



INFOSHEET

Corrosion effects when cooling through the Acid Dew Point

What happens to equipment downstream of a polymer heat exchanger?

Abstract

The Heat Matrix polymer heat exchanger technology allows operators to recover heat to temperatures below the acid dew point. In the polymer heat exchanger, sulphuric acid condenses out, this results in a lower acid dew point of the cooled flue gas. As a result, the corrosivity of the cooled flue gas drops below the design corrosion rate, meaning that the impact on downstream equipment is well within the design envelope.



Heat recovery below the Acid Dew Point is possible



Lower corrosion rates as a result of a lower Acid Dew Point downstream



Impact on downstream equipment within design envelope



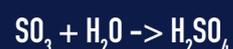
Introduction

Polymer heat exchangers are corrosion resistant. They are used to recover additional heat from potentially corrosive flue gas to temperatures well below the acid dew point. When you decide to recover additional heat from your corrosive flue gas with a polymer heat exchanger, you may be afraid that there will be corrosion effects on the equipment, ducts or stack downstream from the polymer heat exchanger. This infosheet explains why the corrosion rates will be normal and not excessive.

Why do fuels that contain sulphur lead to issues?

Many different types of fuel are used in combustion processes. Most commonly used fuels are natural gas, off-gases, fuel gas, biogas, oil, coal and biomass.

Most of these fuels contain sulphur components like H₂S, mercaptans and thiophenes, which get readily converted to SO_x in the combustion chamber. Mainly SO₂ is formed, but part of this SO₂ (about 2%) oxidizes further to SO₃. The formed SO₃ subsequently reacts with H₂O to form sulphuric acid, when the flue gas cools below the Acid Dew Point (ADP).



The sulphuric acid is highly corrosive and affects equipment surfaces. The rate of corrosion is highest in the range of 100 to 140 °C. At lower temperatures, the corrosion drops, until water vapor in the flue gas condenses out and forms diluted hydrosulphuric acid (figure 1).

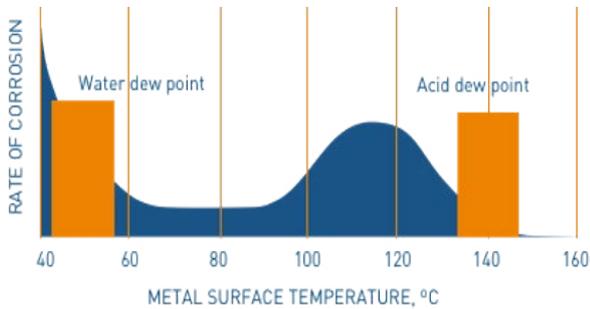


Figure 1

There are a number of equations to determine the Acid Dew Point. They can be found in Appendix A.

Removal of acids in the polymer heat exchanger

The Heat Matrix exchanger has been designed to cool the flue gas down through the acid dew point. Below the ADP, the sulphuric acid condenses on the tube wall in the polymer heat exchanger. As sulphuric acid is highly hygroscopic, a small condensate stream of diluted sulphuric acid is gathered at the bottom of the heat exchanger, which has been specifically designed to handle the acidic fluid. The flue gas temperature remains above the water dew point and the flue gas exiting the air preheater is therefore dry.

Removal of acid means lowering the acid dew point

As a result of the condensation reaction, the level of SO_3 in the flue gas drops significantly. The Heat Matrix Polymer technology has been tested for its selective removal of SO_3 by research organization TNO in the Netherlands. Their lab testing shows that 80 to 90% of the SO_3 will be removed in the polymer honeycomb. The Acid Dew Point reduces accordingly.

Taking for example the Okkes equation and starting with a SO_x level of 200 mg/Nm³, we get a SO_3 level of 1.4 ppmv (based on the SO_3 level being 2% of the total SO_x) and a corresponding ADP of 123 °C. After 80 to 90% has condensed out, the SO_3 level in the cooled gas drops down to 0.14-0.28 ppmv, which equates to an ADP of 108 – 112 °C, so a drop of 11-15 °C. In the Zare-Nezhad approach, the drop is even larger, from 121 °C down to 98 -105 °C (figure 2).

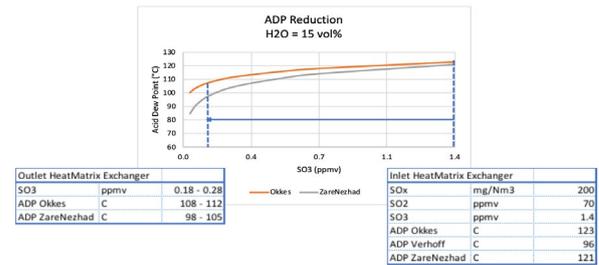
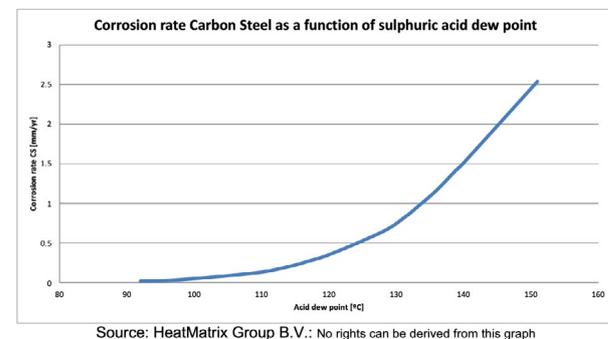


Figure 2

A lower acid dew point means a lower corrosion rate

The following graph (figure 3) shows the corrosion rate of carbon steel as a function of the acid dew point:



Source: HeatMatrix Group B.V.: No rights can be derived from this graph

Figure 3

The graph shows that as soon as the acid dew point drops below 105 °C, the corrosion rate reduces to less than 0.1 mm/year, which is the typical corrosion rate that is used for design. This indicates that cooled flue gas is significantly less corrosive and that the corresponding corrosion rates are within design parameters for the materials downstream.

Field experience

Corrosion test biogas fired boiler

At an operation unit in a biogas fired boiler, a carbon steel material coupon was installed in the exit of the Heat Matrix APH.

The bottom header of the APH itself is constructed of 304L. The flue gas SO_x level in this unit is 500 mg/Nm^3 , corresponding to a SO_3 level of 3.5 ppmv and an ADP (Okkes, ZareNezhad) of $130 \text{ }^\circ\text{C}$. With 80 to 90% of the SO_3 condensing out, the SO_3 level in the cooled gas is in the range of 0.35-0.7 ppmv, which equates to an ADP of $113 - 118 \text{ }^\circ\text{C}$ (Okkes) or $107-114 \text{ }^\circ\text{C}$ (ZareNezhad).

In line with figure 4, a corrosion rate of $0.1 - 0.4 \text{ mm/year}$ would be expected. Over the period of a year, the coupon and bottom header were monitored for any signs of corrosion. None were discernible. In figure 4 for example, the development of the plate thickness and material loss is shown for the carbon steel coupon.



Figure 4

The analysis confirms that downstream of the Heat Matrix polymer heat exchanger, the resulting acid dew point of the flue gas has been lowered to such an extent by the condensation in the polymer heat exchanger, that the corrosion rate has dropped to levels well below the design corrosion rate.

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Appendix A: How to calculate the Acid Dew Point (ADP)?

A number of equations exist to determine the acid dew point.

For example, Okkes¹ suggests the following approach:

$$T_{\text{DEW}} (\text{°C}) = 203.25 + 27.6 \log_{10} (p\text{H}_2\text{O}) + 10.83 \times \log_{10} (p\text{SO}_3) + 1.06 \times (\log_{10} (p\text{SO}_3) + 8)^{2.19}$$

where,

$$p\text{H}_2\text{O} = \text{volume fraction H}_2\text{O in m}^3/\text{m}^3$$

$$p\text{SO}_3 = \text{volume fraction SO}_3 \text{ in m}^3/\text{m}^3$$

Verhoff² suggests:

$$T_{\text{DEW}} (\text{K}) = 1000/[2.276 - 0.02943 \times \ln(p\text{H}_2\text{O}) - 0.0858 \times \ln(p\text{SO}_3) + 0.0062 \times \ln(p\text{H}_2\text{O} \times p\text{SO}_3)]$$

where,

$$p\text{H}_2\text{O} = \text{partial pressure H}_2\text{O in mm Hg (= volume fraction} \times \text{pressure in mm Hg)}$$

$$p\text{SO}_3 = \text{partial pressure SO}_3 \text{ in mm Hg (= volume fraction} \times \text{pressure in mm Hg)}$$

ZareNehad³ proposes the following approach:

$$T_{\text{DEW}} (\text{°C}) = 150 + 8.1328 \times \ln(p\text{H}_2\text{O}) + 11.664 \times \ln(p\text{SO}_3) - 0.38226 \times \ln(p\text{H}_2\text{O}) \times \ln(p\text{SO}_3)$$

where,

$$p\text{H}_2\text{O} = \text{partial pressure H}_2\text{O in mm Hg (= volume fraction} \times \text{pressure in mm Hg)}$$

$$p\text{SO}_3 = \text{partial pressure SO}_3 \text{ in mm Hg (= volume fraction} \times \text{pressure in mm Hg)}$$

1 A. G. Okkes: Get acid dewpoint of flue gas, Hydrocarbon Processing 7 (1987), S. 53–55

2 F.H. Verhoff, J.T. Banchemo, Predicting dew points of flue gases, Chem. Eng. Prog. 70 (8) (1974) 71–72

3 B. ZareNehad, New correlation predicts flue gas acid dewpoints, O&G Journ. 107,35 (2009)

Verhoff's equation results in a 20 to 40 °C lower Acid Dew Point. The ZareNehad equation closely follows the Okkes equation at higher SO₃ levels and calculates a slightly lower ADP at lower SO₃ levels (see Figure 11)

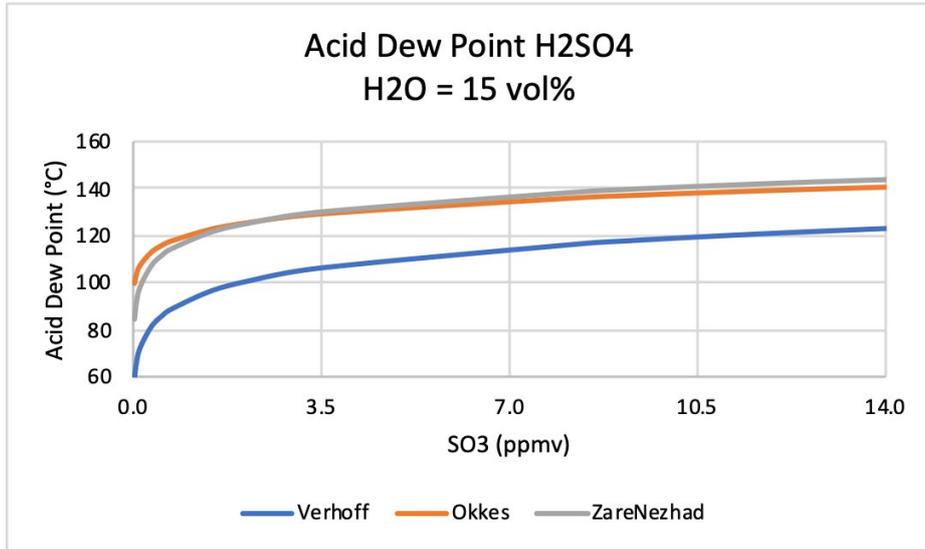


Figure 11

Typical SO₃ levels are in the range of 2 to 4% of the SO₂ level measured. The corresponding graph for the acid dew point related to the SO_x level (in mg/Nm³) in the gas, assuming a 2% SO₃ content is as shown in Figure 12.

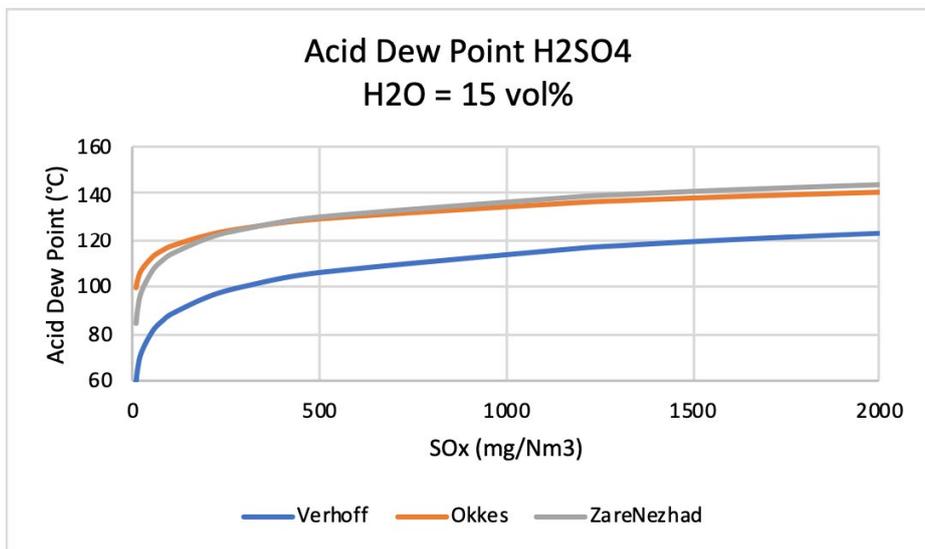


Figure 12