Origin of carbonate

Carbonate Stress Corrosion Cracking in District Heating Systems

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Heat & Power, Vol 3- 1/2006, pg 32-35.

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Summary

Some years ago many Stress Corrosion Cracking (SCC) failures were noticed in the low temperature line of a District Heating System (DHS) in the Netherlands. Extensive research showed that iron carbonate was present in the corrosion scale on the waterside/ inside of the tube as well as in the cracks itself, The authors describe the origin of carbonate in low pressure boilers and in district heating systems.

Introduction

Some years ago many Stress Corrosion Cracking (SCC) failures were noticed in the low temperature line of a District Heating System (DHS) in the Netherlands. Extensive research showed that iron carbonate was present in the corrosion scale on the waterside/ inside of the tube as well as in the cracks itself (Huijbregts et all[1]). Some examples of the scales appear in *Figures 1 and 2*.

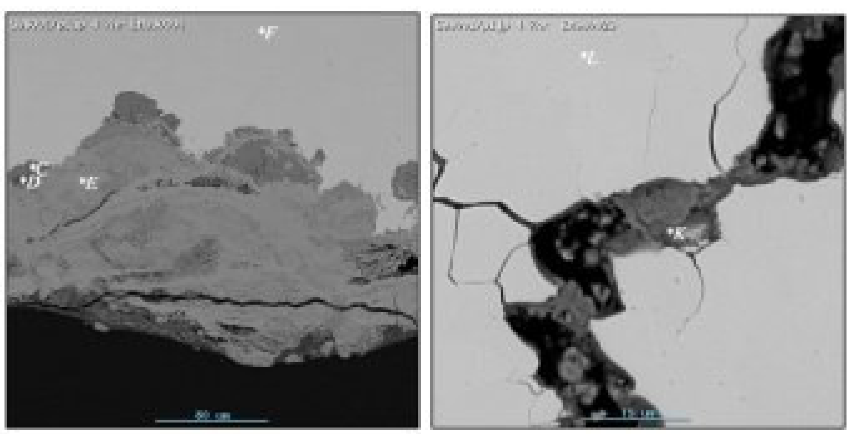

Figure 1. Scanning electron microscope image of a pit and a crack in a DHS tube. The dark gray spots C, D and K contain carbonate.

In the pits where iron carbonate is present and from which SCC starts, there is a equilibrium between ferrous carbonate, ferrous hydroxide and magnetite.

SCC starts from the pits that are filled with iron carbonate. Inside the pits there is a equilibrium between ferrous carbonate, ferrous hydroxide and magnetite.

$Fe^{2+} + 2\ OH^- \Leftrightarrow Fe(OH)_2$ (1)

reaction of Shikorr
$3\ Fe(OH)_2 \Leftrightarrow Fe_3O_4 + H_2 + 2\ H_2O$ (2)

$Fe^{2+} + CO_3^{2-} \Leftrightarrow FeCO_3$ (3)

At pH values above 10 the ferrous hydroxide equilibrium will be shift to the right and the ferrous-concentration in the water will diminish. However, this will result in an increase of the carbonate concentration according to reaction 3.

In equilibrium with ferrous hydroxide (K_s= 1.6 10^{-14} at 80°C) and ferrous carbonate (1.4 10^{-9} at 80 °C) , the carbonate concentration can be calculated. At a pH value of 11 the carbonate concentration is 80 mmol (2). In *Figure 2* the concentrations at various temperatures are shown.

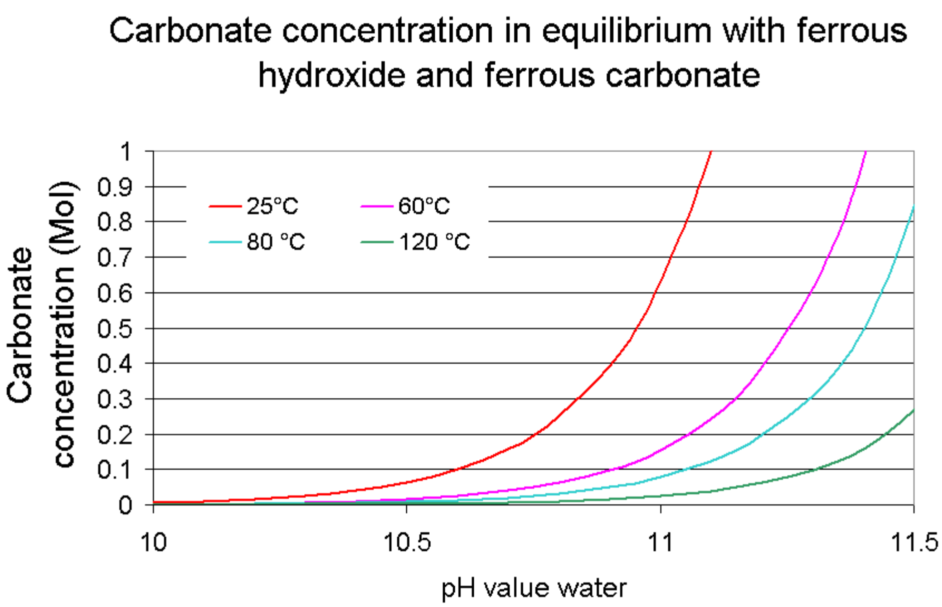

Figure 2. Carbonate concentration in equilibrium with ferrous hydroxide and ferrous carbonate.

Origin of the carbonate

In modern electricity power generating boilers very pure boiler water is used. Modern, highly sophisticated steam turbines are not designed to process steam containing impurities. In addition the water quality specification are very strict to avoid corrosion in the high pressure system . A condensate polishing system is required for high pressure boilers.

When a boiler is used for the production of heat only, the water specifications are less strict and a full 100% condensate polishing is not applied. In fact, this is also the case for a DHS, where a 100% condensate polishing is not needed and is not applied.

An analyzing technique that is still common practice to determine the chemical composition, is titration of the boiler and supply water on the indicators phenolphthalein and methyl orange (p- and m-number). From the p- and m values, the concentration of hydroxyl, carbonate and bicarbonate can be determined with the help of *table 1*. The p- and m-numbers are the amount of millilitres of hydrochloric acid (HCl, 0.1 mol) that is needed for titration of 100 ml of water on the indicators phenolphthalein and methyl orange respectively.

Table 1 Application of p- and m-numbers.

Condition	Concentrations (m.aeq.)		
	OH	CO_3	HCO_3
p=0	0	0	m
2p<m	0	2p	m-2p
2p=m	0	2p	0
2p>m	2p-m	2(m-p)	0
P=m	p	0	0

In *Figure 3* an example has been given for a titration curve with the condition 2p<m.

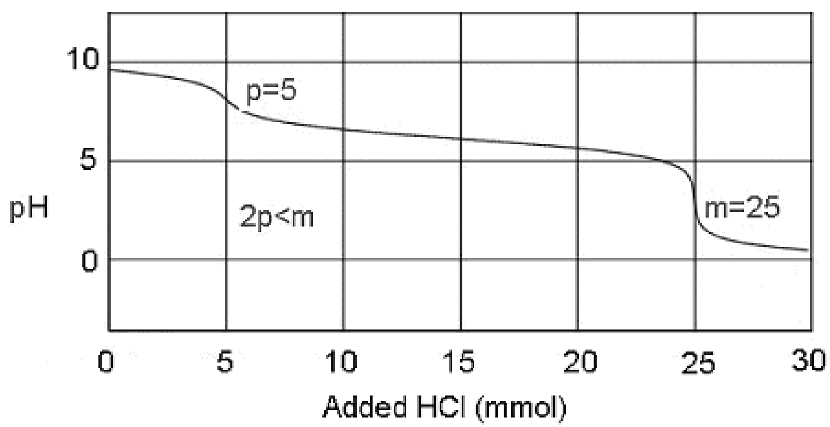

Figure 3. Titration curve of water with 15 mmol bicarbonate and 5 mmol carbonate.

In *Table 2* examples of water qualities in a DHS and a low pressure boiler are compared.
The total carbonate and bicarbonate concentration in the DHS system in supply water and in circulation water contains respectively 0.1 and 0.2 mmol.
In a low pressure boiler the bicarbonate content in the supply water (m=1) is about 1 mmol. In the boiler water (m=8 en p=7) the bicarbonate and the carbonate concentrations are respectively 0 and 1mmol (2maeq). This is a considerable increase over the amounts than found in the DHS.
Despite the low concentration of bicarbonate in the DHS, carbonate was found very obviously in locations where carbonate stress corrosion cracks were present.

Table 2. Example of water qualities of a DHS and low pressure boilers.

System		PH	Conductivity µS/cm	p-value	m-value	p/m condition
DHS	Supply water	5.9 – 7.2	7 – 10	0	0.1	p=0
DHS	Circulation	9 – 11	20 – 40	0.1	0.3	2p<m
Low pressure boiler	Supply water	8.5	300	0,05	1	p=0
Low pressure boiler	Boiler	12	5700	7	8	2p>m

According to Music and co-authors [4] a mixture of basic iron-carbonate and magnetite is formed by exposing C-steel for 1 to 3 weeks already in a 5 mmol Na_2CO_3 environment at room temperature and at 90 °C. When exposed to distilled water no carbonates were found.

It was shown that it is rather easy to crack C-steel by means of Constant Strain Rate experiments in 1500 mmol carbonate environment (Huijbregts et all [1], Wendler-Kalsch [3]). It is very likely that such cracking will occur also in a 80 mmol carbonate environment (the equilibrium concentration of iron-carbonate and iron-hydroxide at pH=11 and at 80 °C). See Figure 2.

To avoid carbonate Stress Corrosion Cracking in the Breda DHS it was advised in 1998 to decrease the pH value of the water in the system to a value of 9.8. Since then, the number of cracking failures decreased drastically as can be seen in *Figure 4*.

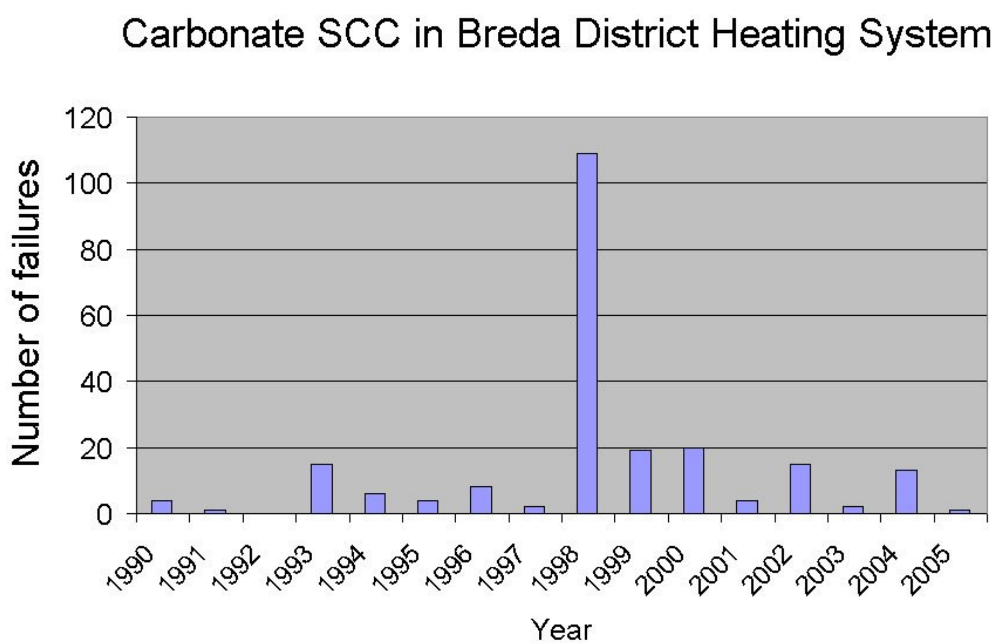

Figure 4. Decrease of in service failures after decreasing the operating pH value in the water of the Breda District Heating System.

References

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