

Corrosion of unalloyed steels in different alkaline solutions at high temperatures and under high pressures

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Abstract

The non-volatile chemicals NaOH, KOH, LiOH and $\text{Na}_3\text{PO}_4 \rightleftharpoons \text{Na}_2\text{HPO}_4$ are used as acid-chloride corrosion inhibitors in evaporators, at high temperatures and under high pressures. The alkaline corrosivities of these chemicals were determined by autoclave studies. There is a critical hydroxide concentration for NaOH, KOH and LiOH above which the corrosion rates increase dramatically. LiOH appears to have the lowest critical concentration (0.5 mol). The corrosion rate in high concentrations of LiOH is five times faster than in NaOH.

Many heats were performed on a number of steel classes in highly concentrated hydroxide solutions. There appears to be a wide variation in the corrosion rates.

Introduction

In evaporators non-volatile alkalisers are dosed for inhibition of acid-chloride corrosion. Cooling water containing chloride, contaminating the boiler feed water via a condenser leakage, can prove to be corrosive, particularly in the evaporator on places with high heat fluxes and on fouled boiler-tube surfaces.

The disadvantage of non-volatile alkalisers such as NaOH, LiOH, KOH and phosphates, is the concentrating and depositing in places with high heat fluxes when, for instance, overdosing take place. It is difficult to determine the exact dosage of the alkaline corrosion inhibitor.

Non-volatile alkalisers will strongly concentrate in evaporators under dryout or steam-blanketing conditions. The maximum concentrations are limited by the boiling-point elevations or the solubility of the alkalisers. NaOH obeys the first-mentioned laws; phosphate obeys the solubility limitations.

Much laboratory research has previously been undertaken in order to understand the mechanism of alkaline corrosion at high temperatures and under high pressures (Harrison, 1965; Castle and Masterson, 1966; Huijbregts and Snel, 1972; Bignold, 1973; Berge et al., 1976). The corrosion mechanisms are known very well nowadays. Some possible weaknesses in the theory are posed by these questions:

1. Does a critical alkaline concentration exist above which linear corrosion takes place?
2. Will the critical concentration depend extensively on the chemical composition of the unalloyed steels? In acid-chloride solutions the corrosion depends considerably on the composition of the steel (Huijbregts, 1981).

These two aspects were considered in the laboratory research; the experiments can be divided into two parts:

1. Corrosion phenomena in alkaline solutions of increasing concentration.
2. Testing of steels in a highly concentrated alkaline solution.

3 Experiments

All of the exposure tests were performed in small stainless-steel autoclaves, with volumes of 25 cm³. In these autoclaves ptfе beakers were used to prevent galvanic contact between the steel specimens and the autoclave wall and also to prevent corrosion of the autoclave. The ptfе beakers were filled with 15 ml of test solution and small steel specimens (surface ca 4 cm²).

Experiment number	Environment		Temperature (°C)	Steels
1	NaOH	nondeaerated	250	St 35.8, 15Mo3, 14Mn4
	NaOH	nondeaerated	250	13CrMo44, 10CrMo910
2a	LiOH	nondeaerated	250	St 35.8
	NaOH	nondeaerated	250	St 35.8
	KOH	nondeaerated	250	St 35.8
2b	NaOH	nondeaerated	310	St 35.8
	LiOH	nondeaerated	310	St 35.8
2c	NaOH	nondeaerated	250	15Mo3
3	NaOH	nondeaerated	310	15Mo3
	NaOH	nondeaerated	250	10CrMo910
	NaOH	nondeaerated	250	10CrMo910
4	Na ₃ PO ₄	nondeaerated	250	St 35.8
	Na ₂ HPO ₄	nondeaerated	250	St 35.8

Table 1: Experiments to determine critical concentrations of alkalisers.

Some test solutions were deaerated by means of nitrogen. In these cases the autoclaves were filled and closed in a glove box under nitrogen atmosphere. The glove box was purged for two days to remove the oxygen. The oxygen content of the atmosphere was measured, and found to be 40 ppb. The test solutions were made oxygen-free by purging nitrogen through the solutions. The test specimens were machined from tube materials, degreased, pickled and weighed before each test. The surface area was measured in order to calculate the weight loss after pickling, and thus, the corrosion rate.

3.1 Critical concentration of alkalisers

In table 1 the experiments under this aspect are summarized. Various parameters were studied.

1. In experiment number 1 special attention was given to the influence of the chemical composition of steels (table 1) with respect to alkaline corrosion.
2. In experiment number 2 the influence of the type of alkaliser was studied at two temperatures and on two different steels.
3. In experiment number 3, the autoclaves were filled with deaerated liquids in the glove box, under nitrogen cover gas. For these tests a 2.25 % Cr steel was chosen.
4. The last experiment, number 4, dealt with the corrosion of carbon steel in phosphate solutions.

3.2 Experiment 1

A number of steels were exposed at 250°C to solutions of different NaOH concentrations (see tables 1 and 2). Two carbon steels (specimen numbers 1 and 2), two 15Mo3 (numbers 3 and 4), two 14Mn4 (numbers 5 and 6), two 13CrMo4.4 (numbers 7 and 8) and three 10CrMo9.10 (numbers 9, 10 and 11) steels were chosen for these experiments.

Specimen number	C	Mn	Si	P	S	Cr	Mo	Al	Cu	Ni
1	0.08	0.50	0.18	0.012	0.012	0.06	0.01	0.02	0.04	0.04
2	0.10	0.65	0.18	0.021	0.024	0.08	0.02	0.01	0.14	0.08
3	0.16	0.70	0.19	0.006	0.019	0.02	0.38	0.01	0.04	0.02
4	0.16	0.71	0.24	0.013	0.029	0.23	0.50	<0.01	0.22	0.15
5	0.16	1.03	0.33	0.022	0.029	0.08	0.02	0.01	0.11	0.17
6	0.16	1.17	0.30	0.022	0.033	0.03	0.01	<0.01	0.12	0.07
7	0.11	0.54	0.23	0.018	0.024	0.99	0.44	~;0.01	0.12	0.22
8	0.11	0.50	0.81	0.012	0.012	1.83	0.26	0.02	0.08	0.05
9	0.10	0.48	0.30	0.014	0.023	2.44	1.04	<0.01	0.10	0.24
10	0.18	0.47	0.25	0.006	0.021	1.68	0.73	<0.01	0.03	0.08
11	0.10	0.48	0.30	0.016	0.010	2.33	1.01	0.02	0.03	0.01

Table 2: Chemical composition (in %) of steels tested in autoclaves.

The weight losses are given in **Figure 1**.

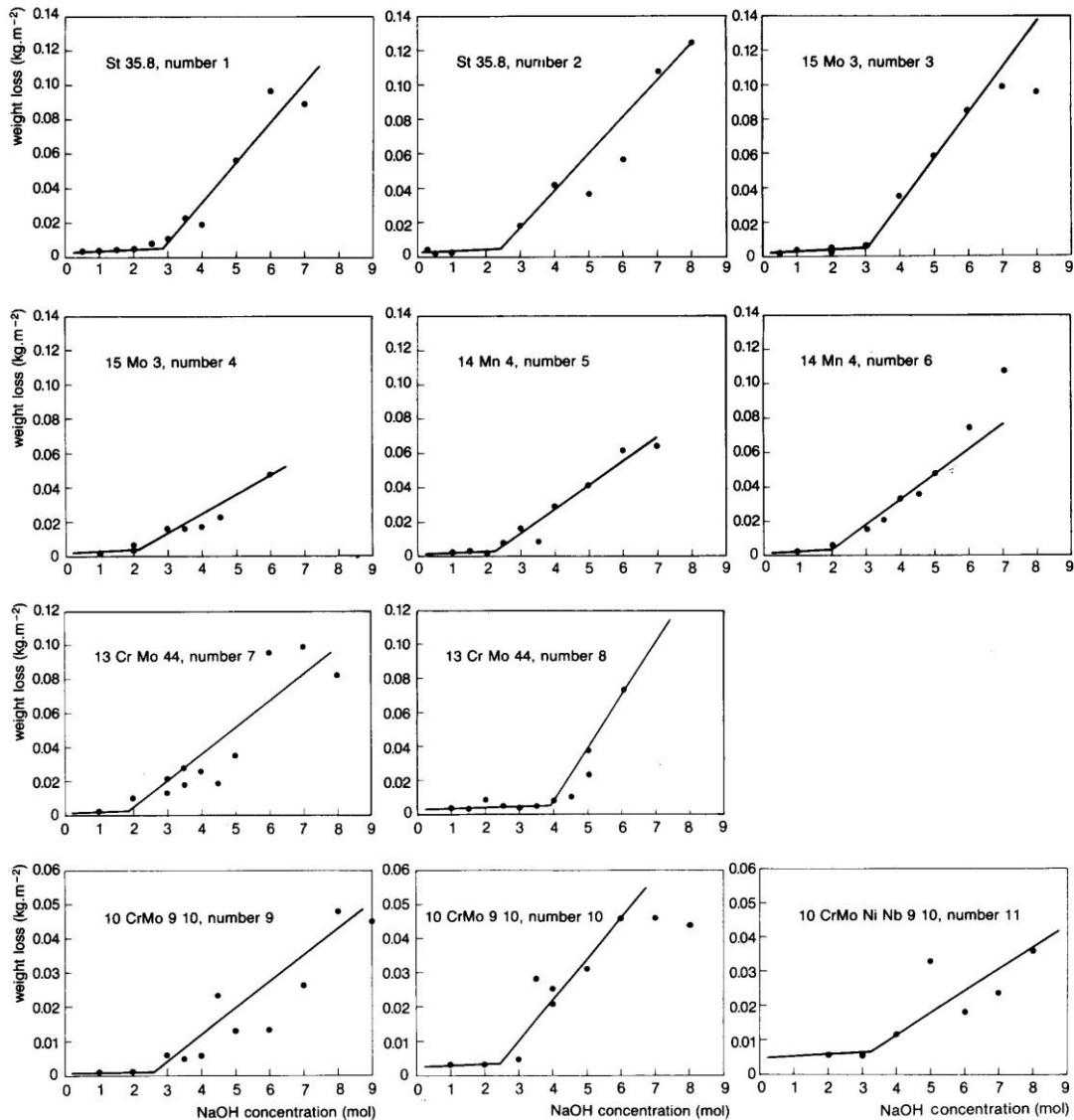


Figure 1: Weight losses after a 4-day exposure to NaOH under non-deaerated conditions at 250 °C (experiment 1)

As can be concluded from these results for all the steels, a sharp increase in the corrosion rate was found at an NaOH concentration between 2 and 3 molar. Only one steel, 13CrMo44, has a rather high critical concentration of 4 molar (perhaps because of the high percentage of Si).

3.3 Experiment 2

A simple carbon steel was exposed to NaOH, KOH and LiOH environments at 250 °C. From **Figure 2** it appears that the critical concentration in LiOH was rather low, only 0.5 molar. The critical values for KOH and NaOH were higher (1.5 and 2.8 molar respectively).

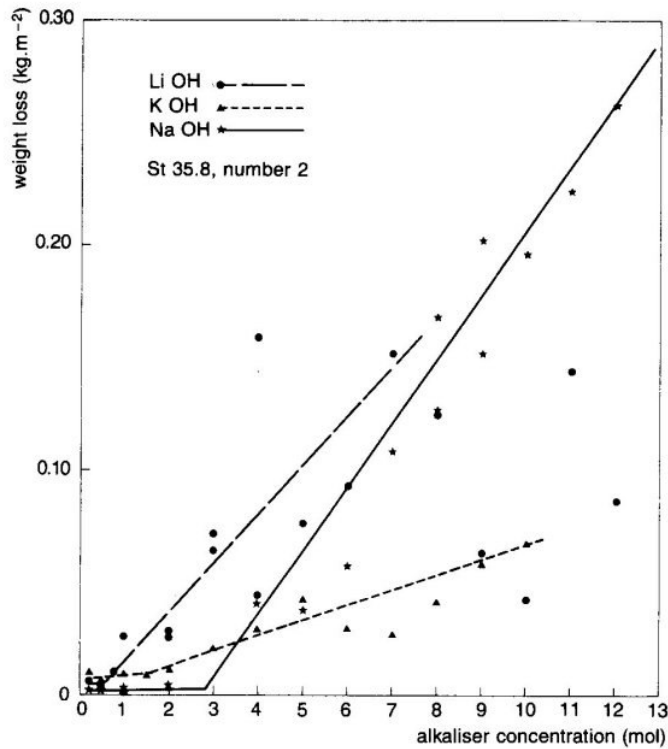


Figure 2: Weight losses after a 4-day exposure under non-deaerated conditions at 250 °C (LiOH, KOH and NaOH)(experiment2a)

Beyond the critical value the variation in weight losses for the concentrated solutions is rather high, in particular for LiOH. However, it can be said that the corrosion in KOH is certainly lower than in the other alkalisers (NaOH and LiOH).

To study the influence of temperature, two more tests were performed on carbon steel and steel 15Mo3 (experiments 2b and 2c). At 310 °C a low critical concentration for LiOH was found (0.5 molar), whereas NaOH showed a critical value of 2 molar (**Fig. 3**). There is no clear difference in corrosion rates for the two temperatures 250 °C and 310 °C (exposure time 4 days) in dependence of the alkaline concentration beyond the critical value (compare **Figures 2 and 3**). In experiment 2c only NaOH was used as a test solution for the 15Mo3 steel (**Fig. 4**). The critical NaOH value amounts to 3 molar for both temperatures. The corrosion rate above this critical NaOH value does not differ for both temperatures either.

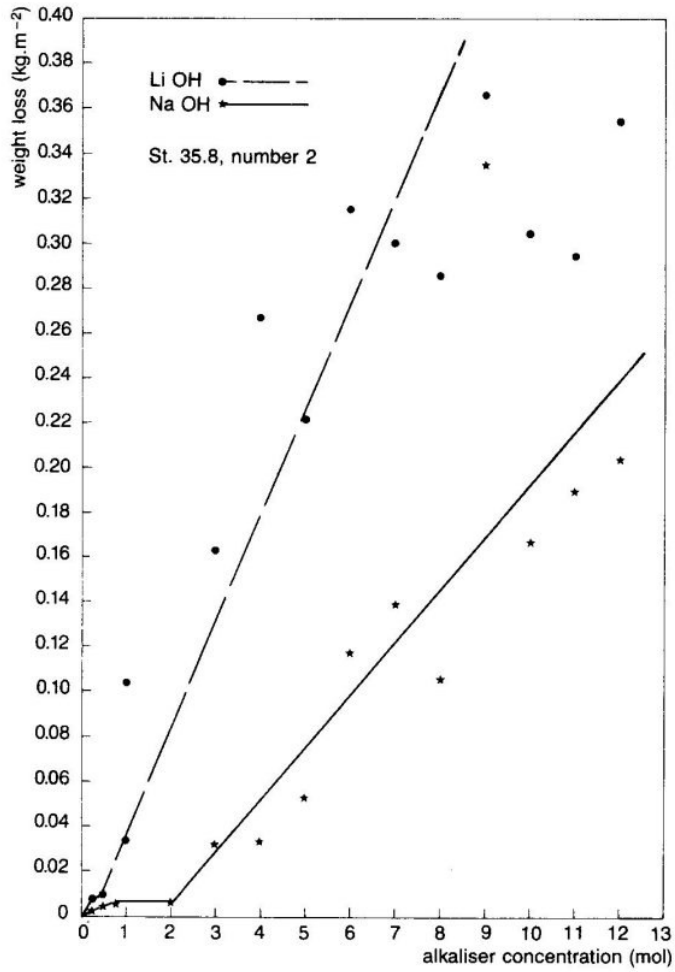


Figure 3: Weight losses after a 4-day exposure under non-deaerated conditions at 310 °C (LiOH and NaOH)(experiment 2b).

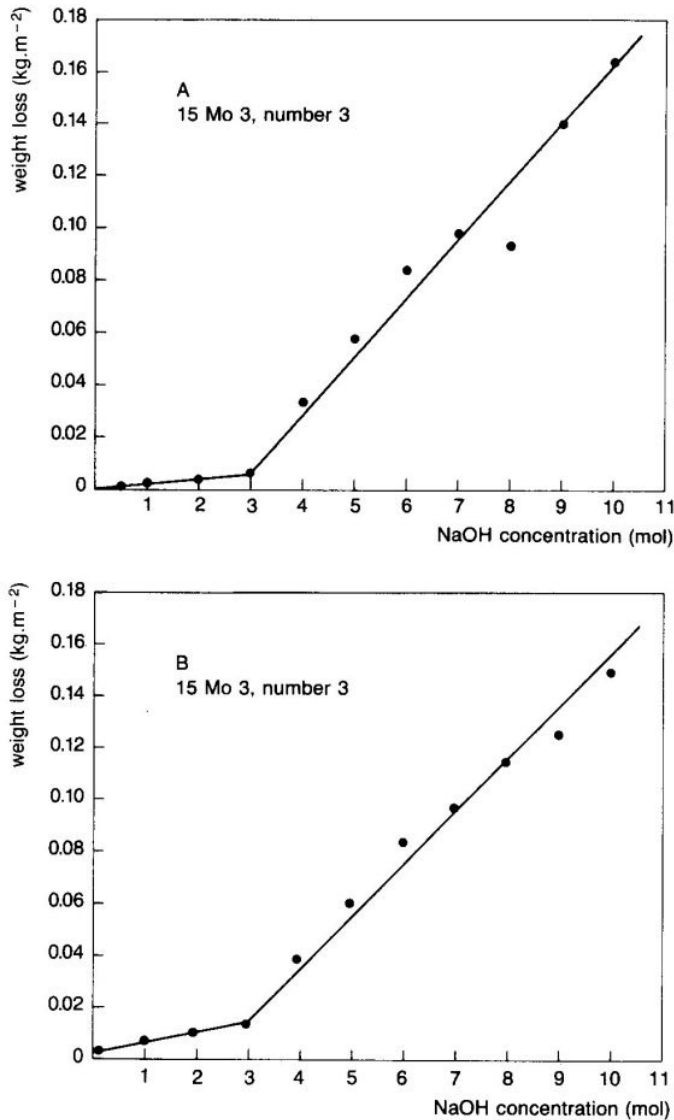


Figure 4: Weight losses after a 4-day exposure to NaOH under nondeaerated conditions at 250 °C (A) and 310 °C (B), respectively (experiment 2c).

As in experiment 2b (compare Figure 3) the weight loss for the samples in the low-alkaline solutions after pickling was at its highest at 310 °C. This can be explained because of the thicker protective oxide layer at higher temperatures.

3.4 Experiment 3

From **Figure 5** it is clear that the corrosion in NaOH solutions for the two 2.25% Cr steels is not substantially influenced by the presence of oxygen.

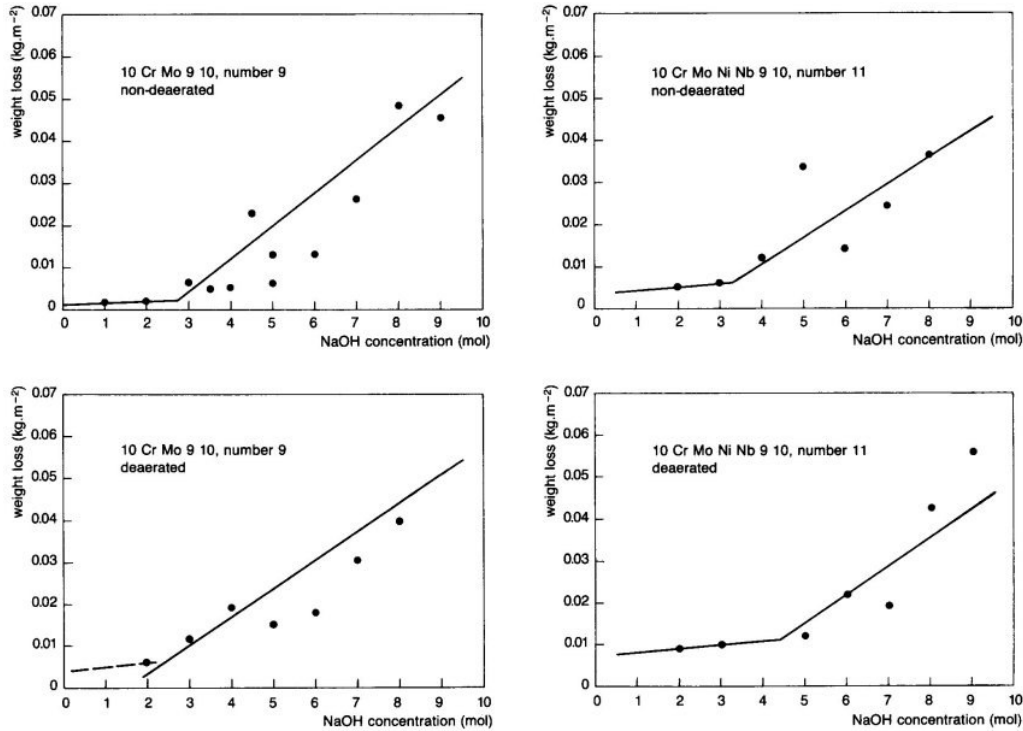


Figure 5: Weight losses after a 4-day exposure to NaOH under various conditions at 250 °C (experiment 3).

3.5 Experiment 4

Experiments in phosphate cannot be performed in highly concentrated solutions, because of the limited solubility. The effect of phosphate could only be studied up to a 0.5 molar concentration.

Figure 6 gives the result of the test. As could be expected in these low-phosphate solutions, there was no critical concentration above which fast corrosion took place.

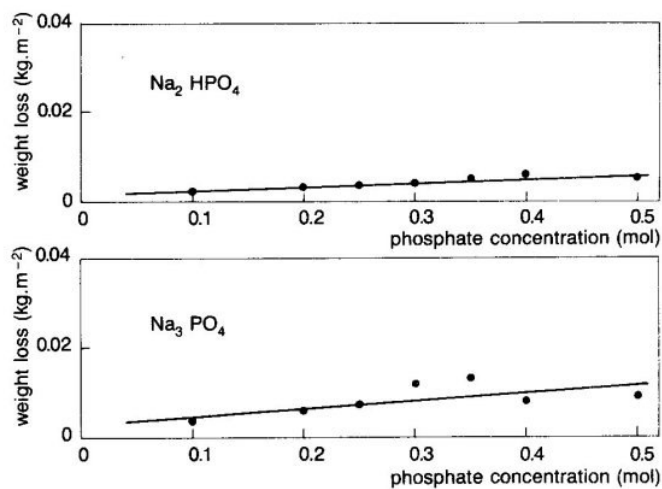


Figure 6: Weight losses of St 35.8, number 2, after a 4-day exposure under deaerated conditions at 250 °C (Na₂HPO₄ and Na₃PO₄) (experiment 4)

3.6 Highly concentrated solutions

In concentrated alkaline solutions two test conditions were chosen:

1. 4 mol OH, deaerated, 250°C
2. 10 mol OH, non-deaerated, 310°C

In both environments two types of exposure tests were performed. They are summarized in table 3. The first type of experiment was performed in order to study the influence of exposure time, the second to study the corrosion-rate frequency-distribution of many heats.

Exp.	Temp. °C	Environment	Steel	Number of heats	Parameter to study
5a	250	NaOH, LiOH, KOH deaerated 4 mol	St 35.8	1	exposure time
5b	250	NaOH, LiOH deaerated 4 mol	15Mo3	23	frequency distribution
6a	310	NaOH, LiOH non-deaerated 10 mol	St 35.8	1	exposure time
Bb	310	NaOH non-deaerated 10 mol	St 35.8	83	frequency distribution
6b	310	NaOH non-deaerated 10 mol	15Mo3	27	frequency distribution
sn	310	NaOH non-deaerated 10 mol	14Mn4	20	frequency distribution
6b	310	NaOH non-deaerated 10 mol	13CrMo44	23	frequency distribution
sb	310	NaOH non-deaerated 10 mol	1 OCrMo910	13	frequency distribution

Table 3: Experiments in concentrated alkaline solutions

3.7 Experiment 5

The results of experiment 5a are given in **Figure 7**. It is obvious that the corrosion rate in LiOH is linear, while KOH and NaOH result in formation of protective oxide layers under the isothermal autoclave conditions. No difference is found between the corrosion rates in NaOH and KOH.

Twenty three heats were run, exposing 15Mo3 steel, for four days, to 4- molar NaOH. The weight losses after pickling are given in **Figure 8**. As can be concluded from Figure 8, the corrosion rate in LiOH is about 5 times faster than in NaOH.

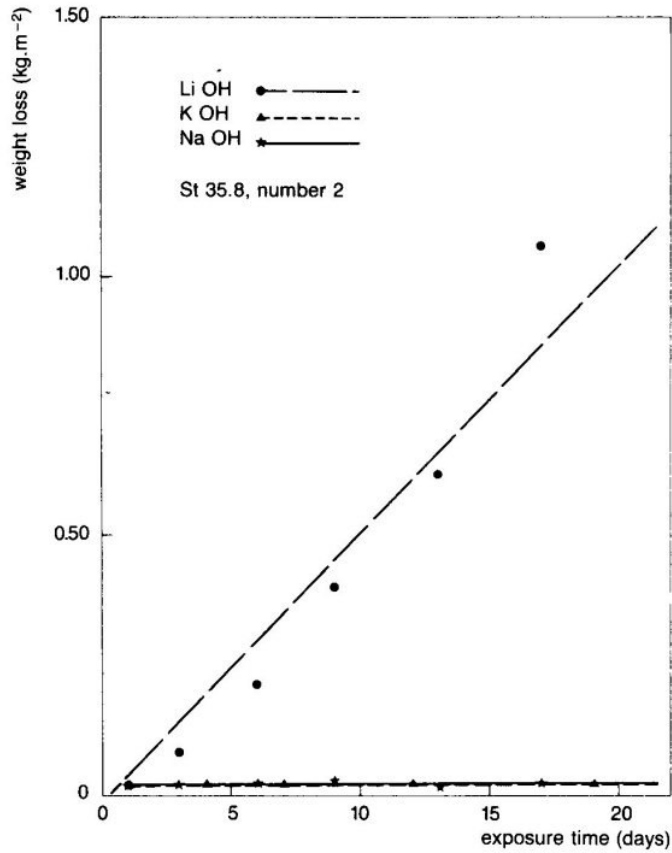


Figure 7: Weight losses after exposure to 4-molar alkaline solutions under deaerated conditions at 250°C (experiment 5a)

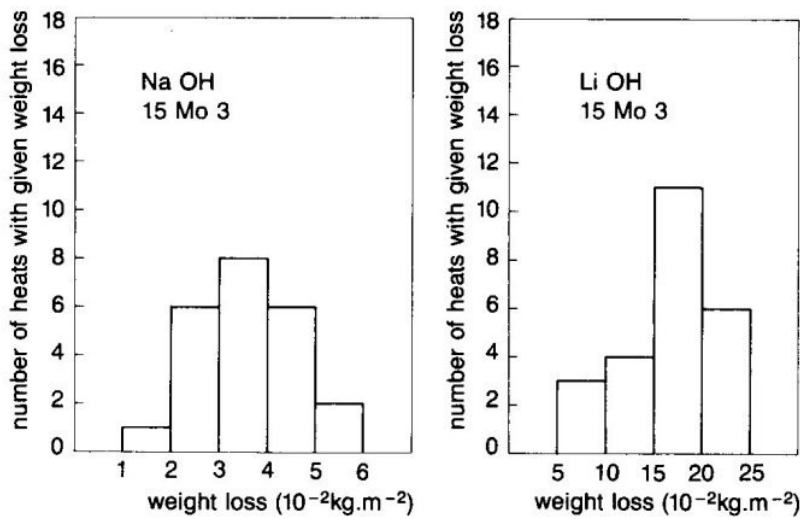


Figure 8: Frequency distribution of heats after a 4-day exposure in 4 molar alkaline solutions under deaerated conditions at 250°C (exp. 5b)

3.8 Experiment 6

Figure 9 shows the results of experiment 6a. At the high temperature of 310°C and in 10-molar solutions the corrosion rate in LiOH is also linear and that in NaOH indicates the formation of a somewhat protective layer. After an exposure time of 31 days two specimens were prepared for microscopic examination of the formed oxide layer.

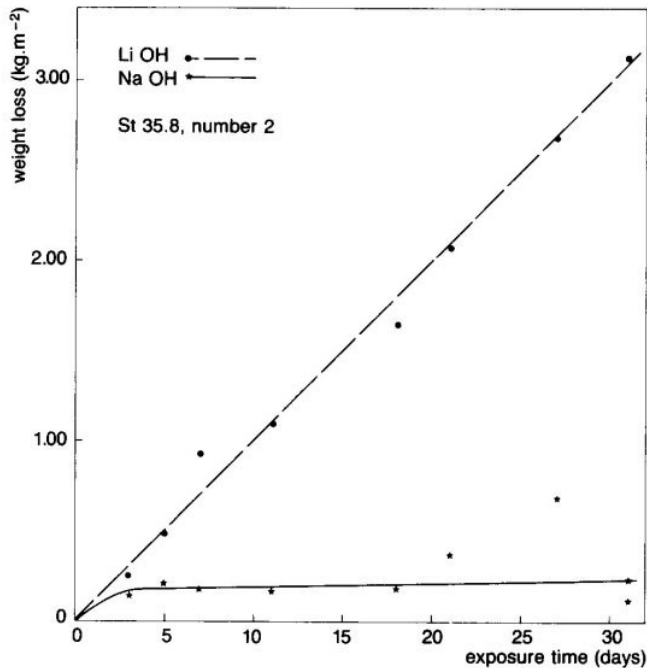


Figure 9: Weight losses after exposure to 10-molar alkaline solutions under non-deaerated conditions at 310°C (experiment 6a)

Figure 10 shows the oxide layers. The layer in NaOH can be described as a so-called Potter and Mann layer. There is an inner porous layer with coarse magnetite crystals on the outside. The layer formed in LiOH, however, is very porous and has an open structure. A columnar character of the oxide can be discerned. The LiOH test solutions after exposure contained a large amount of loose oxide, too. Contrarily the NaOH solutions were always clear and free of oxides.

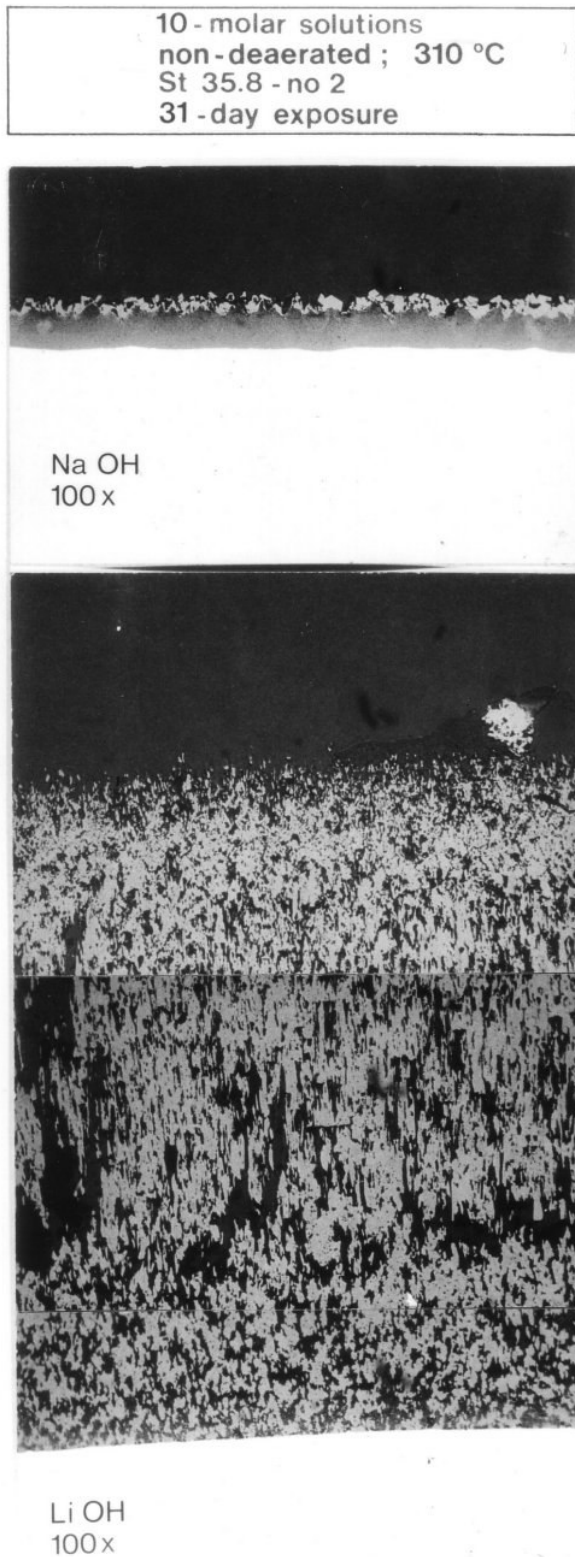


Figure 10: Oxide layers ($\times 100$) formed on St35.8, number 2, after a 31-day exposure to NaOH (A) and LiOH (B) in 10-molar solutions under non-deaerated conditions at 310 °C (experiment 6)

In **Figure 11** the corrosion-rate frequencydistribution is given for the five types of steel. The carbon steel shows a rather broad distribution and has the lowest corrosion resistance. The steels 15Mo3, 14

Mn4 and 13CrMo44 are somewhat better. The 2.25 % Cr steel is the best, but the difference in alkaline corrosion resistance with the other three steels is not so great.

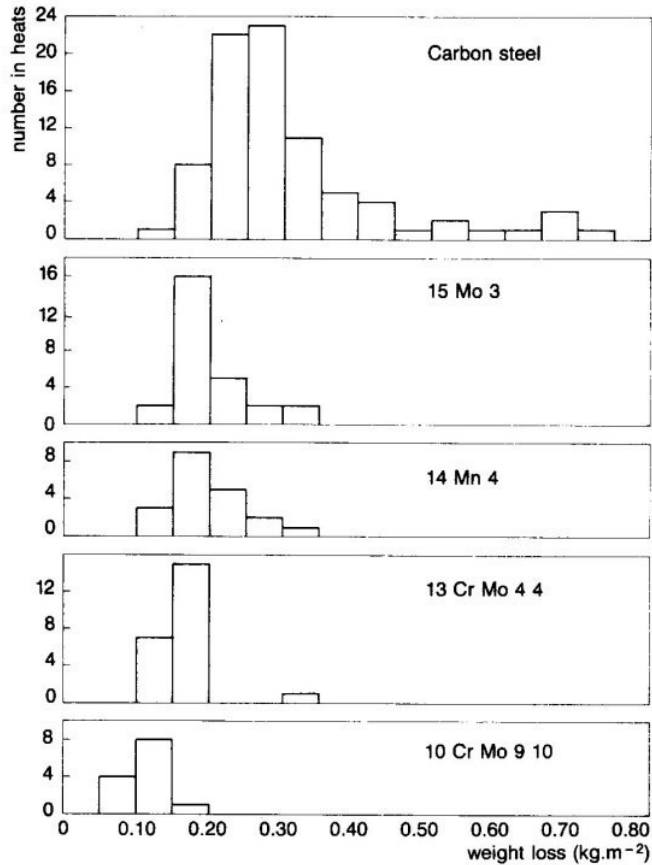


Figure 11: Frequency distribution of heats after a 4-day exposure to 10-molar NaOH solutions under non-deaerated conditions at 310°C (experiment 6b)

4 Discussion

The danger of non-volatile alkalisers (NaOH, KOH and LiOH) to inhibit acid- chloride corrosion in evaporators occurs when the inhibitor concentrates at places with high heat fluxes. High hydroxide concentrations can arise, causing alkaline corrosion of the carbon or low-alloyed steel boiler tubes. Though these experiments were performed under isothermal autoclave conditions, the results might be used for evaluation of the various alkaline inhibitors used in the evaporators. The concentrating, due to the boilingpoint elevation at the heat-loaded metal surfaces, is supposed to be independent of the type of the inhibitor mentioned.

It is obvious that rapid alkaline corrosion will not occur as long as the alkaline inhibitor concentration on the metal surface is kept below the critical value, as determined in the autoclave tests. It has been shown that in the case of LiOH the critical concentration will soon be exceeded. The inhibitors KOH and NaOH show higher critical concentrations. Moreover, the corrosion rate in strongly alkaline solutions is highest in LiOH, lower in NaOH and lowest in KOH considering the equal concentrations. All these electrolytes are highly soluble.

Na₂HP0₄ and Na₃P0₄ were tested up to 0.5 molar because of their much lower solubility. The corrosion rate in these concentrations was very low and a critical concentration was not found. So the danger for

alkaline corrosion when using the phosphate inhibitor will be very low, but deposition and fouling of the heat-loaded tube surfaces will be a greater risk (Huijbregts, 1979). Fouling can result in overheating and mechanical creep of the steel.

From the results it is clear that in the case of steam blanketing or local dry-out, due to circulation disturbances in the boiler, NaOH and KOH are better corrosion inhibitors than LiOH. Phosphate is considered to be the best corrosion inhibitor, but it has the great disadvantage of fouling the tube wall. This second effect can notably influence the in-service behaviour of the boiler. Of course, boiler-water treatment is often a matter of compromise, when searching for the right inhibitor for a troublesome boiler.

It must be mentioned that LiOH has a positive effect on decreasing the amount of boiler sludge. Earlier studies showed that the physical properties of the magnetite are better when it is formed in LiOH (Huijbregts and Snel, 1972). The tensile strains of oxide formed on St35.8 in 0.01 mol NaOH and LiOH amounted to 0.05 and 0.08% respectively. From that research it also appeared that, though corrosion rates in LiOH under pre-break-away conditions are higher, the break-away times are longer in LiOH than in NaOH (**Fig. 12**). These facts indicate that a boiler-water treatment with LiOH instead of NaOH will probably result in less boiler sludge. In this light LiOH is the more favourable. In the case of a fouled boiler and danger for steam-blanketing, a change from NaOH to LiOH water treatment will increase the alkaline-corrosion risk.

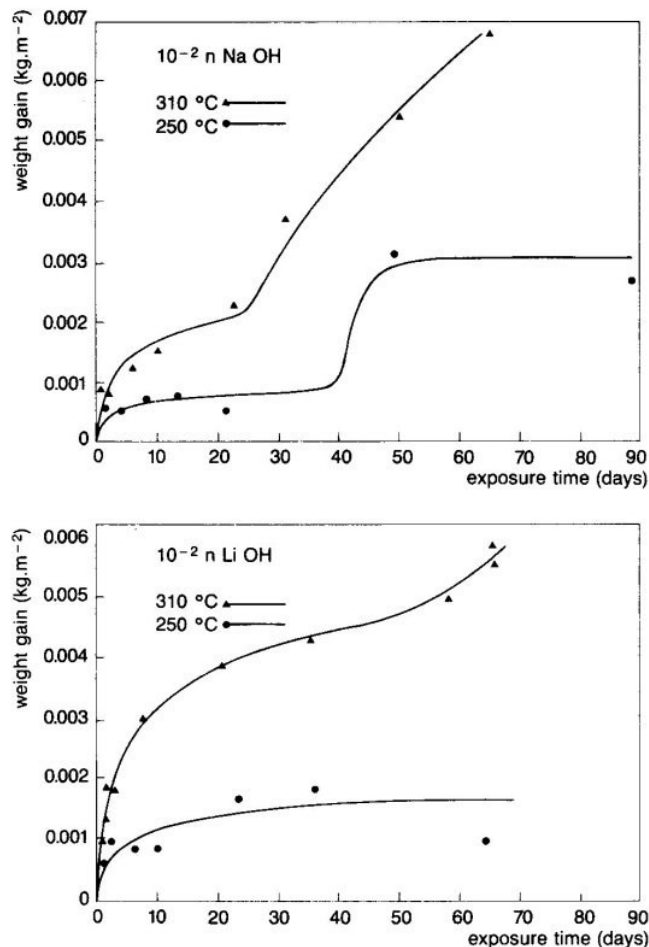


Figure 12: Oxidation of iron specimens in non-deaerated solutions (after Huijbregts and Snel, 1972).

In highly alkaline solutions (4 molar NaOH and LiOH and 10 molar NaOH) a high variation in the corrosion rates for the various steel types was found after many heats. For some heats only, the critical hydroxide concentration was determined. In our opinion it is very important that the boiler steel has a highly critical concentration value for high-alkaline corrosion resistance. If highly concentrated solutions are formed under deposits, the absolute corrosion rates are less interesting. It can

be expected that the critical hydroxide concentration will also depend on the chemical steel composition and thus will vary considerably through the various heats. In the past this effect has been studied extensively for acid-chloride corrosion in boilers (Huijbregts, 1981). Because determination of the critical hydroxide values is very time consuming, this has not been worked out. For acid-chloride corrosion resistance, the following regression formulae were found:

Above the critical FeCl_2 value (molar) linear corrosion starts.

It cannot be excluded that other alloying elements control the critical hydroxide concentration values for the alkaline corrosion. For scientific purposes the influence of composition variations within one steel class will be a very interesting field of study.

Steel	Critical FeCl_2
Carbon steel	$- 0.0235 + 0.18 \text{ C} + 0.12 \text{ Si} + 0.07 \text{ Cr} + 0.1 \text{ Mo}$
15Mo3	$- 0.39 + 2.26 \text{ C} + 0.26 \text{ Mo}$
14Mn4	$- 0.52 + 1.15 \text{ C} + 0.89 \text{ Si} + 0.96 \text{ Cu} + 1.35 \text{ P}$

Table 4: The regression formulae for acid-chloride corrosion resistance

5 Conclusions

1. Above a critical hydroxide concentration the corrosion rate increases rapidly with increasing hydroxide concentrations.
2. The critical concentration of LiOH amounts to about 0.5 molar and that of NaOH. 2-3 molar. KOH shows a critical concentration of 1.5 molar.
3. The critical concentration for alkaline corrosion was only determined for a few heats of the 5 steels tested. It is not clear whether this critical concentration is also controlled by the chemical composition of the steel within the broad range of the various steel specifications.
4. The critical alkaline concentration at 250 °C does not differ from that at 310 °C.
5. The corrosion rate in highly concentrated (4 and 10 molar) LiOH is five times higher than that in NaOH.
6. Under the isothermal autoclave test conditions in 4 mol NaOH a so-called Potter and Mann oxide layer formed, leading to a parabolic corrosion rate. In 4 mol LiOH, however, a porous columnar oxide structure was formed which results in linear corrosion.
7. The corrosion rate in 10 mol NaOH for carbon steels varied considerably for the 83 different heats. Carbon steel showed the highest corrosion rates. Steels 15Mo3, 14Mn4 and 13CrMo44 had about the same corrosion rates but were only slightly better than carbon steel. Steel 10CrMo910 had the lowest corrosion rate.
8. In the case of a fouled evaporator and the consequent danger of steam blanketing, NaOH and KOH are considered to be better acid-chloride corrosion inhibitors than LiOH. LiOH will give a high alkaline corrosion risk because of the low critical hydroxide concentration. Phosphate is a good inhibitor but due to its low solubility it gives a high fouling effect.

6 References

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