

## Nitrate stress corrosion cracking in Waste Heat recovery boilers

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### Abstract

Waste Heat Recovery Boilers (WHRB's) enhance the thermal efficiency of gas turbine power generating plants by capturing the heat from the exhaust gas and utilising it to raise steam for increased electricity production or district heating. Under normal conditions the exhaust gas from the turbine is cooled from around 550°C to 80°C. Care is taken that condensation will not occur in the cooler parts of the boiler.

Nevertheless, during normal operation, dry ammonium nitrate deposits can be formed in the WHRB. These deposits will become wet when the unit is started, shut down, when the temperature falls below the dew point. The deposits may also 'sweat' (i.e. absorb atmospheric moisture and become liquid) during extended plant outage periods. In consequence, Intergranular Corrosion Attack (IGA) and Stress Assisted Intergranular Corrosion Attack (SA-IGA) (in general called stress corrosion cracking) can occur in carbon steel construction materials.

For a total of 86 steels, with known compositions, the sensitivity to IGA was tested. The steels were subjected to aerated ammonium nitrate solutions of 90°C with concentrations ranging between 2 and 35%. After an exposure of 65 hours, cross sections of the steels were studied. If IGA occurred, the steel was considered sensitive to ammonium nitrate at that (critical) percentage.

During this investigation it was observed that alloying elements in several types of steel influence its resistance to IGA in ammonium nitrate. Elements such as molybdenum, manganese and chromium have a positive effect on the resistance to nitrate induced IGA, SA-IGA and stress corrosion cracking, whereas carbon and copper are detrimental.

The microstructure of the steel also appeared to be important. In many specimens taken from in-service failures, strings of carbide precipitates were found to be present at grain boundaries. The precipitates were identified to be ternary carbides. It seems, therefore, that the presence of carbides at grain boundaries increases the susceptibility of a steel to intergranular corrosion.

**Keywords:** CCGT, WHRB, waste heat recovery boilers, intergranular attack, nitrate stress corrosion cracking, carbon steel, 15Mo3

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## Introduction

In a combined cycle power plant, electricity is generated by means of a gas turbine. The exhaust gas from a gas turbine has a temperature of approximately 550 °C and still contains a lot of energy. In a waste heat recovery boiler, heat in the exhaust gas is used to produce steam which may be used to drive a steam turbine to produce additional electricity or exported for use in a district heating system.

If only water vapour and carbon dioxide were present in the flue gas condensation would only occur at the water dew point. Even when gases such as nitric oxides ( $\text{NO}_x$ ) and hydrochloric acid ( $\text{HCl}$ ) are present, condensation still will occur at temperatures very close to the water dew point. However, the presence of sulphur trioxide ( $\text{SO}_3$ ) has a major impact on the dew point of the flue gas. Based on data from literature a program was written to calculate the dew points and corrosiveness of various gas compositions (Kiang 1981, Land 1977, KEMA report 1990). Figures 1 and 2 show the huge difference in dew point between the  $\text{SO}_3$  gas and the other gasses.

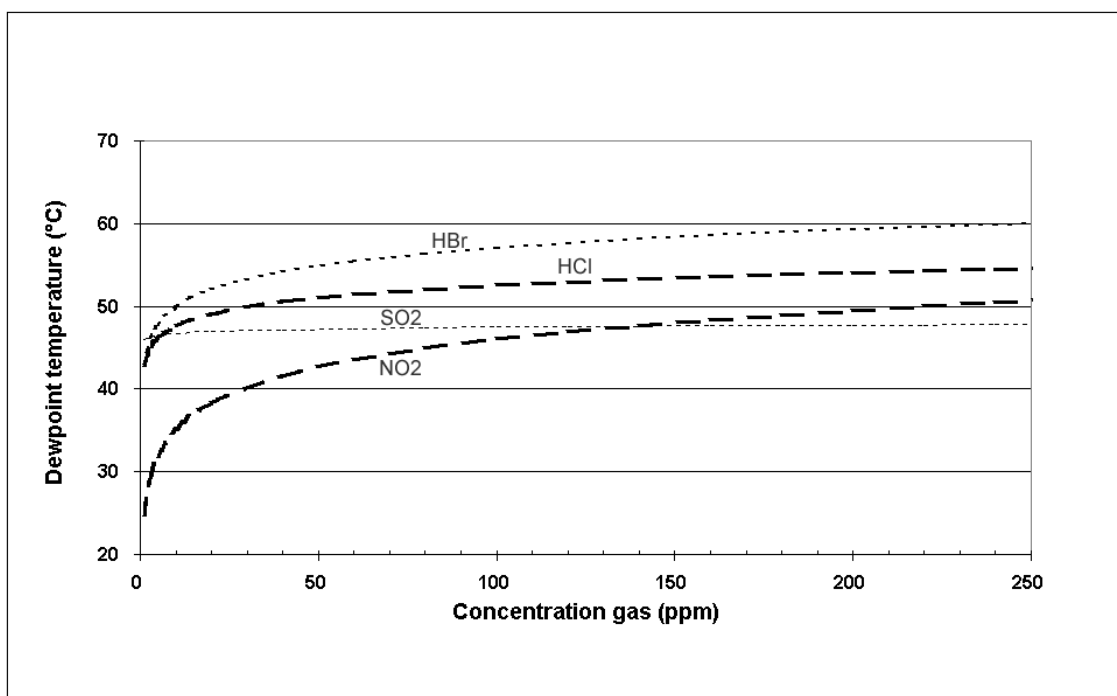


Figure 1. Dewpoint of  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{SO}_2$  and  $\text{NO}_2$  containing gasses with 18% water content.

$\text{SO}_3$  is an oxidation product of  $\text{SO}_2$  which, in turn, is formed when sulphur-bearing compounds are burnt. At temperatures below about 300 °C,  $\text{SO}_3$  starts to react with water to form concentrated sulphuric acid. Even at low  $\text{SO}_3$  concentrations in flue gas, the temperature at which sulphuric acid will begin to condense (often referred to as the sulphuric acid dew point) is well above the water dew point.

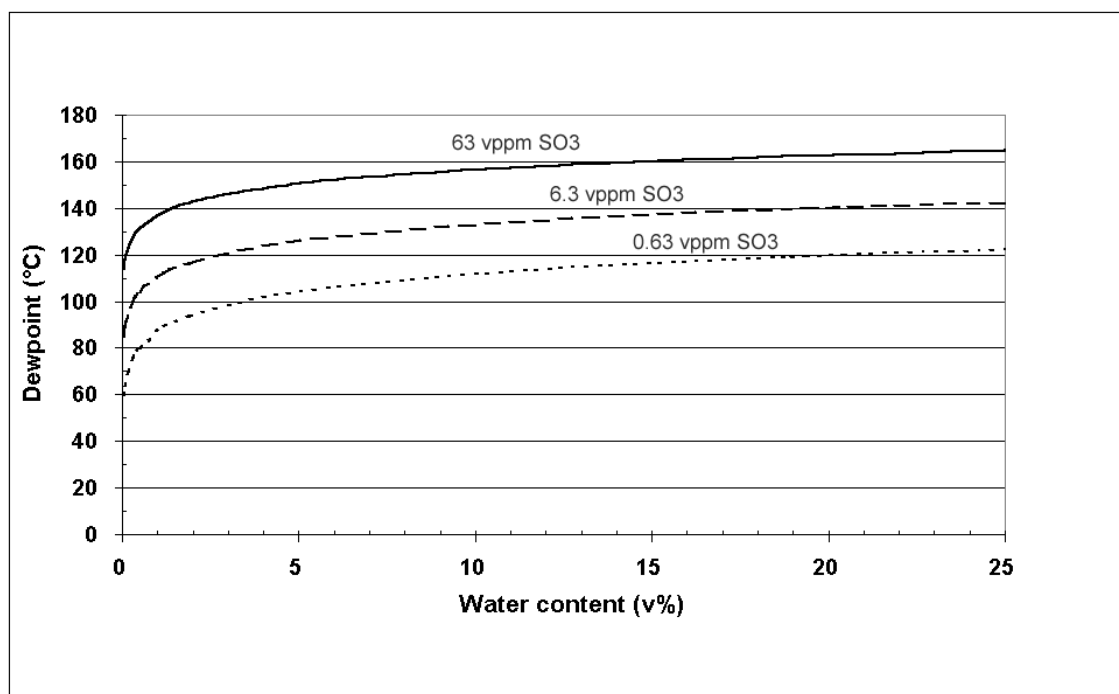


Figure 2 Dewpoints of SO<sub>3</sub> containing gasses with increasing water content. The presence of even minute amounts of SO<sub>3</sub> will result in a profound increase in dew point temperature.

When the temperature drops below the sulphuric acid dew point the sulphuric acid starts to condense either as small fog droplets or as a film onto the walls. If a fog is formed most of the droplets are carried away with the flue gas and the corrosion rate of exposed, unprotected steel exposed will be low. However, if film type condensation occurs the corrosion rate of unprotected steel can be quite high, due to direct contact with the sulphuric acid film. If calculations are to be made for the corrosion rates for new boiler designs it is strongly advised to assume that film condensation will occur.

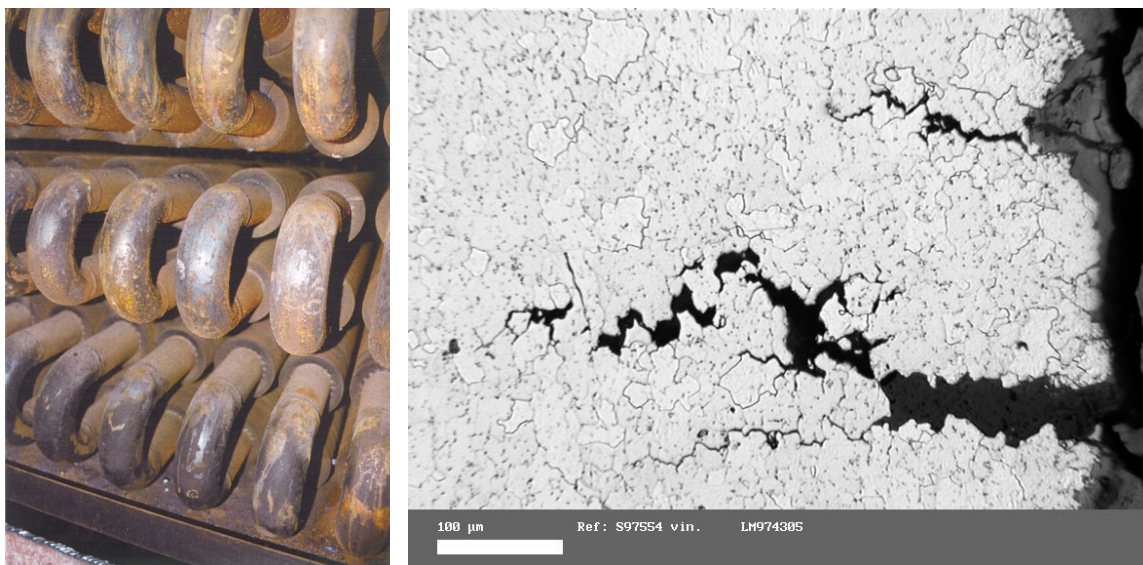
In most installations the formation of sulphuric acid is simply prevented by keeping the temperature above the sulphuric acid dew point. However during start-up and shut-down operations the temperature will necessarily fall below the sulphuric acid or water dew points and condensation will occur.

When waste heat recovery boilers were first introduced it was considered that dew point corrosion would be the most important problem to be overcome. In recent years, however, an unforeseen corrosion problem has emerged: that of nitrate stress corrosion cracking (SCC).

## Field Experience

In the 1990's several failures caused by SCC occurred in the WHRB of combined cycle power plants in the Netherlands (KEMA 2000). The cracks were mostly found in the low temperature heat exchangers. In general, these had been fabricated from steel 35.8, a standard plain carbon steel. Most cracking occurred in bends where mechanical stresses were relatively high. Microscopic

analysis of samples revealed that intergranular corrosion had occurred and it was frequently reported that complete grains of material had become detached.



*Figure 3 A - Overview of an area where SCC occurred. Finned pipes are used to increase the surface area of the heat exchangers. 3B - Cross section of tube material reveals stress corrosion cracking.*

Because in a few cases very thick deposits of ammonium nitrate were found near the damaged areas, nitrate SCC was identified as the cause. Initially the affected tubes were replaced with alloy 15Mo3 because it was presumed that this material had a higher resistance to nitrate SCC. This assumption was based on various published papers on the better corrosion resistance of the steel 15Mo3 (Bunning et al 1990, Dahl et al 1987, Drodten et al 1991, Krautschick et al 1988). Heat treatments to reduce stress levels were also tried as a remedy. However the material 15Mo3 later also failed by nitrate SCC. See Table 2.

Because of the uncertainties surrounding the failures, the Netherlands electricity companies jointly funded a research project to investigate the causes of nitrate stress corrosion cracking.

## The possible cause of stress corrosion cracking in low alloyed steel

It was agreed that an important step would be to find the source of ammonium nitrate, as it was not a component of natural gas, the fuel used in combined cycle units in the Netherlands.

Combustion air for a gas turbine is filtered before it is used to burn the fuel and cool turbine components. However, small particles (smaller than 5 µm in diameter) such as aerosols can slip through the filter.

The major components of aerosols in the Netherlands monitored over a ten year period were reported to be: 7 µg/m<sup>3</sup> SO<sub>4</sub><sup>2-</sup>, 3 µg/m<sup>3</sup> NO<sub>3</sub><sup>-</sup>, 3 µg/m<sup>3</sup> NH<sub>4</sub><sup>+</sup> and 2 µg/m<sup>3</sup> Cl<sup>-</sup> (present as NaCl). These amounts are low. However, gas turbines use vast quantities of air and just 25 % of the oxygen intake is used to burn natural gas. This means that a considerable amount of ammonium nitrate can enter the recovery boiler.

Another source for the nitrate is transition of NO<sub>x</sub>. NO<sub>x</sub> has been formed in the gas turbine in a considerable amount. The exact mechanism for the transition of NO<sub>x</sub> into the nitrate is not known. However, Feitelberg and Correa [2000] identified CO as one of the most important promoters for the formation of NO<sub>2</sub> in the combustion turbine exhaust gas. He mentioned a NO and CO concentration in the exhaust gas of 25 ppmv and 50 ppmv respectively. At temperatures between 450 and 750 °C up to 50% of the NO can be oxidised to NO<sub>2</sub> within just one second. Since NO<sub>2</sub> is a precursor for nitrate, these compounds may very well be formed inside the recovery boiler.

The most likely nitrates to form are ammonium nitrate and sodium nitrate. Because most of the components in a recovery boiler are made of unprotected steel, iron nitrate may form as well. A summary of the physical properties of these nitrates is presented in Table 1.

Table 1: Physical properties of nitrates that may be present in a waste heat recovery boiler.

Material	Formula	Solubility in water at 0 °C (g/l)	Solubility in water at 100 °C (g/l)	Melting point (°C)	Boiling point (°C)
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	1183	8710	170	210
Iron nitrate*6H <sub>2</sub> O	Fe(NO <sub>3</sub> ) <sub>3</sub> *6H <sub>2</sub> O	150	-	35	Decomposes at 125
Iron nitrate*9H <sub>2</sub> O	Fe(NO <sub>3</sub> ) <sub>3</sub> *9H <sub>2</sub> O	soluble	Soluble	47	Decomposes at 125
Sodium nitrate	NaNO <sub>3</sub>	921 (at 25 °C)	1800	306	Decomposes at 380

From Table 1 it can be concluded that iron nitrates would not be sufficiently stable to remain in the boiler. Both sodium and ammonium nitrate are fairly stable. Ammonium nitrate is remarkable because of its relatively low melting and boiling points. Because of this, ammonium nitrate will deposit in the cooler parts of the boiler, near the flue gas outlet. Based on the physical data, sodium nitrate should be deposited nearer to the middle of the recovery boiler because of its higher melting point.

To date, only ammonium nitrate deposits have been found in the cooler parts of recovery boilers, close to the chimney stack. Under normal conditions, the flue gas will be cooled to about 80 °C. At this temperature, however, ammonium nitrate is solid and is most likely to have been deposited on the tube walls. Because ammonium nitrate can not leave the recovery boiler in a vapour state it will accumulate over time on the heat exchanger surfaces near the stack. As long as the temperature of the flue gas is well above the dew point this will not produce problems despite the fact that ammonium nitrate is slightly hygroscopic. However, if the temperature drops below the dew point, for instance during start-up, shut-down or periods of downtime, only a limited amount of water will be necessary to produce a very concentrated solution of ammonium nitrate on the heat exchangers.

SCC in carbon- and low alloy steels can occur in environments that contain carbonates, phosphates, hydroxides and nitrates (Perdieus et al 1977, Mc Evely 1990). The areas of susceptibility to SCC for several ionic species are identified in a corrosion potential/pH - or Pourbaix - Diagram (see Figure 4).

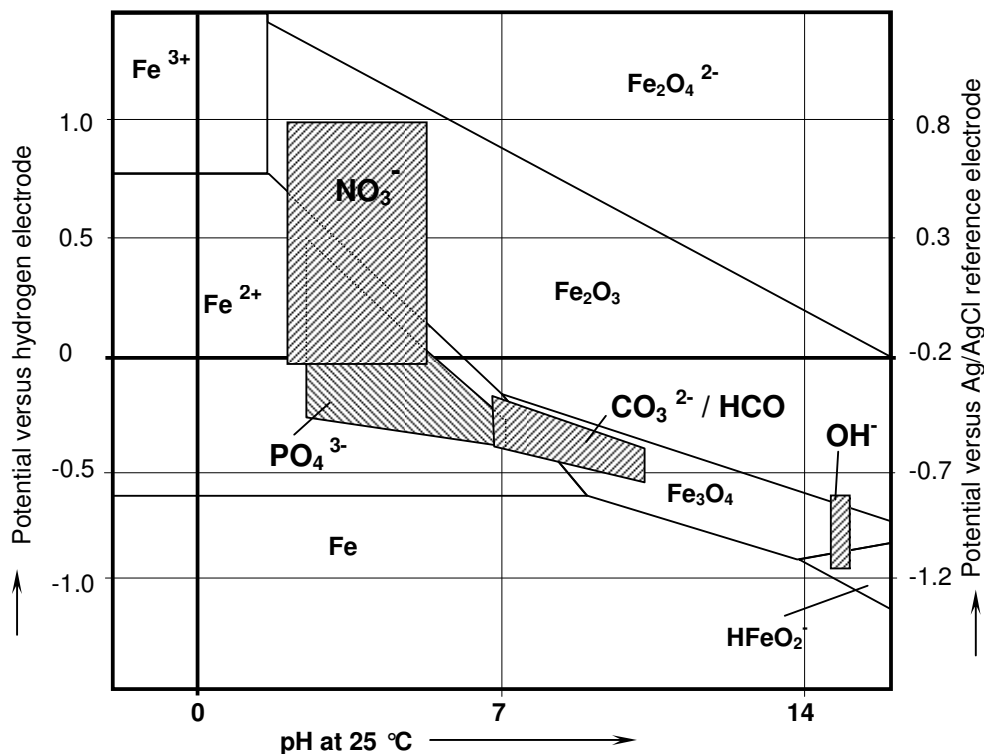


Figure 4: Pourbaix diagram of iron. Shaded areas indicate danger zones where SCC caused by nitrates, phosphates, carbonate/bicarbonate and hydroxide respectively can occur.

Due to small amounts of  $\text{SO}_3$  that are often present in flue gas, condensed moisture will be acidic. In addition, the relatively high oxygen content in the exhaust from the gas turbine (approx. 15% oxygen) means that, in general, the corrosion potential will be relatively high. Both conditions increase the likelihood of SCC in steels that are exposed to nitrates.

## Causes of Nitrate induced Stress corrosion cracking

Steel that is in contact with a more concentrated ammonium nitrate solution is attacked along the grain boundaries by intergranular corrosion. In locations where high mechanical stresses occur and/or a critical deformation rate is exceeded, IGA will lead to the development of cracks (SA-IGA). This, in turn, is called often in general SCC, which was observed in the WHRB failures.

In this investigation, the influence of the following factors on intergranular corrosion were studied:

- corrosion potential
- chemical composition of steel
- structure of the steel.

## Influence corrosion potential (related to oxygen content).

To investigate the influence of the corrosion potential, a carbon steel was exposed in a 5% ammonium nitrate solution at 50 °C at different constant potentials. At a potential of  $-400$  mV versus a Saturated

Hydrogen Electrode (SHE) the corrosion was minimal. At a potential of +100 mV SHE severe IGA occurred in the steel. Within a period of 16 hours steel was attacked to a depth of 300  $\mu\text{m}$ . The observed intergranular corrosion showed a remarkable resemblance to the microstructure found in the failures from recovery boilers.

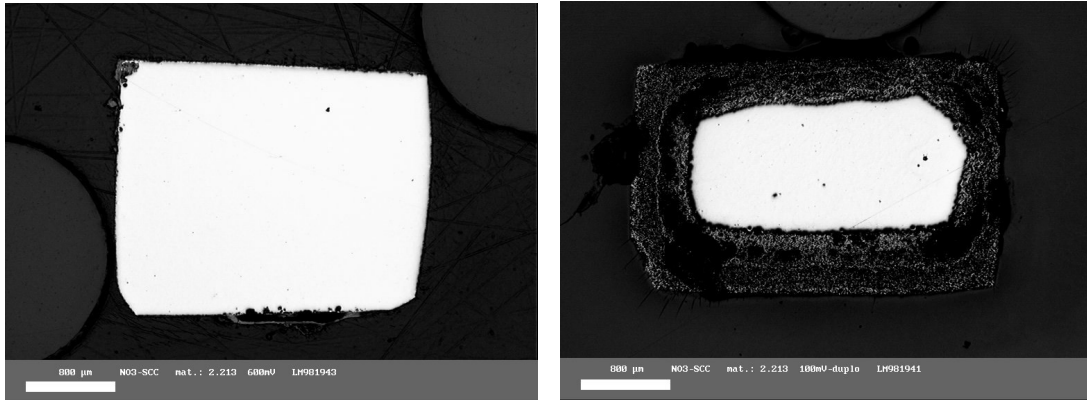


Figure 5A: Sample held at a potential of  $-400$  mV SHE in a 5%  $\text{NH}_4\text{NO}_3$  solution at  $50$  °C; just some pitting occurred.

Figure 5B: Sample in the same solution but at  $+100$  mV SHE. Intergranular corrosion consumed a large part of the sample within 16 hours.

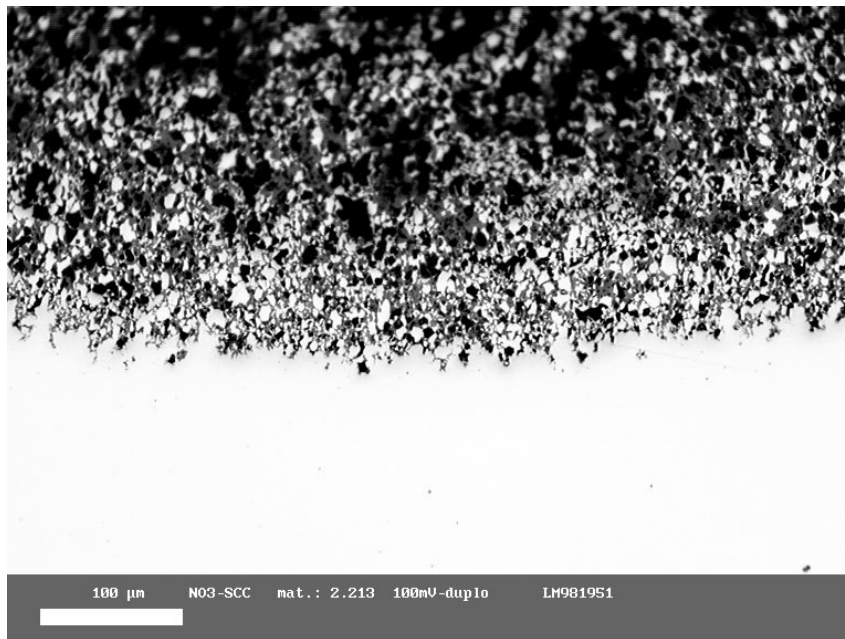


Figure 6: Detail of the corrosion front in the sample from figure 3b shows the intergranular nature of the attack.

These results indicate that IGA only occurs above a certain potential. Taking into account the relative high oxygen content in the exhaust of a gas turbine of around 15% it will be difficult to remain below the critical potential.

## Chemical composition of steel

Much research has been done on SCC; in particularly the corrosion resistances of carbon steel and 15Mo3 were compared . (Bunning et all 1990, Dahl et all 1987, Drodten et all 1991, Krautschick et all 1988).

In our investigation steels ranging from carbon steel up to 9% Cr steel were tested, with emphasis on the real chemical composition. For a total of 86 steels, with known compositions for at least 10 elements, the sensitivity to Intergranular Attack (IGA) was tested. The steels were subjected to aerated ammonium nitrate solutions of 90 °C with concentrations ranging between 2 and 35%. After an exposure of 65 hours, cross sections of the steels were studied. If IGA occurred for 3 grains deep or more, the steel was considered sensitive to ammonium nitrate at that (critical) percentage.

A correlation between the critical nitrate percentage and the chemical composition was found. For carbon steel, 15Mo3, 13CrMo4.4, 10CrMo9.10, 9 % Cr and 12 % Cr steels the regression formula was calculated to be:

$$\text{Critical nitrate \%} = 6\text{Mo} + 2\text{Cr} + 1\text{Mn} + 8 - 12\text{Si} - 8\text{Cu} - 1\text{C} \quad (R^2=0.85)$$

The correlation between measured and calculated critical nitrate percentages is given in Figure 7.

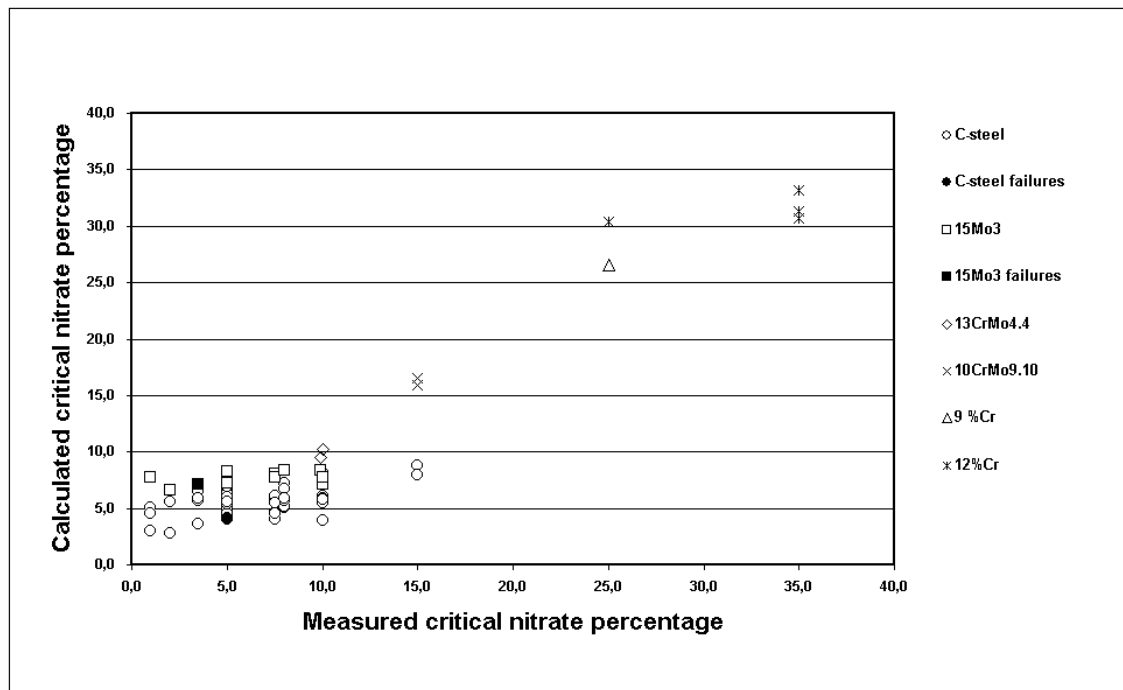


Figure 7: Correlation between measured and calculated critical nitrate concentrations for C-steels, 15Mo3, 13CrMo4.4, 10CrMo9.10, 9% Cr and 12% Cr steels.

With an  $R^2$  of 0,85 the fit of the formula is fair. However, if the carbon steels are left out a better fit can be obtained. For the steel 15Mo3, 13CrMo4.4, 10CrMo9.10, 9% Cr and 12% Cr the regression formula becomes:

$$\text{Critical nitrate \%} = 20\text{Mn} + 10\text{Mo} + 2\text{Cr} + 1\text{Si} - 5 - 35\text{C} - 7\text{Cu} \quad (R^2=0.95)$$

The correlation between measured and calculated critical nitrate percentages is given in Figure 8 for the last mentioned group of steels.

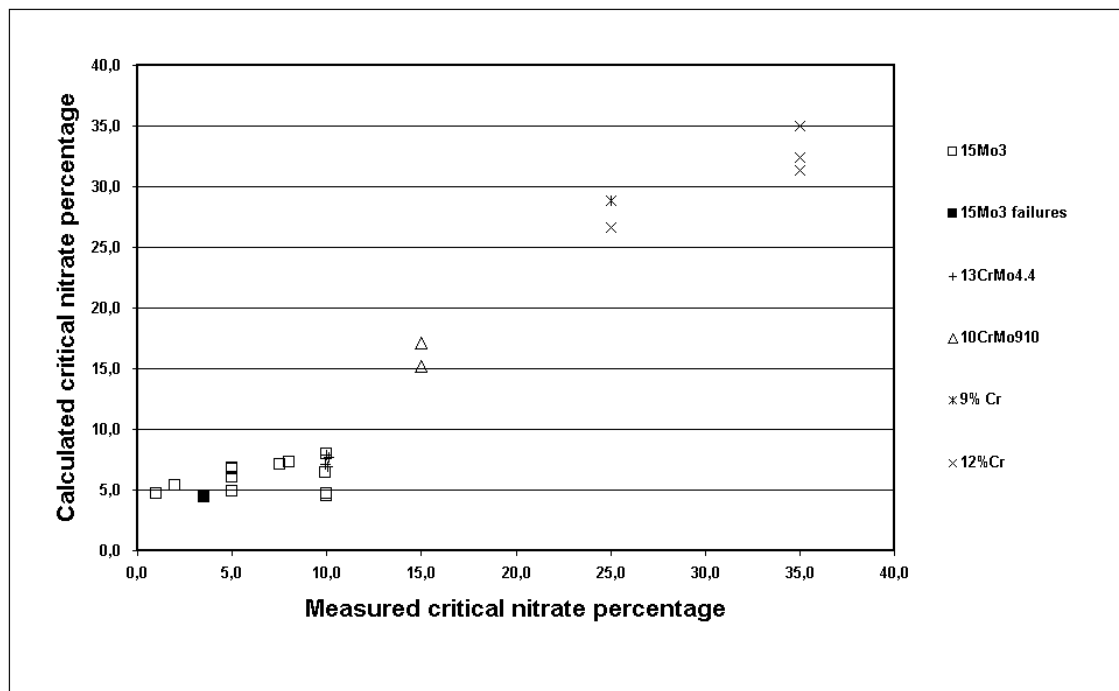


Figure 8: Correlation between measured and calculated critical nitrate concentrations for 15Mo3, 13CrMo4.4, 10CrMo9.10, 9% Cr and 12% Cr steels.

From this work it can be concluded that the elements Mo, Mn and Cr have positive effect on the resistance to nitrate induced IGA, whereas the elements C and Cu are detrimental. If Si has any effect it is uncertain. From this study it can be concluded that the resistance to nitrate induced IGA can be estimated quite reliably, based upon the chemical composition of the steel alone.

As a rule of thumb it can be stated that carbon steels and 15Mo3 have the same resistance to IGA. The steel 13CrMo44 has a slightly higher resistance than carbon steel and 15Mo3. Steel 10CrMo9.10 is obviously better than these steels.

All steels from heat exchanger failures from recovery boilers had a rather low calculated critical nitrate percentage. They all were lower than 6.5 %. These field data are summarised in Table 2 (KEMA 1995) From these field examples only the steels of cases A 1994 and B 1995 were tested, because the tests were finished in 1997.

Table 2: The calculated critical nitrate value for IGA of the materials from heat exchanger failed due to nitrate induced stress corrosion cracking.

Case	Steel	Analysis						Calculated critical nitrate	
		C	Mo	Mn	Cu	Si	Cr	Form. 1	Form. 2
A 1994	St 35.2	0,11	0,02	0,61	0,21	0,31	0,08	3,4	2,7
B 1995	15Mo3	0,17	0,25	0,67	0,14	0,22	0,08	6,4	4,4
B 1997	15Mo3	0,15	0,27	0,61	0,18	0,23	0,14	6,2	3,9
C 1997	St 35.2	0,12	0,02	0,46	0,20	0,22	0,07	4,4	-0,7
D 1997	St 35.2	0,11	0,01	0,48	0,04	0,25	0,06	5,3	1,0
D 1997	15Mo3	0,12	0,33	0,61	0,32	0,21	0,08	5,5	4,5
E 1999	St 35.2	0,08	0,01	0,49	0,14	0,15	0,07	5,8	1,5

The idea is that in practice most of the time the corrosive nitrate environment will not exceeded the concentration of about 10%. Thus, a steel with a composition similar to, or better than, 10CrMo9.10 (a calculated critical nitrate percentage of at least 10%) is advised, because this steel will resist the IGA under practical conditions..

So far no attention had been given to the contribution of the microstructure of the steel. It was expected that an even better correlation would be found if the microstructure were taken into account.

## Microstructural Effects

During the study of samples of material from the failed recovery boilers it was noticed that the steels often had considerable amounts of grain boundary carbide precipitation. Sometimes all grain boundaries were covered with carbides (carbide ribbons). The carbides were identified as ternary cementite. An example of this can be seen in Figure 9.

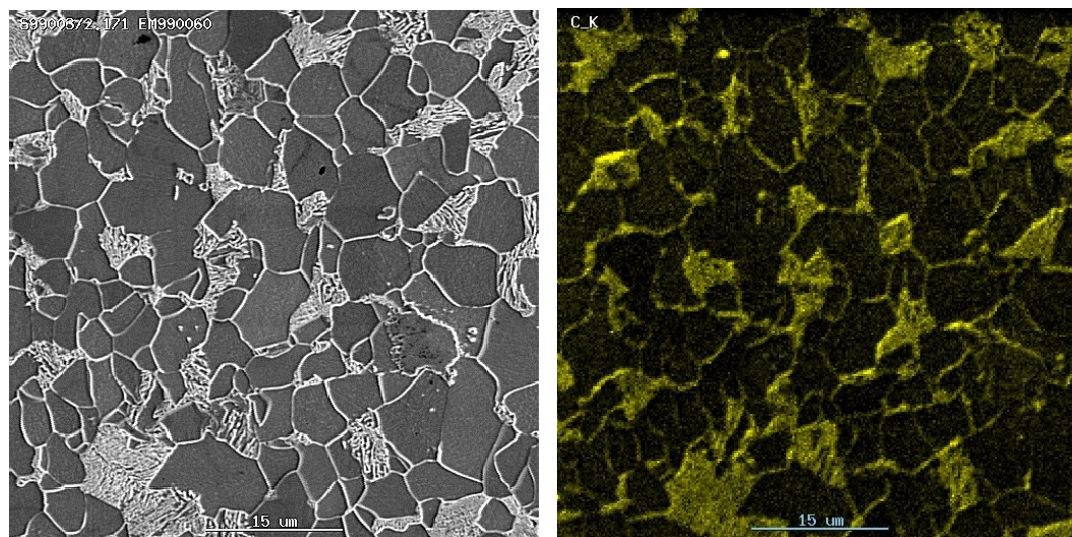


Figure 9A: SEM image of the microstructure of a 15Mo3 steel that showed nitrate induced SCC. Figure 9B: Carbon WDX mapping of the same area shows the distribution of carbon (white is carbon, black is no carbon). The pearlite islands are normal in this material. The large amount of ternary cementite that has deposited on the grain boundaries is not normal, however.

Ternary\_cementite is formed in heat treatment during cooling in the temperature range between 723 and 400°C. At 723°C up to 0.025% carbon will dissolve in ferrite. However during cooling the solubility of carbon will decrease. At these temperatures carbon can diffuse to the grain boundaries where it will precipitate as a thin layer of cementite ( $\text{Fe}_3\text{C}$ ). Pearlite (a eutectic mixture of ferrite and cementite) is partly dissolved and converted to ternary cementite on the grain boundaries. Cold work will accelerate the formation of ternary cementite even at low temperatures.

The present work on in-service material failures has shown that in addition to the corrosion potential and chemical composition of a steel, ternary carbides are also of great influence at initiating nitrate induced stress corrosion cracking. In the past, the microstructure of a material was hardly considered during design and construction of WHRB's.

As far as we know in literature only one paper has been published in which was mentioned that carbide precipitates on the grain boundaries of carbon steel had a detrimental effect on the resistance to SCC (Langenscheid 1989).

However, results from the present study indicated that microstructure also appears to have a significance influence on field service life. Further studies are planned with carbon and low alloy steels to measure the influence of ternary cementite on the sensitivity to SA-IGA and SCC.

## Conclusions

Ammonium nitrate was found in waste heat recovery boilers and is most probably formed by the combination of  $\text{NO}_x$  from the exhaust of the gas turbine with aerosols in the combustion air. Crystals of nitrate tend to deposit in the cooler regions of a WHRB.

During start-up and shut-down the metal temperatures in the boilers tend to fall below the dew point. Condensing water (with some sulphuric acid) will dissolve the precipitated ammonium nitrate, resulting in the formation of a concentrated nitrate solution on the steel surface.

Carbon steel and low alloy steel are sensitive to IGA in ammonium nitrate solutions if the nitrate concentration is above a critical composition, and the corrosion potential of the material in the environment is more anodic than a critical potential.

The critical concentration for nitrate induced IGA can be calculated from the chemical composition. The elements Mn, Mo and Cr have a positive effect on the corrosion resistance while Cu and C have a negative effect.

Ternary cementite precipitated as a continuous ribbon on the grain boundaries of carbon and low alloy steels will increase the sensitivity to nitrate induced IGA.

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