



Stress Corrosion Cracking in District Heating Pipes

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Abstract

Failures due to stress corrosion cracking has occurred in the return pipes of a district heating system. Extensive in service failure investigations were carried out on the pipe sections. Stress analyses were made for various scenarios. The pipes are exposed to a slow strain rate of approximately 10^{-7} per second on heat consumption. It is concluded that the residual stresses along the welds, in combination with the critical strain rates, are sufficient to cause SCC given unfavourable water conditions.

The steel in the pipes complies with the normal specifications of St37.0 and St37.2

Iron carbonate is present in the corrosion products of the pits. As a result of the chemical equilibrium in the pits between iron hydroxide, iron carbonate and the high pH of the water, a high carbonate concentration arose in the pits. Cracking started from the carbonate filled pits. Intergranular SCC was simulated in laboratory experiments under various carbonate conditions. A first requirement to prevent carbonate SCC is maintenance of water quality with respect to pH value in accordance with the applicable guideline.

1. Introduction

In 1998, leaks occurred in a return pipe of the main ring of a district heating network. Leaking was noticed in both the expansion bends and the straight pipe sections. The steel pipes are laid inside a casing filled with a mixture of bitumen and cork (Lebit system).



Figure 1. A cracked zone near the weld.

In response to these pipe leaks, a very wide-ranging investigation was launched, comprising the following components:

- In-depth microscopic examination of the pipe material, corrosion products and cracks
- Stress analyses according to different scenarios for the piping systems
- Experiments research in the laboratory using the slow strain rate technique to determine the precise chemical conditions at which SCC occurs.

2 Investigation of cracked pipe sections

2.1 Microscopic examination

Cracks are not only present in the weld and the heat-affected zone, but also at a distance of approximately 12 mm from the weld, an area which does not lie directly in the heat-affected zone. Figure 2 shows a weld in the etched condition, so that the different zones can be distinguished.

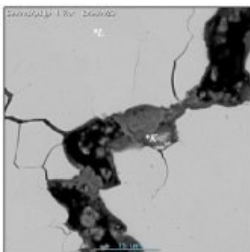
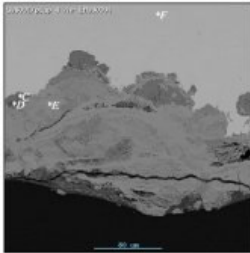


Figure 3

A selection of the SEM images of the corrosion deposit and a part of the crack with the analysis points indicated

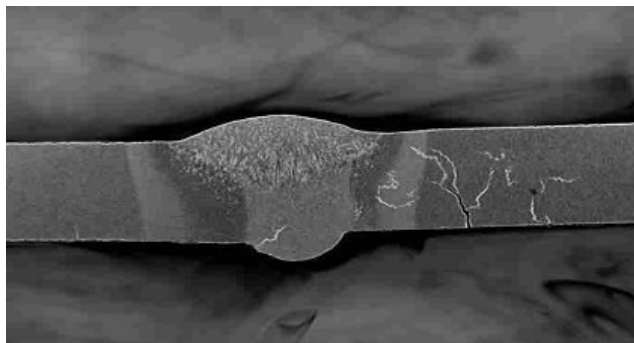


Figure 2. The macro-etching technique shows the different areas in the heat-affected zone and the cracks.

Leaking occurs adjacent to the welds. In addition, intergranular corrosion is also found in the pipe at a considerable distance from the welds. The structures of the pipe material and the heat-affected zones exhibit no distinct differences. The perlite exhibits slight globularization, and a relatively large quantity of carbide is precipitated at the grain boundaries (carbide bands).

Figure 3 shows a Scanning Electron Microscope picture of a characteristic oxide layer in the pit. Magnetite (Fe_3O_4) is found in the corrosion scale. Dark grey corrosion products inside the pits on the metal surface are present. It became clear that the intergranular SCC originates from these dark grey pits. The corrosion products in the corrosion layer and in the cracks were analysed (Table 1). The table gives the atomic percentages, enabling the calculation of the most likely products present at the indicated points.

Table 1 Overview of analysis results in at % for the locations shown in Figure 3.

Element	Position C	Position D	Position E	Position F	Position K	Position L
C	10.3	28.7	-	-	5.8	-
O	59	46.7	56.2	-	54.7	-
Al	0.1	0.2	-	-	1.9	-
Si	0.1	0.1	1.0	0.7	5.1	0.6
Mn	-	-	-	0.4	-	-
P	-	-	0.1	-	0.5	-
S	0.1	0.1	-	-	-	-
Fe	30.5	24.2	42.7	98.9	32.0	99.4
Compound most likely to be present:						
Position C	Iron oxide and iron carbonate					
Position D	Iron carbide and iron oxide and iron carbonate					
Position E	Iron oxide					
Position F	Steel					
Position K	Iron carbonate and iron oxide					
Position L	Steel					

The analysis shows that the pits are filled with iron oxide and iron carbonate (dark grey areas). The iron carbonate is also present in the cracks themselves. A small percentage of chloride is found at the crack tips. The chloride may originate from the district heating water, as approximately 5 mg/L is present in it.

3 Analysis of maximum stresses and strain rates

3.1 Maximum stresses

The Lebit insulation material deforms easily, even at low temperatures. So, the total stresses on the inside of the straight pipe are primarily determined by the stresses resulting from internal pressure and residual stresses. A maximum axial stress of 207 MPa on the inside of the straight pipe was calculated. This value is a summation of the measured residual stresses at the weld (175 MPa), the internal pressure (17 MPa), and effects of prestressing and expansion (15 MPa). The value of 207 MPa is clearly below the minimum strain limit for the steel of 235 MPa.

3.2 Strain rates

The strain rates of a pipe moving freely inside the Lebit insulation were calculated as a function of the measured temperature changes during normal operation of the district heating pipe. For a rigid expansion loop, the strain rate lies in the range 2 to 12 x 10⁻⁷ while for a pipe section with an active free expansion loop, the strain rate is low at 0.2 to 1.8 x 10⁻⁷.

4 Stress corrosion experiments in a carbonate medium

Wendler-Kalsch indicates that SCC can occur in a narrow potential range in a 1.5 Mol carbonate solution with a pH of 9.5. The corrosion potential must lie in the active-passive transition of the steel. This area is only about 150 mV wide, and depends also on the concentration of carbonate in the corrosion deposit (Figure 4). The critical potential range in the 1.5 Mol carbonate solution measured by Wendler-Kalsch (1980) lay between -500 and -350 mV SHE. Only under these conditions intergranular SCC was initiated.

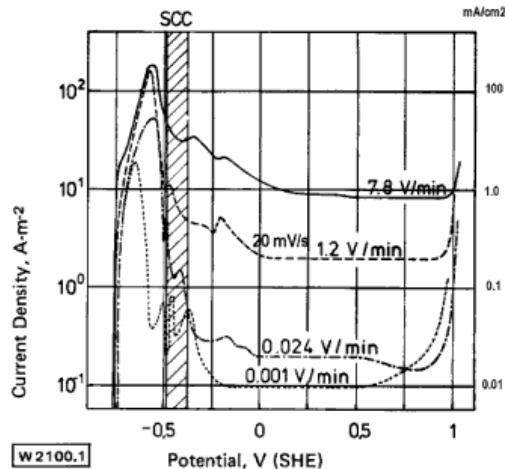


Figure 4. The critical range for stress corrosion in a 1.5 Mol carbonate/bicarbonate medium indicated by Wendler-Kalsch.

Polarization curves were measured on the steel from the district heating piping in a carbonate medium (1.4 Mol) and SCC tests were made in particular in the critical potential range indicated by Wendler-Kalsch (1980). Table 2 shows the data for the relevant tests.

Table 2 Overview of the relevant SCC slow strain rate experiments: strain rate: 1.4×10^{-6} , temperature 70 °C, corrosion potential: -430 mV SHE

Test number	Medium CO ₃ /HCO ₃ g/l	Results of microscopic examination on tensile test bars
1	12 / 53	Small intergranular cracks
2	0.12 / 0.53	No intergranular cracks, completely ductile fracture
3	12 / 53 **	Large intergranular cracks over the whole length of the test bar

** NaCl was added (1 g/l)

In the tests a potential was selected which was just below the maximum of the active-passive transition. In the first test clear intergranular cracks are found both in the straight part of the bar and in the necked part. In the second experiment the carbonate concentration was considerably reduced.

Fracture was completely ductile, and intergranular cracks were not observed. In the last experiment some NaCl was added to the high carbonate concentration. As Figure 5 shows, very clear intergranular cracks are present.

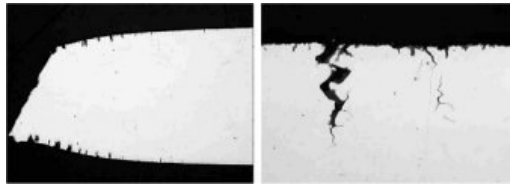


Figure 5 Intergranular cracks in the tensile test bar after testing in the active-passive transition.

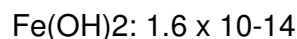
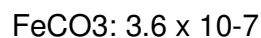
5 Discussion

It was obvious from the first investigations that the leaks were the result of SCC. Three factors (medium, strain rate and material) have to be investigated with respect to SCC. The investigation focused fully on these three factors.

5.1 Medium

The pH value of the circulating water is fairly high for a district heating system. Values between 9.5 and 11.1 were measured, with an average of approximately 10.5. The guideline value is a pH between 9.5 and 10.0.

The pH value of 10.5 is not high enough in itself to cause alkaline SCC. For this reason, investigations were oriented toward carbonate SCC. Water measurements showed no directly high carbonate values. On the basis of the certainty that carbonates are present in the corrosion pits in the return pipe, the carbonate concentration can be calculated at the point at which the ferrous hydroxide formed on the surface of the steel is in equilibrium with the iron carbonate. The solubility products of the relevant compounds are:



At the prevailing temperature of approximately 80 °C, the magnetite layer is formed as a result of the Schikorr reaction, whereby Fe(OH)_2 is further oxidized to Fe_3O_4 . The Fe^{2+} concentration will thus be in equilibrium with the Fe(OH)_2 .

At a pH value of 10.0, the concentration of Fe^{2+} will be equal to 1.6×10^{-6} . As the FeCO_3 is found in the corrosion deposit, the carbonate concentration must have been high, approximately 0.23 Mol.

At a pH value of 11 the iron concentration will be 1.6×10^{-8} , making the carbonate concentration theoretically as high as 23 Mol.

It is clear that, at the high pH value of the water, the carbonate concentration in the corrosion pits is in the critical range for SCC (1 - 2 Mol)

Using laboratory experiments, intergranular SCC was simulated in a carbonate medium of 1.4 Mol. This medium can certainly be considered representative of the medium prevailing in the pits. It is striking that the intergranular SCC only occurs in a narrow potential range. It is possible that this critical condition may also not prevail on a constant basis during the period of operation. It must therefore be assumed that the intergranular SCC which led to the leaks occurred at irregular times over the whole operating period.

It is very likely that chloride found at the crack tips will also cause a negative effect in combination with the carbonate. It is thus assumed that the chloride reactivates the carbon steel at points subjected to high mechanical stresses, as a result of which intergranular SCC occurs sooner in combination with the high carbonate concentration in the corrosion layer.

Iron carbonate is less stable at the higher temperature in the feed pipe (>95 °C). Therefore the high carbonate concentrations are not reached in the feed pipe and explains why SCC is not noticed in the feed pipes.

5.2. Strain rate

The strain rate also influences SCC crack growth rate. An example of this is shown in Figure 6 (Wendler-Kalsch, 1980). From this graph it can be concluded that the low strain rate in the district heating system seems sufficient to cause stress corrosion cracking in a carbonate medium.

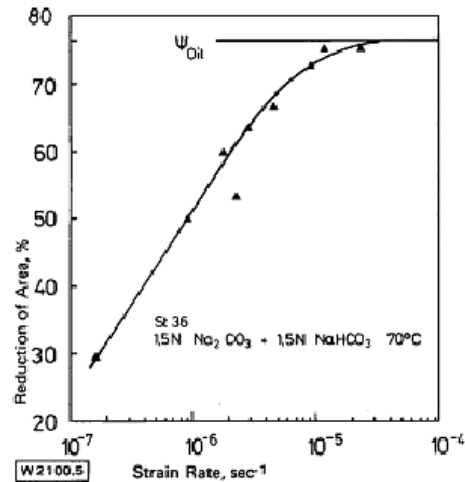


Fig. 5. Effect of strain rate upon the reduction of area of mild steel in 1.5 N ($\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$) at a potential of -0.45 V (SHE)
 Abb. 5. Einfluß der Dehngeschwindigkeit auf die Bruchminderung des Stahls in 1,5 N ($\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$) beim Elektrodenpotential $-0,45$ V

Figure 6

Sensitivity to SCC as a function of strain rate

If low deformation rates are applied in slow strain rate SCC tests, intergranular SCC can very easily be generated. The SCC sensitive strain rate range (expressed in the Reduction of Area in Figure 6) is broad in the experiments in the carbonate medium and at the required potential. Moving toward lower strain rates, sensitivity to SCC increases from a strain rate of 4×10^{-5} . The fracture surface becomes increasingly brittle at lower strain rates.

As the literature and the SCC tests performed at KEMA show, high stress is not necessary to cause SCC. A given strain rate combined with critical water conditioning is already sufficient to cause increased intergranular SCC. The high residual stresses adjacent to the weld and the possibly slightly more sensitive structure in the heat-affected zone, in combination with the strain rates resulting from temperature fluctuations in the return pipe, will cause increased intergranular SCC in the zone adjacent to the weld.

A low level of intergranular corrosion in combination with the presence of carbonate in pits is found in a large number of places in the pipes, including in straight pipe sections at a considerable distance from the weld joints. It follows from the above that the mechanical load and the strain rate do influence crack growth rate, although they do not directly influence intergranular corrosion. Water conditioning is responsible for the occurrence of intergranular corrosion.

5.3 Material

The material complies with the stated specifications of St 37, St 37.2 and St 54. Auger analysis was used to examine fresh fracture surfaces of the material. No accumulation of the elements S and P was measured at the grain boundaries.

It was shown during the course of the investigation that tertiary iron carbides are present at the grain boundaries (Figure 7).

The fact that such tertiary cementite is also emphatically present in cases of nitrate stress corrosion cracking in waste heat recovery boilers gives grounds for performance of follow-up investigations. Besides it appeared that this also applies to the chemical composition of steels, in particular with respect to the influence of small quantities of the elements Cu, Cr, Mo and Si. (Leferink, 2001). These elements influence the quality of the formed oxide layers, and must therefore also play a role in SCC behaviour of unalloyed steels.

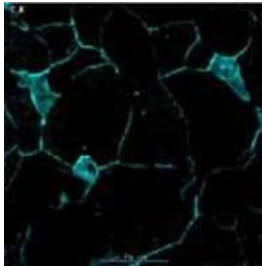


Figure 7

Carbon element mapping. Tertiary cementite is clearly present at the grain boundaries.

In the Netherlands a co-operation project on SCC in carbon steel is starting now.

8 Conclusions

Due to the temperature changes in the return pipe in the event of heat consumption, intergranular SCC is initiated preferentially in the zone adjacent to the weld joints, where the axial residual stresses are also highest. As a result of the temperature changes in the return pipe, the critical strain rate of the steel is $10^{-7}/s$.

SCC only occurs in the return pipe as a result of temperature changes and as a consequence of the stability of carbonate at lower temperature. The carbonate concentration in the pits is governed by the iron carbonate-iron hydroxide equilibrium. At a higher pH value, the carbonate concentration rises sharply.

Intergranular SCC also probably occurs readily due to the large quantity of tertiary carbides present in the steel. In selecting materials for carbon steel components which are susceptible to SCC, greater attention will therefore have to be paid in future to the structure and chemical composition of the steel.

The leaks are the result of carbonate SCC. The high carbonate concentrations occur locally underneath the corrosion layer as a result of the high set pH value in the water.

7 References

1. Wendler-Kalsch E. The effects of film formation and mechanical factors on the initiation of stress corrosion cracking of unalloyed steels in carbonate solutions. *Werkstoffe und Korrosion* 31, 534-542 (1980).
2. Leferink R.G.I., Huijbregts W.M.M., Nitrate stress corrosion cracking in waste heat recovery Boilers. *Anti-Corrosion Methods and Materials*. (to be published in 2001)

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