A STATE OF THE ART REVIEW
OF DEGRADATION PROCESSES
IN LMFBR MATERIALS

Volume I. MECHANICAL PROPERTIES

August 25, 1975

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Volume II. CORROSION BEHAVIOR

August 25, 1975

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Figure 13.3.3.1-1 (Ref. 1)

A Comparison of Sodium Corrosion Characteristics of Ferritic and Austenitic Alloys at Various Oxygen Levels in Flowing Sodium

13.3.3.2 Caustic (NaOH) Corrosion

A chief distinguishing characteristic between ferritic and austenitic materials is their response to caustic solutions, with solutions associated with the sodium cation (NaOH) apparently having the greatest power to discriminate in this respect. ⁽¹⁾ In alkaline solutions, the soluble corrosion product HFeO_2^- , is thought to be largely responsible for the corrosion of ferritic materials. Other, possibly successive, corrosion products in alkaline media are: $\text{Fe}(\text{OH})_2$, Fe_3O_4 , gamma Fe_2O_3 , and gamma FeOOH . This complex of reaction products, of various structural properties, can lead to alternate periods of passivation and corrosion in caustic solutions, as exemplified by Fig: 13.3.3.2-1, depending on the physical and chemical conditions of the corrosion system. Generally, the corrosion layer of ferritic alloys will be comprised of several layers of different structure and somewhat different chemical composition. Fig: 13.3.3.2-2 shows a typical layer development on mild steel under 13% NaOH at 340°C.

The corrosion response of ferritic alloys to caustic solutions is a complex function of the OH concentration, the associated cation (e.g. Na^+ , K^+ , Li^+), the temperature, the physical conditions which affect the interchange of reactants and products with the metal surface, and species in the solution (e.g. Cl, O, Pb, Si, nitrate, chromate, etc.) which affect the protective quality of the corrosion products. The influence of caustic concentration, for relatively low caustic levels, is indicated in Fig: 13.3.3.2-3, for mild steel at 340°C. The influence of temperature for a relatively weak solution (13%) is shown in Fig: 13.3.3.2-4. Table: 13.3.3.2-1 gives some measure of the concentration and temperature effects for lower concentrations and temperatures, for pure iron. Within this low concentration and temperature regime, it is seen that the reaction gradient w.r.t temperature is substantially greater than for concentration, considering percentage changes in corrosion parameter w.r.t to percentage changes in concentration and temperature.

Figure 13.3.3.2-1 (Ref. 1)

Corrosion Rate-Time Characteristic Showing Effect of Alternate Passive and Active Modes of Mild Steel in Caustic Solution

Figure 13.3.3.2-2 (Ref. 1)

Typical Layer Development on Mild Steel in NaOH

Figure 13.3.3.2-3 (Ref. 1)

Effect of Concentration of NaOH on Corrosion Rate

Figure 13.3.3.2-4 (Ref. 1)

Effect of Temperature on Mild Steel Corrosion in NaOH

Table: 13.3.3.2-1 (Ref. 2)

Corrosion Rate of Pure Fe in NaOH Solutions

T(°C)	Corrosion Rate (anodic current, $\mu\text{A}/\text{cm}^2$)	
	0.5w/o NaOH	4w/o NaOH
30	2.1	4.1
50	7.1	15.1
90	11.0	41.0

The Pourbaix diagram has been widely used to depict the various products of reaction between metals and solutions on an electrochemical potential-pH grid. These diagrams are based on equilibrium thermodynamics predictions and, accordingly, permit only a very limited translation to practical corrosion situations. To the extent that the important reactions are considered, however, these diagrams are a valuable preliminary to kinetics analysis or, at least, qualitative speculations on corrosion. A serious limitation of many of the available Pourbaix type diagrams has been their confinement to the standard 25°C temperature. Various techniques for estimating high temperature thermodynamic data are gradually extending the Pourbaix analysis to higher temperatures. For example, recent work by Townsend⁽³⁾ and Ashworth and Boden⁽²⁾ on the Fe-H₂O system has revealed certain changes in the Pourbaix diagram for this system which have relevance for the caustic corrosion problem of Fe alloys. In particular, the work of Townsend has shown that the domain of stability (the potential-pH field) of the corrosion critical ion, HFeO_2^- , is progressively enlarged with temperature increase, up to the limits of his study (200°C). Fig: 13.3.3.2-5 shows the partial Pourbaix diagrams for the Fe-H₂O system at 25 and 200°C, respectively. Fig: 13.3.3.2-6 is a schematic showing the progressive enlargement of the HFeO_2^- domain with temperature increase. The principal corrosion implications of this temperature effect are that, with temperature increase, caustic attack will tend to occur over a wider range of pH (caustic concentration) and a wider range of natural corrosion potential. The possible influence of alloying elements, and various aggressive and inhibiting species, on the caustic corrosion situation is somewhat beyond the scope of the conventional Pourbaix analysis.

Table: 13.3.3.2-2 is a summary of industrial corrosion experience with mild steel and nickel/Inconel over a range of NaOH solutions and temperatures.

Fig: 13.3.3.2-5 (Ref. 3)

Pourbaix Diagrams for the Fe-H₂O System at 25 and 200°C

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Fig: 13.3.3.2-6 (Ref. 3)

Schematic Showing Progressive Enlargement of the HFeO_2^- Domain with Temperature Increase

Table: 13.3.3.2-2 (Ref. 4)

Comparative Unstressed NaOH Corrosion Data for Mild Steel
and Nickel/Inconel

NaOH Concentration(w/o)	T(°C)	Corrosion(mils/yr)	Ratio*
5-10	21	nickel/Inconel: 0.12 mild steel : 4.0	1 33
14(multiple effect evap.)	88	nickel/Inconel: 0.025 mild steel : 8.2	1 330
30-50(single effect evap.)	82	nickel/Inconel: 0.1 mild steel : 3.7	1 37
50(162 days)	38	nickel/Inconel: 0.008 mild steel : 0.7	1 88
50(135 days)	57	nickel/Inconel: 0.02 mild steel : 5.0	1 250
50(30 days)	66	nickel/Inconel: 0.02 mild steel : 8.0	1 400
70(90 days)	102	nickel/Inconel: 0.2 mild steel : 57.	1 285
73(126 days)	110	nickel/Inconel: 0.014 mild steel : 39.	1 2780
73(200 days)	129	nickel/Inconel: 1.0 mild steel : 80.	1 80
100	400	nickel/Inconel: 1.0 2.25Cr-1Mo : 1580.	1 (Refs. 5&6) 1580
100	1000	nickel/Inconel: 5460 2.25Cr-1Mo : 8.3×10^5	1 (Ref. 7) 152

* ratio = rate /rate nickel/Inconel

These data represent a wide variety of conditions (degree of aeration, misc. chemical species present, etc.). The relative corrosion response of these materials to these environments is, however, of interest in attempting to establish some perspective on the caustic corrosion characteristics of low alloy steels. The ratio of the mild steel to the nickel/Inconel corrosion rates is given in the last column of the table. It will be noted that in no case does the ratio decrease below about 30, and it exceeds a thousand in several instances, some of the latter data coming from Refs. 5, 6, and 7, for high temperature tests under laboratory conditions. Fig: 13.3.3.2-7 is a plot of unstressed caustic corrosion data in NaOH solutions as a function of reciprocal temperature, allowing a somewhat better fix on the corrosion of mild steel, and the 2.25Cr-1Mo steel, in relation to nickel and the Inconel type alloys. In this figure, the data for mild steel given in Table: 13.3.3.2-2 are plotted, together with a curve based on Rubright's⁽⁵⁾ data for the 2.25Cr-1Mo steel, for NaOH solutions ranging from 24-49w/o. It is seen that, considering the difference in test conditions, there is rather good agreement between the mild steel and the 2.25Cr-1Mo steel data. This fact tends to justify the claim that, with respect to unstressed caustic corrosion at least, the mild steels and the 2.25Cr-1Mo steel are virtually equivalent. Data for near 100% NaOH solutions obtained by Newman⁽⁷⁾ and Rubright⁽⁵⁾ are also given in the figure, together with data for nickel/Inconel (Harwell data cited in Ref. 6) for this concentration of NaOH. It is interesting that there appears to be a transition zone in the corrosion characteristic, for near 100% NaOH solutions, in the 600-700°C range for both the 2.25Cr-1Mo steel and the nickel/Inconel materials. Furthermore, there appears to be some convergence of the caustic corrosion effect on the ferritic and austenitic materials, irrespective of caustic concentration, toward the higher temperatures. The latter indication may be supportive of recent high temperature wastage data which suggest an increasing equivalence between the 2.25Cr-1Mo steel and Inconel (800), w.r.t wastage effect, with increasing temperature (e.g. Ref. 8).

Fig: 13.3.3.2-7

Caustic Corrosion Data for Mild Steel
2.25Cr-1Mo Steel and Nickel/Inconel

8/18/75

Characterization of caustic corrosion with respect to temperature and NaOH concentration is not well established for any material. Fig: 13.3.3.2-8 presents some indications of this dependance from various sources, and for various metals, over temperatures ranging from 100 to about 300°C. Overall, the data suggest an increase in caustic effect with NaOH concentration, with a maximum corrosion power possibly in the range 40-60w/o NaOH. Under low oxygen conditions, which did not allow passivation ability for the iron, Mayne et al⁽¹⁴⁾ observed caustic corrosion on iron with a NaOH solution of less than 0.5w/o at room temperature. A possibly minor observation, indicating, however, the sensitivity of data such as in Fig: 13.3.3.2-8 to the specific exposure conditions. On the basis of his tests with 24.2, 48.8 and 98.6w/o NaOH, Rubright⁽⁵⁾ obtained a measure of the temperature dependance of the caustic corrosion of 2.25Cr-1Mo steel for these concentrations. His data are summarized in Fig: 13.3.3.2-9. Rubright reported a simple solution attack (uniform penetration), with intergranular attack and oxide formation observed only at the higher temperatures of his work. He also studied the corrosion of this steel in the Na-NaOH system at temperatures ranging from 200-760°C. For the latter tests, he reported intergranular attack, oxide formation, and whole grain removal, at the higher temperatures. Rubright's data for the aqueous NaOH and the Na-NaOH systems, are given in Table: 13.3.3.2-3.

Available data (e.g. Fig: 13.3.2-7) do not support the assertion that the 2.25Cr-1Mo steel composition represents a significant advance in caustic corrosion resistance relative to mild steel. While the wastage phenomenon discussed in Chapter 12, is a complex of many factors beyond the purview of the corrosion data presented here, it patently does involve caustic corrosion. It would be expected, therefore, that wastage data would provide some additional reflection of the relatively poor caustic corrosion resistance of low alloy steels. Table: 13.3.3.2-4 is a sampling of the corroborative data in this respect, and is typical of the results of the extensive, continuing, wastage study which has involved ferritic and austenitic materials of interest to the LMFBR program. The convergence tendency of the wastage characteristics of ferritic and austenitic materials at high temperatures, noted above, is evident in this table.

Fig: 13.3.3.2-8

Misc. Indices of Relative Aggressive Power of NaOH Solutions
For Low Alloy Steel and Ni-Cr-Fe Alloys

Figure 13.3.3.2-9 (Ref. 5)

Corrosion of Croloy 2-1/4 in Aqueous NaOH

Table: 13.3.3.2-3 (Ref. 5)Corrosion of 2.25Cr-1Mo Steel in Aqueous NaOH and Na-NaOH
Solutions-Aqueous NaOH Solutions-

w/o NaOH	Pressure	T(^o C)	Corrosion Rate(<u>inches/yr</u>)
24.2	atm.	60	0.0001
24.2	atm	76	0.015
24.2	atm	93	0.032
24.2	atm	110	0.002
48.8	atm	93	0.035
48.8	atm	110	0.077
48.8	atm	127	0.141
48.8	atm	141	0.519
98.6	atm	371	1.00
98.6	40 psig	482	2.67

-Na-NaOH Solutions-

medium	t(^o C)	Corrosion Rate(<u>inches/yr</u>)
Na(90 ppm Na ₂ O)	204	0.002
"	482	0.0019
"	677	0.0023
"	760	0.073
Na+0.1w/o NaOH	482	0.002
Na+5.0w/o NaOH	482	0.0072
Na+10.0w/o NaOH	482	0.022
Na+0.25w/o NaOH	677	0.036
Na+5w/o NaOH	677	0.105
Na+5w/o NaOH	746	0.341
Na+5w/oNaOH+H ₂ overpressure	482	0.0052

Without strong composition fortification against caustic corrosion, the low alloy steels, and specifically the 2.25Cr-1Mo steel, appear to be vulnerable to caustic corrosion over an extensive temperature-NaOH concentration field, possibly extending to room temperature and less than 0.5w/o NaOH at the low ends of these coordinates. Caustic attack would be expected to show an increasing severity with temperature increase and, up to the neighborhood of 40-60w/o concentration, with NaOH concentration increase. In addition to these factors, the specifics of caustic corrosion will depend on the metallurgical condition of the steel (physical-chemical dissimilarities in structure caused by fabrication/installation/service conditions; plastic strain accumulation; prior corrosion damage; various chemical compound overlays, crevices, dead-end geometries, etc., which permit chemical excursions (including OH concentration) favorable to chemical and electrochemical corrosion action. A quantitative, comprehensive, analysis of these influences is far beyond the capability of current corrosion science. The totality of these factors does, however, provide an ample warning signal. The current dialogue with respect to large scale commitment of low alloy steels to caustic corrosion sensitive zones of LMFBR plants should be duly considerate of the caustic corrosion vulnerability of these materials.

Table 13.3.3.2-4

Relative Wastage Data for 2.25Cr-1Mo Steel and Inconel 800
at Various Temperatures

T(°C)	Ratio*	Ref.
316	70	15
343	100	8
500	110	16
510	4	8
1200	4	7

* Ratio= $\frac{\text{(wastage 2,25Cr-1Mo steel)}}{\text{(wastage Inconel 800)}}$, under identical conditions

Refs. for Section 13.3.3.2

1. D. V. Subrahmanyam, R. W. Staehle, "Stress Corrosion Cracking and General Corrosion of Iron, Nickel, Chromium, and Their Alloys in Caustic Solutions"; Report No. Coo-2018-4(Q-1), Ohio State Univ. 1969.
2. V. Ashworth, P. J. Boden, "Potential-pH Diagrams at Elevated Temperatures;" Corrs. Sci, 10, 1970, p. 709.
3. H. E. Townsend, Jr., "Potential-pH Diagrams at Elevated Temperatures For the System Fe-H₂O;" Corr. Sci, 10, 1970, p. 343.
4. P. J. Gegner, Proc. Short Course on Process Industry Corrosion, NACE, Ohio State Univ.
5. M. M. Rubright, "The Corrosion of Croloy 2.25Cr-1Mo Steel in the Products of a Sodium-Water Reaction; Systems of Sodium Hydroxide in Water and Molten Sodium;" BAW-1280-30, Nov. 15, 1965.
6. Corrosion Resistance of Nickel and Nickel Containing Alloys in Caustic Soda and Other Alkalies; Tech Bulletin CEB-2, International Nickel Co., Inc.
7. R. N. Newman, C. A. Smith, "Sodium/Water Combustion and the Chemistry of Wastage at Sodium, Water Leak Sites;" J. Nucl Matls, 52, 1974, p. 173.
8. D. A. Greene, "Preliminary Results From Small Leak Tube Wastage Scoping Tests;" CONF-740401, 1974, p. 1.
9. M. J. Humphries, R. N. Parkins, "Stress Corrosion Cracking of Mild Steels in NaOH Solutions Containing Various Additional Substances;" Chem Sci, Nov. 7, 1967, p. 747.
10. R. K. Swandby, "Corrosion Charts-Guide to Material Selection;" Chem Engr, Nov. 12, 1962, p. 186.
11. P. P. Snowden, "Stress Corrosion of Austenitic Stainless Steel by High Temperature Solutions and Contaminated Steam;" J. Iron Steel Inst, Feb. 1960, p. 181.
12. O. Asai, CA, 63, p. 12761f(1965).
13. R. S. Thornhill, CA, 57, p. 569f (1969).
14. J. E. O. Mayne, J. W. Menter. M. J. Pryor, "The Mechanism of Inhibition of the Corrosion of Iron by Sodium Hydroxide Solutions;" J. Chem Soc (London), 1950, p. 3229.
15. H. V. Chamberlain, J. H. Coleman, E. Kovacic, A. A. Shoudy, "Wastage pf Steam Generator Materials by Sodium-Water Reaction;" ANL 7520-Pt1. p. 384.
16. R. A. Davies, J. A. Bray, J. M. Lyons, "Corrosion of Steels in the Vicinity of a Sodium-Water Reaction;" Proc. Conf. on Alkali Metal Coolants, Vienna, 1967, p. 263.

13.3.4 Effects of Metal Cleaning Procedures

The cleaning of structural components which have been exposed to sodium, preparatory either to reuse, storage, or disposal, poses a number of problems due to the chemical reactivity of sodium and its propensity for permeating a metallic structure and subsequently 'bleeding' under appropriate environmental conditions. Apart from personal hazard potential, residual sodium--either surface or absorbed--may participate in the gamut of reactions discussed previously and generate corrosion products which are inimical to reuse of such components, and to those components which come within the radius of action of such products in the service, or storage, environments.

A number of schemes are under test for cleaning sodium affected materials and for tailoring cleaning procedures to specific components representing particular problems of sodium retention (e.g., steam generator). A recent review of current work by Atomics International on this aspect of sodium is given in Reference 1. Reference 2 discusses the general scope of sodium cleaning work within the purview of the ERDA and is an excellent concise review of sodium cleaning problems.

Cleaning agents may react chemically with sodium, or they may dissolve sodium. Examples of the former are water, alcohol, alkyl halides. Examples of the latter are mercury, molten lead, liquid ammonia. The current tendency is to emphasize the chemically reacting agents, such as water and alcohol. Water is usually applied as steam in the early stages with an inert diluent, usually nitrogen, for closer control of possible sodium and hydrogen reactions. Final cleanup usually involves liquid water for more complete removal of sodium and sodium products, and for ease in monitoring the cleanup efficacy. Of the alcohols, the low molecular weight varieties are more reactive with sodium. Tertiary butyl alcohol reacts slowly with sodium. It is, however, miscible with water. Various combinations of alcohol and water may be used depending on the severity, or stage, of the cleaning problem.

The final problem in cleaning is removal of the last cleaning agent(s) in the cleaning cycle. Following a final water treatment, a more volatile,

Reference for 13.4.3.1

1. H. Schnauder, R. A. Muller, "Modification of the Design of Intermediate Heat Exchangers for Sodium Cooled Reactors Using Ferritic Materials," EURFNR-924, 1971.

13.4.3.2 Caustic Stress Corrosion Cracking

The phenomenon of cracking of ferritic alloys in caustic environments has been a prime subject of corrosion literature for more than 50 years. Riveted boiler plates apparently provided favorable sites for caustic concentration which, under stress and appropriate temperature conditions, caused severe cracking problems. Considerable additional information on the behavior of ferritic alloys in caustic media has been provided by industrial manufacturers, and users, of caustic solutions. Berk and Waldeck⁽¹⁾ presented some definition of the 'danger zone' for caustic cracking based on U-bend tests with SAE 1020 steel. This is given in Figure 13.4.3.2-1, which suggests a maximum effect for solutions in the range of roughly 20-35% NaOH and a corresponding temperature limit for these concentrations of about 180°F. Schmidt et al.⁽²⁾ presented a somewhat more restrictive definition of the danger zone on the basis of an extensive NACE survey of caustic cracking. Their summary is presented in Figure 13.4.3.2-2, which gives a critical temperature-concentration characteristic somewhat more rigorous than Figure 13.4.3.2-1 with respect to temperature. Their data suggest a maximum effect at NaOH concentrations somewhat higher than the 20-35% range noted above and their 'critical' temperature comes close to 100°F. Table 13.4.3.2-1 gives some caustic cracking data with specimen specifics. The first entry in this table, namely, cracking at 35°C (95°F) for solutions in the range 4-60% would imply even more restrictive conditions than Figure 13.4.3.2-2. Electrochemical studies reported by Reinoehl and Berry⁽³⁾ indicate that, under conditions favoring electrochemical action, caustic solutions down to roughly 4% are aggressive to ferritic alloys at a temperature of 93°C (200°F), in agreement with the critical cracking characteristic established in Figure 13.4.3.2-2.

The effect of stress on caustic SCC is complex and depends on specific exposure conditions, time of exposure, and the chemical and metallurgical history of the metal. Figure 13.4.3.2-3 is a typical stress-failure time (θ_f) characteristic for a given temperature and caustic concentration. Plastic strain, rather than stress per se, is now considered

Figure 13.4.3.2-1 (Ref. 1)

Caustic SCC Danger Zone

Figure 13.4.3.2-2 (Ref. 2)

Relation of Temperature and Concentration
of NaOH to Cause Cracking

Table 13.4.3.2-1 (Ref. 3)

NaOH Concentrations at Which Caustic Cracking
Has Been Observed for Mild Steels

Caustic Cracking Concentration Range, % NaOH	Threshold Temperature,		Exposure Conditions	Reference
	F	C		
4-60	(95)	35	0.12% C-0.47% Mn steel (1/8" boiler plate)	10
5-73	130	(55)	NACE survey (service)	3
10-50	(160)	70	Boiler service	7
10-75	-	-	0.8% C steel, slow strain rate tensile tests	11
15-33	-	-	0.03, 0.09% C steels 3 mm thick U-bends	9
15-40	(175)	80	Various	8
18-40	180	(85)	1020 steel 1/4" thick U-bends	6
20-55	(180)	85	Bayer plants service	4
35-70	(160)	70	De-enamelling tanks service	2

Points	C	N	Al	Si	Mn	P	S	Cu	O
○—○ B	0.04	0.014	0.001	< 0.001	< 0.001	0.003	0.002	--	0.002
△—△ C	0.02	0.006	< 0.003	0.003	0.018	0.011	0.009	< 0.003	--
●—● D	0.11	0.009	0.004	0.01	0.31	0.022	0.039	0.03	--

Figure 13.4.3.2-3 (Ref. 4)

Effect of Stress on Failure Times of Mild Steels in NaOH Solution
 ($\sim 250^\circ\text{C}$)

to be critical to SCC and the concept of a 'critical' stress appears to be of limited value. In other words, once sufficient plastic strain has developed as a result of various service conditions (temperature, stress cycling, steady stress, etc.), SCC will occur in the presence of caustic and sufficient stress to propagate the crack.

Relatively modest changes in temperature can drastically change the SCC tendency under given caustic and stress conditions. This is indicated by Figure 13.4.3.2-4 where the θ_f is given as a function of applied potential. It is seen that a temperature change of 50°C effects roughly an order of magnitude change in the failure time (θ_f). Strain rate is an important variable in SCC, with a slow strain rate generally being more harmful in the respect of SCC. This is indicated in Figure 13.4.3.2-5, where the cracking parameter (in this case reduction in area at fracture) is plotted against applied potential for various strain rates. Applied potentials which produce serious cracking at a strain rate of $1.6 \times 10^{-6} \text{ sec}^{-1}$, have no effect at the highest strain rate ($4.2 \times 10^{-5} \text{ sec}^{-1}$).

The ability of a metal to develop passive layers is crucial to its resistance to SCC. Figure 13.4.3.2-6 shows the effect of cold work on the ability to achieve passivation. Here the corrosion potential is plotted against time for mild steel in the 50%, 80% and zero cold worked conditions. The less negative potential is in the direction of passivity and it is seen that while the zero cold worked material exhibits a tendency to passivation after roughly 30 min, the cold worked materials persist in an active (corrosion mode) potential throughout the exposure to the caustic solution.

The damaging effect of caustic SCC is indicated by Figure 13.4.3.2-7 where maximum load sustained by the specimen, and the resulting reduction in area at fracture, are plotted against the applied potential for given caustic concentration, strain rate, and temperature conditions. While applied potential tests provide a possibly unnatural acceleration of the SCC process, the damage effects of these 'synthetic' tests is more than matched by observations of 'natural' SCC damage reported in surveys such as Reference (2). Summary remarks given by Schmidt et al. after their

13.4.3.2-6

Figure 13.4.3.2-4 (Ref. 4)

Effect of Temperature on the Failure Time of Mild Steel in NaOH Solution

Figure 13.4.3.2-5 (Ref. 4)

Effect of Strain Rate on SCC

Figure 13.4.3.2-6 (Ref. 4)

Effect of Cold Deformation of Steels on Open Circuit Potential-Time Curves in NaOH Solution

Figure 13.4.3.2-7 (Ref. 4)

Embrittlement Effects of SCC at Various Applied Potentials

extensive survey of industrial participants are somewhat pertinent to this discussion. The following recommendations for minimizing caustic SCC were made:

- A. Decrease stress (residual and applied)
 - 1. Change design
 - 2. Stress relieve
- B. Decrease Temperature
 - 1. Change design
 - 2. Change operating conditions
- C. Change materials of construction
 - 1. Different metal
 - a. nickel
 - b. Monel metal
 - c. nickel clad steel
 - 2. Coatings
 - a. spraying with nickel
 - b. spraying with steel
 - c. organic coatings (rubber has been used with considerable success in minimizing caustic attack)

While some of the above recourses are irrelevant to LMFBR plants, some are not, namely: the general suggestions embodied in items A, B and C, which might be paraphrased as follows: minimize the opportunity for stress concentration, caustic concentration and temperature excursion; in considering a material for critical LMFBR service within caustic corrosion sensitive zones, the ability to resist caustic attack should obviously be given prime weight in the materials competition.

Fig: 13.4.3.2-8 is a consolidation of industrial experience, some cited previously, which attempts to define safe working limits for mild, low alloy steels with respect to caustic SCC. These data embody a wide, and in many instances, unknown range of variables (stress history, misc. chemical species involved, quality of technical management of equipment, service time, temperature history, etc.). Such experience, however, constitutes the principal reservoir of caustic SCC information at this time. Curve (E), based on Shell Development Co. information for non-stress relieved steel, cited in Ref. 6, is nearly coincident with the recommendation of the Schmidt survey (Ref. 2). The latter limit 'lines' impose severe temperature-concentration restrictions on those steels which fall within the mild, and low alloy, category with respect to caustic corrosion

Fig: 13.4.3.2-8

Delineations of Possible Caustic (NaOH) SCC
Regime for Low Alloy Steels

resistance, or more specifically, caustic SCC resistance. Section 13.3.3.2 discussed the unstressed corrosion behavior of the 2.25Cr-1Mo steel in NaOH solutions. Evidence was presented indicating that the composition of this steel does not represent a significant improvement in protection against caustic corrosion, relative to mild, or low alloy, steels. Despite the prominence of this particular steel for some years as a candidate for critical LMFBR applications within the action scope of sodium, caustic SCC data for this steel (as opposed to wastage and Na corrosion data) are remarkably sparse. The most recent summaries of the caustic SCC behavior of this steel are uniformly encouraging (e.g. Refs. 8,9). It is submitted, however, that the caustic SCC tests to-date with this steel represent only a very limited penetration into practical operating regimes which might be experienced in LMFBR service. During the operating history, NaOH concentration, stress and temperature history, and structural sensitization factors will probably be involved which are somewhat beyond the purview of the published caustic SCC information for this steel. Specifically, the NaOH concentration limits of current SCC studies should be expanded substantially. The tests should also allow some opportunity to study the SCC influence of mechanical (e.g. hardness, strength) and physical-chemical (e.g. precipitates, phase island, alloy segregation) dissimilarities to which this steel might be susceptible during the fabrication/installation/service phases. Caustic SCC has been notoriously difficult to reproduce under laboratory conditions for many materials which have a proven, or suspected, susceptibility to this attack. In order to effect a practicable incidence of caustic SCC for laboratory observation, recourse has been had to crevices, and/or various types of defects (machined and fatigued). The well known technique of determining a stress intensity threshold (K_{ISCC}) for SCC (involving a prior machined + fatigued defect under static loads of various intensity) has apparently had little application in caustic SCC analysis for LMFBR materials.

The conventional wastage test is essentially a study of a post facto corrosion phenomenon, i.e., it is a study of the sodium/water/steam reaction

consequences of a penetration of a high pressure water/steam conduit within a dynamic sodium reservoir. The corrosion action which is the prelude to wastage has received relatively little attention. For example, a tubing defect allowing sodium-water/steam contact could conceivably present an array of NaOH solutions to the stressed tubing ranging from zero to virtually 100% concentration. The response of an LMFBFR tubing candidate to this situation is of obvious importance in an assessment of useful potential. In recent French work so oriented (Ref. 10), water and steam pressurized 2.25Cr-1Mo tubes, containing various size prior defects, were tested in a sodium loop at temperatures ranging from 350-450°C. Profiles of the corrosion effect for two water tests and a steam test, involving different size defects, are given in Fig: 13.4.3.2-9. The test times before the damage necessitated shutting down are given in the figure. Whether, or not, the damage shown here is attributable to SCC, to some 'stress assisted' corrosion mechanism, or to a purely chemical process, would seem to be immaterial as far as the functional utility of the tubing is concerned. These tests are additional corroboration of the caustic corrosion sensitivity of the 2.25Cr-1Mo steel, a characteristic which, as noted previously, has had considerable reflection in unstressed NaOH corrosion and wastage studies with this steel.

LMFBFR materials decisions for many applications involve difficult projections of past service experience, and laboratory studies, into working arenas which, in many respects, defy small-scale simulation. Unfortunately, the caustic SCC problem has not been emphasized sufficiently in LMFBFR related work to provide a good basis in this respect for design decisions. At least one comprehensive program so oriented (Ref. 4) was discontinued. A primary objective of this program was the relation of general caustic corrosion susceptibility to SCC tendency, under the spectrum of possible working and material conditions. This is precisely the information which is needed now to bolster materials decisions for LMFBFR plants.

Vue de l'éprouvette avec son entaille mécanique
et schéma de la fissure de fatigue.

specimen & prior defect details

Fig: 13.4.3.2-9 (Ref. 10)
Corrosion Effects from Penetration of Sodium/Water/Steam Barrier
2.25Cr-1Mo Steel

References for 13.4.3.2

1. A. A. Berk. W. F. Waldeck, "Caustic Danger Zone," Chem. Engr., June 1950, p. 235.
2. W. W. Schmidt, P. J. Gegner, G. Heinemann, C. F. Pogacar, E. H. Wyche, "Stress Corrosion Cracking in Alkaline Solutions," Corrosion, Sept. 1951, p. 295.
3. J. E. Reinhoehl, W. E. Berry, "Natural Conditions for Caustic Cracking of a Mild Steel," Corrosion, 28, No. 4, April 1972, p. 151.
4. D. V. Subrahmanyam, R. W. Staehle, "Stress Corrosion Cracking and General Corrosion of Iron, Nickel, Chromium and Their Alloys in Caustic Solutions," Ohio State Univ. Report No. C00-2018-4(Q-1), 1969.
5. M. J. Humphries, R. N. Parkins, "Stress Corrosion Cracking of Mild Steels in NaOH Solutions Containing Various Additional Substances;" Corr. Sci, 7, 1967, p. 747.
6. R. J. Schmitt, "The Use of Iron, Carbon Steel and Alloy Steel in the Chemical Industry;" Proc. Short Course on Process Industry Corrosion, Ohio State Univ., NACE, p. 31.
7. R. K. Swandy, "Corrosion Charts-Guide to Material Selection;" Chem Engr. Nov. 12, 1962, p. 186.
8. J. S. Armijo, J. L. Krankota, C. N. Spalaris, K. M. Horst, F. E. Tippets, "Materials Selection and Expected Performance in Near Term LMFBR Steam Generators;" Proc. Intl. Conf. on Fast Reactor Power Stations, London, March 1974, p. 189.
9. Steam Generator Materials Engineering First Quarterly Rept., July-Sept. 74, GEAP-14029-1, Oct. 1974, p.2.
10. J. R. Donati, M. Grand, P. Spiteri, "Etude Des Phenomenes de Corrosion Consecutifs a Une Micro-Reaction Sodium-Eau dans une Fissure Transversante d'un Tube de Generateur de Vapeur de Reacteur Rapide;" J. of Nucl. Matls, 54, 1974, p. 217.

conditions which can create plastic strain concentrations become increasingly significant as a damage agency with increasing temperature and time of exposure to the corroding media. As in the unstressed corrosion case, the austenitic stainless steels and high nickel alloys are substantially superior to the low alloy ferritic materials in their tolerance of these factors for caustic solutions. Inattention to sodium excursion events in the external system could, however, cause serious corrosion and stress corrosion effects on highly stressed austenitic materials. The ferritic materials, and in particular the 2-1/4 Cr - 1Mo steel, now being considered for wide application in the LMFBF plants, exhibit very little tolerance for caustic media throughout the temperature range of the external environment. Increases in stress, caustic concentration, and temperature, aggravate the caustic attack on ferritic materials. Tolerable exposure times to a dangerous combination of these factors would be expected to be very short. Any internally pressurized ferritic alloy component, irrespective of wall thickness, subject to a sodium spill/leak under conditions which could generate some caustic (and this would appear to apply to virtually all spills/leaks) should be given whatever in situ inspection is possible to determine the extent of structural damage.

Probable location and cause of sodium leaks and spills are not likely to be predictable until details of plant design and operation are known. The history of sodium facility operation shows that leaks have been discovered by operators inspecting the system visually rather than by the leak detection system.

At CRFBF operating temperatures and in areas covered by nitrogen plus 1% oxygen atmosphere sodium leaks may be expected to produce corrosion rates of tens to hundreds of mils/year. During shutdown, when the system is maintained at lower temperatures and where stresses equal or exceed yield stress for the material, failure through stress corrosion cracking can occur much more quickly.

Except under hopefully extreme and rare circumstances permitting prolonged contact of liquid sodium with structural material under a nitrogen atmosphere at temperatures in excess of roughly 450°C, nitriding is

not expected to be a significant problem in the LMFBR external environment. Within the scope of alloy compositions of present interest, high chromium contents appear to present the greatest potential for nitriding under the above circumstances.

References for 13.7.3

1. N. D. Tomashov, Theory of Corrosion and Protection of Metals; The MacMillan Co., N.Y. 1966.
2. H. A. Klein, "Corrosion of Fossil Fueled Steam Generators," Combustion, January 1973, p. 5.