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# On the Corrosion Adequacy of the 2 1/4 Cr-1Mo Steel for LMFBR Steam Generation System Service

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## ABSTRACT

The 2 1/4 Cr-1 Mo ferritic steel has been selected for the evaporator and superheater components of the U. S. LMFBR demonstration plant (Clinch River). The focus of this review is on the long-term serviceability of this steel under the water-side conditions presented by an LMFBR plant of commercial scale. The basic question related to material behavior is to what extent the water side physico-chemical environment will affect the favorable performance of a given material under operating experience. In present light water reactors, the steam generator corrosion problems in part are attributable to complex interaction between the localized secondary water environment and the mechanical design of the components (i.e., tube/tube support crevice, tube/tubesheet crevice, flow pattern, etc.) in the steam generating system.

Much excellent work has been done in system design, fabrication, materials specifications, mechanical property analysis, and general quality control, in support of the demonstration plant working assignments for 2 1/4 Cr-1 Mo steel. The correlative corrosion studies have also yielded much excellent work under difficult experimental conditions. These facts notwithstanding, the degree of overlap between the field of conceivable water-side working conditions and the field of reasonably acceptable working conditions for this steel needs more clarification. The importance of the water-side corrosion qualities of this steel to its practical utility in the subject application will be influenced by the design, the construction quality control, and the operation and maintenance history, of the total water-side system of the LMFBR plant.

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## INTRODUCTION

Carbon and low-alloy steels are fundamental to industry and render economical service over a wide range of engineering environments. Potential problems with the availability of certain alloying elements, chromium in particular, obligate a continual effort to enlarge the scope of application of these steels under reasonable public and operational safety constraints. A concomitant obligation is the identification of limits of application of these steels.

This report continues an earlier review<sup>(1)</sup> of the corrosion adequacy of the unstabilized 2 1/4 Cr-1Mo ferritic steel for LMFBR steam generator system service, and is based primarily on publicly accessible information subsequent to about May 1977.

Much excellent work has been done in the system design, mechanical property analysis, fabrication and general material quality control in support of LMFBR system assignments for the 2 1/4 Cr-1Mo steel (e.g., 2). These aspects of the qualification program, while having many important implications with respect to general corrosion behavior, are, however, peripheral to the question of the water-side corrosion adequacy of the basic unstabilized 2 1/4 Cr-1Mo steel. Accordingly, as in the previous review, this report will focus on water-side corrosion information pertinent to the LMFBR steam generation system environment.

## CONCLUSIONS AND RECOMMENDATIONS

The decision to select the unstabilized 2 1/4 Cr-1Mo steel for the steam generation (SG) system of the LMFBR Demonstration Plant (CRBRP) had a number of bases, including: fossil plant experience, fabrication experience, certain economies associated with the low-alloy content, ASME code acceptance of mechanical properties, and the opinion that the limited LMFBR plant experience with this steel adequately supported the subject assignment.

Carbon and low-alloy ferritic steels have rendered satisfactory service for many years in the lower temperature regimes of fossil plant steam generation systems and the excellent record of the 2 1/4 Cr-1Mo steel in this respect is frequently cited in support of LMFBR assignments for this steel. While the public literature on fossil plant steam generation systems is remarkably uninformative on the performance of specific steels it has revealed a number of corrosion problems, particularly with recirculating boilers which continue to account for a significant fraction of plant outages. 'Satisfactory performance' is certainly a subjective attribute. Within the fossil plant frame of reference, in view of well publicized corrosion problems, it implies that the frequency of equipment (primarily tubing) failure, and the direct/indirect costs of corrective action, are within manageable economic limits. An LMFBR plant of commercial scale poses a number of factors which makes the fossil-to-LMFBR translation of materials performance difficult. In the LMFBR case: the Na-H<sub>2</sub>O and the conceivable follow-on H<sub>2</sub>-O<sub>2</sub> reactivity requires more restrictive plant operational guide-lines upon tube leak detection; the compactness of the heat exchangers and the secondary sodium presence complicate inspection, maintenance and repair operations; under current secondary water chemistry control limitations, certain physico-chemical conditions in the evaporator and superheater components (primarily higher heat flux in some zones than generally experienced in fossil plants) pose potential environmental conditions whose corrosion implications are still not well understood for any candidate material. However, apart from improbable temperature excursions potential to massive Na-H<sub>2</sub>O reactions, an important constraint on destructive corrosion processes in the LMFBR SG system is the limit on maximum

tubing temperature imposed by the secondary sodium, which is low relative to the flame-side temperature regime of fossil plant boilers.

The fabricability attribute of the 2 1/4 Cr-1Mo steel poses a difficult question with no pat answers. Ferritic steels have, in general, a more complex metallurgy than the austenitic materials under the thermal/mechanical treatment experienced during the melting/processing/fabrication chain. While this metallurgy affords considerable opportunity for tailoring properties to a specific application, it also imposes very substantial constraints on fabricability and on working environments which can induce long-term microstructural alterations inimical to mechanical and corrosion properties. LMFBR SG system assignments for this steel will impose fabricability standards unique to the experience with this steel, with particular emphasis on self-self and transition welds. Technique gains in this respect for the 2 1/4 Cr-1Mo steel will most certainly benefit all candidate materials for LMFBR service.

Conformance of as-fabricated mechanical properties with the various applicable codes is a prerequisite of LMFBR SG system materials. This qualification, however, takes only qualitative cognizance of environmental effects on form and structure which can degrade the ability of a given component to sustain its working stresses or fulfill its various containment functions. Integrating corrosion influence into long term mechanical property/structural assessment remains a major problem of materials science. Specifically, corrosion fatigue is an important consideration for LMFBR SG system materials. This problem is being addressed with the 2 1/4 Cr-1Mo steel over a range of caustic (NaOH) concentrations under prototypical temperatures and pressures.

The limited LMFBR plant experience with the 2 1/4 Cr-1Mo steel has been, in general, encouraging. The EBRII is a classic in this regard although the literature is quite sparse on the specifics of the corrosion response under the EBRII conditions. The chief limitation on weighting the LMFBR plant experience with 2 1/4 Cr-1Mo steel is that the water-side environmental conditions of the LMFBR plants using this steel have barely penetrated the possibilities potential to commercial plants presenting a variety of condenser cooling



expedients, water management philosophies, and operational/maintenance standards. These factors have been important to the service history of LWR SG system materials and there is no obvious justification for discounting their importance with respect to the LMFBR plants. The Fermi plant history and some foreign experience with this steel in LMFBR applications indicate, or suggest, the necessity for rigorous fabrication quality control, and post-fabrication environmental control. These limitations have been recognized in National Program work with this material.

From the corrosion perspective, the basic question to be asked is to what extent does the field of water-side physico-chemical conditions reasonably favorable to a given material overlap the field of conditions potential to the service environment. In the case of the austenitic material candidates for the subject service (principally Incoloy 800, possibly other alloys of the Fe-Cr-Ni family), localized corrosion (stress corrosion cracking emphasis) may be encountered under adverse water-side conditions. The 'uniform' corrosion behavior of these materials should pose no significant problems. In the case of the low-alloy Cr-Mo ferritic steels, e.g. 2 1/4 Cr-1Mo, the 'uniform' corrosion (oxidation) response under adverse chemistry conditions may be an important limitation on the serviceability of these steels. While oxidation has been observed to blunt cracks of the stress-corrosion cracking (SCC) type with the 2 1/4 Cr-1Mo steel, in more extreme forms the oxidation of this steel has some potential for significant structural degradation depending on its contribution to local buildup of aggressive ions and/or the development of adverse electrochemical situations.

The evaporator component of the LMFBR SG system is generally considered to be the principal arena for significant corrosion action under adverse water chemistry conditions. The various parameter limits for this component allowing economic service with the 2 1/4 Cr-1Mo steel, or any other candidate material, are not well identified. Considering the complex of mechanical, physical and physico-chemical factors operating under the service conditions of the LMFBR SG system, a significant advance from the present position will be made by additional evaporator testing now underway, or pending to supplement the in-plant trials of this steel. This work will include a full size CRBRP

evaporator prototype test for part power performance and transient testing<sup>(2)</sup>. The concerted action of heat exchanger design practice and strategies and standards for fabrication, plant maintenance and water chemistry management is an important determinant of a material's service history. In the author's opinion, the water chemistry management factor poses the greatest uncertainty in the current corrosion assessment of LMFBR SG materials. Test cognizance of this factor should be based on a realistic appraisal of the state-of-the-art ability to hold various base-line specifications for corrosion significant species. Continuous development of in-plant detection methods for such species will be a powerful aid to better water chemistry management.

In summary, the Cr-Mo ferritic steel family shows considerable promise in the development of economic LMFBR SG system materials providing working conditions can be maintained which minimize massive oxidation and local corrosion of these steels. The austenitic steel candidates, principally Incoloy 800 and possibly other Fe-Cr-Ni alloys, also display a number of promising characteristics for the subject service given conditions which minimize the propensity of the austenitic steels to pitting and stress corrosion attack. In cognizance of the international work with the austenitic and other ferritic steels proposed for LMFBR SG system service, the U.S. program is focused on establishing the position of the unstabilized 2 1/4 Cr-1Mo ferritic steel in the hierarchy of the candidate materials.

## FOSSIL PLANT EXPERIENCE WITH FERRITIC STEELS

Ferritic steels are used extensively in fossil plant SG systems. Carbon and low alloy ferritic steels are used for furnace water walls and economizers. Carbon steel is also the economic choice for superheater and reheater sections where service temperatures are less than about 510°C (950°F). Ferritic and austenitic alloy steels are used for SG system applications at higher service temperatures.<sup>(3)</sup> Although the economic serviceability of the ferritic steels (including the low Cr-Mo steels such as 2 1/4 Cr-1Mo) can be supported by vendors and utilities alike, water-side corrosion of boiler tubing, particularly with recirculating boilers, continues to be a major factor in forced plant outages for fossil plants. A recent description of corrosion problems in fossil plants by Schwleger and Strauss<sup>(3)</sup> conforms in virtually all respects to descriptions given earlier by Klein et al.<sup>(4)</sup> and Klein<sup>(5)</sup>, a fact indicating a persistence of these corrosion problems extending to the present despite decades of observation, analysis, and presumably progressive improvement in control of the working environment for these plants. In the face of these well publicized corrosion problems, 'serviceability' within the fossil plant frame of reference implies that the effects envelope of the fossil plant boiler corrosion problems has been held within manageable economic bounds.

The status of the 2 1/4 Cr-1Mo steel in this problem assessment, and the limits of various operating parameters (T, contaminant levels, heat flux, etc.) allowing economic service with this steel in fossil plant SG systems cannot be obtained to any extent from publicly accessible literature. Lux<sup>(6)</sup> has noted that oxide exfoliation under superheater and reheater service of fossil plants has not been a problem for Cr-Mo steels (1/4 to 9% Cr) up to a temperature of roughly 540°C (1000°F). A number of authors have noted that below roughly 590°C (1090°F), Cr alloying confers no significant advantage relative to carbon steel with respect to steam oxidation. On the basis of oxidation behavior, these observations suggest a limit of serviceability of 2 1/4 Cr-1Mo steel for fossil plant boilers somewhat in excess of 540°C (1000°F). ORNL studies<sup>(7)</sup> of the oxidation characteristics of the 2 1/4 Cr-1Mo steel, under a heat flux substantially lower than the values expected for the lower stage

of the CRBRP superheater, revealed extensive oxide instability for this steel at a somewhat lower temperature (470-500°C steam). Indig's<sup>(8)</sup> corrosion studies with NaOH impurity under superheated steam at 480°C (896°F) showed that the oxidation response of 2 1/4 Cr-1Mo steel is strongly conditioned by aggressive ion presence (see Table 9).

Table 1 presents some of the very sparse corrosion observations for ferritic steels under fossil plant SG system service. The salient observations from the ASME survey on fossil power plant steam generation system corrosion problems are also included in the table, as well as the principal conclusions from the ASME/Edision Electric Institute (EEI) model boiler program oriented toward verification and elucidation of the various corrosion processes identified in the fossil power plant corrosion survey. The conclusions of the latter program, given in the following table, have a number of important implications for the use of low-alloy ferritic steels in LMFBR SG system service. The observations of this study regarding the limitations of the all volatile treatment (AVT) in combating aggressive ion intrusion are particularly noteworthy. A similar concern has been expressed by a number of water treatment specialists and this issue is reviewed briefly in a following section on secondary water-chemistry control.

Table 1 is concluded by observations from two recent papers on fossil plant SG experience (entries 8 and 9). The summary of Mai and Drucks<sup>(9)</sup> (from an earlier study by Uebing and Oudenhengel cited in the paper) is particularly noteworthy, indicating the importance of the general plant technical management on the SG system performance.

TABLE 1. Fossil Plant Corrosion Experience and Model Boiler Studies

Entry #/ (Ref.)	Experience/ Observation	
1/(10)	Bull Run (TVA)	<ul style="list-style-type: none"> <li>• pin hole leaks in the tube-tubesheet welds of carbon steel high pressure heaters have occurred continually; 50-100 leaks in one of these units can be found during any outage</li> <li>• early in operation, numerous leaks in reheater superheater section, thought to be related to SCC and vibration; 1 1/4 Cr-1/2Mo, 2 1/4 Cr-1Mo and 347 SS used, depending on metal wall temperature</li> <li>• accumulation of pre-boiler corrosion products is concern</li> </ul>
2/(10)	Paradise (TVA)	<ul style="list-style-type: none"> <li>• 46 startups during 1st 10 months of operation attributable to boiler tube leaks and boiler control problems (1/2Cr-1/2Mo boiler tubes)</li> </ul>
3/(6)	General Observation	<ul style="list-style-type: none"> <li>• exfoliation has not been a problem with 1 1/4, 2 1/4, 5 and 9 Cr ferritic steels for tubing at Ts greater than about 537°C (997°F)</li> <li>• chemical cleaning on regular basis, under careful control, is generally best control measure</li> </ul>
4/(11)	Fossil Plant	<ul style="list-style-type: none"> <li>• corrosion damage resulting in boiler tube failure can occur within a few hours, or even a few thousand hours under adverse corrosion conditions</li> <li>• no specifics of boiler tube material performance</li> </ul>
5/(12)	CEGB (UK)	<ul style="list-style-type: none"> <li>• SCC observed in mild steel boiler tubing and turbine blades made of Cr ferritic steel</li> <li>• 2 1/4 Cr-1Mo steel used extensively in final superheater for oil-fired stations and 3rd stage superheater for coal-fired stations up to main steam Ts of about 540°C and mid-wall tube Ts up to 580°C</li> </ul>

TABLE 1. (Continued)

Entry #/ (Ref.)	Experience/ Observation
	<ul style="list-style-type: none"> <li>• where oxidation and creep resistance of 2 1/4 Cr-1Mo have proved inadequate (no details), higher Cr alloys (5,9,12% Cr) are used</li> <li>• 1 Cr-1/2Mo is substantially inferior to 9Cr-1Mo under aggressive heat flux and solute concentration conditions over T range 450-520C</li> <li>• 1 Cr-1/2Mo and 2 1/4 Cr-1Mo showed improvement in scaling resistance of 3-10X compared to C steel under acid chloride condition in RC boilers;</li> <li>• under high heat flux and tube locations conducive to steam blanketing, or dry-out, local concentration of corrosion species can occur; this can lead to very rapid attack of boiler tubes; 1 Cr-1/2Mo tubes operating under above conditions fail after &lt;1000 hrs; 9 Cr-1Mo steel can effect up to 8-fold decrease in rate of attack under adverse NaOH conditions; adherence of oxide believed to be a major factor in superiority of 9 Cr-1Mo steel</li> <li>• although no comments relating to specifics of 2 1/4 Cr-1Mo performance under upset chemistry conditions, these authors assert that above a Cr content of about 2 1/4%, the Cr/Mo steels display roughly comparable corrosion behavior</li> </ul>
6/(4,5)	<p>Fossil Plant</p> <ul style="list-style-type: none"> <li>• debilitating corrosion has occurred almost exclusively in evaporator units under boiling conditions; seldom found in superheaters or reheaters or economizers where single phase flow predominates</li> <li>• the change from high pH caustic treatment to lower alkalinity (phosphate, AVT) treatment correlates with the change from predominantly caustic (ductile gouging) attack to predominantly brittle failures; high Cl in condenser coolant correlates with incidence of brittle failure</li> </ul>

TABLE 1. (Continued)

Entry #/ (Ref.)	Experience/ Observation
7/(5,15)	ASME/EEI Model Boiler Program  Conclusions

- 3 conditions judged to be important to corrosion failure:  
50% of cases---deposit buildup  
30% of cases---condenser in-leakage  
20% of cases---design deficiencies
- up to end of 1970, about 20% of fossil plants had a corrosion failure (single, or multiple tube failure); this figure is probably very conservative (optimistic) due to difficulty in obtaining operational specifics from commercial plants

SA 192 carbon steel used in this study (1.5" OD x 200 mil wall); tube wall Ts ranged from 777<sup>o</sup>-1062<sup>o</sup>F (415<sup>o</sup>-571<sup>o</sup>C) OD and 690<sup>o</sup>-975<sup>o</sup>C (365<sup>o</sup>-523<sup>o</sup>C) ID; heat flux ranged from 110,000-150,000 Btu/hr/ft<sup>2</sup> (347-473 kW/m<sup>2</sup>) ID

- with clean heat exchanger (HX) surfaces, corrosion is unlikely over a wide range of pH and boiling conditions regardless of water treatment practice
- corrosion will not occur with AVT treatment or coordinated phosphate treatment of pure water (less than 2 ppm dissolved solids) even with fouled surfaces and DNB conditions, i.e., a corrosion aggressive agent is needed
- in all cases where corrosion was experienced, prior fouling of HX surfaces was necessary for initiation of attack
- once surfaces were fouled with pre-boiler corrosion products, precipitation of various salts occurred within porous matrix of deposit and significant metal T increases observed; this effect is aggravated in DNB zones where cyclical T variations due to DNB are superimposed on gradual T rise due to salt concentration

TABLE 1. (Continued)

Entry #/ (Ref.)	Experience/ Observation	
		<ul style="list-style-type: none"> <li>• AVT provides little or no buffering action at high temperatures, therefore even low contamination can result in a corrosive situation; bulk pH measurements are not valid as a control parameter under acid contamination and fouled conditions</li> <li>• AVT treatment caused formation of difficult-to-remove deposits</li> <li>• the pH reduction resulting from acid condenser leakage resulted in corrosion damage with <u>all</u> types of chemical treatment; corrosion could be reduced by <u>raising</u> the pH with phosphate or caustic treatment; however once HX surfaces have been <u>sufficiently</u> fouled, the introduction of caustic caused caustic attack</li> <li>• acid forming condenser cooling water leaks can cause lowering of pH in boiler water; under fouling, hydrogen embrittlement can occur and rate of attack is rapid in a matter of hours)</li> </ul>
8/(3)	General Observation	<ul style="list-style-type: none"> <li>• internal (water-side)corrosion of boiler tubes is a major factor in many forced outages</li> <li>• the most prevalent forms of corrosion (water-side) in drum-type utility boilers are: hydrogen embrittlement; bulk under-deposit corrosion, corrosion fatigue; stress corrosion cracking; oxidation</li> </ul>
9/(9)	General Observation	<ul style="list-style-type: none"> <li>• on basis of many years observation, 47-70% of failure time of fossil power plants caused by boilers</li> <li>• in analysis of 1200 fossil power plant boiler damage cases, the following cause attribution is given:</li> </ul>



TABLE 1. (Continued)

Entry #/ (Ref.)	Experience/ Observation	principal cause(a)	~% of cases
		operation/maintenance errors	32
		planning errors	25
		construction/erection/repair errors	18
		inadequacy of technology	13
		material failure	11

(a) Verbatim from reference

## LMFBR PLANT EXPERIENCE WITH THE 2 1/4 Cr-1Mo STEEL

In terms of total service time, the EBRII history represents the most satisfactory testimony to date on the attributes of the unstabilized 2 1/4 Cr-1Mo steel under LMFBR steam generation system conditions. Corrosion details for the duplex tubing used in this plant and correlative data on water-side chemistry conditions have been sparse. Of the other USA LMFBR plants, the Fermi plant experience provides some valuable guide-lines for the use of this steel (see Table 2).

Foreign experience with the stabilized and unstabilized 2 1/4 Cr-1Mo steel has apparently not been well documented in the public literature with respect to the corrosion and fabricability specifics for this steel, and particularly for the crucial interplay between the fabricability (welding and post-weld heat treatment emphasis) and corrosion factors. The French report on the Phenix plant experience, given at the BNES Conference on Ferritic Steels in 1977, implied that there was still considerable uncertainty regarding the ability of this steel to sustain waterside chemistry transients under LMFBR SG system environmental conditions. The National Program work with 2 1/4 Cr-1Mo steel has addressed various aspects of the desired corrosion test areas mentioned by Robin and Birault.<sup>(16)</sup> One of the desirable performance criteria noted by these authors, namely, no excessive corrosion rate under adverse chemistry conditions, has not been satisfied by the unstabilized 2 1/4 Cr-1Mo steel as shown by National Program work reviewed in the following section on water-side corrosion studies.

The brief text of this section is concluded with two quotations from a recent paper by K. M. Horst<sup>(17)</sup> summarizing worldwide LMFBR experience.

- "Essentially all countries are using the ferritic steel 2 1/4 Cr-1Mo with minor alloy additions in some cases to achieve a stabilized grade for the evaporators. This material has been shown to be highly corrosion resistant." (page 533)
- "The steam generators have given the most difficulty among LMFBR plant components. The most consistent trouble has been with the welded joints

at the tube/tubesheet interface and other joints in the tubes. Major efforts are underway in each of the national programs to develop reliable units." (from summary, page 529)

While any use of a quotation is subject to the charge of 'out-of-context distortion,' the author submits the above quotations as a commentary on one aspect of the LMFBR plant experience with the 2 1/4 Cr-1Mo steel. The degree of involvement of corrosion processes in the weld problems noted by Horst is not identified to any extent in this paper.

Table 2 presents a brief summary of commentary/observations on LMFBR plant experience with the 2 1/4 Cr-1Mo steel. A resume of LMFBR plant experience with steam generator tubing given by Horst<sup>(17)</sup> is the last entry of this table. Some of this experience is given in slightly more detail in preceding entries of this table. Observations from tests of prototype components for LMFBR SG systems are given in Table 3 of the following section on water-side corrosion studies.

TABLE 2. LMFBR Plant Experience with 2 1/4 Cr-1Mo Steel

Entry #/ (Ref.)	Items
1/(13)	<p><u>EBR11</u></p> <ul style="list-style-type: none"> <li>the steam generation system, using duplex 2 1/4 Cr-1Mo tubes, has operated reliably for over 11 years (now 15); no details on corrosion response of section of piping taken from circuit downstream of superheater</li> </ul>
2/(18)	<ul style="list-style-type: none"> <li>no leaks between Na-H<sub>2</sub>O have <u>ever</u> occurred; performance of secondary sodium-to-water steam generator has exceeded <u>expectations</u>; no corrosion particulars</li> </ul>
3/(19)	<ul style="list-style-type: none"> <li>after 12 years operation, results of first mechanized inservice inspection of SG tubing gave no indication of corrosion effects that would be detrimental to continued use of the evaporator; no evident damage from appearance of scale; scale extremely hard and adherent</li> </ul>
	<p><u>Fermi</u></p>
4/(20)	<ul style="list-style-type: none"> <li>SCC of 2 1/4 Cr-1Mo tubes in No. 2 SG was experienced during preoperational testing; Na-H<sub>2</sub>O leak in No. 1 SG during operation lead to Na-H<sub>2</sub>O reaction which was adequately contained</li> <li>major factors in failure of tubing and tube-tubesheet joints thought to be: preoperational residual stresses resulting from improper stress relief of welds; poor weld quality; vibration induced stresses; improper quality control through-out the manufacturing sequence and improper environmental control of fabricated units up to operational stage</li> </ul>
	<p><u>PFR</u></p>
5/(21)	<ul style="list-style-type: none"> <li>12 small leaks in 2 1/4 Cr-1Mo tube-tubesheet welds during operation in 2 out of 3 evaporators; welds were not given PWHT; lab tests showed that stressed welds can crack in pure water</li> </ul>

TABLE 2. (Continued)

Entry #/ (Ref.)	Items
	<ul style="list-style-type: none"> <li>• leaks in one evaporator believed associated with long dryout during lay-up period; leaks in other evaporator believed due to caustic SCC</li> <li>• water contamination during storage led to considerable pitting and sufficient corrosion to require chemical cleaning</li> <li>• while 'normal' operation appears entirely satisfactory for 2 1/4 Cr-1Mo steel, the tolerance for water contaminants is not well known</li> </ul>
	<p><u>Phenix</u></p>
6/(22)	<ul style="list-style-type: none"> <li>• the Phenix (250 MWe) plant comprises 36 evaporators, 36 SHs and 36 reheaters; 24 evaporators are made of 2 1/4 Cr-1Mo, 12 of 2 1/4 Cr-1Mo-Nb; all SHs and RHs are made of 321 SS; since October 1973, the plant has experienced a number of start-ups and shut-downs and some 9000 hr of operation at full load; experience to date may be summarized as follows:             <ul style="list-style-type: none"> <li>• still too early to say that correct choice of materials was made</li> <li>• the general T level has been lowered for the Super Phenix; this change is mainly directed toward a possible improvement in reliability that is 'highly needed' because of large size of the power plant; <u>no qualification given for this statement</u></li> <li>• for beyond Super Phenix plants, a number of materials will be evaluated, including Nb stabilized 2 1/4 Cr-1Mo steel and the higher Cr alloys; some concern expressed over fabricability of ferritic steels</li> </ul> </li> </ul>
	<p><u>Phenix</u></p>
7/(16)	<ul style="list-style-type: none"> <li>• since 1973, over 17,000 hr of exposure to flowing sodium at about 470°C; no problems mentioned</li> </ul>

TABLE 2. (Continued)

Entry #/ (Ref.)	Items
7/(16)	<ul style="list-style-type: none"> <li>• the question of resistance of 2 1/4 Cr-1Mo steel to off-chemistry conditions is still not well resolved (Cl and OH emphasis in this reference)</li> <li>• no specifics of operating experience with 2 1/4 Cr-1Mo steel</li> <li>• the water/steam affecting SG performance can conceivably be contaminated to some extent by corrosion aggressive species; the margin of tolerance of ferritic materials to water-side chemistry upsets should be given more study, specifically:               <ul style="list-style-type: none"> <li>stressed specimens under [Cl] to 100 ppm at 350°C; at least 3000 hr duration;</li> <li>stressed specimens under [NaOH] up to 1%, at 350°C; 5000 hr duration</li> <li>stressed specimens under 10% NaOH at maximum sodium T for up to 100 hr</li> </ul> </li> <li>• under test conditions, no localized corrosion (cracking) or excessive corrosion rates should be observed</li> </ul>
8/(23)	<p data-bbox="378 826 441 867"><u>PFR</u></p> <ul style="list-style-type: none"> <li>• sensitivity of 2 1/4 Cr-1Mo to rapid pitting was demonstrated by severe pitting of evaporator tubing during storage; water was inadvertently trapped inside tubes in presence of warm air</li> </ul>

TABLE 2. (Continued)

Entry #/ (Ref.)	Items				
	LMFBR <u>Plant</u> Experience with Steam Generator Tubing				
9/(17)	<u>Plant</u>	<u>MW(e)</u>	<u>Tubing Material</u>	<u>Evaporator Type</u>	<u>Observation</u>
	EBR-II	20	2 1/4 Cr-1Mo	double wall tubing; st. tube; recirculating	over 12 years (now 15) without failure
	FERMI	60	2 1/4 Cr-1Mo	single wall tubing; U-tube; once-thru	failures <sup>(a)</sup>
	BN-350	350	1 Cr-2Mo	single wall bayonet tubing; recirculating	over 4 years operation; failures <sup>(b)</sup>
	PHENIX	250	2 1/4 Cr-1Mo	single wall serpentine tubing; once-thru	over 3 years successful operation (as of June 1977, 9000 hr (~1 yr) full load operation; ref. 22)
	PFR	250	2 1/4 Cr-1Mo Nb stabilized	single wall tubing; U-tube; recirculating	failures <sup>(c)</sup> under partial load condi- tions (as of June 1977, full load condi- tions had not been reached; ref. 21)

(a) corrosion problems related to fabrication procedures; pre-service environmental control

(b) related to faulty welds

(c) welds have been principal source of problems

## WATER-SIDE CORROSION STUDIES WITH THE 2 1/4 Cr-1Mo STEEL

The question of the relevance of a given set of test conditions to the proposed LMFBR working environment is virtually impossible to answer satisfactorily without a substantial backlog of plant working experience for comparison. Among the factors which complicate this assessment of relevance are:

- bulk stream levels of corrosion aggressive species on a steady-state, or sporadic basis;
- dissolved oxygen level on steady-state or sporadic basis;
- the cognizance taken of the deposition potential of the pre-boiler circuits for the test zone;
- the time of exposure to various test conditions;
- the influence of nominal and emergency transient environmental conditions (primarily during startup and shutdown) on the long term corrosion behavior of test materials under the principal plant operating modes;
- the extent to which design features of the LMFBR SG system components can obviate buildup of oxidation/deposit layers conducive to aggressive ion concentration under the heat flux levels obtaining in LMFBR SG system heat exchangers and under the current standards for control of water quality;
- the extent to which the gradual evolution in the ability to control water quality (boiler feedwater in particular) can be expected to eliminate corrosion aggressive ions as a factor of LMFBR SG system operation.

Many of the above factors cannot be addressed to any extent at this time considering the complex synergism which evidently involves many, if not all, of these factors under actual plant working conditions. Brief comments on several of these factors are, however, in order.

Focusing on the chloride and caustic contaminant levels of the bulk test fluid (water/steam), the laboratory and prototype studies to date with the 2 1/4 Cr-1Mo steel could be characterized as generally pessimistic and optimistic, respectively, relative to the actual working environment. This assessment



is derived from several factors; the sparse information on the average levels and variability of various chemistry parameters of the secondary water system of commercial nuclear power plants; the ability to manage deposit build up via periodic chemical cleaning; the ferritic steel side of the current denting phenomenon which is manifest evidence that chloride levels damaging to ferritic steels can be obtained in current secondary water systems under appropriate concentration conditions (deposit buildup and heat flux) and ORNL studies which relate this chloride action to a Cr-Mo alloy content at least as high as that represented by the 2 1/4 Cr-1Mo steel under the oxygen levels used in the tests (see Table 7, entry #8); concentration factors for corrosion aggressive species which can range over many decades depending on local conditions conducive to concentration and operational strategies.

One of the most difficult questions in the current appraisal of the ferritic steels for LMFBR SG system service is the influence of dissolved oxygen on the stability and corrosion characteristics of these steels. This issue was discussed briefly in the first review.<sup>(1)</sup> In the ASME/EEI model boiler program reviewed above, the dissolved oxygen variable was excluded from the test program for the main reason that it was felt that the presence of oxygen was not a prerequisite for the various corrosion processes of interest to this study, namely: caustic attack (the so-called 'ductile gouging'), plug-type corrosion (local zones of massive oxidation), and the embrittlement type attack thought to be related to hydrogen action on ferritic steels. In the ASME/EEI work, it was postulated that the principal cathodic process for driving the electrochemical action responsible for the various corrosion processes was hydrogen ion reduction. As noted in the first review,<sup>(1)</sup> there is considerable justification for reexamination of the current low dissolved oxygen specifications for the secondary water system for continuous operation, particularly during periods of minimal contamination by potentially aggressive species. In the report of entry #1 of Table 7, reference is made to EBRII studies showing that the hydrogen flux from the water-side of the 2 1/4 Cr-1Mo steel was increased 3-fold when the hydrazine ( $N_2H_4$ ) concentration was deliberately increased from 13 to 150 ppb. If this  $[N_2H_4]$  increase can be related to a decrease in the dissolved oxygen content of the water-side, then this suggests

additional evidence of the beneficial effect of some oxygen on water-side corrosion of ferritic steels, particularly in the absence of corrosion aggressive species. In a recent review, Tyzack<sup>(24)</sup> advanced the thesis that ferritic steels presented generally attractive corrosion properties under the neutral, oxygenated, conditions of the BWR plants. Under the conditions of the PWR secondary water system, the detrimental/ beneficial influences of dissolved oxygen have apparently not been quantitatively related to any extent to water chemistry despite considerable lip-service to this subject.

A third factor which is difficult to relate to the actual service environment is the exposure time of the test specimens to the detrimental conditions. One of the important findings of the ASME/EEI model boiler studies, oriented toward fossil plant SG system corrosion elucidation, was that caustic and chloride affected corrosion processes can proceed rapidly, e.g., a 200 mil tube wall can be penetrated in a matter of hours under an adverse conjunction of factors. In a recent paper,<sup>(11)</sup> Pocock and Lux of Babcock & Wilcox also affirm the rapidity of corrosion attack under adverse chemistry conditions for a working boiler (see entry #4 in Table 1). Further information on the tolerance of candidate materials to off-chemistry conditions is desirable.

Observations from recent LMFBR prototype tests involving the 2 1/4 Cr-1Mo steel are given in Table 3. Thermal parameters for this work are given in Table 4. Water chemistry data for the various test programs are given in Table 5.

The DNB studies of General Electric and Westinghouse were designed to study the corrosion response of the 2 1/4 Cr-1Mo steel under the DNB (departure from nucleate boiling) conditions expected in the CRBRP evaporator. At about 64% and 100% of full power, critical heat fluxes of about 1260 kW/m<sup>2</sup> and 750 kW/m<sup>2</sup> respectively, are expected. The GE program employed a single tube with a heated section length of 16 feet. The Westinghouse program used a single duplex tube, 60.9 ft long, in a "J" tube configuration evaporator module. After exposures of roughly 0.5 year (GE) and 1 year (Westinghouse) these tests gave no evidence of unusual uniform corrosion, exfoliation, or local attack which would appear to compromise the performance of the CRBRP evaporator.<sup>(28)</sup> The individual reports on this work<sup>(26,27)</sup> present photomicrographs of the

TABLE 3. Corrosion Observations from Prototype LMFBR Evaporator Tests Using 2 1/4 Cr-1Mo Steel

Entry #/ (Ref.)	Observations
1/ (25,26,28)	<p><u>Facility:</u> General Electric DNB Test</p> <p><u>Unit:</u> single tube with heated length of 6 feet; 2 1/4 Cr-1Mo steel tubing</p> <p><u>Duration:</u> 4181 hr within 10% of test specifications; 2820 hr within 1% of test specs.</p> <p><u>Observations:</u>  <u>scaling:</u> tube corrosion observed to be essentially uniform throughout length and within design tolerance; scale thickness (comprised of tube oxidation plus deposit) was about 15 <math>\mu\text{m}</math>. Some difference in scale morphology at various zones  <u>localized attack:</u> no significant localized attack observed on any part of tubing</p>
2/(27,28)	<p><u>Facility:</u> Westinghouse DNB Test</p> <p><u>Unit:</u> single, duplex tube of 60.9 feet in a 'J' tube configuration; 2 1/4 Cr-1Mo</p> <p><u>Duration:</u> 8494 hr</p> <p><u>Observations:</u>  <u>scaling:</u> scale layer generally characterized by a compact inside oxide layer overlaid with a porous deposit; dense layer thickness was thickest at DNB zone (22 <math>\mu\text{m}</math>) and thinnest at nucleate and film boiling zones (14 <math>\mu\text{m}</math>); the porous layer showed same thickness profile: about 12 <math>\mu\text{m}</math> at DNB zone and about 6 <math>\mu\text{m}</math> at nucleate and film boiling zones  <u>localized attack:</u> no pitting or anomalous oxidation behavior noted in nucleate boiling, DNB, and film boiling zones; some shallow pitting, (95 <math>\mu\text{m}</math>) and exfoliation were observed in sub-cooled zone</p>
3/(29)	<p><u>Facility:</u> BN-600 prototype test</p> <p><u>Unit:</u> tube-in-tube single tube units and multi-tube models using vertical shell-and-tube configuration; heated length of tubing averaged 44 feet; tubing material was Russian designation 1KH2M, which is similar to 2 1/4 Cr-1Mo</p> <p><u>Duration:</u> up to 12,000 hours, with intermediate inspections</p> <p><u>Observations:</u>  <u>scaling:</u> in sub-cooled and nucleate boiling zones, a thin brown scale was observed; in upper section of evaporator, deposit consisted of porous lumps superimposed on a smooth layer; the deposit thickness reached 1000 <math>\mu\text{m}</math> in some instances in this section</p>

TABLE 3. (contd)

Entry #/  
(Ref.)

Observations

Observations (contd):

localized attack: shallow pitting (up to about 20 m) was developed primarily during startup periods without any prior deposit using single tube models tested for up to 3000 hr; in multitube models, in zones where some superheating took place, pits up to 350  $\mu\text{m}$  were found under the thicker deposits (see scaling comments above) under the same test conditions, 12% Cr ferritic steel displayed less tendency to pitting; in particular, it gave no evidence of pitting worsening under the conditions of the upper evaporator stage; shallow pitting was fairly uniformly distributed over tubing length and showed a greater tendency to passivation

4/(30)

Facility: BOR-60 prototype test

Unit: Once thru, serpentine design for evaporator and coupled superheater; tubing length in evaporator was 55 ft; 45.5 ft in superheater; Russian steel designation 1KH2M (similar to 2 1/4 Cr-1Mo)

Duration: 18,000 hr with intermediate inspections

Observations:

scaling: in evaporator unit, a dark brown deposit was observed over entire length of tubing; layer was comprised of a compact and a loose layer of total thickness ranging up to about 250  $\mu\text{m}$ ; the deposit was thickest near the upper end of the evaporator; in the superheater, the deposit ranged up to 200  $\mu\text{m}$ , with the thickest deposit near the steam inlet end; in both evaporator and superheater units, the deposit tended to be thicker in bend sections relative to straight sections

localized attack: in the evaporator, pitting up to 125  $\mu\text{m}$  was observed, with the highest pitting incidence near the outlet end of the evaporator; in the superheater, the deepest pits were concentrated near the steam inlet end; the density of shallow pits increased toward the outlet end of the superheater

TABLE 4. Thermal Data for Prototype Testing (Evaporators)

Parameter	Test Facility(a)				References
	GE	W	BN-600	BOR-60	
$T_{in}(H_2O)(^{\circ}C)$	313	286	270-320	188	
$T_{out}(H_2O)(^{\circ}C)$	316	327	350-370	302	GE(26,28)
P (psia)	1631	1815	2130	1320	W(27,28)
$T_{in}(Na)(^{\circ}C)$	446	459	450	398	BN-600(29)
$T_{out}(Na)(^{\circ}C)$	338	344	320	295	BOR-60(30)
$\phi_{max}(kW/m^2)$	1260	750	790-1390	444	

(a) typical for a principal operating mode

TABLE 5. Water Chemistry Data for Prototype Testing

Parameter	Test Facility			
	GE	W	BN-600	BOR-60
Na (ppb)	9	32	5-8	8
Cl (ppb)	30	50	16-20	NS
O (ppb)	3	0.9	3-10	10
Fe (ppb)	12	8	5-8	10-15 (oxide)
Cu (ppb)	2	4	3-5	5 (compounds)
SiO <sub>2</sub> (ppb)	18	52	15-57	18
pH	8.8	9.3	9.2	6.7
cationic cond( $\mu S/cm$ )	0.4	0.7	NS	NS

NS = not specified

local oxidation response. Both studies revealed an internal oxidation zone which preceded the main oxidation front in some instances by the depth of the main oxidation layer. The long-term structural significance of this zone is difficult to assess. A limited study of the sub-cooled water zone of the Westinghouse test revealed that some pitting had occurred. There was also indication of some oxide exfoliation. None of these effects had been well characterized at the time of the report.<sup>(27)</sup>

Observations from Russian prototype test work with the 2 1/4 Cr-1Mo steel (Russian designation 1KH2M) are also given in Table 3, with test details in Tables 4 and 5. Under roughly comparable thermal and fairly similar water chemistry conditions with respect to the General Electric and Westinghouse studies, the Russians observed somewhat thicker deposits and more skewing of the thickest deposits toward the outlet (H<sub>2</sub>O) end of the evaporator unit (and toward the inlet end of the superheater unit) than was reported for the GE and W work, wherein a fairly uniform oxidation/deposit layer was observed over the entire length of the heated section. The Russian work also identified pitting action, particularly under the thickest deposits, ranging up to 14 mils in depth. The correspondence of observed corrosion phenomena in the Russian work with exposure time and particular test units was somewhat ambiguous in the available translations of this work. It was a conclusion of this work, however, that the observed pitting gave enough evidence of passivation to support economical use of the 2 1/4 Cr-1Mo steel in the subject application.

In comparing the water chemistry parameters of the above prototype tests with average, standard deviation and maximum values cited by Jonas<sup>(31)</sup> for PWR recirculating boilers under AVT treatment (see Table 14), there appears to be some basis to question the degree of reality represented by these tests in respect of water quality. As noted in a following brief section on water quality control, however, Jonas' data do not reflect the control potential possible with current ion-exchange purification systems. The pitting observations of the BN-600 and BOR-60 tests and the kind and thickness of the deposits observed in the upper stage and the lower stage of the evaporator and superheater units, respectively, are somewhat disquieting, although some aspects of the water chemistry control for this Russian experience are unknown.

Some earlier LMFBR SG system prototype tests for various reactors are briefly noted in Table 6. The reported water-side corrosion response of the 2 1/4 Cr-1Mo steel under these tests is generally favorable.

Table 7 presents a summary of laboratory corrosion studies with the 2 1/4 Cr-1Mo steel. The entry (#1) on waterside corrosion assessment in LMFBR plants, based on hydrogen flux measurements, is included here for use in a later comparison with uniform corrosion levels under contamination by chloride or caustic. Brief comments will be made on some of the entries of Table 7.

The most recent ORNL work (Table 7, entry #2) on the influence of heat flux on the oxidation behavior of 2 1/4 Cr-1Mo in pure steam was conducted under conditions which partially overlap CRBRP superheater (SH) conditions. Metal temperatures (510-540°C) were roughly 40°C higher than SH sodium-side temperatures (see Figure 2). The average heat flux for this study (126 kW/m<sup>2</sup>) was at the low end of the heat flux range predicted for the SH (38kW/m<sup>2</sup> outlet to 820 kW/m<sup>2</sup> inlet). The test steam temperature (ranging from about 470 to 500°C) partially overlapped the range of SH bulk steam temperatures (330-485°C). This work corroborated earlier findings from a number of studies that heat flux tends to increase water/steam oxidation. The oxidation response of internally or externally heated specimens was virtually identical. Under the test heat flux, the oxidation layer exhibited porosity, cracking and poor adherence to the metal. Exfoliation occurred after short periods, resulting in a linear oxidation characteristic. This work was discussed at the recent ORNL SG Materials and Process Development review (June 1978).<sup>(32)</sup> The authors concluded that there was very little basis for extrapolating the results of this program to the lower temperatures and higher heat flux regime of the CRBRP SH. No other new work close to CRBRP SH operating parameters has been noticed in the course of the present report, a situation which leaves the question of heat flux influence on SH oxidation under nominal purity steam at an unsatisfactory juncture. The author suggests that the matters of exfoliation and the development of cracked, porous, oxidation layers, have substantially more important implications for the concentration of contaminants, and the development of a damaging local chemistry, than for the uniform corrosion allowance.

With the exception of a corrosion fatigue program under 5% NaOH (deaerated) solution at 316°C<sup>(38)</sup> no new work on corrosion fatigue testing of 2 1/4 Cr-1Mo was noticed for this review. The General Electric program (Table 7, entry #4) has not yet reached definite conclusions on caustic influence over a range of caustic concentration under the present test parameters.

TABLE 6. Additional Tests of LMFBR SG System Prototypes

Entry #/ (Ref.)	Test/Observation Particulars
1/(33)	<p data-bbox="363 427 545 455"><u>MSG Testing</u></p> <p data-bbox="363 459 1414 523">Atomics International (AI) examination of modular steam generator (MSG) after large leak tests observations:</p> <ul data-bbox="363 555 1414 853" style="list-style-type: none"> <li data-bbox="363 555 1300 583">• steam-side was given only a cursory visual examination;</li> <li data-bbox="363 619 1414 683">• superficial oxidation and minor pitting was found in some tubes but not investigated in detail</li> <li data-bbox="363 719 1398 783">• no evidence of significant degradation except at tube rupture sites used for wastage tests;</li> <li data-bbox="363 819 1414 846">• abrasive wear at tube support plates was limited to about 3 mil</li> </ul>
2/(34)	<p data-bbox="363 883 545 910"><u>MSG Testing</u></p> <p data-bbox="363 915 1373 1055">AI examination of MSG prototype EV after steam generation tests included 9305 hrs of Na operation; 4015 hrs of steaming; 37 start-up/shut-down cycles; maximum steam condition was 930°F (499°C) at 2340 psig; maximum power transfer was 32.1 MW (t);</p> <p data-bbox="363 1076 1097 1112">observations of <u>water-side</u> corrosion response:</p> <ul data-bbox="363 1144 1455 1374" style="list-style-type: none"> <li data-bbox="363 1144 1162 1172">• no evidence of fouling, exfoliation or erosion;</li> <li data-bbox="363 1208 1455 1236">• no evidence of tube deterioration due to vibration and T cycling;</li> <li data-bbox="363 1272 1195 1300">• no evidence of tube/tubesheet weld deterioration;</li> <li data-bbox="363 1336 1357 1364">• the magnetite scale had a maximum thickness of about 1 mil.</li> </ul>
3/(35)	<p data-bbox="363 1404 756 1432"><u>Monju (Prototype Testing)</u></p> <p data-bbox="363 1436 1406 1500">Loop testing of 50 MW SG prototype (helical, once-through design) for 3400 hr revealed the following:</p> <ul data-bbox="363 1532 1455 1702" style="list-style-type: none"> <li data-bbox="363 1532 1357 1559">• slight compressed traces observed in contact zones of tubes</li> <li data-bbox="363 1596 951 1623">• no anomalous water/steam corrosion</li> <li data-bbox="363 1659 1455 1687">• no evidence of pitting/cracking in tubes or tube/tubesheet joints</li> </ul>



TABLE 6. (Continued)

Entry #/ (Ref.)	Test/Observation Particulars
4/(36)	<p data-bbox="332 388 771 430"><u>SNR-300 (Prototype Testing)</u></p> <p data-bbox="332 430 1411 493">Loop testing of Nb stabilized 2 1/4 Cr-1Mo tubing in straight tube and helically coiled SGs revealed following:</p> <ul data-bbox="332 514 1411 787" style="list-style-type: none"><li data-bbox="332 514 1411 598">• no corrosion problems; no details given of water-side corrosion chemistry and test details sparse</li><li data-bbox="332 619 1411 661">• some tube wear noted for 10 out of 1200 tubes at support plates</li><li data-bbox="332 682 1411 787">• the few tubes from straight tube SG that were examined for water-side corrosion response showed rather porous total layer, with areas of loose oxide</li></ul>

TABLE 7. Water-side Corrosion Tests/Observations with 2 1/4 Cr-1Mo Steel

Entry #/(Ref.)	Test/Observation Particulars			
	LMFBR Plants			
1/(14)	overall water-side corrosion determined from H flux data from various LMFBR plants;			
Plant	Steady-state Uniform Corrosion Rate (mil/yr)	Average T Water Inlet (°C)	Steam Outlet	Comment(a)
Phenix proto-type (Renadier)	0.82	245	515	EV flux only
MSG (U.S.)	0.32	235	503	total EV & SH flux
Phenix (France)	0.69	246	513	EV flux only
Monju proto-type (Japan)	0.59	240	487	EV flux only
PFR (UK)	0.72-1.4	288	514	EV flux only
EBR-II (U.S.)	0.19	286	450	total EV & SH flux
CRBRP (U.S.)	---	286	331	EV

(a) flux data applies to 2 1/4 Cr-1Mo evaporator(EV) and superheater(SH) units  
 (b) calculated from hydrogen flux data given in report as follows:  $t(\text{mil/yr}) = 3.28 \times 10^{10} [\text{gm H cm}^{-2} \text{ sec}^{-1}]$ , assuming the following reaction accounts for metal loss:  $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$

Laboratory Studies

- 2/(7) ORNL SH test for oxidation behavior of 2 1/4 Cr-1Mo steel under SH steam and heat flux conditions; to compare oxidation response of internally and externally heated specimens;  
 see text of this section for comments on this test and test parameters.
- 3/(37) ORNL SH test for oxidation behavior of various materials under isothermal SH steam conditions;

TABLE 7. (Continued)

Entry #/(Ref.)	Test/Observation Particulars
	<p>temperature 482°C and 538°C;</p> <p>observations:</p> <ul style="list-style-type: none"> <li>• under isothermal conditions up to 12,000 hr no exfoliation of oxide layer noted for any material;</li> <li>• all ferritic steels (2 1/4 Cr-1Mo, 9 Cr-1Mo, HT-9 (Sandvik)) exhibited similar oxidation behavior;</li> <li>• the austenitic materials (I-800, I-617, 304SS) showed substantially lower oxidation rates;</li> <li>• no material showed evidence of local attack except I-800 which had been furnace sensitized and damaged by HF pickling; IG attack for this material did not progress under SH steam oxidation.</li> </ul>
4/(38)	<p>GE corrosion fatigue test under deaerated 5% NaOH at 316°C, over strain range of 0.2-1%, 1 cps, strain rate range of <math>1.7-5.0 \times 10^{-3} \text{ sec}^{-1}</math>;</p> <p>observations:</p> <ul style="list-style-type: none"> <li>• the safety factor of design allowable fatigue curve adequately accounts for possible degradation of properties in 5% NaOH at 316°C over strain range studied;</li> <li>• fracture morphology at 316°C in both air and NaOH is branching and TG; with multi-crack initiation somewhat more extensive under the NaOH environment;</li> <li>• the occurrence of strain aging at the test T (316°C) complicates interpretation of caustic influence; further high cycle (<math>&gt;10^6</math>) tests needed to quantitatively establish caustic influence (author's statement).</li> </ul>
5/(39)	<p>GE evaluation of tube/tubesheet welds of 2 1/4 Cr-1Mo; constant load tests under 10 and 20% NaOH at 323°C were used to simulate CRBRP shutdown and requalification following a Na-H<sub>2</sub>O reaction resulting from a tubing penetration;</p>

TABLE 7. (Continued)

Entry #/(Ref.)	Test/Observation Particulars
observations:	<ul style="list-style-type: none"> <li>• in 10-20% NaOH at 232°C, <u>air melted</u> 2 1/4 Cr-1Mo weld metal exhibited SCC under <u>tensile stress</u> near the weld YS in both <u>as-welded(AW)</u> and <u>post-weld heat treated(PWHT)</u> conditions;</li> <li>• electroslag remelt/vacuum arc remelt tube/tube sheet welds crack in the AW condition under tensile loading near YS; one PWHT specimen given the minimum PWHT of 7070°C (1305°F)/20 min cracked, otherwise PWHT specimens have resisted caustic SCC;</li> <li>• a one hour PWHT at 727°C appears required to reduce weld metal hardness and UTS enough to avoid susceptibility to in-service cracking and embrittlement;</li> <li>• no observation on general corrosion attack given in this report other than comment (p.3) that the mode of fracture was partially obscured by chemical attack; according to text, this remark apparently applies to both air melted and ESR/VAR material;</li> <li>• these authors noted that one air-melted AW specimen under constant load failed within about 10 min after exposure to 20% NaOH at 232°C.</li> </ul>
6/(40)	<p>ORNL test with I-625 loop to test corrosion response under alternate wet/dry conditions under Cl contamination; T<sub>sat</sub> was 604°F/316°C; [Cl] 10 ppm; T<sub>sh</sub> was 725°F/385°C; [Cl] 2.7 ppm; [O] was about 8 ppm;</p> <p>constant stress tube specimens (internally pressurized with test fluid to give stresses of 0.5, 1.0, 1.5 S<sub>m</sub> at 725F/385C)</p> <p>6475 hours duration;</p> <p>observations:</p> <ul style="list-style-type: none"> <li>• no SCC evidence;</li> <li>• heavy oxidation caused tube failures;</li> <li>• see text of this section for comments on this test.</li> </ul>
7/(40)	<p>ORNL test with 9 Cr-1Mo loop under simulated SH conditions with periods of pure steam oxidation followed by period with Cl contamination; 1st 4626 hrs, [O] less than 7 ppb; 2nd 5958 hrs, [O] about 8 ppm; [Cl] 2 ppm; 900°F/482°C; 1625 psig; constant stress tube specimens as above and flat specimens</p>

TABLE 7. (Continued)

Entry #/(Ref.)

Test/Observation Particulars

observations:

- several T transients of unknown extent obscured test results to some extent;
- after 3120 hr at low [O] numerous small pits were noted; no pitting for Nb stabilized grade;
- during test phase with 8 ppm [O], corrosion product randomly spalled;
- at end of exposure of 9078 hr, pits in unstabilized grade showed no evidence of enlargement;
- all specimens corroded at faster rate in high [O] plus chloride environment than low in [O] environment;
- see text of this section for comments on this test.

8/(41)

ORNL boiling loop studies; for all tests average heat flux was 150 kW/m<sup>2</sup>; 2 1/4 Cr-1Mo specimens (sleeves) were sprung onto a 2 1/4 Cr-1Mo sleeve which covered an I-800 clad electric heater; method of mounting specimens gave a stress gradient with a maximum stress exceeding the YS

Test 1

nucleate boiling under NaOH contamination

conditions:

test T gradient: 100-350°C; 100 ppm NaOH; oxygen 8ppm (air exposed)

observations:

- heavy loose scale for specimens at unheated end (<100°C);
- throughout most of heated section specimens showed thin, adherent scale; widely scattered pitting; no significant crevice corrosion;
- near max T end of heated section, specimens had heavy deposits of needle-like oxidation product under all specimens; no SCC evidence;

TABLE 7. (Continued)

Entry #/(Ref.)	Test/Observation Particulars
	<p><u>Test 2</u> exposure to typical cooling tower water treated with proprietary corrosion inhibitors</p>
	<p>318°C maximum T; oxygen about 8 ppm (air exposure); 1481 hr exposure; misc. contaminants (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>)</p>
	<p>observations:</p>
	<ul style="list-style-type: none"> <li>• much heavier attack than in 1st test;</li> <li>• many shallow pits at low T end of mounting rod;</li> <li>• on all heated areas, specimens and sleeve were heavily attacked; near max T end, 30 mil sleeve completely penetrated; many deep pits under heavy scale both within and outside crevice regions;</li> <li>• oxide filled SC crack noted</li> </ul>
	<p><u>Test 3</u> exposure to Cl contaminated water</p>
	<p>Cl 10 ppm; 318°C T max (1600 psi); oxygen about 8 ppm (air exposed); 2065 hr</p>
	<p>observations:</p>
	<ul style="list-style-type: none"> <li>• numerous shallow pits on specimens in unheated zone (&lt;100°C);</li> <li>• at low T end of heated section, occasional mounds of oxide overlying large pits; no noticeable crevice attack;</li> </ul> <p>on upper heated section, the following was observed:</p> <ul style="list-style-type: none"> <li>• very heavy crevice attack on sleeve and specimens;</li> <li>• voluminous oxide expanded specimens with worse attack in crevice regions;</li> <li>• one sharp SC crack (IG about 15 mil deep) noted; search for SCC evidence was very limited and authors state probably more SCC cracking could be found.</li> </ul>

TABLE 7. (Continued)

Entry #/(Ref.)	Test/Observation Particulars
<u>Test 4</u>	oxide buildup under pure boiling H <sub>2</sub> O at 318°C (T maximum) for 2 weeks with air exposure of condensate followed by caustic contamination under low oxygen conditions
	during caustic phase: [NaOH]100 ppm; N <sub>2</sub> blanketing used to reduce oxygen; after one week oxygen ran as high as 0.5 ppm
	heater failure due to corrosion terminated test after 618 hr
	observations:
	<ul style="list-style-type: none"> <li>• about same appearance as for Test 1;</li> <li>• no localized attack on unheated section (&lt;100°C);</li> <li>• few isolated oxide mounds covering broad pits in lower heated section;</li> </ul>
	proceeding up heated section:
	<ul style="list-style-type: none"> <li>• pitting was less frequent but crevice attack noted under all specimens; attack greater than for test 1; under some specimens 30 mil sleeve was penetrated;</li> <li>• crevice attack was noted only on heat transfer surfaces; inner surface of one heavily attacked specimen showed numerous shallow penetrations (1-5 mil deep);</li> <li>• under these test conditions the attack on the I-800 cladding was essentially nil and no SCC noticed; both sensitized and annealed 304 and 304L specimens also showed no appreciable attack.</li> </ul>
9/(42)	Autoclave study of ferritic steels in NaOH solutions; 350°C; [NaOH] 0.1-5.0 molar; up to 5000 hrs exposure;
	observations:
	<ul style="list-style-type: none"> <li>• duplex layer on all materials; inner layer of 2 1/4 Cr-1Mo had grainy appearance similar to that on mild steel and occupied about 2X volume of metal corroded whereas for other materials inner layer had about same volume as metal;</li> </ul>

TABLE 7. (Continued)

Entry #/(Ref.)	Test/Observation Particulars
	<ul style="list-style-type: none"> <li>• both 9 Cr-1Mo and 2 1/4 Cr-1Mo Nb exhibited substantially better corrosion resistance than unstabilized 2 1/4 Cr-1Mo, with margin of superiority going down with conc. of NaOH;</li> <li>• a linear loss characteristic was established for all materials;</li> <li>• relative superiority of Nb stabilized grade of 2 1/4 Cr-1Mo could be due to greater amount of Cr available for corrosion protection;</li> <li>• the very poor resistance of unstabilized 2 1/4 Cr-1Mo limited tests with this material to NaOH concentrations less than about 1 molar (see following table).</li> </ul>

Test Results for This Work

M(NaOH)	Uniform Corrosion Rate ( $\mu\text{m}/1000 \text{ hr}$ )		
	2 1/4 Cr-1Mo	2 1/4 Cr-1Mo Nb	9 Cr-1Mo
2.5	X	X	8.2
1.0 (3.6 w/o)	54.0	5.0	2.7
0.5 (2.0 w/o)	30.0	4.3	1.5
0.1 (0.4 w/o)	7.0	2.9	1.5

X = massive corrosion

10/(43)

Corrosion study of Nb stabilized 2 1/4 Cr-1Mo steel under heat flux conditions

test conditions:

water is circulated through 24 in (0.6 m) heat transfer section (0.8 in ID x 0.98 in OD) using electrical heating and a static sodium annulus to facilitate heat transfer; hydrogen flux into sodium monitored by argon flowing through nickel capillary mounted in sodium;

steady-state heat flux:  $660 \text{ kW/m}^2 - 250 \text{ kW/m}^2$ ;  
 water inlet T =  $343^\circ\text{C}$  (2550 psi)  
 pH = 8.5-9.2  
 O = 10-30 ppb

for transient conditions, water was shut off and tube T allowed to rise to  $510^\circ\text{C}$



TABLE 7. (Continued)

Entry #/(Ref.)	Test/Observation Particulars
	<p>water chemistry varied as noted below</p> <p>observations: <u>under 1ppm NaCl; heat flux 250 kW/m<sup>2</sup>; 650 hr:</u></p> <ul style="list-style-type: none"> <li>• no unusual corrosion action; no evidence of pitting;</li> </ul> <p><u>under 7 ppm NaOH, 630 kW/m<sup>2</sup>; 1400 hrs: water flow adjusted to give steam quality of 6%</u></p> <ul style="list-style-type: none"> <li>• no change in H emission upon NaOH introduction</li> <li>• no measurable build-up of NaOH in test section</li> <li>• no unusual corrosion resulting from NaOH</li> </ul> <p><u>under presence of artificial defects (spark-eroded pits of various depth/diameter ratios):</u></p> <ul style="list-style-type: none"> <li>• no unusual corrosion effects attributable to defects; substantial crud deposition was observed in defects of depth/diameter ratio &gt;1. Crud believed derived from dissolved species; possible aggressive salts could concentrate in similar way in a working situation</li> </ul> <p><u>general comments on test</u></p> <ul style="list-style-type: none"> <li>• metal corrosion appeared largely independent of heat flux; extra oxide buildup being derived from <u>deposition from solution</u>;</li> <li>• in all zones of test section there was a net <u>deposition</u> of oxide (largely Fe<sub>3</sub>O<sub>4</sub>) from the solution; this deposition occurred at a constant rate of about 1 μm/1000 hr for the heat flux zone;</li> <li>• metal loss appeared to follow a logarithmic law, consistent with steady buildup by deposition from solution; metal loss appeared to be largely independent of steam quality, from sub-cooled water to 10% quality region</li> </ul>

Entry #5 of Table 7 outlines the results to date of a tube/tubesheet weld evaluation program being conducted by General Electric. Corroborating earlier findings of the National Program,<sup>(8)</sup> air melted stock exhibited SCC under the corrosion evaluation conditions for both as welded (AW) and post-weld heat treated (PWHT) conditions. Electroslag remelted (ESR) and vacuum arc remelted (VAR) material have thus far shown good resistance to the caustic test conditions of this evaluation. Cracking was reported for one ESR/VAR welded couple given the minimal PWHT (20 min. at 1305°F/707°C). This report gives no details on the uniform corrosion attack other than a comment that the mode of fracture for both air-melted and ESR/VAR material was obscured by the 'chemical attack'.

A recent ORNL report of considerably earlier work (entry #6), under oxygen conditions not likely to be encountered in practice, discusses the corrosion effects of alternate wet/dry cyclic conditions under a temperature range of 316°C (saturated) to 386°C (superheated), and Cl contamination ranging from 10 ppm (sat.) to 2.7 ppm (SH), with about 8 ppm oxygen for both phases of the test. Tube specimens were internally pressurized by the test medium and evacuated at the outer surface. Tube wall thickness was adjusted to provide hoop stresses ranging from 0.5 to 1.5 of the allowable design stress for 386°C. Under these isothermal conditions, tube sections failed via gross oxidation thinning at various times, depending on the stress level. At the end of the total test exposure (6475 hours) all tube specimens at the 1.5  $S_m$  and 1.0  $S_m$  level had failed, 5 had failed at the 0.55  $S_m$  level and the authors state that the remainder would have failed had the test continued much longer. A total of 27 out of 35 specimens had failed at the end of the test period. No SCC evidence was found. In the face of uniform oxidation rates of the magnitude shown in these tests, whether or not SCC was evidenced would appear to be completely irrelevant. Under conditions which developed the above damage to the 2 1/4 Cr-1Mo steel, I-800, I-625, and 304L SS exhibited only a light oxidation layer. This report also discusses a test (entry #7) to simulate SH conditions under Cl contamination. After a period of 4626 hours under low [O] and pure steam to develop a protective oxide layer, constant stress tube specimens and flat coupons were exposed for an additional 5958 hours under 8 ppm [O] and 2 ppm [Cl]. After 3120 hours of the first period, some shallow pitting was

noted, but not for the Nb stabilized steel. These pits showed no tendency to enlarge during the subsequent test. Under the second test, some exfoliation of the oxide layer was observed. Specimens corroded at a faster rate under the chlorinated, oxygenated, environment. Again, there was no evidence of SCC for any of the test materials even under the unrealistic condition of 8 ppm oxygen. For the second test, 2 1/4 Cr-1Mo gave a uniform corrosion rate of about 1.5 mils/yr while I-800 gave rates ranging from 0.04-0.09 mils/yr under the same conditions.

The ORNL boiling loop studies are summarized briefly in entry #8 of Table 7. While these were reviewed in the previous report<sup>(1)</sup>, they are repeated here for the reason that, in the author's opinion, they remain among the most significant tests of the National Program for their indication of the possible adverse effects of bulk stream excursions of aggressive ions under concentrating conditions. Specifically, these tests revealed: SCC of the 2 1/4 Cr-1Mo steel near 300°C under high oxygen and Cl concentrations, under concentrating conditions (test #3); under high Cl and oxygen concentrations and concentrating conditions, the 2 1/4 Cr-1Mo steel displayed a massive oxidation response similar to that of the carbon steel support plates involved in the current 'denting' phenomenon affecting some PWR evaporators (test #3). The oxygen level (8 ppm) used in these ORNL tests is considered unrealistic for LMFBR evaporators unless total breakdown occurs in coolant chemistry control.

Newman et al.'s corrosion study of the Nb stabilized 2 1/4 Cr-1Mo steel under heat flux conditions is outlined in Table 7 (entry #10). These authors found no significant corrosion effect attributable to Cl or NaOH contaminants and no effect of heat flux on either general, or localized, corrosion under Cl and NaOH contamination. These findings are at considerable variance with National Program studies with unstabilized 2 1/4 Cr-1Mo (see Table 7 entry #8,) involving, in some instances, roughly comparable concentrations of contaminant and similar temperature levels. The [O] level of this British work was substantially lower (10-30 ppb) than that for most of the ORNL work (ranging from 7 ppb to 8 ppm). Furthermore, the other differences between the test conditions of these studies makes comparison of test results difficult.

The tendency of 2 1/4 Cr-1Mo steel to accelerated oxidation under high Cl and NaOH concentrations, and possibly unrealistic oxygen levels, has been well substantiated by the National Program work to date. Some of this work was reviewed in the previous corrosion assessment<sup>(1)</sup> and additional observations relating to this corrosion aspect of the 2 1/4 Cr-1Mo steel are given in Table 7 of this report. Figure 1 presents a graphical summary of those National Program observations which permit an estimate of uniform corrosion rate. Tables 8, 9, 10 present a more detailed data summary. Entry #1 of Table 7 gives values of the steady-state corrosion rate for 2 1/4 Cr-1Mo steel (estimated from hydrogen flux measurements from the sodium side) of the EV and SH components of various LMFBR plants. The data field for the EV components is plotted in Figure 1 to illustrate the very substantial difference between 'uniform' corrosion characteristics of 2 1/4 Cr-1Mo steel under nominal purity water and under water contamination of various degree of severity. Indig's data for stressed tubing under SH steam and roughly 5-10 ppm NaOH contamination are also given in Figure 1.

Figure 2 represents an attempt to summarize what we regard as some of the most important National Program observations of 2 1/4 Cr-1Mo corrosion response over a wide range of temperatures, heat flux conditions and contaminant concentration. While no single plot can adequately present such a data complex, the data citations indicate if heat flux was present, the principal contaminant, and the plot coordinates give the bulk fluid concentration of the contaminant and the temperature, or temperature range, of the citation. Brief data details for this figure are given in Table 11, some of which as noted, are given in previous tables of this report. Using the Na values for the contaminant index, the General Electric and Westinghouse DNB tests<sup>(26,27)</sup> (reviewed previously, see Tables 3, 4, 5) are also plotted in Figure 2. At the top of the figure an indication of the possible range for the maximum concentration of Na and Cl ions under crevice concentration conditions is given. These data are from an interesting paper by Balakrishnan<sup>(44)</sup> on the possible effects of condenser in-leakage on SG system water and were calculated for a variety of fresh water cooling sources, with 300°C primary and 250°C secondary water.

Although the pitting and stress corrosion cracking indications of the Figure 2 data are of importance to the proposed LMFBR applications of the 2 1/4 Cr-1Mo steel, clearly the dominant aspect of Figure 2 is the large T-[X] field over which this steel has displayed a tendency to massive oxidation. The question of the relevance of this characteristic of the 2 1/4 Cr-1Mo steel to economic service in the SG system of LMFBR plants cannot be answered satisfactorily without substantially better knowledge of the bulk fluid contamination species and levels, and the concentration agencies for these species potential to the heat exchangers of LMFBR plants under a spectrum of water quality management and equipment maintenance practice. Oxidation has been observed to blunt cracks of the SCC type with the 2 1/4 Cr-1Mo steel.<sup>(8)</sup> In more extreme forms, oxidation of this steel has some potential for significant structural degradation depending on its contribution to local buildup of aggressive ions and/or the development of adverse electrochemical situations.

The corrosion information to date from National Program and general sources clearly identifies the evaporator component as the most probable arena for significant corrosion action under adverse water-side physico-chemical conditions. There are several reasons for this: the liquid phase is the principal medium for the various electrochemical processes which drive the uniform and local corrosion processes of the water-side system; the boiling process is the principal mechanism for concentrating corrosion aggressive species; deposition of dissolved and particulate products of the pre-boiler circuits, an important precursor of abnormal local chemistry development, is favored by the heat flux obtaining in the evaporator. Some aspects of water chemistry control affecting these factors are considered briefly in a following section.

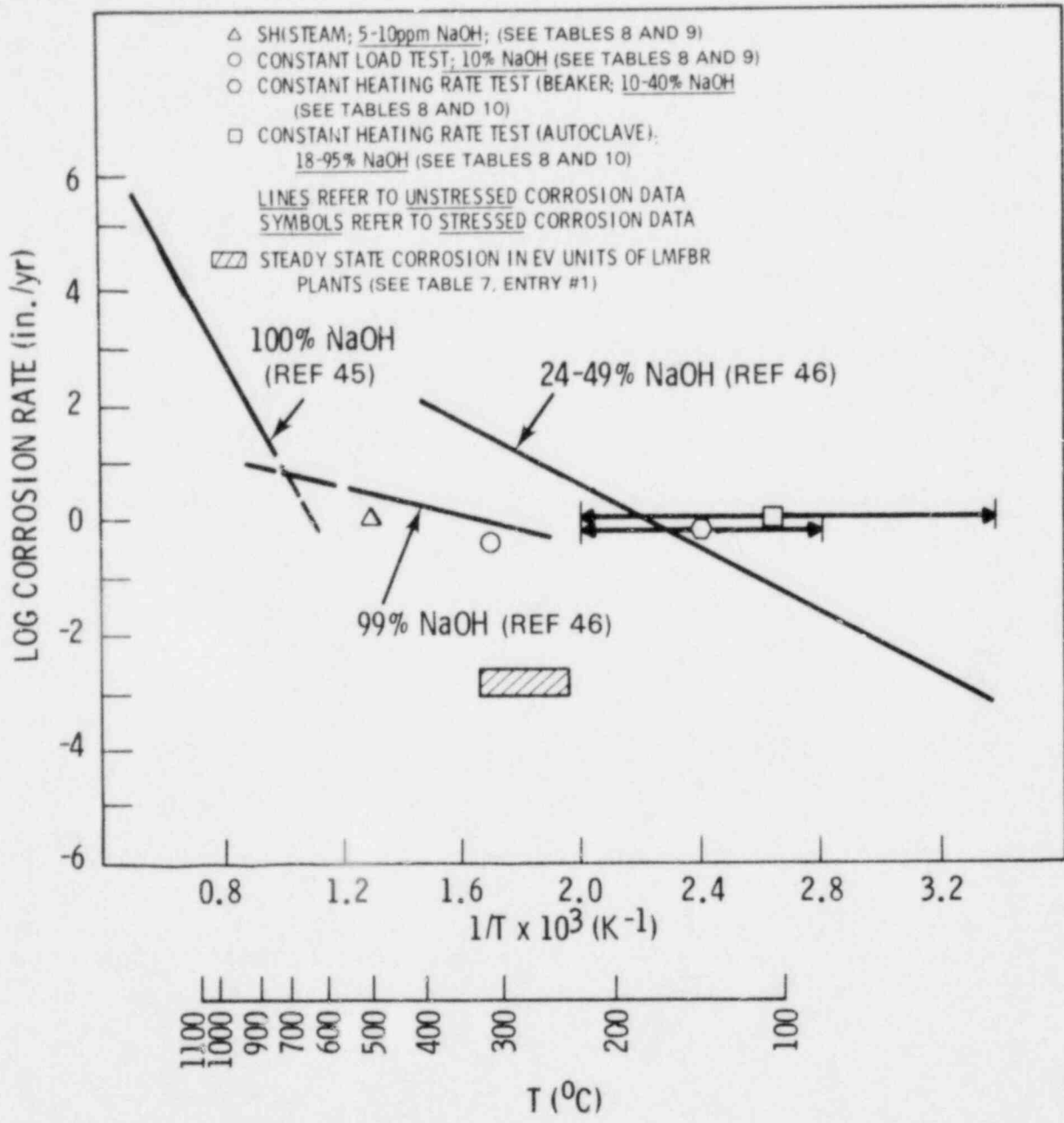


FIGURE 1. Uniform Corrosion Rate Data for 2 1/4 Cr-1Mo Steel Under Stressed and Unstressed Conditions for Various NaOH Solutions and Temperatures

TABLE 8. Summary of Uniform Corrosion Observations for  
2 1/4 Cr-1Mo Steel Under Stressed Conditions

Test	T (°C)	[NaOH] %	Uniform Corrosion Rate <sup>(a)</sup> (mil/yr)
• <u>constant load test</u> ; average for base and HAZ sites of stress relieved weld material	316	10	320 (see Table 9)
• <u>constant heating rate test</u> ; autoclave; N <sub>2</sub> atmosphere; average for annealed and normalized/tempered material	RT-316	18-95	820 (see Table 10)
• <u>constant heating rate test</u> ; beaker, air exposed	82-232	10-40	610 (see Table 10)
• <u>superheater test</u> (steam)	482	5-10(ppm)	650 (see Table 9)
Misc. observations reported in GE work which give no particulars of uniform corrosion response			
• <u>constant extension rate test</u>	316	5 & 10	in general, samples showed fairly thick oxide layer which cracked during straining (p. 6, Ref. 47)
• <u>evaluation of prototypical CRBRP SG tube/tubesheet welds</u> ; constant load stress corrosion tests and U-bend tests	232	10 & 20	mode of fracture obscured by chemical attack; presumably this remark applies to both air melted and ESR/VAR specimens (p. 3, Ref. 39)

(a) average of data computed from cross-sectional area changes, or actual penetration rate data reported in references

TABLE 9. Summary of Uniform Corrosion Data for  
2 1/4 Cr-1Mo Steel from Constant Load Test(8)

10% NaOH; 316°C, stress range 35-65 ksi

<u>Metallurgical Condition</u> (a)	<u>Sample Region</u>	<u>Exposure (hr)</u>	<u>Uniform Corrosion Rate</u> (b) (mil/yr)
Welded & Stress Relieved	base	836	210
	HAZ		280
	fusion line		560
	weld		160
	fusion line		130
	HAZ		380
	base		290
	base	298	320
	HAZ		400
	fusion line		5
	weld		2
	fusion line		
	HAZ		390
	base		320
ESR, Annealed	average gage	1895	3
	average gage		1
Annealed	--	2033	14
Normalized & Tempered	--	1324	10

- uniform corrosion from SH test reported in Reference 8

T: 482°C

[NaOH] 5-10ppm

internally pressurized tube specimens; stress range 20-50 ksi uniform  
corrosion rate reported by Indig: 400-900 mil/yr

(a) ESR refers to electroslag remelt heats; other heats air-melted;

(b) computed from cross-sectional area change data given in Reference 8; no  
estimate given of area change increment due to plastic strain



TABLE 10. Summary of Uniform Corrosion Data for 2 1/4 Cr-1Mo Steel from Constant Heating Rate Tests<sup>(48)</sup>

Autoclave tests: constant heating rate - data for specimens stressed at, or below, YS; flat tensile specimens; Nitrogen ambient atmosphere

T nominal (°C/hr)	NaOH (w/o)	T range (°C)	t (hr)	Uniform Corrosion Rate <sup>(a)</sup> (mil/yr)		
				2 1/4 Cr-1Mo	C steel	304SS
10	18-65	RT-160	14	1300	170	~0
10	33-95	RT-316	29	990	850	170
10	33-95	PT-316	29	790	~0	~0
20	33-95	RT-316	15	1100	-	230
20	33-95	RT-316	15	290	-	~0
4.5	33-95	RT-316	64	460	-	90
Average:				820	340	80

(a) data calculated from cross-sectional area change data given in Reference 48; 2 1/4 Cr-1Mo tested in annealed and normalized and tempered condition; C steel in as-received condition; 304SS tested in mill-annealed, solution annealed, and furnace sensitized conditions; corrosion data showed no particular sensitivity to condition of test materials; where more than one specimen used, data represent average for all specimens.

Beaker Tests: 'C' type specimens heated in open air; spot welds placed on both sides of specimen; residual stress approached YS

T nominal (°C/hr)	NaOH (w/o)	T range (°C)	t (hr)	Uniform Corrosion Rate <sup>(a)</sup> (mil/yr)		
				2 1/4 Cr-1Mo	C steel	304SS
5	33	82-232	30	380	760	150
10	10	82-182	10	1200	500	110
5	10	82-182	20	570	350	88
2.5	10	82-182	40	290	260	77
Average:				610	470	110

(a) data calculated from cross-sectional area change data given in Reference 49

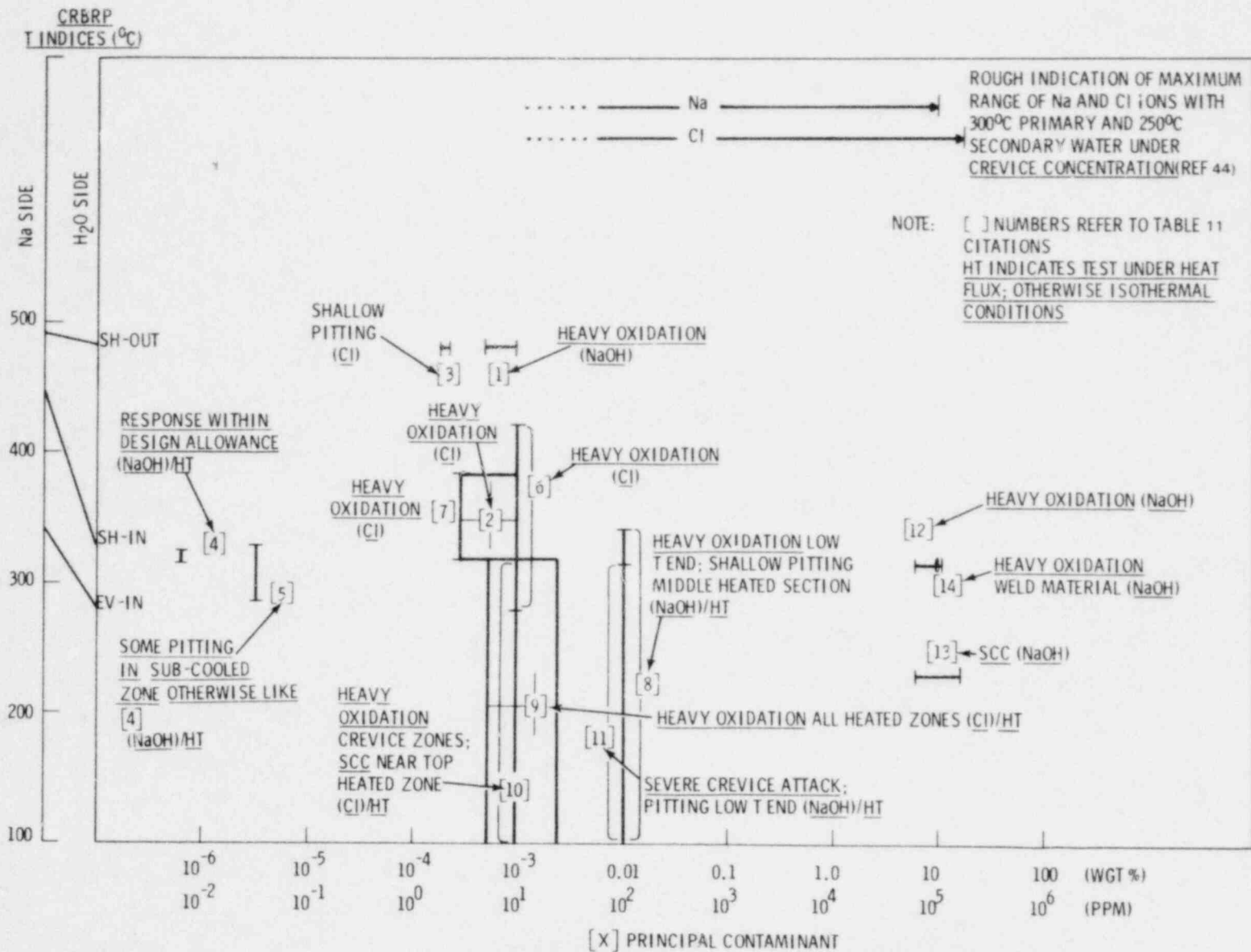


FIGURE 2. A Partial Summary of National Program Corrosion Observations for the 2 1/4 Cr-1Mo Steel

TABLE 11. Data Citations Used in Figure 2

(All tests cited below done under various stressed conditions)

Citation Fig. 2	H <sub>2</sub> O Phase	T (°C)	[X] (ppm)	[O] (ppm)	Heat Flux (kW/m <sup>2</sup> )	Corrosion Observations			Reference
						Uniform Attack	Pitting	Cracking	
1	SH	482	NaOH 5-10	-	IT	heavy	-	-	8 (see Table 9)
2	sat- SH	316- 385	Cl 3-10	8	IT	heavy	-	-	40 (see Table 7, #6)
3	SH	482	Cl 2	7ppb- 8ppm	IT	--	numerous shallow pits	-	40 (see Table 7, #7)
4	liq- sat.	313- 318	Cl ~30ppb Na 6ppb	7ppb max	1260	no unusual effects in DNB zone after 4181			26,28 (see Table 3, #1)
5	liq- sat.	286 327	Cl <50ppb Na 31ppb	0.9ppb	750	no unusual effects in DNB zone after 8500 hrs; in subcooled zone some pitting, anomalous ID increase and possible exfolia- tion of oxide			27,28 (see Table 3, #2)
6	sat.- SH	282- 371/ 427	Cl 10 max	20 max		heavy	-	-	49
7	sat.- SH	318- 385	Cl 3-4	9		heavy	-	-	50
8	sat.	100- 350	NaOH 100	-	150	heavy low T end	shallow pitting middle heated zone	-	41 (see Table 7, #8) (1st test)

TABLE 11. (Continued)

(All tests cited below done under various stressed conditions)

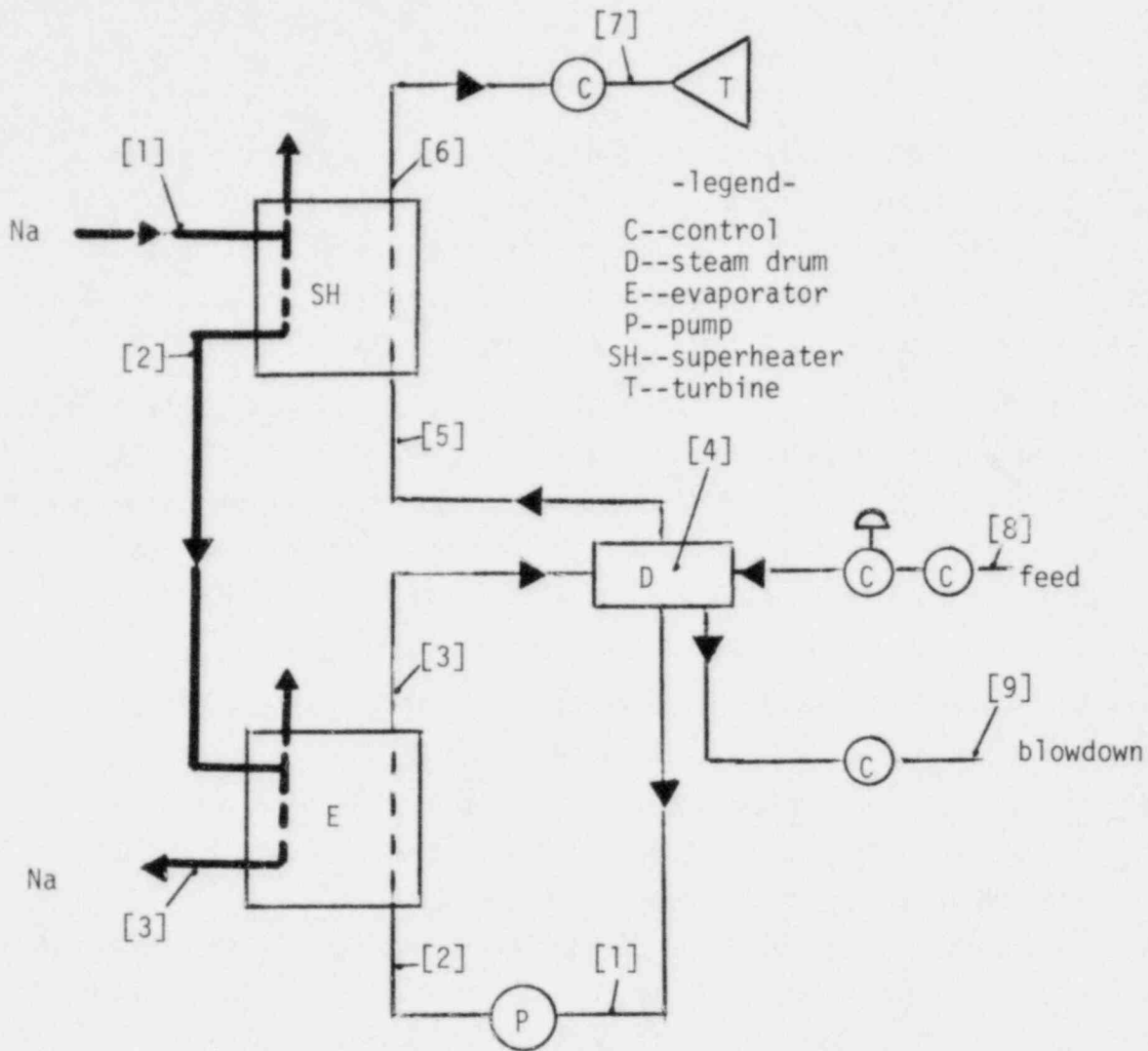
Citation Fig. 2	H <sub>2</sub> O Phase	T (°C)	[X] (ppm)	[O] (ppm)	Heat Flux (kW/m <sup>2</sup> )	Corrosion Observations			Reference
						Uniform Attack	Pitting	Cracking	
9	liq.	<100 318	Cl 6-27 & other ions	8	150	heavy all heated zones	deep pits under oxide	oxide filled cracks upper (high T) section	41 (see Table 7, #8) (2nd test)
10	liq.	<100 318	Cl 10	8	150	heavy crevice attack	small to large pits low T end	IG cracking upper section	ibid; (3rd test)
11	liq.	<100 318	NaOH 100	-	150	heavy crevice attack	broad pits low T end	shallow cracks	ibid; (4th test)
12	liq.	316	NaOH 5-10%	low- 8	IT	heavy crevice attack	-	numerous shallow cracks	18 (see Table 8)
13	liq.	232	NaOH 5-15%	-	IT	-	-	IG & TG cracking	8
14	liq.	316	NaOH 10%	-	IT	heavy on weld specimens	-	none	8 (see Table 9)

## WATER QUALITY CONTROL

Probably the most important resultant of the past decade's experience with SG system materials in nuclear power plants has been a fairly general consensus that the best possible control of secondary water quality is an imperative of long-term economic operation. Furthermore, this appears to be the case for every SG material within the current perspective.

Some of the details of the CRBRP recirculating SG system are given in Figure 3. The latest feedwater specifications proposed for the CRBRP are given in Table 12. For comparison, Table 13 presents feedwater and drum water specifications for the PFR LMFBR plant. Table 14 presents a summary of blowdown water chemistry experience compiled by Jonas<sup>(31)</sup> for PWR plants using recirculating SGs and either AVT or phosphate water treatment.

The boiler water/feedwater concentration factor for the PFR plant given in Table 13 is 100 and yields a boiler water chloride value close to the average value for the boiler (blowdown) water for the AVT plants given in Table 14. This concentration factor for the CRBRP plant is expected to be about 6.<sup>(51)</sup> and is reflected in the specifications for the CRBRP given in Table 12. For operation above 5% of full power the Cl specifications for the feedwater and boiler (recirculating) water are 9 and 50 ppb, respectively. This boiler value is roughly 1/3 of the average value (135 ppb) reported by Jonas for AVT plants. The Na specification for the CRBRP for greater than 5% power (6 ppb for boiler water) is substantially lower than the 160 ppb average value reported for the AVT plants in Table 14. The standard deviation and max/min data given by Jonas in Table 14 are indicative of the degree of control for the units surveyed. It is to be noted, however, that to the author's knowledge most of the plants contributing data to Table 14 did not use ion-exchange purification to any extent, whereas this feature is planned for the CRBRP. Further, the CRBRP water chemistry specifications and analytical capability are being continually upgraded to state-of-the-art-standards by General Electric.



state point	T(F)	T(C)	P(psia)	Flow(lb/hr x10 <sup>-6</sup> )
[1]Na	921	494	158	13.49
[2]Na	845	452	112	13.36
[3]Na	651	344	104	13.10
[1]H <sub>2</sub> O	548	286	1905	2.22
[2]	548	286	2024	
[3]	628	331	1896	
[4]	628	331	1889	
[5]	625	329	1857	
[6]	906	486	1550	
[7]	900	482	1465	
[8]	468	242	2032	1.14
[9]	659	348	1890	0.11

FIGURE 3. Some Operating Parameters of the CRBRP SG Circuit(2,52)

TABLE 12. Water Chemistry Specifications, CRBRP(f)

<u>Parameter</u>	<u>Units</u>	<u>Preheat and Operation Below 5% Power</u>	<u>Operation Above 5% Power (a)</u>	<u>Mandatory Operator Shutdown</u>
<u>Maximum Allowable Feedwater Impurities</u>				
Solids, Suspended	ppb	NA	16(e)	NA
<u>Dissolved Oxygen</u>	ppb	10	7	100
Silica	ppb	30	20	NA
Iron (Fe)	ppb	50	10	NA
Copper (Cu)	ppb	10	<1.5	NA
Hydrazine (Residual)	ppb	100	5	NA
Sodium	ppb	NA	1(e)	NA
pH at 77°F	NA	8.6-9.6	8.7-9.1	<8.0
Conductivity (cation) at 77°F	μmho/cm	NA	0.3(e)	NA
Chlorides	ppb	NA	9(e)	NA
<u>Maximum Allowable (Recirculation) Water Impurities</u>				
Chlorides	ppb	100	50(d)	150
Solids, Suspended	ppb	250	90	90
Sodium	ppb	60	6	30(b)
pH	NA	8.5-9.6	8.5-9.0	<8.0
Conductivity (cation) at 77°F	μmho/cm	6.0	2.0(c)	9.0

- (a) Operation above these limits is allowable for up to 24 hrs at any one instance. Total time above these limits shall not exceed 525 hrs in any twelve month period.
- (b) Operation up to 60 ppb recirculation water sodium levels is allowable below 45% power for times specified in (a) above.
- (c) Action to determine location of leaks should be initiated upon detecting change in trend (increase in conductivity) of conductivity in condenser outlet water.
- (d) Action to determine location of leaks should be initiated upon detecting change in trend (increase in concentration) of chlorides concentration.
- (e) For reference only. Value could vary depending on power level, drum drain rate, and impurity deposition rate in evaporator. Control and alarm to be on recirculation water.
- (f) Supplied to author by C.N. Spalaris of General Electric

TABLE 13. PFR (Downreay) Water Specifications for Recirculating Boiler System<sup>(23)</sup>

Item	Feed Water	Boiler Water
Total dissolved solids (TDS)	0.07 $\mu\text{mho/cm}$	$\pm 7.0 \mu\text{mho/cm}$
Sodium (Na)	0.001 ppm	"0.10 ppm
Chloride (Cl)	0.0016 ppm	"0.16 ppm
Silica (SiO <sub>2</sub> )	0.002 ppm	"0.20 ppm
Calcium/Magnesium (Ca/Mg)	0.0002 ppm	"0.02 ppm
Iron (Fe)	0.01 <sup>(a)</sup>	Measured for record purposes
Copper (Cu)	0.002	Measured for record purposes
Nickel (Ni)	} Total	
Zinc (Zn)		$\pm 0.01$
Oxygen (O <sub>2</sub> )	0.007 ppm	"0.007 ppm
Carbon Dioxide (CO <sub>2</sub> )	0.015 ppm	"0.015 ppm
pH	8.8 - 9.2	>8 (pH units)

(a) Integrated iron level 800 ppm hours  
Max 0.2 during start up

Condenser in-leakage, particularly where brackish (sea, estuarine) coolant is involved, has been the primary cause of serious contamination of the secondary water system from a corrosion standpoint. A number of strategies have been proposed for minimizing this contamination source, including: redundant containment of coolant in condenser, use of titanium condensers, redundant condenser capacity and quick isolation of defective condenser units and contaminated condensate. Apart from minor sources attributable to the vagaries of commercial plants during construction, lay-up and chemical cleaning phases, the water treatment system itself is probably the most important source of corrosion aggressive species after condenser in-leakage. The all volatile (AVT) and phosphate techniques, solely or in combination, are the principal water treatment techniques used in modern nuclear powerplants. AVT is currently specified for the CRBRP.<sup>(52)</sup> Condenser cooling is provided by river water and a cooling tower.



TABLE 14. Water Chemistry (Blowdown) for Recirculating PWR Steam Generators<sup>(31)</sup>

	AVT (19 units)				PO <sub>4</sub> (10 units)			
	Specified	Average	Std	max min <sup>(1)</sup>	Specified	Average	Std	max min <sup>(1)</sup>
pH	8.5-9.0 <sup>3</sup> -9.6 <sup>4</sup>	8.87	0.36	10.3 6.4	8.5-10.6	9.5	0.44	10.6 8.1
Cation Cond. (μmhos/cm)	<2.0	3.33	9.16	100 0.2				
Total Cond. (μmhos/cm)	-	4.65	5.1	62.0	-	66.6	41	
Dissolved Oxygen (ppb)	<5				<5	3.3	2.4	
Sodium (ppm)	<0.1	0.16	0.70	15.0	-	16.8	10.6	6.0 1.0
Free OH as CaCO <sub>3</sub> (ppm)	<0.15	0.25	0.51	10.5	0			
Chlorides (ppm)	<0.15	0.135	0.48	7.8	<75	1.6	3.9	33 <0.01
Silica (ppm)	<1.0	0.32	1.19	22.0	<5	1.4	1.7	
Ammonia (ppm)	<0.25	0.39	0.36	4.2 0.0	-			
Phosphates (PO <sub>4</sub> ) (ppm) 0.7	-				10-80 <sup>5</sup> 25-80	25.7	16.1	110 0.7
Na/PO <sub>4</sub>	-				2.3-2.6 <sup>6</sup>	2.5 <sup>6</sup>	2.6 <sup>6</sup>	6.5/1.9 <sup>6</sup>
Molar Ratio						3.3 <sup>7</sup>	9.8 <sup>7</sup>	13.0/1.24 <sup>7</sup>
Copper (ppb)	-				<10	14	15.1	

- NOTES: 1. max and min bi-weekly average  
 2. estimated  
 3. copper alloy preheaters  
 4. no copper in the system  
 5. brackish or seawater cooling  
 6. Marcy-Halstead  
 7. analytical ratio

8. (To the author's knowledge, most of the plants in the above survey did not use ion-exchange purification to any extent)

As well demonstrated by a number of model boiler studies, (15,44,41) and identified by the ASME survey on fossil plant boiler corrosion, (4,5) there are two principal factors involved in a debilitating corrosion situation, namely: some bulk water contamination by an aggressive ion (e.g. Cl, OH, SO<sub>4</sub>, etc.); conditions conducive to concentrating the ion(s) (heat flux, mechanical crevice or prior deposit) or, in general, conducive to a local buildup of an abnormal chemistry stimulative of anodic/cathodic processes which drive the corrosion processes. The presence of continuous or cyclic stress conditions causing plastic deformation at sites within the affected zone will certainly exacerbate the corrosion damage potential of such a situation. The pre-boiler corrosion product fouling of heat exchanger surfaces is an important potential contributor to the concentration process. More attention is now being paid to a general upgrading of the secondary water circuit materials in general in an attempt to minimize this factor.

In recent conferences, Garnsey has given two comprehensive reviews of the problems of water quality control. (53,54) His remarks focus attention on two important problem areas:

- it is generally not possible to quantify the improvement in boiler corrosion suppression achievable by water quality specifications due to:
  - a) the complex relationship between bulk water and local conditions;
  - b) current uncertainty over local environmental conditions harmful to various SG materials;
- the concentration of aggressive species in porous deposits is of concern in subcritical boilers.

Consideration of the concentration process by a number of authors (53,54,44) indicates that the concentration factor (CF) (local/bulk concentration) may range over roughly six decades, depending on the particular species involved and the specifics of the local concentration environment.

Details of water treatment technology are outside the scope of this review. Because of its importance to long-term corrosion response of SG system materials a few qualitative comments on water treatment are, however, in order. These are given in Table 15. It is obvious that mere specification

TABLE 15. Water Quality Control Observations for Secondary Water of Nuclear Powerplants

Area	Observation	Refs.
Detectability of significant ions	Hideout of soluble species and precipitation of hardness salts during normal operation may give below limit of detection complacency. During transients (startup, shutdown) significant levels of various species (Ca, Mg, Na, Cl) can reappear.	55
Cu ion significance	There has been some correlation of the massive oxidation of carbon steel under concentrating conditions and Cl presence with Cu ions in the feedwater	56
Contaminant input from ion-exchangers	<p>The condensate polishing plant (CPP) could be a significant source of corrosion aggressive species as a result of:</p> <ul style="list-style-type: none"> <li>• leakage of ions thru the CPP due to resin exhaustion;</li> <li>• contamination of resins by organics, anion and cation regenerants;</li> <li>• thermal decomposition of resin fines which bleed into SG water</li> </ul>	57,58,59 60,61
Water treatment option limitations	<p>The chemicals used in AVT treatment (e.g. ammonia, morpholine, cyclohexylamine) do not appreciably affect solute concentration because the AVT reagent distributes preferentially to the steam, is a weak base and almost completely un-ionized at evaporator temperatures. Model boiler studies with Cl ions under concentrating conditions have confirmed the inefficacy of AVT in combating Cl corrosion action, whereas phosphate treatment inhibited both local and general corrosion under the same conditions.</p> <p>While the buffering power of phosphate treatment can limit local pH excursions, excess phosphate can lead to tubing wastage in zones of poor circulation.</p> <p>Each of the various options for water treatment: AVT, phosphate and CPP has advantages and limitations. Steady and transient combinations of two, or more, of these options are being used in commercial plants to achieve acceptable control over the chemistry of SG system water.</p>	15,44,61 62,63

of full flow condensate polishing does not eliminate concern over aggressive ions. Furthermore, there is considerable uncertainty regarding the ability of the AVT treatment to cope with off-chemistry transients if not properly protected by water management philosophy. Rapid detection of aggressive ion presence is crucial to successful quality control of the water contacting the materials of the SG system. Continuous upgrading of in-plant water chemistry monitors will be a powerful aid to this vital area of plant operation.

AN ASSESSMENT OF CORROSION PROBLEM AREAS OF THE 2 1/4 Cr-1Mo  
STEEL FOR LMFBR SG SYSTEM SERVICE

The focus of the present review is on the margin of protection afforded by the 2 1/4 Cr-1Mo steel for water-side physico-chemical perturbations common to present commercial plants. While the proposed Clinch River Breeder Reactor demonstration plant has been used as the principal reference point for the corrosion discussions, the author chose not to limit the review to the specifics of this particular plant design and location.

From the present perspective, an assessment of the water-side corrosion credentials of the 2 1/4 Cr-1Mo steel would involve the following documented characteristics of this steel.

- In liquid and steam phases, over a T-[contaminant] field which includes transient values for many present nuclear powerplants using recirculating boilers, this steel has displayed a propensity for accelerated oxidation. Under contamination by Cl and caustic, to name two of the most prominent and probable contaminants, this accelerated oxidation could affect metal areas ranging from that corresponding to a few grains to piping sections, depending on the extent of the conditions favorable to such action.
- An important correlative factor of accelerated oxidation is surface roughness which encourages deposition of pre-boiler corrosion products. The morphology and increasing thickness of the buildup comprised of deposition and intrinsic tubing corrosion can develop a progressively more favorable local environment for the concentration of corrosion aggressive species, particularly in zones of high heat flux. Depending on the particular species involved, the corrosion consequences of this action can be manifested in a broad spectrum of pitting types, 'gouging', or stress corrosion cracking under appropriate temperature, stress and prior metallurgical state conditions.
- The T-[bulk contaminant] field cannot per se identify limits for the occurrence of the above corrosion effects inasmuch as the complex of

factors of the local environment, noted above, is involved. The National Program studies have identified SCC of the 2 1/4 Cr-1Mo steel up to roughly 300°C under Cl contamination and concentrating conditions.

While the competition between uniform and local corrosion processes may be expected to favor uniform attack with temperature increase, it would be imprudent in the author's opinion to characterize SCC of 2 1/4 Cr-1Mo steel as a phenomenon of conceivable significance only during transient operational phases (e.g., for tubing temperatures below about 250°C).

With respect to the other principal form of localized attack, a wide range of pitting types has been observed with this steel over an extensive area of the T-[contaminant] field.

Deposition of pre-boiler corrosion products, as noted above, can be an important precursor of significant corrosion activity. The design of the LMFBR SG system heat exchangers confines the secondary water to the inside of the tubing. In the case of the CRBRP EV and SH units (identical), only a single mild tubing bend is involved and the tube-tubesheet weld connection minimizes the mechanical crevice factor. Thus, the possibilities for deposit buildup in this equipment are much less than in PWR units where the secondary water is external to the tubing and there are various sites within heat flux zones presenting opportunity for deposit buildup. A concentrating situation is conceivable, however, in the interior environment of the tubing under the accidental conjunction of local conditions favoring the progressive deposition phenomenon (heat flux, surface irregularities, hydrodynamics) and the presence of dissolved/particulate products from the pre-boiler circuits. Periodic chemical cleaning of heat exchanger tubing is expected to be very helpful in maintaining the nominal interior surface condition.

The second principal factor of a significant corrosion situation is aggressive species presence. The state-of-the art ability to manage the water chemistry for the SG systems of LMFBR plants needs substantial clarification. This factor, in the author's opinion, constitutes the chief uncertainty in the current appraisal of the corrosion credentials of the 2 1/4 Cr-1Mo steel. Laboratory corrosion studies of this steel have tended to be pessimistic in

this respect, while prototype tests appear to have been optimistic. Continuous development of the in-plant detection methods for adverse chemical species, coupled with advances in purification ability for the various water circuits affecting the SG system, will undoubtedly enlarge the economic operational window for this steel and other candidate materials now under consideration.

The Cr-Mo ferritic steel family shows considerable promise in the development of economic LMFBR SG system materials providing working conditions can be maintained which minimize massive oxidation and local corrosion of these steels. The austenitic steel candidates, principally Incoloy 800 and other Fe-Cr-Ni alloys, also display a number of promising characteristics for the subject service. While uniform oxidation behavior appears to pose no problems for the austenitic materials, localized attack (pitting and stress corrosion cracking) can occur under adverse conditions. In cognizance of the international work with the austenitic and other ferritic steels proposed for LMFBR SG system service, the U.S. program is focused on establishing the position of the unstabilized 2 1/4 Cr-1Mo steel in the hierarchy of the candidate materials.

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The focus of this review is on the long-term serviceability of 2 1/2-1 Mo steel under the water-side environmental conditions presented in the steam generator of an LMFBR commercial scale plant. The basic question related to material behavior is to what extent the water side physico-chemical environment will affect the favorable performance of a given material under operating experience. In present light water reactors, the steam generator corrosion problems in part are attributable to complex interactions between the localized secondary environment and the mechanical design of the components (i.e., tube/tube support crevice, tube/tubesheet crevice, flow pattern, etc.) in the steam generating system.

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