



## WHITEPAPER

# Corrosive flue gas is no longer a showstopper for heat recovery

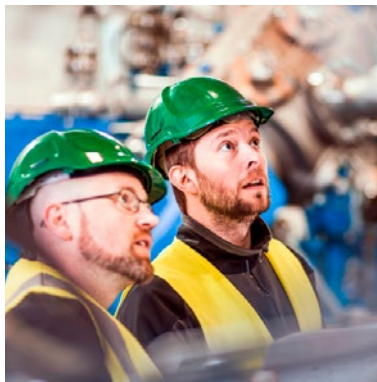
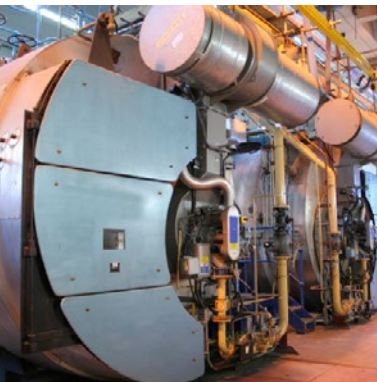
A significant amount of waste heat from flue gas or exhaust air remains untapped due to acid dew point corrosion. Read this whitepaper to find out how to overcome this limitation.

- ✓ Solve Acid Dew Point corrosion
- ✓ Reduce CO<sub>2</sub> emissions
- ✓ Learn about the Polymer Honeycomb Technology



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## Abstract

Many companies want to become more sustainable. They are searching for possibilities to reduce the CO<sub>2</sub> emissions from their thermal processes. Reducing fuel usage is one of the first actions to take. The highest short-term gain can be achieved by recovering heat from flue gas or exhaust air. But risk of corrosion prevents them from cooling their flue gas or exhaust air any further.

Losses of heat via stacks are significant, as they represent highly concentrated points of energy loss at elevated temperature. Typically, flue gas is sent out the stack at elevated temperatures of 150 °C and up. As a result, 10% or more of the process heat is still lost to the atmosphere. Corrosion concerns have up to now stopped operators from recovering this heat any further. This corrosion arises from sulphuric acid condensation from the flue gas at temperatures below the acid dew point (ADP). The Heat Matrix polymer-based technology allows operators to recover more heat from the flue gas by cooling through the ADP.

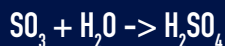
The recovered heat can be used in an air preheater (Heat Matrix APH) to directly preheat the combustion air and thereby reduce the fuel consumption in thermal processes. If air preheating can't be applied, the recovered heat from the corrosive flue or exhaust gas can be captured by using water as the heat transfer medium. For this application, the Heat Matrix ECO is ideally suited.

This paper looks at acid and temperature related corrosion and explains how cooling flue gases through the acid dew point not only recovers significant amounts of energy, but also reduces the corrosivity of the flue gas, thereby taking away the corrosion concerns that stopped heat recovery in the first place.

# 1. The issue with heat recovery from corrosive flue gas

Many different types of fuel are used in combustion processes. Most commonly used fuels are natural gas, off-gases, LPG and biogas, but also naphtha, fuel oils and solid fuels (such as biomass and coal) are applied.

Most of these fuels contain sulphur components like  $\text{H}_2\text{S}$ , mercaptans and thiophenes, which get readily converted to  $\text{SO}_x$  in the combustion chamber. Mainly  $\text{SO}_2$  is formed, but part of this  $\text{SO}_2$  (about 2%) oxidizes further to  $\text{SO}_3$ . This  $\text{SO}_3$  becomes the source of Sulphuric acid, when the flue gas cools below the Acid Dew Point (ADP). At the ADP the  $\text{SO}_3$  reacts with  $\text{H}_2\text{O}$  to form sulphuric acid:



## Elements that cause corrosion

The sulphuric acid is highly corrosive and affects susceptible equipment surfaces. For example, in metal air preheaters, local cold spots will lead to rapid corrosion and break down of plates and tubes. Note that other acids ( $\text{HF}$ ,  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$ , etc.) can also cause corrosion, though these typically have lower acid dew point temperatures.

## Result is leakage

Degradation of heat exchangers will go unnoticed for a while, but the leaks will result in a shortcut between hot and cold fluids. In an air preheater for combustion air, combustion air will leak into the flue gas, and thereby cause an energy loss through reduced recovery efficiency and increased power consumption by the combustion air fan. Such leakage can even impact the production rate, once the combustion air fan starts hitting its limitation.

**“ A typical thermal efficiency loss could be up to 10% or more, of which around half can be recovered with help of a Heat Matrix APH or ECO.**

In economizers, water will flash into the flue gas, leading to loss of water side pressure, loss in heat recovery performance and an increase in electricity consumption of the water pump(s).

Cold spots leading to integrity loss can already occur when the flue gas bulk temperature is still as high as  $250^\circ\text{C}$ , because the cold fluid is keeping the tube surface temperature below the acid dew point.

To minimize the potential for cold spot corrosion, operators have traditionally chosen to stay well above the acid dew point. As a result, significant amounts of energy are sent out the stack. A typical thermal efficiency loss could be up to 10% or more, of which around half can be recovered with help of a Heat Matrix APH or ECO.

## 2. Reasons why conventional solutions do not work

In order to improve energy efficiency several techniques have been applied in corrosive duties with mixed success. In air preheaters, heat recovery by cooling the flue gas down to approximately 180 °C in a carbon steel air preheater can potentially lead to cold spot corrosion issues as described before.

Recycling of part of the heated combustion air to the inlet of the forced draft air fan will lift the air temperature and subsequent the local cold spot temperature. Alternatively, the combustion air can be first warmed up in a steam air preheater. Both these measures consume energy themselves and still limit the recovery of the heat in the flue gas to approximately 20 °C above the acid dew point.

In economizers, the inlet water temperature can be held high, but variations in operational conditions can still lead to corrosion issues.

### Corrosion resistant metal alloys are too expensive

To increase the energy efficiency further, the flue gas has to be cooled below the acid dew point.

Under the condensing conditions, standard metal exchangers are not suitable and advanced metals need to be used, which make the heat recovery uneconomical. From a variety of exotic metals, only tantalum and zirconium can withstand acid dew point corrosion at acid dew points higher than 150 °C (Figure 1).

### Glass or coating solutions are not robust

Alternative materials like glass (air preheaters) or coated tubes (air preheaters and economizers) have been implemented at times. Glass tubes are however susceptible to flow induced vibrations and thermal shocks, which lead to tube breakage or rupture. Coated tubes can still lead to acid attack through hair-line cracks in the coating. Both solutions can have corrosion issues in the tubesheets, especially on the cold fluid inlet side, even if the tubesheet has a protective layer. The subsequent shortcut between hot and cold side leads to consequences as described above.

“ To increase the energy efficiency further, the flue gas has to be cooled below the acid dew point. ”

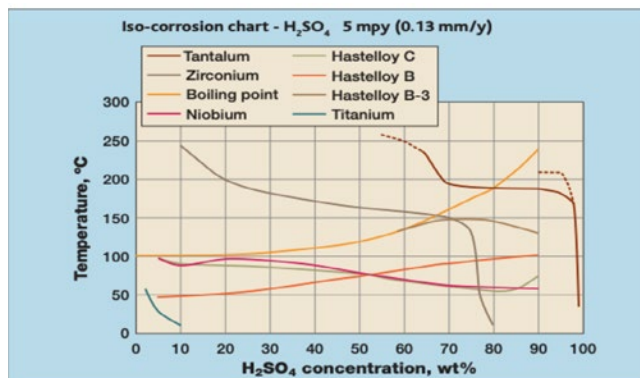


Figure 1: Resistance of metals against acid dew point corrosion



### 3. The air preheating solution that works: Polymer Air PreHeater (APH)

Heat Matrix Group has developed an innovative polymer-based heat exchange technology, that allows recovery of heat from corrosive and/or fouling flue and exhaust gases. This heat can be used to warm up (combustion) air or water.

In air preheating, the technology enables operators to:

- Replace their existing glass tube or glass lined air preheater or steam air preheater by a reliable, more efficient solution, or;
- Operate the existing metal air preheaters closer to the acid dew point without cold spot corrosion concerns, independent of variations in fuel sulphur content, or;
- Recover even more heat from the flue gas or dryer exhaust air down to temperatures well below the acid dew point.

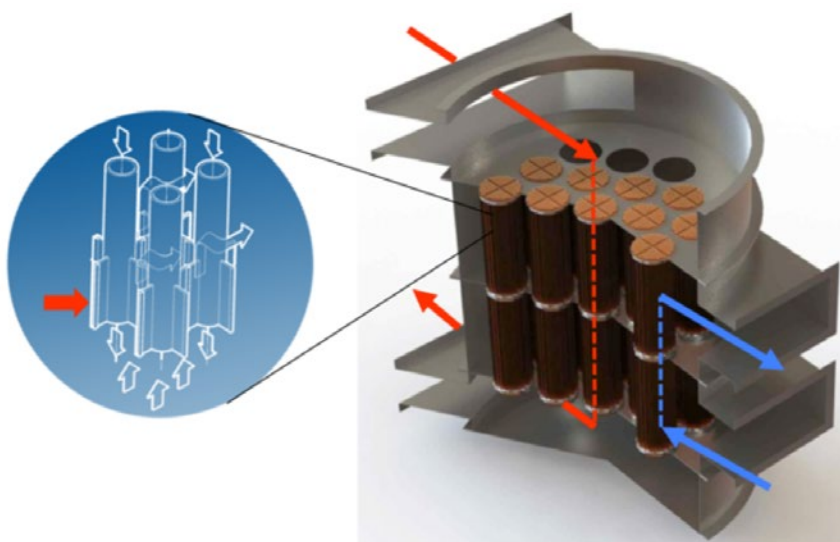
#### **Polymer is corrosion resistant**

The Heat Matrix® APH consists of multiple corrosion resistant polymer tube bundles mounted into a metal casing. The proprietary polymer bundle design is built up from multiple tubes that are connected to each other over a significant length of the tube.

#### **Robust, efficient and low weight**

The resulting structure creates a strong rigid matrix grid that is able to resist high gas velocities and thermal shocks. The geometry creates at the same time a counter-current flow configuration between the flue gas and air streams. This configuration improves the effective temperature difference by up to 20% compared to cross flow type exchangers. Flue gas flows from top to bottom through the tubes (red arrow in Figure 2) and combustion air flows in opposite direction around the tubes (blue arrow in Figure 2). The lightweight bundles are retractable from the top and can be cleaned or replaced without demounting the complete exchanger.

**“ This configuration improves the effective temperature difference by up to 20% compared to cross flow type exchangers. ”**



### Easy to install

The low weight of the bundles allows flexible installation of the heat exchanger, even at height, when plot space is limited (see Figure 3).



Figure 3: Examples of installed Heat Matrix Air Preheaters

### Easy to clean

In the case of fouling flue gas or dryer exhaust air, each bundle can be equipped with an in-line spraying nozzle, which thoroughly cleans each bundle in an alternating cleaning sequence during operation.



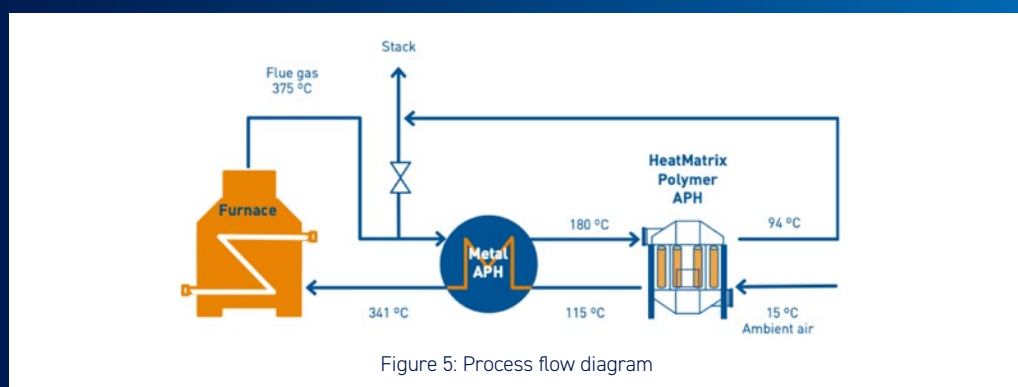
Figure 4: In-line cleaning system for Heat Matrix Polymer Air Preheaters

## Case study

### Air Preheater on Refinery Crude Furnace

The Heat Matrix Air Preheater technology has now been proven in a wide range of applications, ranging from small steam boilers, to large oil refinery furnaces.

Here is a case study for a refinery. On a refinery furnace, a metal air preheater (APH) recovered part of the heat remaining in the flue gas. To protect the existing metal APH and to improve the refinery's energy performance, an extra metal APH in combination with a Heat Matrix polymer APH is installed. The combined additional recovery amounts to an energy saving of 9 MW, of which about 30% is recovered in the polymer APH.



The combined additional heat recovery of 9 MW is obtained by reducing the flue gas temperature from 375 °C to 94 °C. The overall pay-back time for this project is less than 5 years.

Duty	9 MW
Payback time	Less than 5 years
Flue gas flow	kg/hr 103,000
Flue gas inlet temperature	375 °C
Flue gas outlet temperature	94 °C
Air flow	98,000 kg/hr
Air inlet temperature	15 °C
Air outlet temperature	341 °C



## 4. The water heating solution that works: Polymer Economiser (ECO)

Heat Matrix Group has developed an innovative polymer-based corrosion-resistant economizer, that permits recovery of heat from corrosive and/or fouling flue and exhaust gases. The Heat Matrix PCT (Polymer Concentric Tube) technology gives the ECO Gas/Water (or thermal oil) heat exchanger several advantages:

- Resistance to corrosion and/or fouling from flue gas;
- Recovering heat from flue gas temperatures up to 250 °C;
- Allowing for water pressures up to 30 barg;
- Impermeable barrier for acids between flue gas and water;
- Enhanced equipment durability through stress free thermal expansion

**“ The Heat Matrix ECO recovers heat from challenging flue gases and boosts efficiency without corrosion risks. ”**

### **Substantial additional heat recovery**

The Heat Matrix ECO system lets operators recover more heat from challenging flue gases, with which (boiler feed) water can be heated up. Alternatively, the recovered heat can be exported to a warm water or (district) heating grid, thereby reducing the overall CO<sub>2</sub> emission.

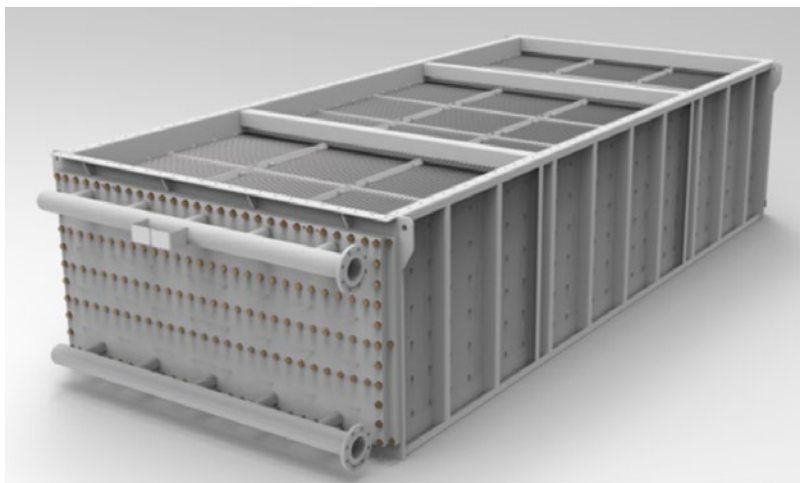


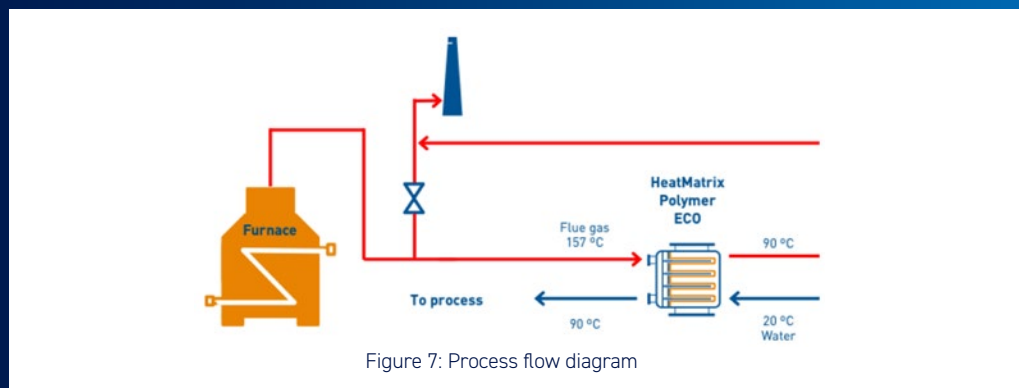
Figure 6: Heat Matrix ECO

## Case study

### Economiser on flue gas from industrial furnace

The Heat Matrix Economizer technology can be applied in a wide range of applications, ranging from small cylindrical flame tube steam boilers, to large industrial water tube boilers, as well as for exporting heat recovered from (furnace) stacks.

Here is a case study for a chemical site. On an industrial site, significant amounts of energy were lost through the stack. To improve the energy efficiency, a polymer ECO was installed to recover 5.3 MW from the residual heat in the flue gas.



The overall pay-back time for this project is less than 5 years.

Duty	5.3 MW
Payback time	Less than 5 years
Flue gas flow	240,000 kg/hr
Flue gas inlet temperature	157 °C
Flue gas outlet temperature	90 °C
Air flow	65,000 kg/hr
Air inlet temperature	20 °C
Air outlet temperature	90 °C



Figure 8: Installed Heat Matrix Polymer ECO

## 5. No impact on downstream corrosion rates

Heat Matrix' solutions allow for more heat to be recovered from corrosive flue gases. The question arises what impact cooling through the acid dew point has on equipment that is present after the polymer heat exchanger.

Corrosion rates are being lowered by two phenomena occurring during the heat transfer in one of Heat Matrix' exchangers.

- Firstly, part of the corrosive sulphuric acid is being condensed and removed as condensate, which brings the resulting acid dew point of the flue gas down.
- Secondly, the flue gas temperature drops, which reduces the corrosion rate.

Both phenomena shall be discussed separately. This chapter describes in general terms how corrosion rates downstream of the heat recovery are held within manageable boundaries. If you want to learn more about this topic, please feel free to contact us.

### Condensing the sulphuric acid

The Heat Matrix APH and ECO exchangers have been designed to cool down the flue gas through the acid dew point. As a result, sulphuric acid condenses on the tube wall in the polymer heat exchanger. Since sulphuric acid is highly hygroscopic, it will absorb moisture from the flue gas leading to a small condensate stream of diluted sulphuric acid which is collected at the bottom of the heat exchanger.

Consequently, the level of  $\text{SO}_3$  in the flue gas drops significantly. In the Heat Matrix APH, typically 80 to 90% of the  $\text{SO}_3$  will be removed (TNO research the Netherlands, December 2018). This reduction in concentration of  $\text{SO}_3$  reduces the acid dew point and as a consequence the corrosion rate. An example of the reduction of the acid dew point due to sulphuric acid condensation is shown in Figure 9.

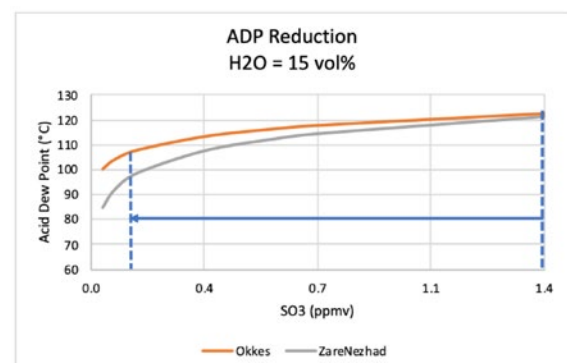


Figure 9: Reduction of the acid dew point due to condensation of sulphuric acid

**“ In the Heat Matrix APH, typically 80 - 90% of the  $\text{SO}_3$  will be removed. ”**

Source: TNO research the Netherlands, December 2018

### Outlet temperature in a reduced corrosion regime

Flue gas typically enters the Heat Matrix heat exchanger at temperatures ranging from 160 – 200 °C. Inside the heat exchanger the flue gas is cooled down to temperatures of around 85 – 105 °C. The resulting outlet temperature will be in a region with a much lower rate of corrosion as is shown in Figure 10.

### Field results

In the previous paragraphs, the theoretical background of the reduced corrosion rates by the two phenomena is discussed. Field results confirm the reduced corrosion rates.

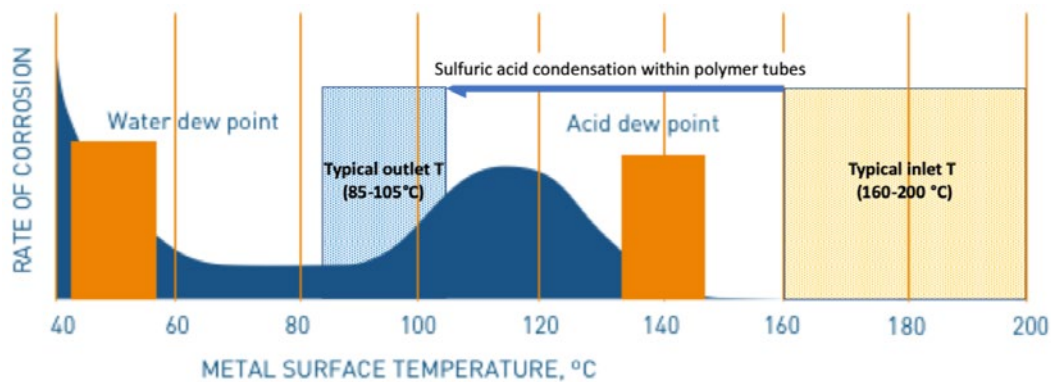


Figure 10: Effect of temperature on corrosion

“ Inside the heat exchanger the flue gas is cooled down to temperatures of around 85 - 105 °C “

At an operating unit in a biogas fired boiler, a carbon steel material coupon was installed at the outlet of the Heat Matrix APH. The flue gas  $\text{SO}_x$ -concentration in this unit is 500 mg/Nm<sup>3</sup>, corresponding to an  $\text{SO}_3$ -concentration of 3.5 ppmv and an ADP (Okkes, ZareNehad) of 130 °C. With 80 to 90% of the  $\text{SO}_3$  condensing, the  $\text{SO}_3$ -concentration in the cooled gas is in the range of 0.35 - 0.7 ppmv, which equates to an ADP of 113 - 18 °C (Okkes) or 107 - 114 °C (ZareNehad).

Over the period of a year, the coupon was monitored for any signs of corrosion. None were discernible. The analysis confirms that downstream of the Heat Matrix APH, the resulting acid dew point of the flue gas has been lowered to such an extent by the condensation in the heat exchanger, that the corrosion rate has dropped to levels well below the design corrosion rate.



## 6. How much heat can you recover?

Stacks offer a clear opportunity for energy saving by recovering the heat from the flue gas. The recovered heat can be used to for example preheat the combustion air or alternatively used to warm up water that can be used in other processes or thermal demands. The many references of the Heat Matrix technology have shown that concerns around acid dew point should no longer be a showstopper for this kind of energy saving.

If you recover 50% of your waste heat currently going to stack, you can take a significant step forward towards achieving your efficiency and sustainability targets. The actual amount of heat that you can recover depends on several factors and needs to be determined case by case. Share your case with us and find out what the savings can be.

### Heat Recovery Scan

Our process engineers assess the technical feasibility of additional heat recovery on your process. The potential reduction in CO<sub>2</sub> emissions, energy consumption and costs are determined.

- ✓ Analysis of your thermal process
- ✓ Minimal input data required
- ✓ Business case on savings potential

[Request a Heat Recovery Scan](#)

### Your savings potential?

Our Heat Recovery Scan gives you insight into the most promising heat-integration concepts and their payback period.



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

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

For example, Okkes<sup>1</sup> suggests the following approach:

$$T_{\text{DEW}} (^{\circ}\text{C}) = 203.25 + 27.6 \log_{10}(\text{pH}_2\text{O}) + 10.83 \times \log_{10}(\text{pSO}_3) + 1.06 \times (\log_{10}(\text{pSO}_3) + 8)^{2.19}$$

where,

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

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

Verhoff<sup>2</sup> suggests:

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

where,

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

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

ZareNehad<sup>3</sup> proposes the following approach:

$$T_{\text{DEW}} (^{\circ}\text{C}) = 150 + 8.1328 \times \ln(\text{pH}_2\text{O}) + 11.664 \times \ln(\text{pSO}_3) - 0.38226 \times \ln(\text{pH}_2\text{O}) \times \ln(\text{pSO}_3)$$

where,

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

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

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

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

<sup>3</sup> 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 ZareNezhad equation closely follows the Okkes equation at higher  $\text{SO}_3$  levels and calculates a slightly lower ADP at lower  $\text{SO}_3$  levels (see Figure 11)

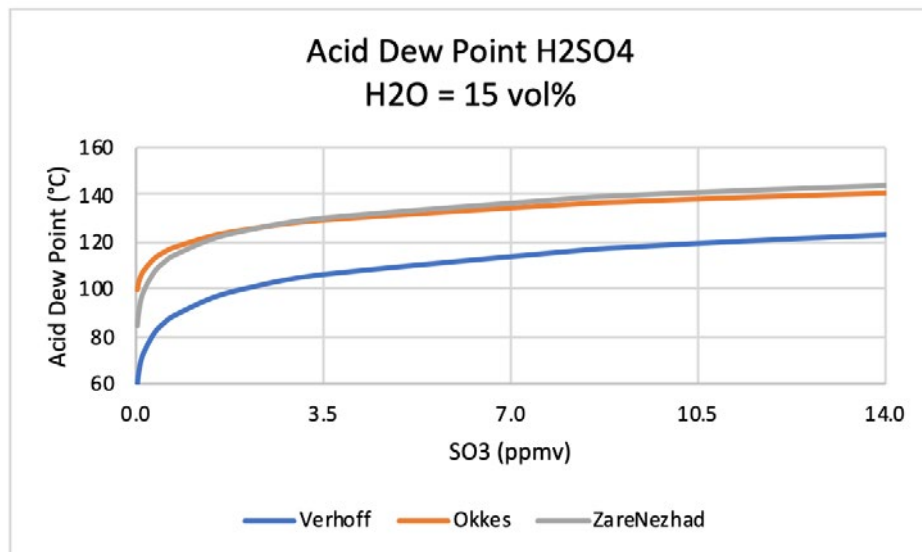


Figure 11: Comparison between the different equations for calculating the acid dew point from the  $\text{SO}_3$ -concentration

Typical  $\text{SO}_3$  levels are in the range of 2 - 4% of the  $\text{SO}_2$ -concentration measured. The corresponding graph for the acid dew point related to the  $\text{SO}_x$ -concentration (in  $\text{mg}/\text{Nm}^3$ ) in the gas, assuming a 2%  $\text{SO}_3$ -concentration is as shown in Figure 12.

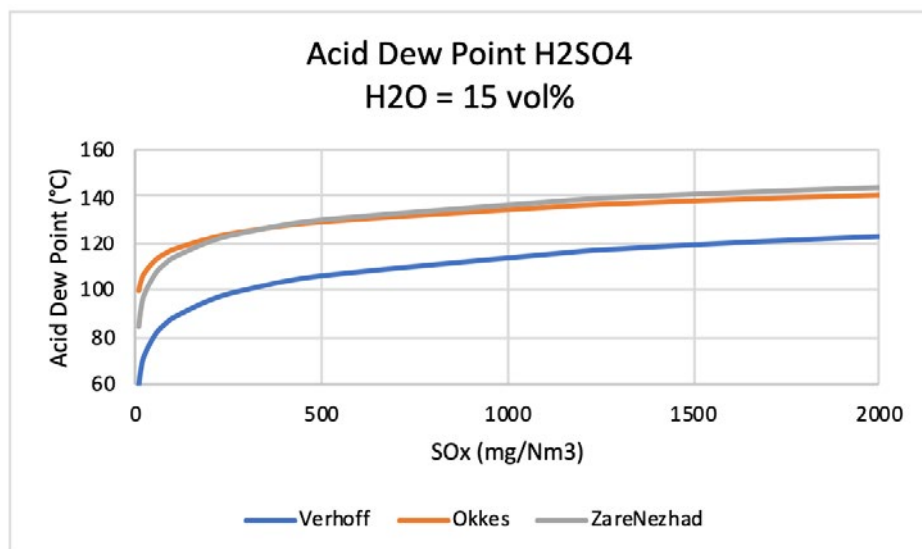


Figure 12: Comparison between the different equations for calculating the acid dew point from the  $\text{SO}_x$ -concentration assuming 2%  $\text{SO}_3$



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