TABLE 20—Effects of Concentration, Stress, and Temperature with KOH and NaOH Solutions (Snowden[51])

Effect of Concentration at 300 C and 10 tons/in.²			Effect of Stress at 300 C			Effect of Temp with 10 tons/in.² Stress		
Wt %	Life with KOH, h	Life with KOH, h	Applied Stress tons/in.²	Life with 30% KOH, h	Life with 20% NaOH, h	Temp. C	Life with 30% KOH, h	Life with 20% NaOH, h
50	7.8	2.1	20	2.0	- - -	300	2.8, 19.8	1.1, 1.8
20	3.8, 19.6	1.1, 1.8	10	3.5, 19.8	1.1, 1.8	250	12.2, 55.7	3.6, 3.6
5	51.2, 17.6	6.4, 15.1	75	- - -	137	200	40.8, 52.6	177.8
1	17.9, 150, UB[1]		5	16.9, 32.3	212, 118	175	43.7, 195	
0.1	551 UB[1]		2	28.5, 88.5	400 UB[1]	150	500 UB[1]	

[1] UB = Unbroken.

However, these equilibria are not equally reducible by the hydrogen ion equilibrium as shown in Figure 14; and only the iron appears to be significantly oxidized with nickel being sparingly so. This trend suggests that increasing nickel would inhibit caustic cracking, which it does. Chromium forms a soluble species (CrO_2^-) but more sparingly than either nickel or iron at the same pH.

1. Environmental Factors. Siderov and Ryabchenkov investigated the effect of NaOH concentration on the cracking of Type 310 at 350 C and obtained the results of Figure 76 showing that the concentration of NaOH below which cracking would not occur is about 0.1 to 1%.[153] Cracks were intergranular and transgranular with the latter predominating. Picket et al investigated the cracking of Type 304 and found similar trends.[47] Snowden[156] used Type 347 to investigate the effects of concentration, stress, temperature and the composition of NaOH with KOH. His results are summarized in Table 20. In general, NaOH appears to be about twice as aggressive as KOH. This same trend was noted by Connou and Grall.[157] The concentration dependance of Snowden's work appears to agree with that of Siderov and Ryabchenkov. The cracking of all specimens showed no prior susceptibility to sensitization. Snowden also investigated the effect of dewpoint and superheat environments on the cracking of contaminated Type 347 in a temperature range of 275-350 C. The contamination was applied by immersing specimens in a 30% solution. The most significant finding of these experiments was the shifting in mode of cracking. Contrary to the results of solution tests described in Table 20, the cracking for the NaOH contaminated solutions was predominantly transgranular. Specimens contaminated with KOH cracked intergranularly below 380 C (the melting point of KOH) and transgranularly above. Figure 77 shows typical intergranular and transgranular cracks from the work of Snowden.

Wheeler and Howells[158] investigated the effect of NaOH concentration on the cracking of Type 347 in liquid sodium and water environments at 360-450 C. Oxygen was purposely excluded. Their results are shown in Table 21. Cracking in very high caustic concentrations at 399 C and 362 C appears to be stifled; whereas cracking was observed

TABLE 21—Incidence of Cracking in Type 347 Stainless Steel U-Bends Exposed to Hydroxide Solutions (Wheeler and Howells[158])

Temp. C	Mixtures	Days	Cracking
454	16% NaOH in Na	30	yes
454	30% NaOH in Na	20	yes
454	60% NaOH in Na	30	yes
454	100% NaOH	14	yes
454	95% NaOH in H_2O	30	no
399	100% NaOH	30	no
399	95% NaOH in H_2O	30	no
362	100% NaOH	30	no
362	80% NaOH in H_2O	1	yes

when the concentration reaches 100%. All cracking in this study was transgranular.

The effect of LiOH on the cracking of Type 347 was studied by Pement using cold formed bellows specimens.[159] Concentrations were varied from 10^{-4} to 5 molar and specimens were tested at 160, 289, and 315 C. Oxygen was purposely excluded from the experiments. Cracking occurred at all three temperatures; an 0.1 molar concentration appeared to be the approximate division for susceptibility with only one crack observed at this concentration. Intergranular cracking was observed in all cases. Pement states that the cracking in LiOH solutions was less aggressive than in NaOH solutions; and he suggests that this may result from the lower ionization and lower solubility of the LiOH.

The effect of additions to caustic solutions has been investigated. Siderov and Ryabchenkov studied the effect of NaCl additions to a 3% NaOH solution at 330 C and found that the cracking was progressively inhibited as the concentration increased according to the trend in Figure 78.[153] Gulyaev et al[154] investigated the effect of air, nitrogen, and argon additions on cracking in NaOH solutions and found that these additions inhibited cracking. However, the mechanism for their effect is not clear.

Wheeler and Howells investigated the effect of phosphate addition to NaOH + KOH solutions and found that an Na_3PO_4/(NaOH + KOH) ratio of 1:4 was sufficient to prevent cracking.[155] Their well known data are shown in Figure 79.