of piping systems is very important. Air trapped in piping systems which are pressurized to reactor pressure, can result in very high local concentrations of oxygen in the water, due to the high partial pressure of oxygen.

The following oxygen control techniques were considered but were not included in the recommended oxygen control scheme for the reasons indicated.

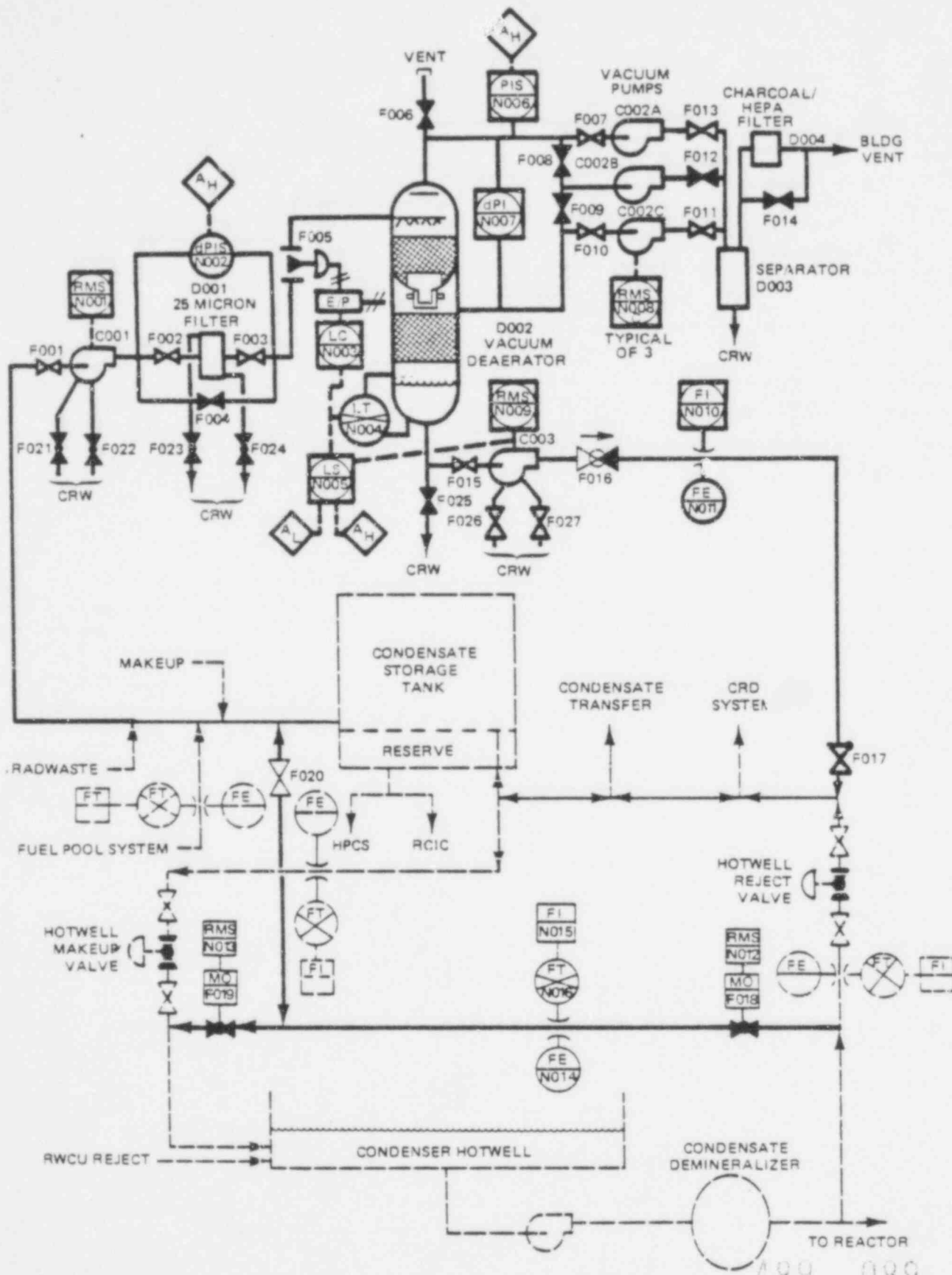


Figure A-1. Vacuum Deaerator System Diagram

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2.4 Thermal Deaeration

In this technique, water is heated to its saturation temperature, usually by direct contact with steam in a tank, then either sprayed, or allowed to spill over an array of trays, while steam sweeps out the noncondensable gases. The steam in this mixture is then condensed while the noncondensable gases are allowed to vent to the atmosphere. Deaerated water exits from the bottom of the tank. In essence, the partial pressure of oxygen is reduced by increasing the partial pressure of water to the point where it is equal to the total pressure. Spraying the water and scrubbing with steam serve to speed removal of noncondensibles.

Advantages of thermal deaeration relative to vacuum deaeration is more compact equipment. A typical 1,000 gpm steam deaerator system would fit in a space of 26 feet long by 11 feet wide by 14 feet high. The main disadvantage is the requirement for an auxiliary steam source during plant shutdown. Most plants have auxiliary boilers for heating and other purposes, but their capacity might not be sufficient. In addition, a reboiler would probably be necessary to keep from mixing the auxiliary boiler water with reactor water. Mixing of these water streams would be undesirable for two reasons. The first is that chemicals used in auxiliary boilers carry over with the steam and have undesirable side effects in a BWR water system. The second is that an amount of water equal to the auxiliary boiler steam supply to the deaerator would have to be processed by the radwaste evaporator to maintain plant liquid inventory constant. Another disadvantage is that the effluent water would have to be cooled, resulting in the need for a heat exchanger. Consequently, a thermal deaerator would not be the most economical alternative at most plants.

2.5 Chemical Scavaging

Chemicals, such as hydrazine, can be used to remove free oxygen from water, but they usually have undesirable side effects in a BWR. General Electric has a long range program to evaluate the use and benefits of adding chemicals to the BWR water system, but currently no chemical additions are permitted.

2.6 Exclusion of Air

Floating tank covers or inert gas blankets can be used to prevent air diffusion into tanks. A floating tank cover, however, could present a difficult retrofit problem. Inert gas blankets might be more easily retrofitted; however, operating costs, in terms of gas and operator time, would be expensive, particularly in tanks where the level varies greatly and frequently. On the other hand, use of an inert gas blanket would have the additional benefit of removing oxygen, since the partial pressure of oxygen, and thus its solubility, would be zero.

In most cases, the amount of air entering a tank is a lower order of magnitude compared to other inputs. Thus, air diffusion at the surface can be compensated by a slight increase in deaerator capacity. It may be desirable to use an inert gas blanket in the reactor as a backup system and for MSIV leak testing.

2.7 Hydrogen Overpressure

It is possible to use a hydrogen overpressure in a reactor to suppress radiolytic oxygen generation rates. However, this technique is considered impractical for a BWR during shutdown conditions.

3. SYSTEM DESCRIPTION

Figure A-1 shows the basic system which has been selected to supply deaerated water for BWR oxygen control. The system employs a vacuum deaerator, as previously described, operating in a "kidney mode" on the condensate storage tank (CST). As explained later in "BWR Oxygen Control Procedures," this system is used in conjunction with existing systems to control oxygen as desired.

Manifolding is an important feature of the piping arrangement. One manifold collects all the aerated water inputs to the system, while the other supplies deaerated water outputs. This arrangement allows the deaeration system to process all aerated water inputs prior to their entering the CST, while providing deaerated water outputs with the lowest oxygen content. At the same time, overall system operation is simplified since deaerator flow rate need not exactly match input or output flows.

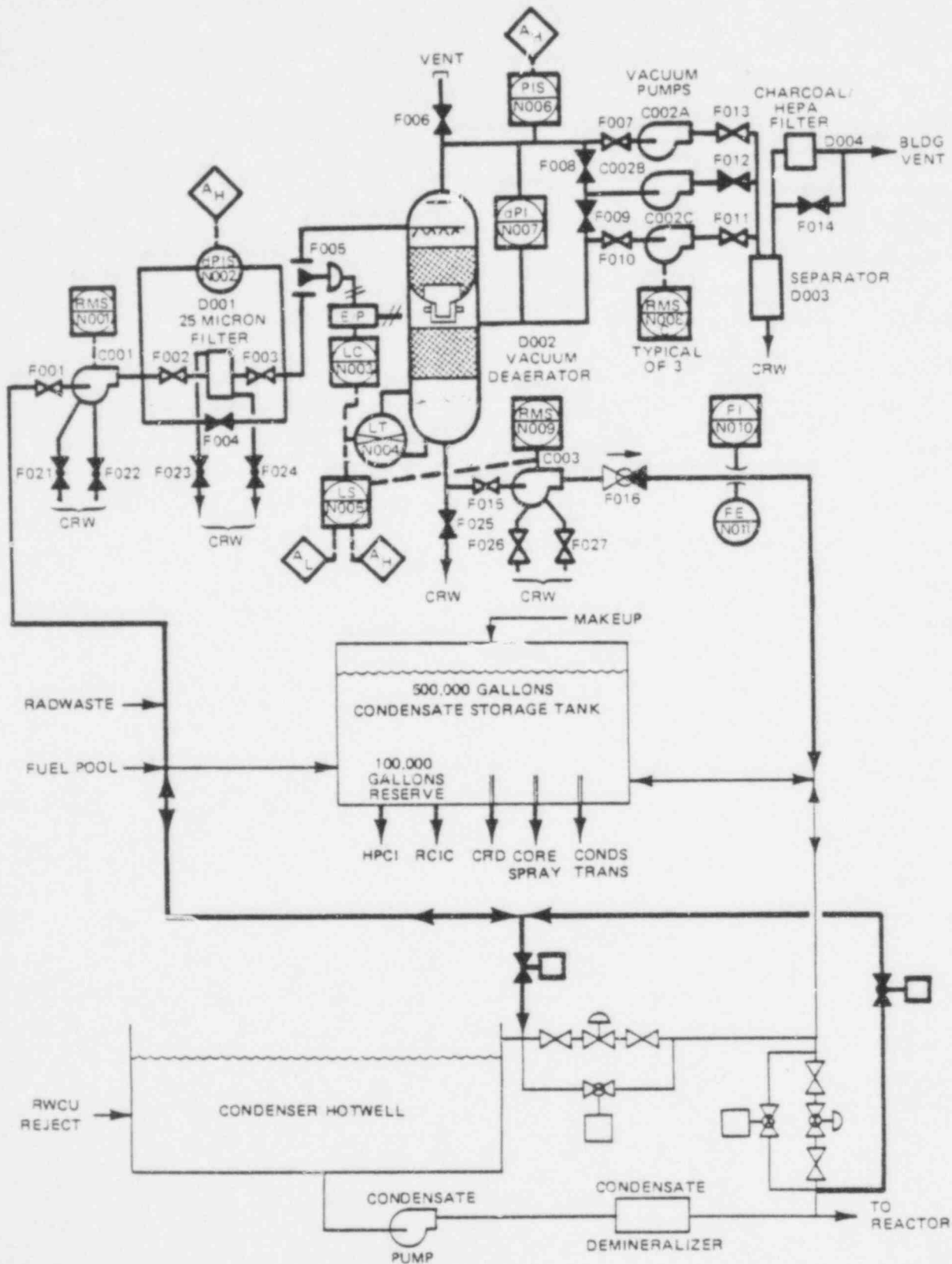


Figure A-2. Condensate Storage Tank Deaerator — Alternate Configuration

Steady-state demand for deaerated water is supplied directly from the deaerator at 0.05 ppm oxygen, and the CST is maintained at 0.2 ppm oxygen to supply high flow, short duration demands (e.g., backflushing of a condensate demineralizer). The CRD connection is arranged so that the CRD system has first priority for water with the lowest oxygen concentration.

A 25-micron, cartridge-type filter is recommended in the deaerator inlet piping to prevent fouling or radiation buildup in the deaerator. A bypass is provided to allow on-line replacement of the filter if necessary.

A charcoal filter is required to remove radioactive isotopes of iodine from the vacuum pump discharge flow. Consistent with the design basis, 100,000 $\mu\text{Ci}/\text{sec}$ off-gas release rate (at the SJAE), an estimated 0.6 $\mu\text{Ci}/\text{sec}$ of iodine isotopes would be discharged from the vacuum pumps. A decontamination factor (D/F) of 100 or more is necessary to reduce this to an acceptable release rate. A charcoal filter with a bed depth of 6 inches will provide a D/F of 1,000 or more, assuming suitable humidity control is provided. The steady-state flow rate is about 3 to 5 cfm for a 1,000 gpm deaerator. A filter bypass valve may be required to handle the deaerator startup air flow rates. Discharge from the filter should be routed to an existing building vent where it can be monitored before being released to the atmosphere.

Additional connections, as shown, are required between the CST and the condensate-feedwater system. During power operation, deaerated water is supplied from the condensate-feedwater system and the vacuum deaerator is not required to be in service. During plant shutdown, water rejected from the hotwell to the CST is aerated and must be processed by the deaerator. This difference requires that connections from the condensate-feedwater system be reversed in going from shutdown to power operation. For power operation, valve F019 is opened to allow water from the aerated water manifold to flow into the condenser hotwell. The hotwell level control automatically opens the hotwell reject valve and delivers deaerated water to the deaerated water manifold. During shutdown, valve F018 is opened to allow aerated water to be pumped out of the hotwell to the aerated water manifold. From there, it is processed by the vacuum deaerator.

Figure A-3 shows another possible arrangement for a vacuum deaerator system. The main difference is that piping to the various systems is connected directly to the CST instead of a manifold. This arrangement requires that the water in the CST be maintained at less than 0.05 ppm. To accomplish this would require all water to be deaerated prior to entering the CST, resulting in a very large deaerator to handle peak input flows. In addition, a means for excluding air from the tank (e.g., floating top, inert gas blanket) is necessary. Recovery time from a deaeration system breakdown would be very long, possibly necessitating redundant vacuum deaeration systems. Consequently, for most plants the arrangement in Figure A-1 is probably the most economical.

4. BWR OXYGEN CONTROL PROCEDURES

The following is a discussion of BWR oxygen control procedures and processes that are used during various plant operating modes. Vacuum deaeration equipment is used principally during plant shutdown, while certain operating procedures and existing plant characteristics, as described below, control oxygen during other plant modes.

4.1 Power Operation

- 4.1.1 Deaerated water is supplied to the CRD system from condenser hotwell reject or from the vacuum deaerator.
- 4.1.2 The balance between inherent BWR oxygen production (radiolysis) and oxygen removal (boiling) processes results in reactor, recirc, and RWCU water being maintained at 0.2 to 0.3 ppm.
- 4.1.3 Water in the condensate-feedwater system is deaerated by the main condenser.
- 4.1.4 The "dead" lines attaching to the reactor vessel are deaerated by thermally-induced circulation of reactor water through them.
- 4.1.5 The condensate storage tank is maintained deaerated by the main condenser or vacuum deaerator.

NOTE: DETAIL OF LINES SHOWN IN DARK IS GIVEN IN FIGURE A-1

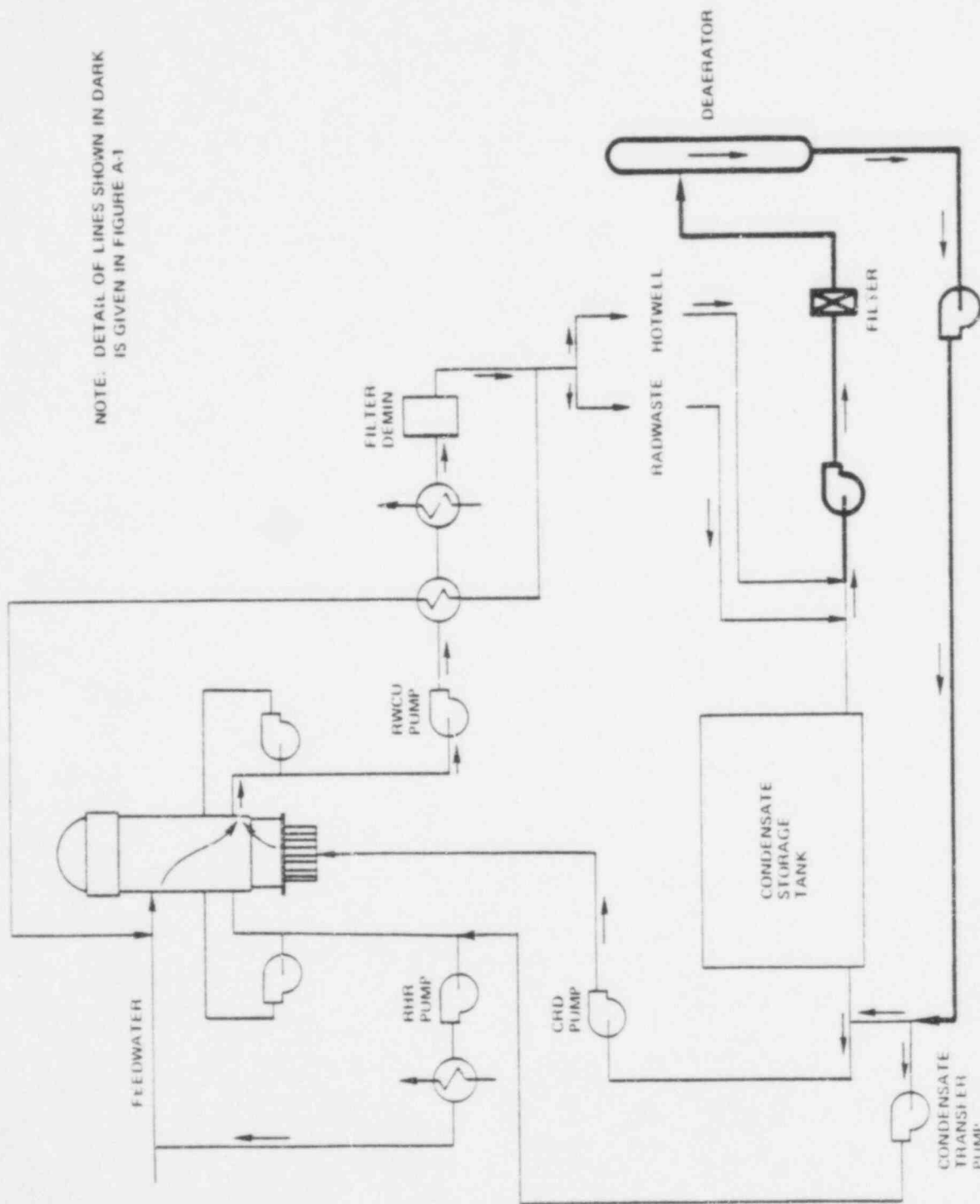


Figure A-3 Shutdown Mode Deaeration Loop

4.1.6 Condensate and RWCU demineralizer vessels are filled with deaerated water from the CST following a backwash or resin replacement. This prevents or minimizes oxygen transients when these filters are placed in service.

4.1.7 ECCS systems are "laid up" by filling the piping between the injection valve and the pump check valve with deaerated water. Water in these systems is then periodically sampled and flushed, if necessary, to maintain oxygen at less than 0.6 ppm.

4.2 Shutting Down

4.2.1 The RHR system is drained, flushed, and filled with deaerated water from CST prior to placing it in the shutdown cooling mode.

4.2.2 When the shutdown cooling system is placed in service (reactor temperature 350°F, pressure 135 psia), the reactor is deaerated by venting while the reactor pressure is greater than atmospheric. The head spray may be used to improve deaeration efficiency. Condenser vacuum is maintained as long as possible, perhaps by using the mechanical vacuum pump, in order to deaerate feedwater being supplied to the reactor. Water level in the reactor should be brought up to the upper limit of the normal range.

4.2.3 When it becomes necessary to break vacuum in the condenser, the CRD pump can be used to supply deaerated water to maintain water level in the reactor.

4.3 Shutdown with Reactor Head in Place

4.3.1 When reactor pressure reaches atmospheric, a flow loop between the CST and reactor vessel, as shown in Figure A-3, is established. Deaerated water from the CST is supplied to the reactor via the CRD system, and the condensate transfer-RHR-feedwater systems. In the latter path, the condensate transfer system uses flushing connections on the RHR system, and the RHR system connects to the feedwater system, which, in turn, connects to the reactor vessel. (In BWR/3 and BWR/5, the RHR system discharges into the reactor recirculation piping.) To maintain constant water level, water is rejected by the reactor water cleanup system to either the main condenser or the radwaste system. From there, water is returned to the CST, completing the cycle.

4.3.2 A small flow through each of the ECCS lines is established by opening the valve in the test connection and deaerated water supply, as shown in Figure A-4. Deaerated water from the CST then flows through the ECCS line into the vessel, thus maintaining the water in these lines deaerated.

4.4 Preparations for Refueling

Preparations for refueling depend on plant type (Mark I, II, or III) and water management scheme. For Mark I and II, water from the CST or refueling water tank is used to bring the reactor to refueling level, and to fill the dryer/separator storage pool. In Mark III, the upper pools are normally full and the reactor well must be drained to allow removal of the drywell head. RPV insulation and head. Water from the CST or refueling water tank is then used to refill the reactor well. Specific operating procedures are as follows:

4.4.1 Water in a special refueling tank (if provided) is deaerated prior to the outage by the vacuum deaerator or main condenser. Water in the CST is maintained deaerated in the same manner as described previously.

4.4.2 The reactor well is drained to the main condenser and stored temporarily. Later, this water is processed through the vacuum deaerator to the CST (Mark III only).

4.4.3 After the reactor head is removed, the reactor is brought up to refueling level. The preferred way to do this would be to use the HPCS, or other ECCS pump having a connection to the CST (this system should be thoroughly flushed before commencing the filling operation). This method is preferable to using a refueling water pump that discharges into the separator/dryer storage pool or reactor well, since aeration problems would be minimized. Surface agitation is minimized and flow is out of the vessel into the pool, both of which favor lower oxygen levels in the reactor.

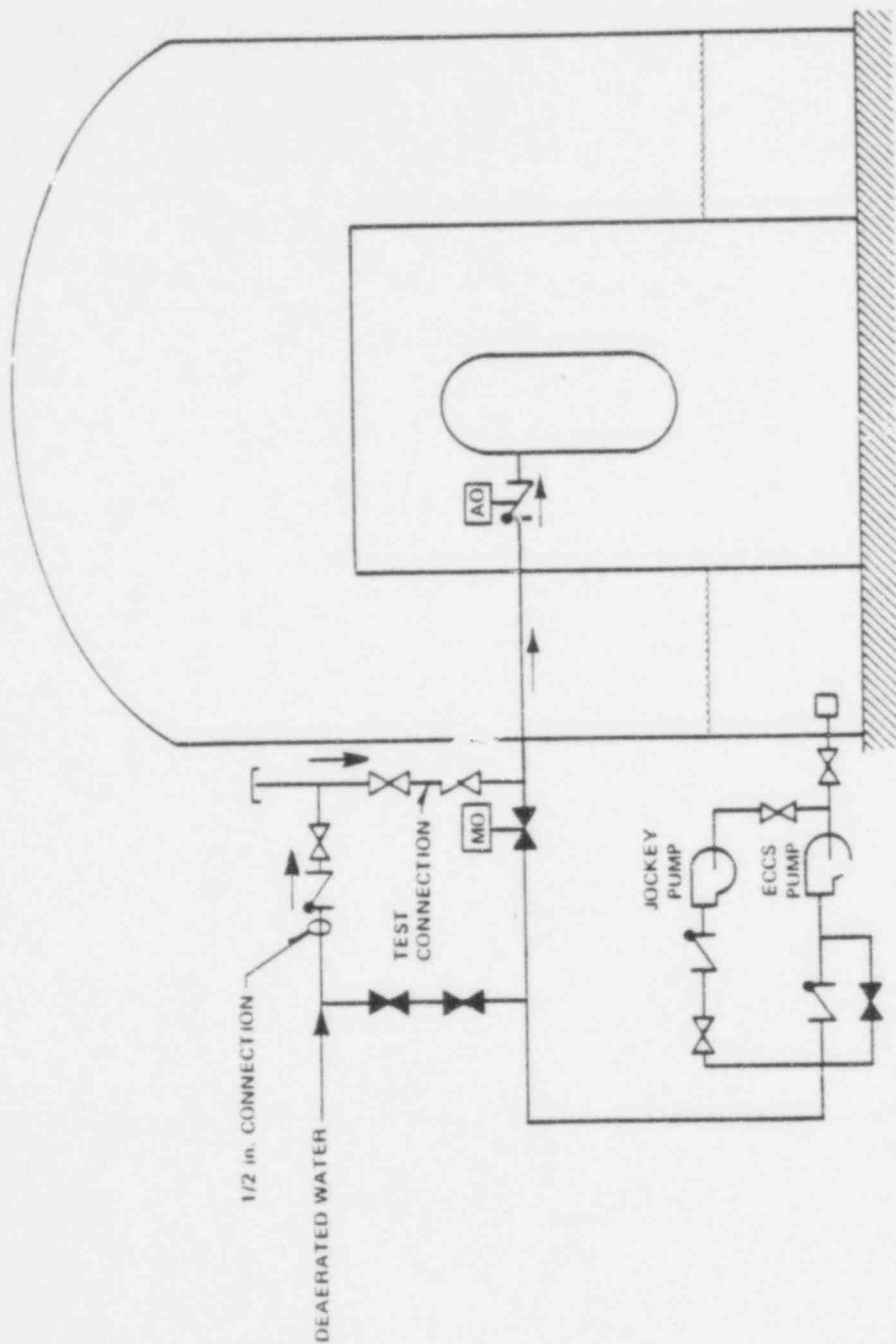


Figure A-4 Typical ECCS Flushing Arrangement

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4.5 Refueling Shutdown

4.5.1 When the reactor has been brought to refueling level, a flow loop between the reactor and the CST is established as shown in Figure A-5. Deaerated water is supplied to the reactor through the CRD and condensate transfer systems as during a shutdown with the reactor head in place. This results in a net flow of water out of the vessel into the upper pool, over the pool weir and into the fuel pool system surge tank. The flow of water into the fuel pool system causes the surge tank level to increase. The surge tank level instrumentation detects this increase and automatically opens a valve that returns water to the condensate storage tank.

4.5.2 The ECCS lines are flushed in the same manner as during a shutdown with the reactor head in place.

4.6 Recovery from Refueling

4.6.1 Drain reactor well (and dryer separator storage area for Mark I and II) to the main condenser hotwell or refueling water storage tank. Process water drained to the hotwell through the deaerator to the CST.

4.6.2 Establish a deaeration flow loop with the reactor as described in "Shutdown with Reactor Head in Place."

4.6.3 After reactor head is installed, perform hydrostatic test. Stop rejecting water through RWCU as necessary to bring level up in the reactor. Isolate the RHR system and pressurize reactor vessel using the CRD system. Control pressure by balancing RWCU reject flow against CRD flow.

4.6.4 After completing the hydrostatic test and restarting the RHR system, bring water in the reactor down to normal level by reducing CRD flow to minimum, stopping condensate transfer flow to RHR, and rejecting through RWCU at maximum rate.

4.6.5 Refill reactor well directly from CST or refueling water tank. Water does not have to be deaerated (Mark III only).

4.7 Starting Up

4.7.1 As soon as reactor water temperature reaches 212°F, the reactor is deaerated by venting as was done during shutting down.

4.7.2 Flushing of ECCS lines can be stopped when reactor water temperature exceeds 212°F.

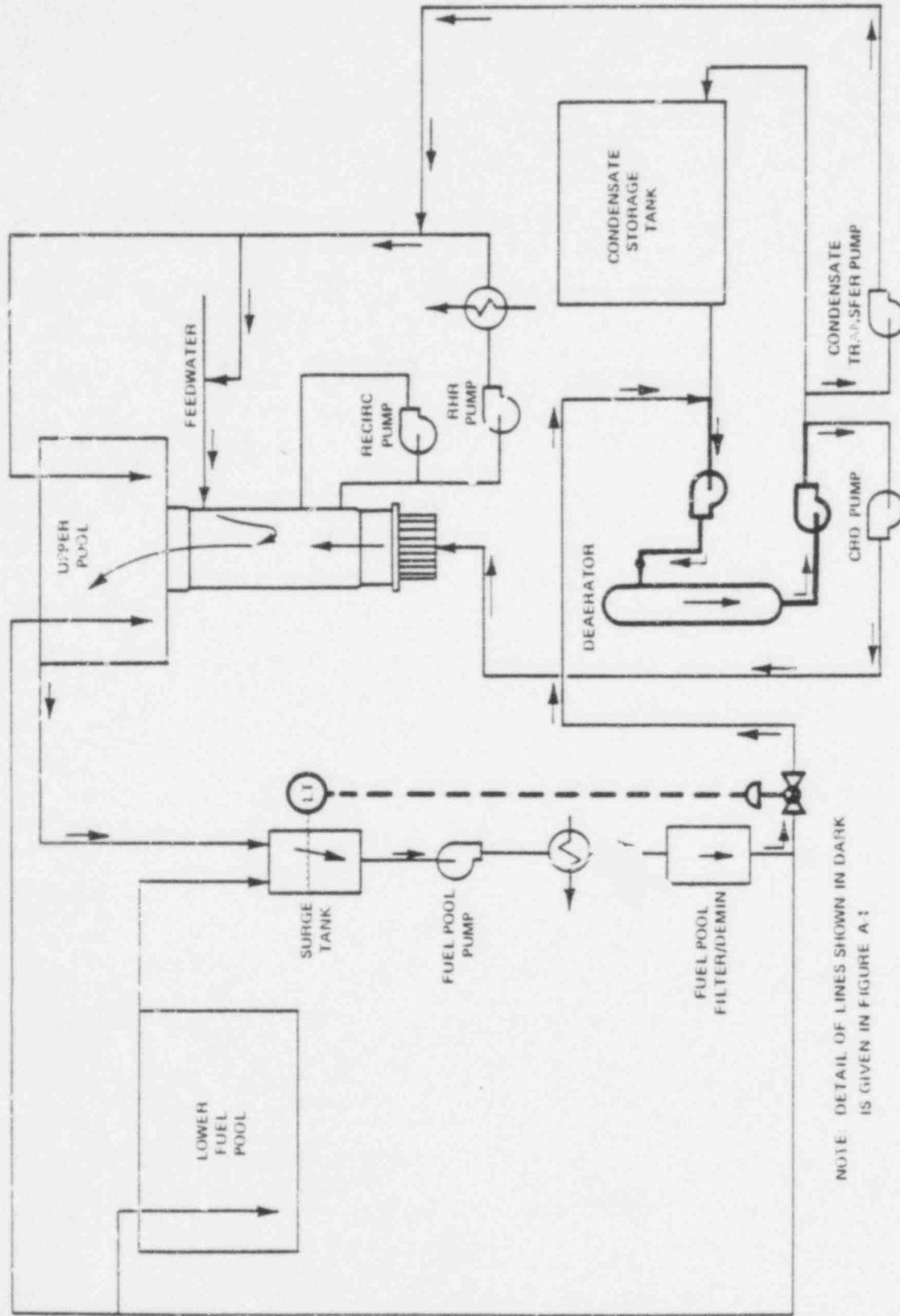
4.7.3 Vacuum in the main condenser is established as soon as possible to deaerate the feedwater. The feedwater system cleanup line, which returns feedwater from downstream of the high pressure feedwater heater to the condenser hotwell, is used to facilitate deaeration and cleanup of the feedwater.

4.8 Off-Normal Conditions

The following procedures minimize the possibility of exceeding maximum limits due to failure of deaeration system components

4.8.1 Perform routine and preventative maintenance of the vacuum deaeration equipment during plant power operation when deaeration can be provided by the condensate-feedwater system. This minimizes the probability of vacuum deaeration equipment failure.

4.8.2 Maintain an inventory of deaerated water in the condensate storage tank. If the vacuum deaerator becomes inoperative, continue the deaeration process using this water. For either the reactor-head-on or refueling modes, reject water through RWCU to radwaste or the hotwell, holding the water there as long as possible. Stop any other inputs of aerated water to the CST. Stop the flow of water from the CST to the vessel when the oxygen concentration in the CST becomes higher than that in the vessel.



NOTE: DETAIL OF LINES SHOWN IN DARK IS GIVEN IN FIGURE A-1

Fig. 1. g Mode Deaeration Loop

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- 4.8.3 Run the reactor recirc pumps or RHR pumps at minimum flow to minimize air absorption in the vessel.
- 4.8.4 Maintain the reactor coolant at a higher temperature to reduce oxygen solubility and buildup.
- 4.8.5 An alternate to items 4.8.3 and 4.8.4 is to place an inert gas blanket in the reactor to prevent air absorption while the deaerator is out of service.

5. OXYGEN SOURCES

In general, there are three sources of oxygen to BWR water system as follows:

5.1 Radiolytic Oxygen

Oxygen is generated in the reactor, and in piping where there is a significant radiation field, by radiolytic decomposition of water. Based on the best available test data, the oxygen generation rate in a reactor is 0.00014 scfm/MWt or less during shutdown (normal) conditions. Radiolytic oxygen generation rate during normal operation is much greater (0.02 scfm/MWt), primarily due to the boiling process which strips away oxygen before it can recombine with hydrogen.

Radiolytic oxygen generation outside the reactor vessel may occur in piping in the vicinity of the reactor core, but is expected to be quite small, particularly during shutdown, although a possibility exists for oxygen to accumulate in localized areas. During plant power operation, thermally-induced circulation of reactor water through critical portions of this piping prevents such an accumulation. A small flow of deaerated water will preclude this possibility during shutdown.

5.2 Oxygen Transport

Oxygen transport from air into pools of water can be described as two processes: (1) diffusion of oxygen into the water surface layer, and (2) mixing of the surface layer with the bulk water.

The relatively low mixing flow rates which occur in the bodies of water of interest in this report, result in the mixing flow rate being the controlling factor. At higher flow rates, oxygen diffusion into the surface layer may be controlling. If there is no mixing, transport of oxygen into water by diffusion alone occurs at a very slow rate. One hour is required for the first 2 millimeters of water to become saturated, and saturation to greater depths takes place at exponentially slower rates.

Solving Equation (1) below will provide an estimate of the oxygen transport rate into the water. The mass transfer coefficient (K) in Equation (1) is very difficult to determine theoretically, and it is recommended that the empirical O'Connor-Dobbins reaeration coefficient, which is widely used to approximate the reoxygenation of streams and lakes, be used. Equation (2) defines the O'Connor-Dobbins coefficient.

$$Q = KA\rho C \quad (1)$$

where

Q = amount of oxygen entering the water (lb/hr)

A = surface area (ft²)

ρ = density of water (lb/ft³)

C = solubility of oxygen in water (lb/lb, see Table A-1)

K = mass transfer coefficient (ft/hr)

$$K = \left[\frac{DG}{h} \right]^{0.55}$$

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where

- D = diffusivity of oxygen in water (ft²/hr, see Table A-1)
 G = average stream velocity (ft/hr)
 h = average stream depth (ft)

Table A-1
 SOLUBILITY AND DIFFUSION OF OXYGEN IN WATER

Temperature (°F)	60	80	100	120	140	160	180	200
Diffusivity (ft ² x 10 ⁹)	6.7	9.2	12.0	15.0	19.0	22.5	26.6	31.4
Solubility* (ppm)	9.9	8.0	6.7	5.6	4.7	3.7	2.6	1.1

* Solubility of oxygen in water in equilibrium with a standard air mixture at 14.69 psia.

5.3 Inputs of Aerated Water

Depending on the system, there may be various inputs of aerated water. This water can contain up to the saturation quantity of oxygen, which for water exposed to air, is a function of water temperature as shown in Table A-1 above.

6. SIZING CONSIDERATIONS

Oxygen removal rate from the reactor system is equal to the difference between the inlet and outlet oxygen concentration times the deaeration flow rate through the reactor system. Inlet flow to the reactor system from the deaerator has an oxygen concentration of 0.05 ppm or less. Exit flow from the reactor may be assumed to be the average reactor system concentration of 0.25 ppm. The oxygen removal rate must equal the source rate if equilibrium conditions are to be maintained. The major sources in the reactor are radiolytic oxygen produced by decay energy in the reactor core, diffusion of air at the water surface, and inputs of aerated water.

Radiolytic oxygen generation rate for a 3500 MWt reactor is about 5×10^{-3} scfm, 4 hours after reactor shutdown. This rate decreases with time after shutdown in proportion to reactor decay energy. To balance radiolytic oxygen production requires a deaerator flow rate through the reactor of about 250 gpm. It is estimated that an additional 50 gpm is required to balance air diffusion, giving a total required flow rate of 300 gpm through the reactor system. The total required deaerator flow rate is determined by a number of factors including the following:

- 6.1 Required reactor system flow rates for various shutdown modes (e.g., reactor head on, refueling).
- 6.2 Flow rate required to maintain the condensate storage tank at 0.2 ppm oxygen to provide large volumes of deaerated water for filling and flushing systems. If no means is provided to exclude air from the condensate storage tank, a deaerated water flow rate through the tank is required to account for air diffusion. In addition, the deaerator should have the capacity to process any sustained inputs, or combination of inputs of aerated water, before they enter the CST. It is much more efficient to deaerate flows of air-saturated water before they enter the CST and mix with low oxygen water. About 25 times as much low-oxygen CST water must be processed to remove an amount of oxygen equivalent to that in an air-saturated water volume.
- 6.3 Depending on water management scheme, there may be a refueling water tank provided, or a scheme where water is drained to, and temporarily stored in the condenser hotwell. Deaeration of this water must be factored into the sizing basis.

It is estimated that a typical BWR/6-238 Mark III plant will require a deaerator capacity of 600 to 800 gpm.