

LATEST ADVANCES IN THE UNDERSTANDING OF ACID DEWPOINT CORROSION: CORROSION AND STRESS CORROSION CRACKING IN COMBUSTION GAS CONDENSATES

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SUMMARY

Corrosion failures very often occur because of condensing flue gasses containing H₂O, SO₃, NO_x and HCl. The corrosion failures can be of the type: general corrosion, pitting and stress corrosion cracking. The chemistry of the condensing gasses is discussed and some examples of corrosion in Blast Stoves, Heat Recovery Steam Generators and waste incineration boilers are described. Mounting of the insulation inside the casing is a main cause for stress corrosion cracking. Nitric acid can react with carbon steel and insulation material forming ammonium nitrate and calcium nitrate, both very hygroscopic materials and very corrosive for Stress Corrosion Cracking, even above the water dew point.

1 INTRODUCTION

In the recent years many corrosion problems arose from condensing gasses. When there is a risk of condensation the designer should have the answers on the following questions:

- Which condensed liquid can be formed (the dewpoints of the various gasses should be calculated)?
- Which amount of condensed liquid can be expected?
- What concentration of corrosive liquid can be expected?
- What is the corrosion resistance of the material in the to be expected environment?

The method of calculation dew points, description and calculation of condensation phenomena and the concentrations of the condense have been published rather well (Handbook of Chemistry and Physics¹, Yen Hsiung Kiang², Land³, Hoftyzer⁴ and Ullman⁵).

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In particularly stress corrosion cracking failures on carbon steels is a common mechanism in condensing nitrate gasses. Much research on general aspects of stress corrosion cracking has been done (McEvily⁶, Dahl⁷, Drodten⁸, Krautschick⁹, Mazille¹⁰, Bunning¹¹, Bohnenkamp¹², Krautschick¹³). More specific problems on stress corrosion cracking in blast stoves and in Heat Recovery Steam Generators has been studied since 1967 (Blekkenhorst¹⁴, Harp^{15,16}, Ullman¹⁷, Kalfa¹⁸, Sucker¹⁹, Buhler²⁰ and Leferink²¹).

The chemistry of condensation will be explained, after which the specific problems in blast stoves of blast furnaces and in Heat Recovery Steam Generators (HRSG's) will be discussed. At last a specific problem of a corrosion problem in HCl containing flue gas in a waste incineration unit will be discussed (de Weijer²²).

2 DEW POINTS OF H₂O, NO₂ AND SO₃

Based on data from literature, the dew points of various gas compositions can be calculated and plotted. The dew point is the temperature at which the first liquid starts to condense from the gas phase. The water dew point can be plotted from the water vapour pressures tables¹.

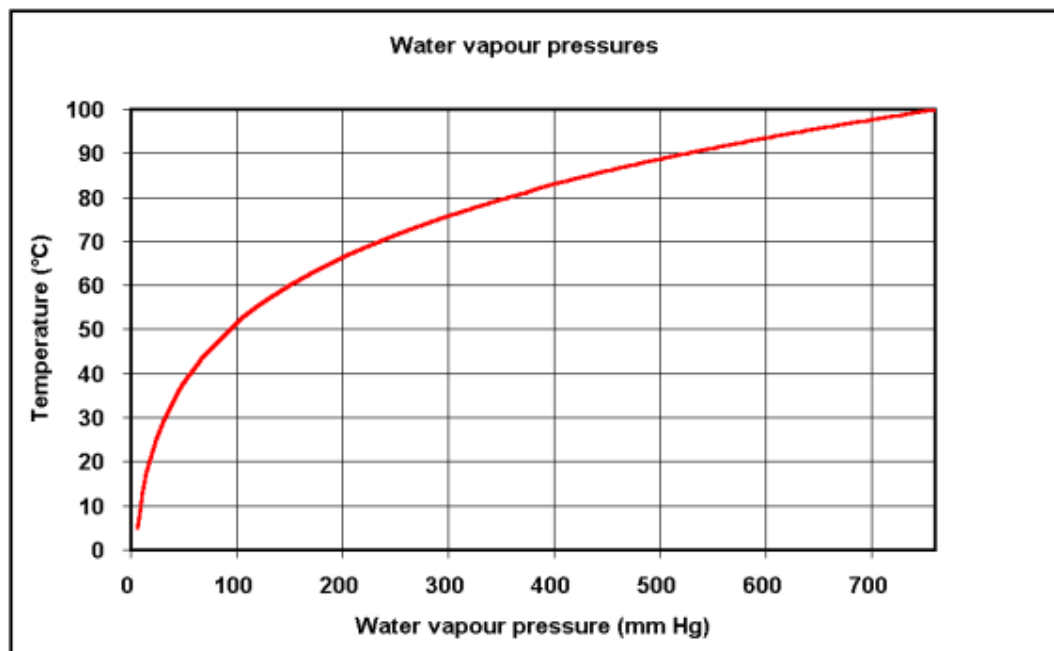


Figure 1. The water vapour pressures from the water vapour table. A gas with 6.5 v% H₂O has a vapour pressure of 49.7 mm Hg (100 v% water has a vapour pressure of 758 mm Hg) and a dewpoint of 38 °C.

Dewpoints (°C) of the gasses SO₃, SO₂, HCl and NO₂ can be calculated by means of the equations of Verhoff, Perry and Kiang².

A: Dewpoint equation of SO₃ according to Verhoff:

$$(1/T)=0.002276 - 0.00002943(P_{H_2O}) - 0.0000858\ln(p \ln PH_2SO_4) + 0.00000620(\ln PH_2SO_4)(\ln P_{H_2O})$$

B: Dewpoint equation of SO₂ according to Kiang:

$$T_d=1000/\{3.9526 - 0.1863*\ln(P_{H_2O}) + 0.000867*\ln(P_{SO_2}) - 0.00091*\ln(P_{H_2O})*\ln(P_{SO_2})\}-273$$

C: Dewpoint equation of HCl according to Kiang:

$$T_d=1000/\{3.7368 - 0.1591*\ln(P_{H_2O}) - 0.0326*\ln(P_{HCl}) + 0.00269*\ln(P_{H_2O})*\ln(P_{HCl})\}-273$$

D: Dewpoint equation of NO₂ according to Perry:

$$T_{d \text{ NO}_2} = 1000/(3.664 - 0.1446*\ln(v\%H_2O/100*760) - 0.0827*\ln(vppmNO_2/1000000*760) + 0.00756*\ln(v\%H_2O/100*760)*\ln(vppmNO_2/1000000*760)) - 273$$

Pressures (P) in the equations A, B, C en D are given in mm Hg.

The Figures 2 up to 5 give the dew points of the gasses SO₃, SO₂, HCl and NO₂. When the calculated dewpoints are lower than the water dew point a straight water dew point line is given (for HCl and NO₂).

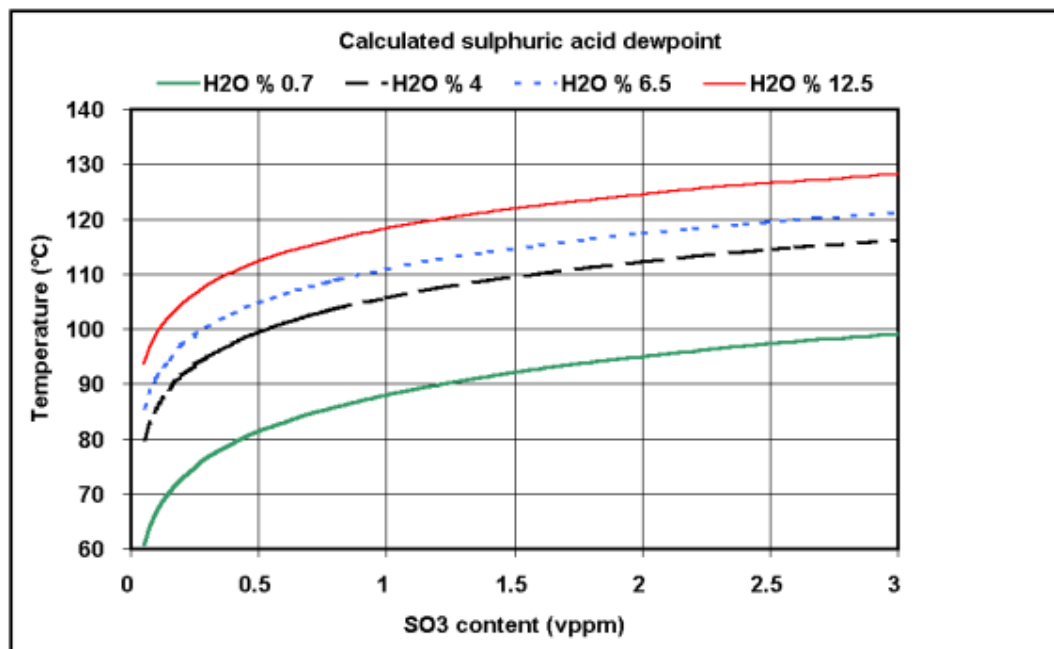


Figure 2. Dew points of SO_3 at various water contents of the gas, calculated from the formula of Verhoff.

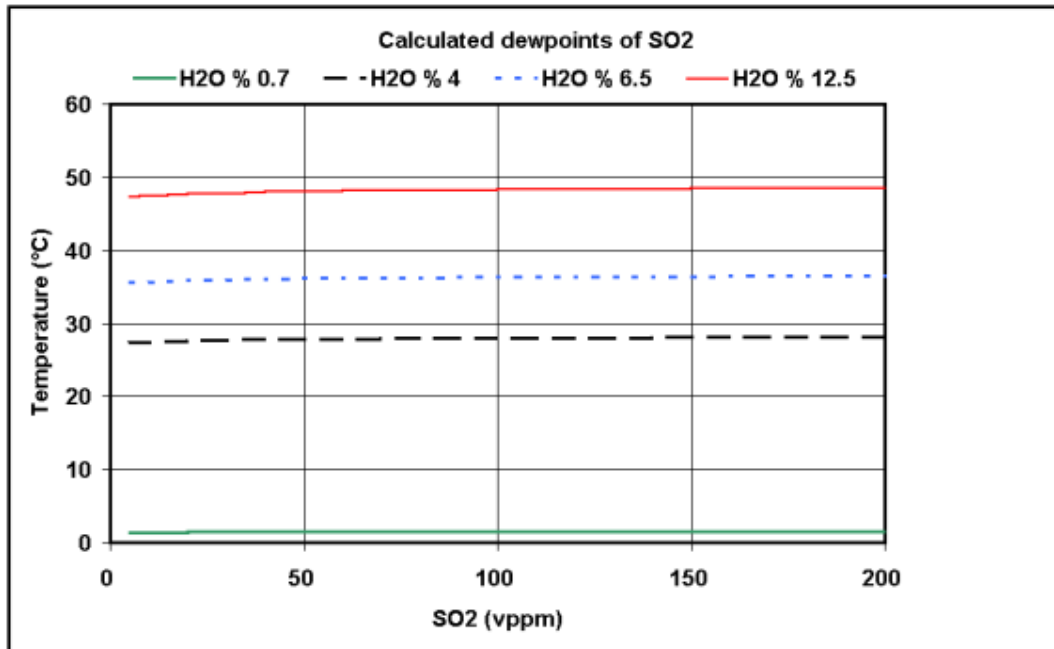


Figure 3. Dew points of SO_2 at various water contents of the gas, calculated from the formula of Kiang. The SO_2 dew points for all gasses are lower than the water dew point of the gasses.

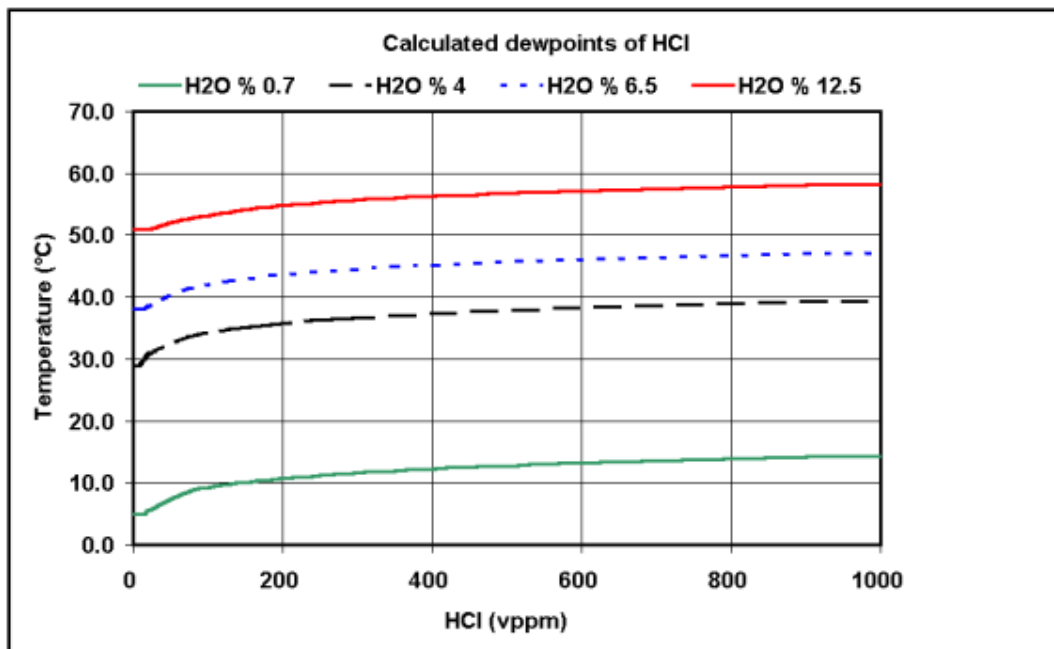


Figure 4. Dew points of HCl at various water contents of the gas, calculated from the formula of Kiang and the water vapour table.

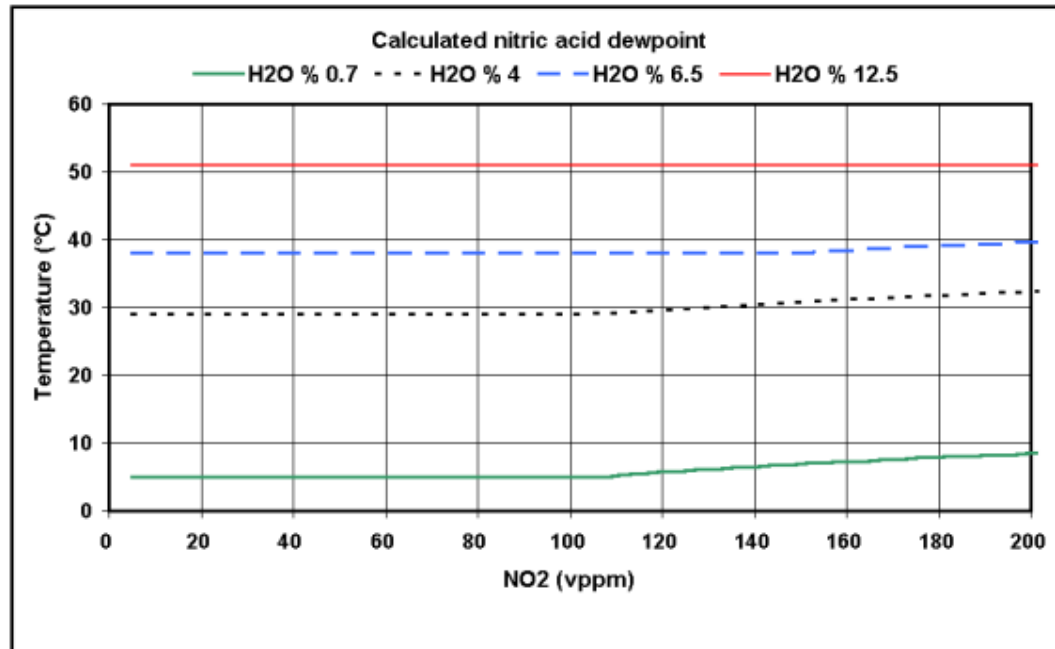


Figure 5. Dew points of NO₂ at various water contents of the gas, calculated from the formula of Perry and the water vapour table.

3 AMOUNT OF CONDENSED ACID

When the temperature drops below the dew point, sulphuric acid, hydro nitric acid and water start to condense either as small fog droplets or as a film onto the walls (Land³). Condensation droplets will be formed very easily on particles in the flue gas, acting as condensation nuclei. For instance fly ash particles (coal fired boilers, waste incineration boilers) can cause the mist condensation. On the other hand in a rather clean gas, as in gas fired units, super-saturation will take place, resulting in film condensation on the cool walls or heat exchanger tubes.

If a mist is formed, most of the droplets are carried away with the flue gas and, in case of acid droplets, the corrosion rate of steel will be low. However, in the case of super-saturation, film condensation will occur and a liquid film will be formed on the bundle tubes or on the flue gas line walls. Besides, in the case of mist condensation, high gas velocities or local high flow disturbances will push the droplets onto the metal walls and a thin liquid film is formed as well by this mechanism

Acid deposition can be quite high under certain conditions. To get some idea of the deposition rates to be expected Land³ produced Figure 6. The calculation method of Land was based on heat transfer

and mass flow equations. It would go to far to describe the method in detail, see for the mathematics the paper of Land³.

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. See Figure 6. As Land³ mentioned in the text under Figure 6: "In practice we may expect to find curves lying anywhere between the two extremes".

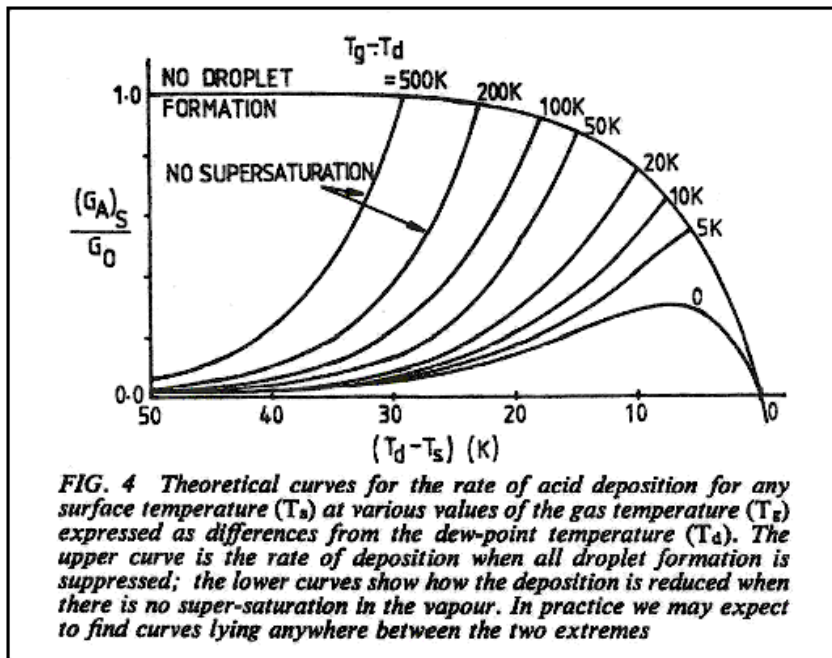


Figure 6 Theoretical curves for the rate of acid deposition according to the calculations of Land³.

Following the calculation method of Land, the sulphuric and nitric acid deposition rate for the gas conditions in table 1 have been calculated. The results of these calculations are given in Figures 7 and 8. Because there are some uncertainties in the exact figures for heat transfer coefficients of sulphuric and nitric acid, the results should be considered more an estimation than an exact figure. Land compared his calculations on sulphuric acid with experimental measurements and the results were very satisfactory. See the paper of Land³.

Table 1. Conditions assumed for the calculation of acid deposition:
gas flow 4 m/s, tube diameter: 4 m, gas temperature 130 °C.

	Gas A	Gas B
SO ₃ (vppm)	0.15	
NO ₂ (vppm)		200
H ₂ O (v%)	6.5	6.5

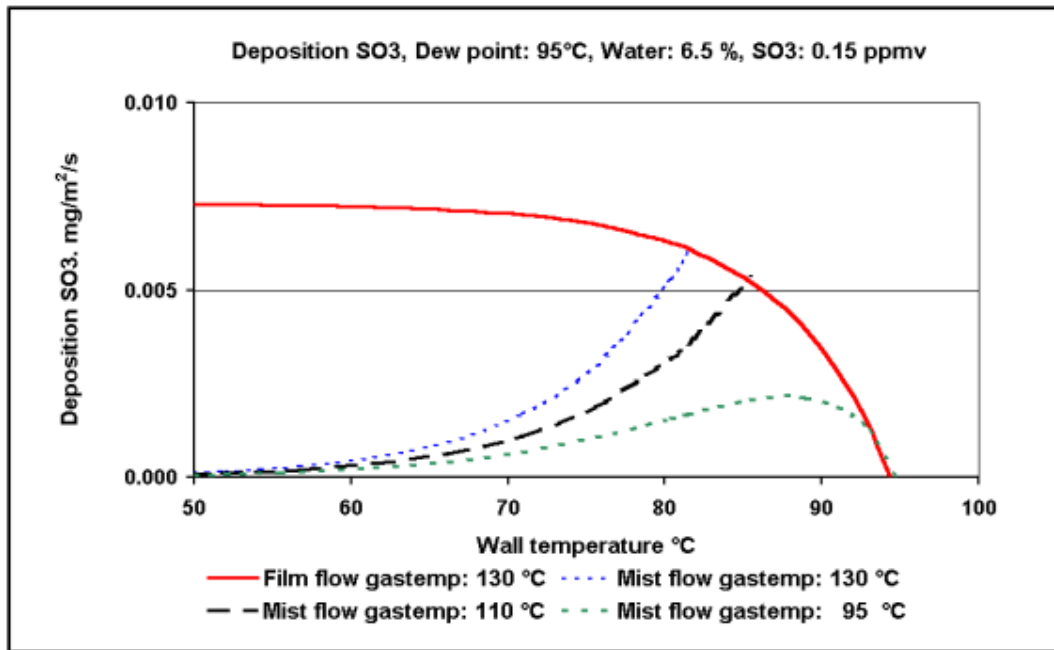


Figure 7 Acid deposition rates in case of sulphuric acid condensation of gas A.

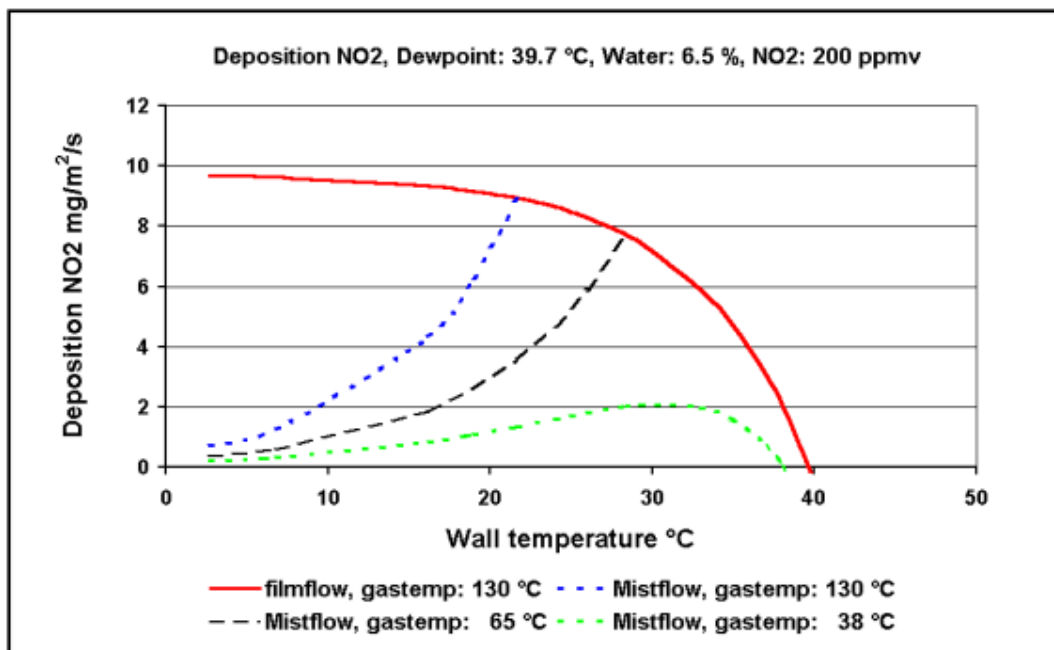


Figure 8 Acid deposition rates in case of nitric acid condensation of gas B.

The calculated deposition rate of sulphuric and nitric acid for both gasses A and B are 0.0073 and 9.7 mg/m²/s respectively in case of film flow. At a lower NO₂ content, e.g. 20 vppm NO₂ the deposition rate of nitric acid is proportionally lower at a level of maximum 0.97 mg/m²/s in case of film flow. However, at a temperature near the dew point of 38 °C the deposition rate is minimal.

4 CONCENTRATION OF THE FIRST CONDENSED LIQUID

The concentration of the sulphuric acid can be concluded from the boiling lines in the phase diagram of SO₃-H₂O. See figure 9.

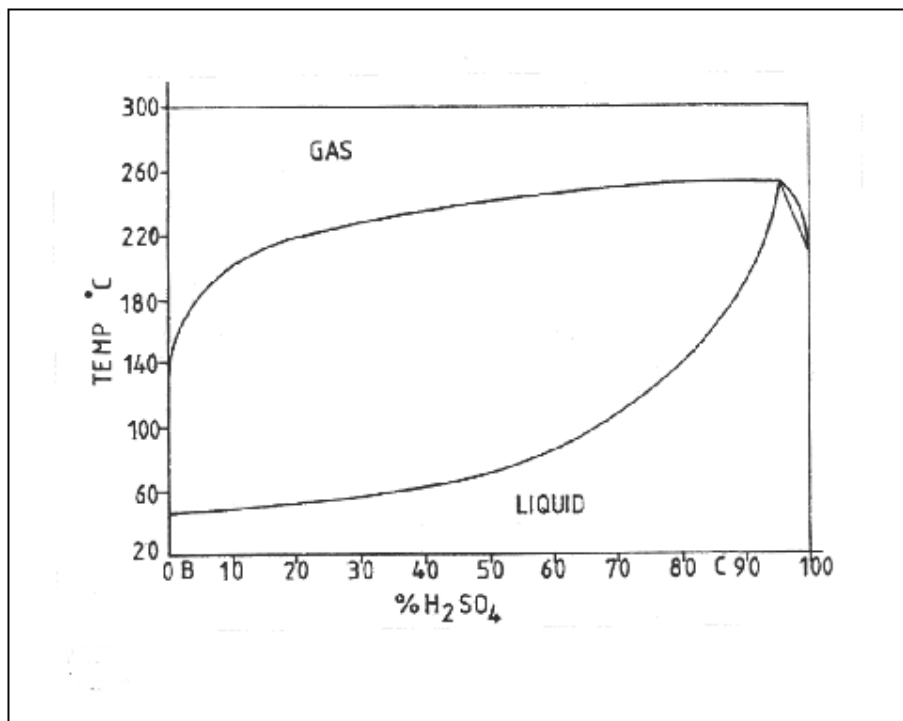


Figure 9. Phase diagram of sulphuric acid Land³ ($P_{H_2O} + P_{H_2SO_4} = 0.1 \text{ atm}$)

At a dew point of 95 °C the condensed sulphuric acid has a concentration of 67%. At lower temperatures the concentration decreases according to the boiling line. So at 60 °C the concentration is still 43%, a very corrosive liquid that will result in uniform corrosion of carbon steel.

It is more complicated to determine the concentration of the condensed nitric acid. Therefore the equilibrium vapour pressure diagram of Hoftyzer⁴ can be used. See Figure 10. The gas pressures are given in mm Hg. A pressure of 1 mm Hg pressure is equal to 1316 vppm or 0.13 v%.

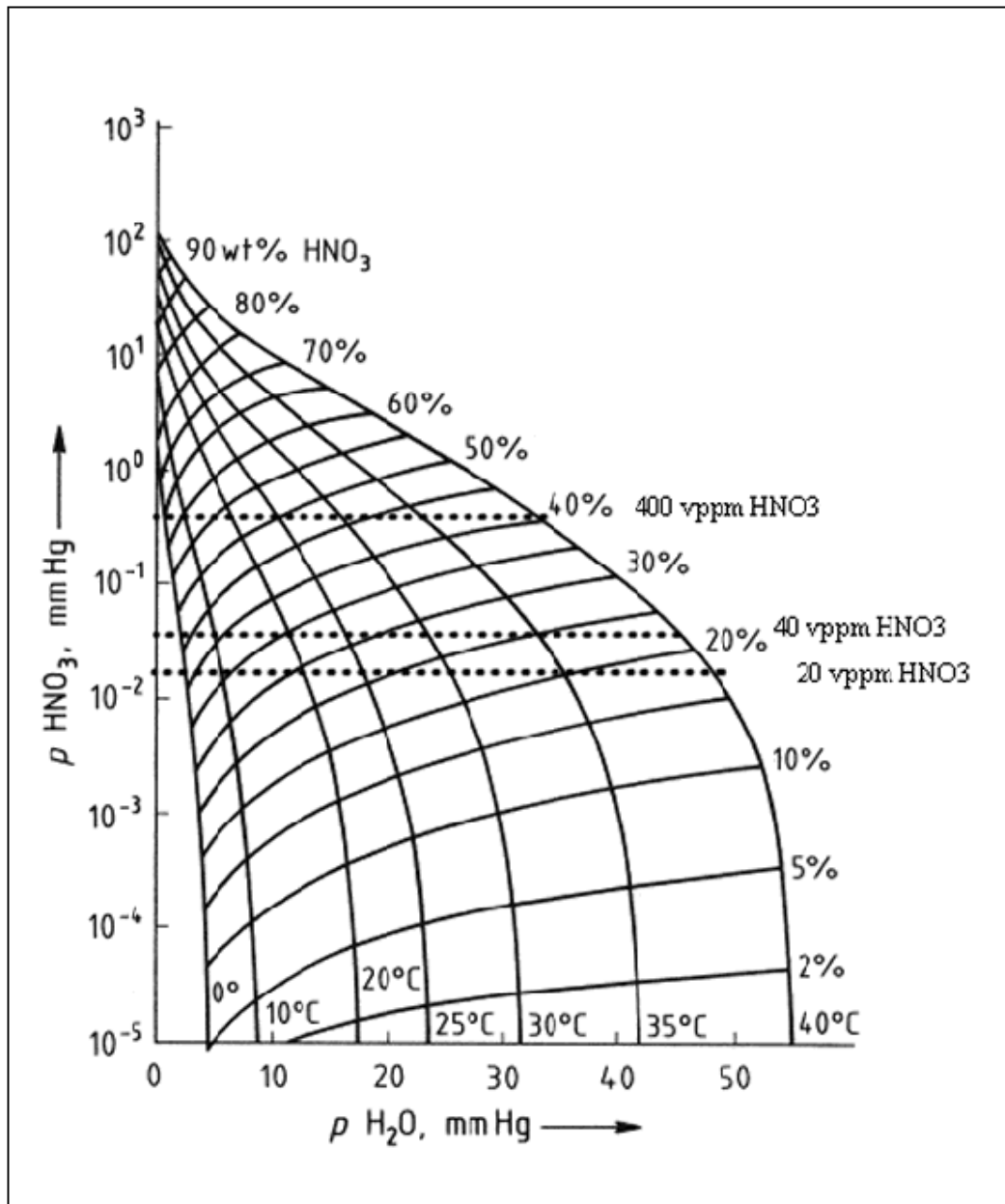
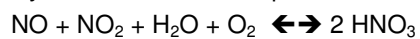


Figure 10. Vapour pressures of nitric acid and water as a function of acid strength and temperature.

Hydro nitric acid is in equilibrium with NO and NO_2 according to the formula:



When 200 vppm NO₂ and 200 vppm NO are present, the reaction will result in 400 vppm (0.305 mm Hg) HNO₃. The water dew point and the NO₂ dew point of the gas are 38 and 40 °C respectively. In the range of 10 to 200 vppm NO₂ (0.015 and 0.305 mm Hg HNO₃ vapour pressure), the concentration of the condensed HNO₃ will be in the range of 17 to 40%. These figures can be derived from Figure 10 by following the 40 °C line until the mentioned HNO₃ vapour pressures.

The nitric acid concentration in the liquid will be high, even at low NO₂ concentrations (17 up to 40 wt %). Such concentrations result in very acidic conditions with pH values of -0.4 and -0.8 respectively. However, at low NO₂ contents (as usual in modern Heat Recovery Steam Generators) the deposition rate will be rather low. For a gas with 10 vppm NO₂ the deposition rate of 17% nitric acid will be 0.45 mg/m²/s. At a temperature of 38 °C (near the dew point) the deposition rate will be minimal. See Figure 8.

5 BLAST STOVES

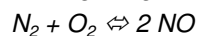
The burning air for a blast furnace in the steel making industry is preheated in a blast stove. The stove is filled with bricks that are heated with the natural gas burners. The air for the blast furnace is preheated by leading the air over the hot bricks.

The outer diameter and the height of the newest stove of the Hoogovens in IJmuiden is 10.7 m and the height is 46.4 mm (Blekkenhorst¹⁴). The maximum dome temperature is 1550 °C. Particularly at such high temperatures NO_x is formed. In older blast stoves where the dome temperature was below 1340 °C NO_x was not formed and stress corrosion cracking did not occur (Bohnenkamp¹²). In 1977 the first stress corrosion cracking was noticed in the stoves in Hoogovens IJmuiden.

There was no insulation on the outside of the stove shells. From the operation of blast stoves it has been observed that nitrate stress corrosion cracking is a well-known cause of failure (Blekkenhorst¹⁴, Harp^{15, 16}, Kalfa¹⁸, Sucker¹⁹ and Buhler²⁰). The blast stoves are insulated on the inside of the casings by means of a brick stone insulation. The first failures in the blast stoves from nitrate stress corrosion cracking were noticed in 1965 (Buhler²⁰). Initially the cause of the cracking was ascribed to formation of nitric acid because of the high amounts of NO₂ in the gas.

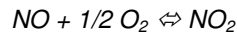
Blekkenhorst¹⁴ describes the corrosion process in the stoves as follows:

"During firing of the stove the NO concentration increases because of the endotherm reaction:



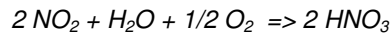
Pressurising the stove at the beginning of the blast period causes diffusion of NO to the steel shell and insulation. During the blasting period the NO concentration is decreased by oxidation to NO₂, diffusing back into the combustion chamber, blowing out etc.

At the start of the blast period, the NO₂ concentration is increased because of the higher NO concentration and the build-up of pressure as can be seen from the following reaction:



Below 650 °C the rate of NO₂-formation is significantly. The formation of NO₂ is fastest in the coldest area of the stove e.g. on the steel shell.

During the blast period the temperature of the steel shell will easily fall below the water dewpoint and NO₂ will dissolve in the water:



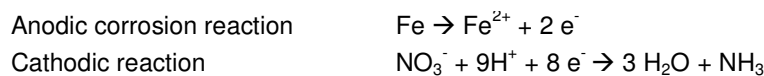
According to Blekkenhorst the reaction of the nitric acid and the dissolution of various compounds of the insulation material into the condense, yield a nitrate solution causing SCC of the stove shell."

Though Blekkenhorst mentioned that reaction products of the nitric acid can be responsible for the nitrate solution that causes SCC, he does not mention which cations are present. Because of the presence of a brick line in the stove calcium nitrate could be one of the products.

The experiences in hot blast stoves is that the NO₂ content in the gas is about 80 vppm (Harp^{15, 16}, Blekkenhorst¹⁴) The measured nitrate concentrations in condense could range from 1 up to 100 g/L. In the insulation layer near the shell much nitrate 4.5 g/kg) and less sulphate (0.6 gr/kg) and chloride (0.1 gr/kg) were found. Near the gas side the amounts of nitrate, sulphate and chloride were respectively 0.7-5.6-0.1 gr/kg (Buhler²⁰).

In literature references the composition of the blast stove environment regarding SO₂, SO₃ and H₂O gasses was not mentioned. The dew point in all relevant references is 67 °C. Because in the deposits sulphates are found it is reasonable to assume that sulphuric acid will condense in the insulation near the gas side at first. Afterwards the NO₂ will condense as nitric acid below the nitric acid dew point or it will dissolve in the condensed water below the water dew point.

Harp¹⁵ analysed the condensed liquid and the deposits at the stove shell. In the condensed liquid they found ammonium and nitrate ions, though the gas did not contain ammonium. They came to the conclusion that the ammonium would have been formed when steel is corroded in the concentrated nitric acid environment. Ammonium is formed from the reduction of nitrate according to the following reactions:



To prove this hypothesis Harp did laboratory experiments in which he exposed steel samples in wet NO and NO₂ containing gas at temperatures above the dew point value of the gas. See Figure 11. The gas atmospheres contained 75 vppm NO and 25vppm NO₂ and by adding water dew points of 30, 45 and 60 °C were fixed. He exposed steel carbon samples at temperatures of 64, 80 and 125 °C during one week. It appeared that in the gas with the dew points of 45 and 60 °C ammonium nitrate deposits were formed on the specimens at an exposing temperature of 64 °C and no deposit formation occurred at 80 and 125 °. The cause of the deposit formation above the water dew point of the gas can be explained from the hygroscopic properties of ammonium nitrate.

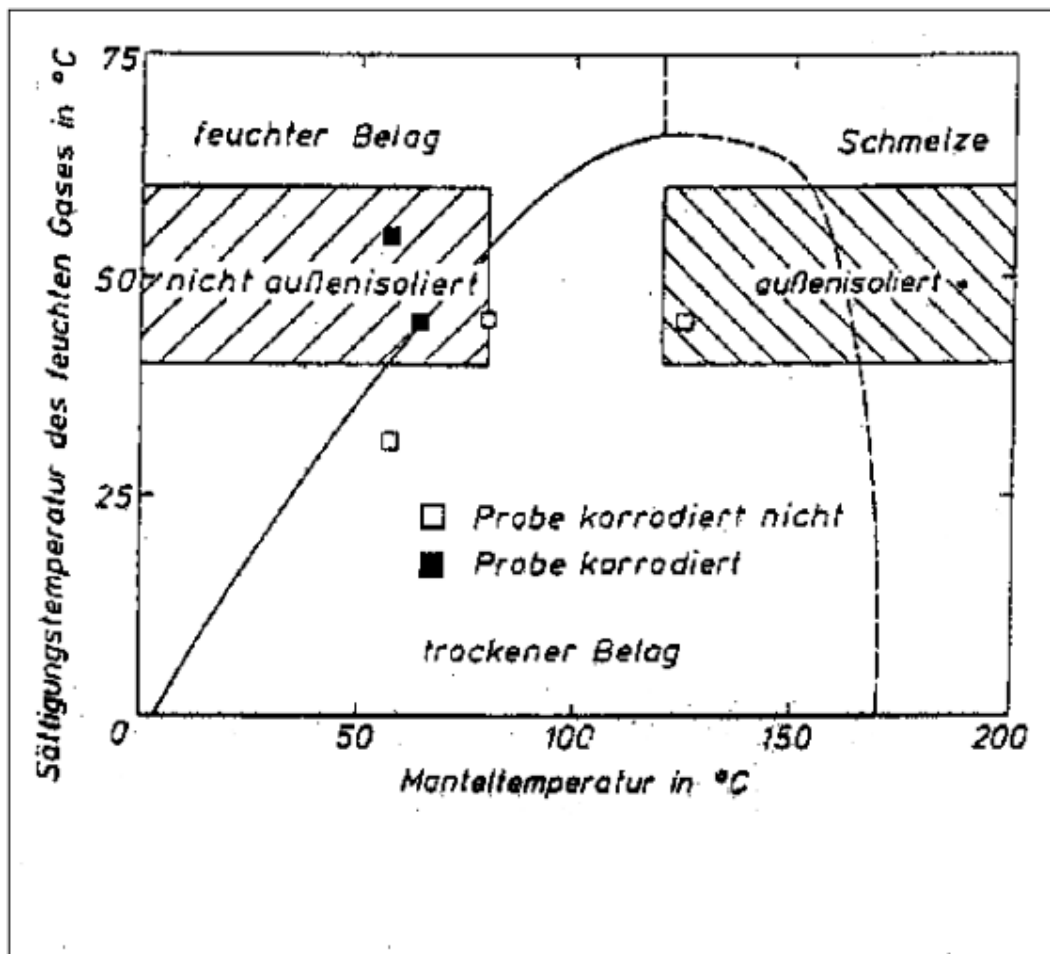


Figure 11. The thermodynamic conditions for the formation of ammonium nitrate containing liquid (Harp¹⁵).

When the shell is warmed above the water dew point the ammonium nitrate will still contain water, because it acts as a rather hygroscopic deposit. In the dry condition ammonium nitrate is not corrosive, but below 160°C it starts to absorb water and high concentrated nitrate liquid films can be formed. Figure 12 shows the solubility at increasing temperature (Ullmann¹³). According to Harp¹⁵ the water content above 120°C is too little (less than 5%) to be a danger for stress corrosion cracking. Therefore, Harp drew the ammonium nitrate saturation line in Figure 11 as a dotted line above 120°C.

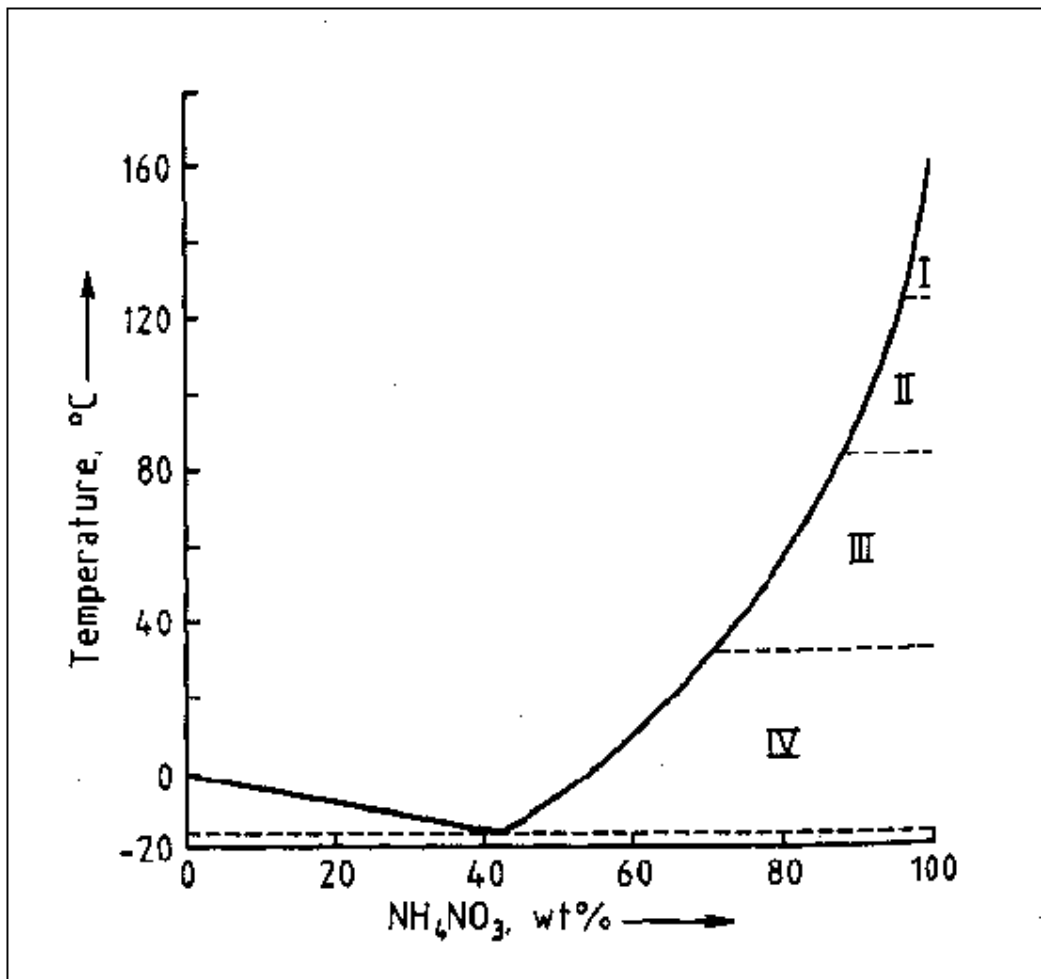


Figure 12. The solubility of ammonium nitrate in water (weight% on x-axis) versus the temperature (°C). Ammonium nitrate has 5 modifications: I: cubic, II tetragonal: III: orthorhombic, IV: orthorhombic and V tetragonal. Very concentrated ammonium nitrate solutions can be formed well above the boiling point of water.

Because the stoves are filled with bricks and there is a cemented brick lining at the shell, presence of calcium nitrate can not be excluded. Calcium nitrate has hygroscopic properties similar to those of ammonium nitrate. However contrary to ammonium nitrate it will prefer to absorb specific quantities of water per molecule Ca(NO₃)₂. See Figure 13 (Uhlman¹⁷).

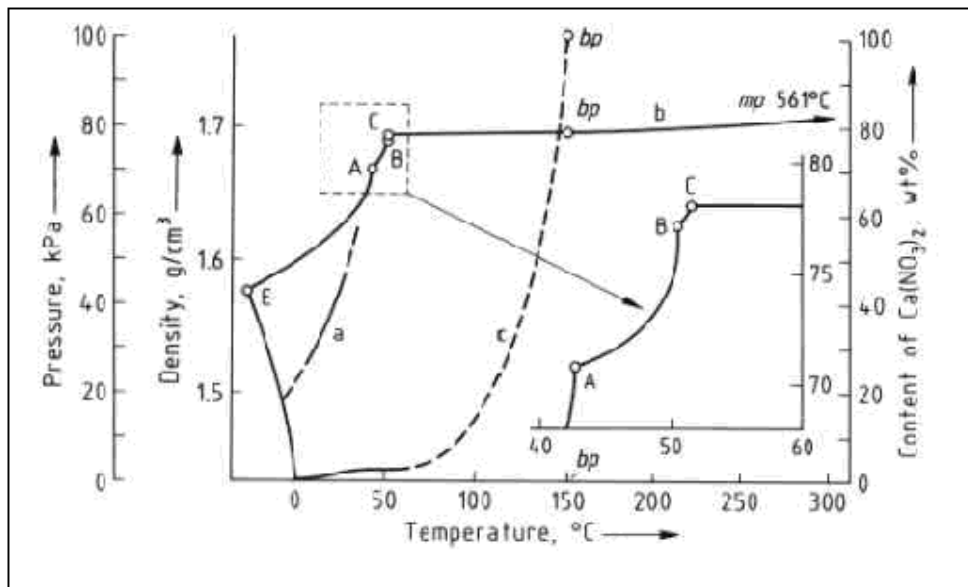


Figure 13 Properties of a saturated solution of calcium nitrate in water (see Table 6 for explanations). The lines a, b and c give density (a), content of calcium nitrate (b) and vapour pressure (c).

Data for the system $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$ (see also Fig. (11))					
Transition point and temperature, °C	Content of $\text{Ca}(\text{NO}_3)_2$, wt%	Range	Stable hydrate formula	m_p , °C	
E*	28.7	42.9			
		E-A	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	42.7	
A	+42.6	70.8			
		A-B	$\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	51.1	
B	+50.6	77.2			
		B-C	$\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$		
C	+51.6	78.1			
		above C	$\text{Ca}(\text{NO}_3)_2$	561	
b_p^{**}	+151	79.0			
Water vapour pressure over saturated solution with solid $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$					
Temperature, °C	0	10	20	30	40
Pressure, kPa	0.36	0.69	1.25	1.99	2.63
*E=cryohydric point. **Boiling point (101.3 kPa) of the saturated solution.					

Figure 14. Data for the system $\text{Ca}(\text{NO}_3)_2\text{-H}_2\text{O}$. See also Figure 13. The nitrates $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2$ are stable in the temperature ranges -28.7 up to 42.6 °C, 42.6 up to 50.6 °C, 50.6 up to 51.6 °C and 51.6 up to 151 °C as given in Figure 13.

The solubility of calcium nitrate is very high, see table 4.

Table 4. Solubility of calcium nitrates.

Temperature	Solubility (kg/L)	
	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	$\text{Ca}(\text{NO}_3)_2$
0 °C	2.66	
18 °C		1.21
30 °C	6.60	
100 °C		3.76

Regarding stress corrosion cracking, it is known that it is not really important which type of nitrate is present. Nitrate SCC was found in calcium nitrate, ammonium nitrate, potassium nitrate, sodium nitrate, lithium nitrate and nitric acid (ASM Handbook 1986).

6 HEAT RECOVERY STEAM GENERATORS (HRSG)

In the 1990's several HRSG's of combined cycle power plants in the Netherlands, had tube failures caused by nitrate SCC. The cracks were mostly found in the low temperature heat exchangers (70 up to 90 °C). In general, these had been fabricated from steel 35.8, a standard low carbon steel. Most cracking occurred in bends and finned tubes 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.

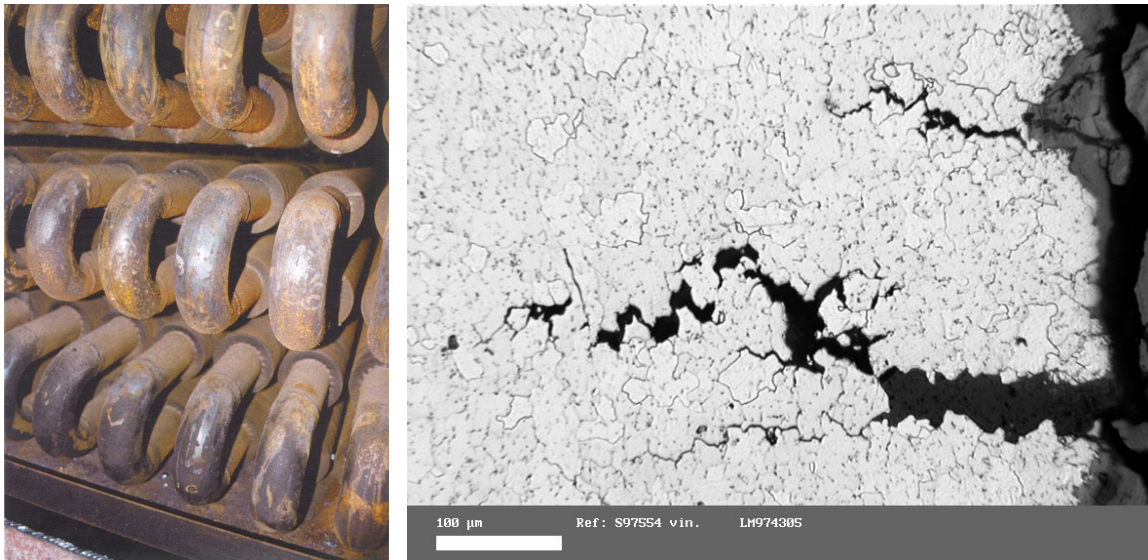


Figure 15. Overview of an area where SCC occurred. Finned pipes are used to increase the surface area of the heat exchangers. Photo right: cross section of tube material reveals stress corrosion cracking.

An average gas composition of an HRSG gas around 1990 was as follows: 18 v% CO, 50 vppm NO₂, 6.5 v% H₂O and 75v% N₂.

Generally, a small amount of sulphur containing odourant (tetra hydro thiofeen) is added in natural gas for safety reasons. Besides some sulphur containing components will be present in the firing air. This will cause a small content of SO₃ in the flue gas of at least 0.15 vppm. From Figure 2 it can be concluded that the dew point for a 6.5 % water containing gas will be 95 °C.

Thus, small amounts of sulphuric acid can condense in the HRSG. In most installations the formation of sulphuric acid is prevented by keeping the temperature above the sulphuric acid dew point as well as possible. However during start-up and shut-down operations the temperature will inevitably fall below the sulphuric acid or water dew points and condensation will occur. Thus, small uniform corrosion by the sulphuric acid can not always be avoided. However, in the case of high NO_x content

in the gas, nitric acid and concentrated ammonium nitrate liquid films will be formed. These nitrates will cause very severe stress corrosion cracking.

In the deposits sulphates and nitrates were analysed. The large amount of sulphate in the deposits was explained by the presence of sulphur salts in the intake air. In the air filter these salts are filtered from the air. However during days with fog these salts will be dissolved and sucked up into the air entering the gas turbine.

Because of the presence of sulphates and nitrates it was concluded that sulphuric acid as well as nitric acid were condensed, causing nitrate SCC.

Changing the material from St 35.8 into 15Mo3 did not give any improvement. Neither annealing of the St 35.8 and 15Mo3 bends, though some publications suggested that this material and treatment should result in a better resistance to nitrate SCC (Bunning¹¹, Dahl⁷, Drodten⁸ and Krautschick⁹).

To prevent SCC initially the following countermeasures were taken:

- The inlet water temperature was increased to 90 °C
- New type of co-firing burners were installed that resulted in a lower NO₂ (< 20 vppm). After installation of these burners the inlet water temperature was decreased again to 70 °C.

In a gas, containing 50 vppm NO₂ and 6.5 % water (a typical high NO₂ containing GT gas) the NO₂ dew point (32.7°C) is lower than the water dew point (38 °C). During operation of the HRSG the inlet temperature is at least 70°C, which excludes water and nitric acid condensing. Only during shutdowns, nitric acid can be formed by solving of the gas in the water droplets. The concentration of the nitric acid will be about 25% (see Figure 10).

Thus the most realistic mechanism for nitrate SCC in the HRSG's in the Netherlands before 1995 is the solving of the NO₂ in the condensing sulphuric acid and aerosols. By increasing the inlet temperature above the sulphuric acid dew point formation of sulphuric-nitric acid mixtures was prevented more or less. However, presence of some sulphate will inhibit nitrate stress corrosion cracking by formation of ammonium sulphate instead of the corrosive ammonium nitrate.

In 1999 a number of new failures occurred in HRSG's (Leferink²¹). Ammonium nitrate was found in large amount in the HRSG's in the east part of the Netherlands. Combustion air for a gas turbine is filtered before it is used to burn the fuel and to cool turbine components. However, small particles (aerosols, smaller than 5 µm in diameter) can slip through the filter. The major components of aerosols in the Netherlands monitored over a ten year period were reported as being: 7 µg/m³ SO₄²⁻, 3 µg/m³ NO₃⁻, 3 µg/m³ NH₄⁺ and 2 µg/m³ Cl⁻ (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 enters the recovery boiler in some of the Dutch HRSG's (rural area in the Netherlands).

To date, ammonium nitrate deposits have been found in the cooler parts of recovery boilers, close to the stack. Under normal conditions, the flue gas will be cooled to about 80°C. Already at 170°C, however, ammonium nitrate is solid and is most likely to have been deposited on the tube walls. Because ammonium nitrate will 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 water dew point this will not produce problems despite the fact that ammonium nitrate is hygroscopic and easy soluble in water (1.183 kg/L at 0°C and 8.710 kg/L at 100°C) (see Figure 12). If the temperature drops to levels of just above the water dew point, because of too low operating temperatures or during start-up and shut-down periods, only a limited amount of water will be necessary to produce a very concentrated solution of ammonium nitrate on the heat exchangers.

At the water dew point (38°C) a liquid film containing 75% ammonium nitrate can be expected on the wall. At 60 °C the ammonium nitrate concentration of the liquid will be increased to 80% (10 Mol). In these environments intergranular corrosion of the carbon steel and low alloyed steel will occur, initiating the stress assisted intergranular corrosion or stress corrosion cracking. According to Harp¹⁴ ammonium nitrate will contain too little water at a temperature of 120°C to be corrosive for SCC in carbon steel.

In some HRSG's the insulation is mounted at the inside of the casing. The advantage is a lower metal temperature of the casing, and therefore no danger for creep of the material. The casing can be build cheaper. However, there is a temperature gradient over the insulation as shown schematically in Figure 16. The dew points of water and the gasses NO₂ and SO₃ are given. The places where the sulphuric acid, nitric acid and water are formed are pointed in the Figure for 2 situations: start-up and normal operation.

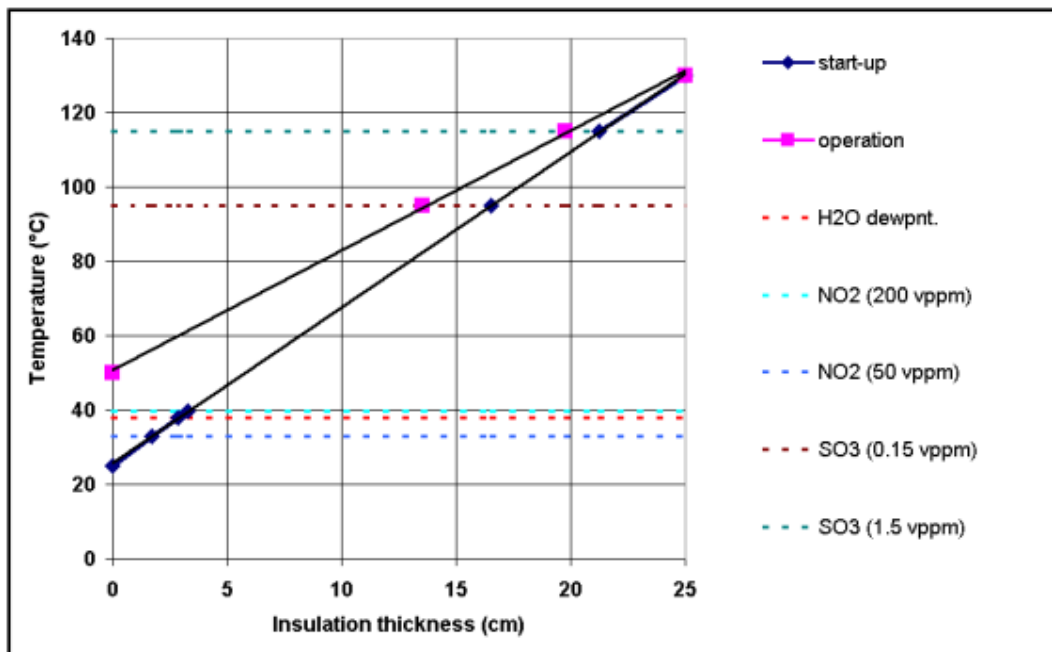


Figure 16. Schematic view of the condensation processes in the insulation for a start-up and a normal operation condition. The casing surface is on position zero, the liner is on position 25 cm. The dotted lines refer to the dew points of the various gasses.

In the start-up situation the temperature at the casing will be below the water dew point. At NO_2 contents smaller than 150 vppm NO_2 and NO will dissolve in water, forming nitric acid. At very high NO_2 contents nitric acid will start to form above the water dew point in the insulation at a depth from the casing of about 3 cm. The SO_3 present in the gas will start condensing as sulphuric acid at a depth of 16.3 cm (at 0.15 vppm SO_3) or 21.3 cm (at 1.5 vppm SO_3). In sulphuric acid NO_2 will dissolve, resulting in sulphuric-nitric acid mixtures.

At normal operation the casing temperature will be over the dew points of water and NO_2 and condensation will not occur. The sulphuric-nitric acid mixture will still be formed in the insulation at a depth of 13.8 and 20 cm.

Because the operation conditions are not stable (gas and casing temperatures will move in a range) the temperature decay lines over the insulation will change too. Over time the insulation will be filled over the whole thickness with sulphuric, nitric acid and reaction products with carbon steel and the insulation. Ammonium and calcium nitrate are hygroscopic. According to Harp¹⁴ ammonium nitrate will be no corrosive anymore at 120°C, because the water content is too low (less than 5%). Calcium nitrate is losing all its crystal water at 51.5°C. That means that at normal operational conditions the nitrate salts are still corrosive.

7 CORROSION IN A WASTE INCINERATION PLANT

In a new build waste incinerator the waste (Refuse Derived Fuel) was burned on a discontinuous moving grate. Regularly overpressure peaks were the result and flue gas and flyash was pushed outside the boiler into the building (de Weijer²²). During the starting up period of the plant a seal in a waterfeed pipeline broke and a large amount of condensed steam entered the boiler house. The seal was repaired and the incineration started in operation again. In about two weeks very severe corrosion was noticed on the galvanised gangways, steel building components, the boiler sheetings and processing lines. The spring discs, applied for hanging the boiler, were cracked because of stress corrosion cracking and had to be replaced all. Directly after the steam leakage many of the discs were fractured as a result of the acid mist in the top of the boiler house. Normal condition in the boiler house is a dry warm atmosphere and condensation is not noticed. Microscopic examination of the coils indicated cracking because of hydrogen embrittlement.



Figure 17 Corroded aluminium isolation plates and steel valves.

The whole building was cleaned with water to remove the acid.

The flue gas concentration in the building as a result of the leakage in the boiler and the overpressure peaks can be calculated approximately. In these calculation the following parameters were taken in consideration: underpressure in the boiler, the value of the pressure peaks and the period of the overpressures, the length of the missing weld and the ventilation in the building. It is assumed that the flue gas had been spreaded homogeneously in the boiler house and that locally acid condensation did not yet occur. In the direct neighbourhood of the leakage a higher flue gas concentration will be present than at the walls of the building.

The increase of the flue gas concentration in the building can be calculated by means of the equation:

$$C = \text{leakage} / \text{ventilation} * (t/(1+t))$$

The ultimately composition of the flue gas in the building together with the dew points are mentioned in the table below.

Table 2. Composition of the boiler gas, the environment in the boiler house and the various dew points.

Gas	Waste Incineration Plant	Boiler house
SO ₃ vppm	18	0.033
SO ₂ vppm	140	0.260
HCl vppm	871	1.6
H ₂ O v%	125 mbar (12,5%)	7.2 mbar (0.72 %)
Dewpoint H ₂ O	54	4.5
Dewpoint SO ₃	146	58
Dewpoint SO ₂	48	2
Dewpoint HCl	42	1

Over the isolation layer from the membrane wall to the aluminium sheets the temperature decreased from about 300 °C down to about 45 °C. The temperature in the boiler hall was about 30 °C, when the boiler was in operation. SO₃ and HCl in the escaped flue gas were the corrosive gasses to be considered.

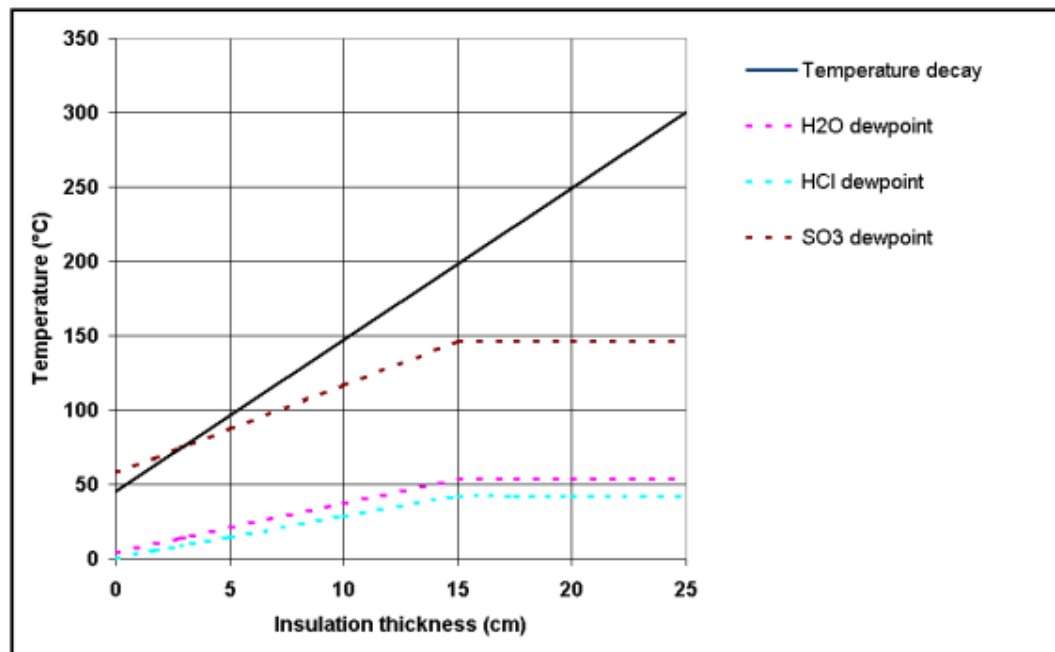


Figure 18. Temperature decay over the insulation outside the membrane wall with the various dew points.

The SO_3 concentration decreased as a result of dilution in the isolation area from maximum 18 vppm at the membrane wall down to the calculated value of 0.033 vppm (diluted fluegas in the boiler house). The calculated dew points for these concentrations are 146 and 58 °C. Because of the temperature decay and the more or less linear dilution in the insulation the sulphuric acid droplets will be formed at about 75°C and 3 cm in the insulation. The sulphuric acid concentration at 75 °C is 60%. See Figure 9. Condensation of sulphuric acid arose already before the flue gas reached the aluminium sheets.

The dew points of the hydrochloric acid in the flue gas at the membrane wall and in the boiler house are very low. The hydrochloric acid concentrations amounted 871 vppm (undiluted flue gas) and 1.6 vppm hydrochloric acid (diluted flue gas). The dew points at the corresponding water vapour pressures are 58 and 1 °C. Hydrochloric acid did not condense in the isolation and inside the aluminium sheets. Dry hydrochloric acid was present in the boiler house as a gas and was removed by the boiler house ventilators.

However, as soon as the boiler house was filled with condensed steam the escaped hydrochloric acid dissolved instantaneously in the water droplets. The ventilators did not remove these acid droplets. The acid remained in the boiler house and this explains the severe corrosion activity. The corrosion was noticed mainly as general corrosion of the steel boiler house walls and the galvanised gangways. The hardened carbon steel spring discs were cracked after the steam leakage too. Besides, a huge damage was the stand still period and the cleaning activities.

8 MATERIAL CHOICE IN RELATION TO NITRATE STRESS CORROSION CRACKING

Using carbon steels in conditions where there is a risk of condensation in the presence of nitrates or NO_x SCC is likely to occur sooner or later. SCC due to nitrates is nearly always associated with intergranular corrosion. Leferink²³ studied the resistance of several ferritic steels to intergranular corrosion in ammonium nitrate solutions in the range of 2 to 35 wt% at 90 °C for a period of 100 hours. After exposure of the steels they were examined with an optical microscope. When the intergranular corrosion was more than three grains deep, the steel was considered to be sensitive for intergranular corrosion in that environment. A clear correlation was found between the steel composition and the molar ammonium nitrate in which the corrosion became three grains deep.

For all tested steels C-steel, 15Mo3, 13CrMo44, 10CrMo910 and 12% Cr steel the correlation is:
 Critical percentage ammonium nitrate = $6\text{Mo} + 2\text{Cr} + 1\text{Mn} + 8 - 12\text{Si} - 8\text{Cu} - 1\text{C}$ ($R^2=0.85$)

The correlation between measured and calculated critical nitrate percentages is given in Figure 19.

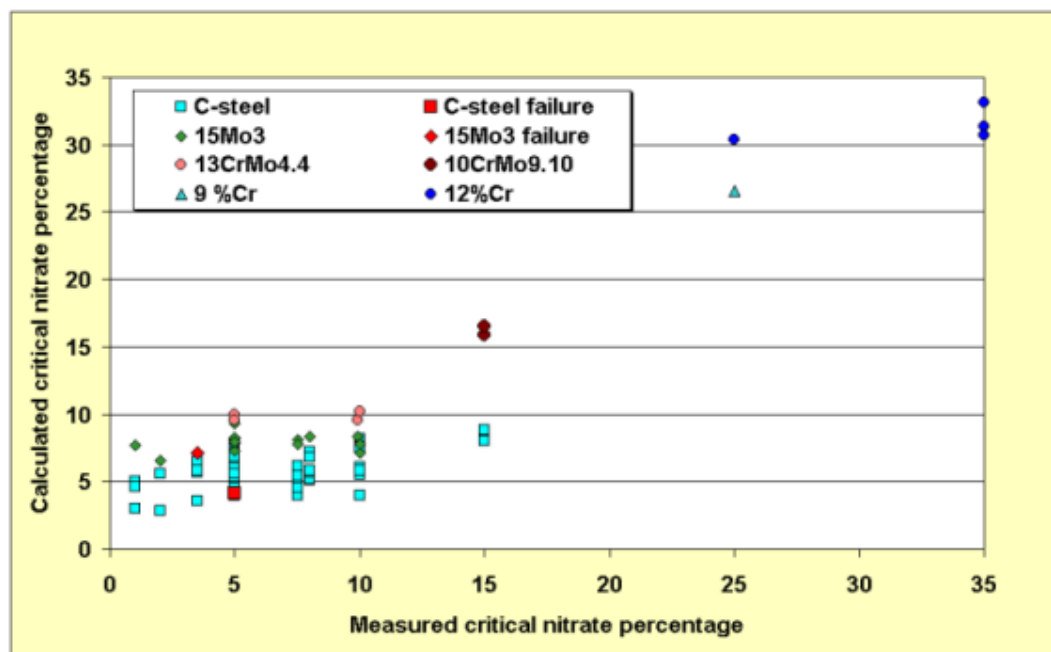


Figure 19 Correlation between measured and calculated critical nitrate concentrations of steels tested in ammonium nitrate solutions of varying nitrate concentrations.

After the results of this study were published, steels that had failed due to nitrate SCC came available from several sources. These steels were analysed for their chemical composition and critical ammonium nitrate concentrations were calculated. Results of the calculations appear in table 5

Table 5: Steels from in service failures

Number	Steel	Chemical analysis of the steels						Calculated Critical % nitrate
		Cr	Cu	Mo	C	Mn	Si	
1*	C-steel	0.08	0.21	0.02	0.11	0.61	0.31	3.4
2	15Mo3	0.08	0.14	0.25	0.17	0.67	0.22	6.4
3	15Mo3	0.14	0.18	0.27	0.15	0.61	0.23	6.2
4	C-steel	0.07	0.2	0.02	0.12	0.46	0.22	4.4
5	C-steel	0.06	0.04	0.01	0.11	0.48	0.25	5.2
6*	15Mo3	0.08	0.32	0.33	0.12	0.61	0.21	5.6
7	C-steel	0.07	0.14	0.01	0.08	0.49	0.15	5.7
8	C-steel	0.08	0.52	0.03	0.05	1.17	0.14	3.6
9	C-steel	0.058	0.42	0.052	0.05	1.09	0.17	4.1
10	C-steel	0.036	0.44	0.03	0.05	1.11	0.17	3.9
11	C-steel	0.036	0.44	0.03	0.05	1.12	0.17	4.0
12	C-steel	0.036	0.48	0.03	0.06	1.16	0.15	3.8
13	C-steel	0.036	0.33	0.03	0.06	1.23	0.19	5.8
14	C-steel	0.036	0.25	0.03	0.07	1.07	0.34	3.2
15	C-steel	0.02	0.021	0.002	0.13	0.959	0.342	4.6
16	C-steel	0.03	0.024	0.006	0.111	1.19	0.193	6.7
17	C-steel	0.1	0.11	0.03	0.07	0.49	0.17	5.9

* Steels were tested in ammonium nitrate.

It is obvious that steels from failed constructions all have a low resistance to intergranular corrosion according to the ammonium nitrate correlation formula. The difference in resistance to intergranular corrosion in nitrate solutions between carbon steels and 15Mo3 steel is minimal.

Using carbon steels in risky condensing conditions will give sooner or later SCC.

9 CONCLUSIONS

- Though the knowledge of condensation of corrosive gasses is well available in literature, many design failures are made in technical installation. Running of equipment with condensing gasses make it necessary to think carefully about the operation temperatures and the condensation risks.
- Application of hot casings is cheaper than a cold casing but risk of stress corrosion cracking is high. Temperatures should be held higher than in case of a hot casing, which can imply that the gasses can not cool enough to attain the aimed efficiency of the HRSG.
- Condensing nitric acid can cause stress corrosion cracking of carbon steel. However reaction products of nitric acid with the steel or insulation can result in formation of ammonium nitrate or calcium nitrate.
- Calcium and ammonium nitrate are both hygroscopic materials that can take up water even above the dew points of the gas, resulting in very corrosive environments regarding stress corrosion cracking up to 120°C.

- Because the nitrate stress corrosion cracking starts with intergranular corrosion SCC is in particularly controlled by chemical corrosion. Annealing of the material or selecting a higher strength material will not be helpful to prevent SCC on the longer times. Select a low alloyed 2 % chromium steel to prevent the intergranular corrosion in nitrates.
- Small amounts of SO₃ inhibit SCC from ammonium nitrate, because of formation of the innocent ammonium sulphate.

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