Corrosive flue gas is no longer a show-stopper for heat recovery

Topics
1. What is the issue with corrosive flue gas?
2. Why do conventional solutions not work?
3. The air preheating solution that works? - The HeatMatrix APH
4. The water heating solution that works? - The HeatMatrix ECO
5. What does it mean downstream?
6. How much can you recover?
7. Appendix: How to calculate the acid dew point?
Abstract

Many governments and institutions are currently investigating short-, medium- and long-term solutions to bring greenhouse gas emissions and most notably CO₂ emissions down. Solutions are sought in capturing CO₂ after it has been formed and in reducing the formation of CO₂, by reducing the combustion of hydrocarbons.

The most straightforward approach for the latter, with the highest short-term gains is to increase energy efficiency by minimizing losses. Stack losses are the most notable, 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 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 HeatMatrix 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 (HeatMatrix 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 HeatMatrix 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.

Content of this White Paper:
1. What is the issue with corrosive flue gas?
2. Why do conventional solutions not work?
3. The air preheating solution that works? - The HeatMatrix APH
4. The water heating solution that works? -The HeatMatrix ECO
5. What does it mean downstream?
6. How much can you recover?
7. Appendix: How to calculate the acid dew point?
1. What is the issue with 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 H₂S, mercaptans and thiophenes, which get readily converted to SO₂ in the combustion chamber. Mainly SO₂ is formed, but part of this SO₂ (about 2%) oxidizes further to SO₃. This SO₃ becomes the source of Sulphuric acid, when the flue gas cools below the Acid Dew Point (ADP). At the ADP the SO₃ reacts with H₂O to form sulphuric acid:

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]

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 (HF, HCl, H₃PO₄, HNO₃, etc.) can also cause corrosion, though these typically have lower acid dew point temperatures.

Degradation of heat exchangers will go unnoticed for a while, but the leaks will result in a shortcut between hot and cold fluids. In air preheater, 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.

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 °C, because the cold fluid 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 HeatMatrix APH or ECO.
2. Why do conventional solutions 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.

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).

![Figure 1](image)

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.
3. The air preheating solution that works? - The HeatMatrix APH

HeatMatrix 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.

The HeatMatrix® 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.

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) and combustion air flows in opposite direction around the tubes (blue arrow). The lightweight bundles are retractable from the top and can be cleaned or replaced without demounting the complete exchanger.

**Figure 2**

---

HeatMatrix Group bv Address: De Ooyen 15, 4191 PB Geldermalsen, The Netherlands
+31(0)85 1302790 | info@heatmatrixgroup.com
The low weight of the bundles allows flexible installation of the heat exchanger, even at height, when plot space is limited (see Figure 3).

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.
Case Study: Air Preheater on Refinery Crude Furnace

Duty: 9 MW  
Payback time <5 years

The HeatMatrix 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 HeatMatrix 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.

- Flue gas flow: 103,000 kg/hr
- 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
- Duty: 9 MW

![Figure 5](image-url)
4. The water heating solution that works? -The HeatMatrix ECO

HeatMatrix 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 HeatMatrix 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 HeatMatrix 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 CO₂ emission.
Case Study: Economizer on flue gas from industrial furnace

| Duty: 5.3 MW | Payback time <5 years |

The HeatMatrix 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.

- Flue gas flow: 240,000 kg/hr
- Flue gas inlet temperature: 157 °C
- Flue gas outlet temperature: 90 °C
- Water flow: 65,000 kg/hr
- Air inlet temperature: 20 °C
- Air outlet temperature: 90 °C
- Duty: 5.3 MW
5. What does it mean downstream?

HeatMatrix’ 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 HeatMatrix’ 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.

5.1 Condensing the sulphuric acid

The HeatMatrix 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 in the bottom of the heat exchanger.

Consequently, the level of SO₃ in the flue gas drops significantly. In the HeatMatrix APH, typically 80 to 90% of the SO₃ will be removed (TNO research the Netherlands, December 2018). This reduction in concentration of SO₃ 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](image-url)
5.2 Outlet temperature is in a reduced corrosion regime

Flue gas typically enters the HeatMatrix 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.

![Figure 10: Sulfuric acid condensation within polymer tubes](image)

5.3 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.

At an operating unit in a biogas fired boiler, a carbon steel material coupon was installed in the exit of the HeatMatrix APH. The flue gas SO\(_x\) level in this unit is 500 mg/Nm\(^3\), corresponding to an SO\(_3\) level of 3.5 ppmv and an ADP (Okkes, ZareNehad) of 130 °C. With 80 to 90% of the SO\(_3\) condensing, 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 °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 HeatMatrix air preheater, 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.

Further reading on acid dew point and the related corrosion:
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 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 HeatMatrix 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.

HeatMatrix
De Ooyen 15,
4191PB Geldermalsen
The Netherlands

+31 85 1302790
info@heatmatrixgroup.com

Disclaimer

While the information has been prepared by Heat Matrix Group BV in good faith, HeatMatrix Group BV cannot guarantee the reliability, accuracy or completeness of the information. The information is provided for information purposes only. The information is not intended to act as advice upon which reliance should be placed. HeatMatrix Group BV cannot be held liable for any damage, loss, expense or cost arising from the use of the provided information. No rights can be derived from the provided information.
Appendix A: How to calculate the acid dew point (ADP)?

A number of equations exist to determine the acid dew point. For example, Okkes\(^1\) suggests the following approach:

\[
T_{DEW} \text{ (°C)} = 203.25 + 27.6 \log_{10}(pH_2O) + 10.83 \log_{10}(pSO_3) + 1.06 \log_{10}(pSO_3) + 8\]

where,

- \(pH_2O\) = volume fraction H\(_2\)O in m\(^3\)/m\(^3\)
- \(pSO_3\) = volume fraction SO\(_3\) in m\(^3\)/m\(^3\)

Verhoff\(^2\) suggests:

\[
T_{DEW} \text{ (K)} = \frac{1000}{[2.276 - 0.02943 \ln(pH_2O) - 0.0858 \ln(pSO_3) + 0.00626 \ln(pH_2O.pSO_3)]}
\]

where,

- \(pH_2O\) = partial pressure H\(_2\)O in mm Hg (= volume fraction \times \text{pressure in mm Hg})
- \(pSO_3\) = partial pressure SO\(_3\) in mm Hg (= volume fraction \times \text{pressure in mm Hg})

ZareNezhad\(^3\) proposes the following approach:

\[
T_{DEW} \text{ (°C)} = 150 + 8.1328 \ln(pH_2O) + 11.664 \ln(pSO_3) - 0.38226 \ln(pH_2O).\ln(pSO_3)
\]

where,

- \(pH_2O\) = partial pressure H\(_2\)O in mm Hg (= volume fraction \times \text{pressure in mm Hg})
- \(pSO_3\) = partial pressure SO\(_3\) in mm Hg (= volume fraction \times \text{pressure in mm Hg})

Verhoff’s equation results in a 20 to 40 °C lower Acid Dew Point. The ZareNehad equation closely follows the Okkes equation at higher SO\(_3\) levels and calculates a slightly lower ADP at lower SO\(_3\) levels (see Figure 11).

---

\(^1\) A. G. Okkes: Get acid dewpoint of flue gas, Hydrocarbon Processing 7 (1987), S. 53–55
\(^3\) B. ZareNehad, New correlation predicts flue gas acid dewpoints, O&G Journ. 107,35 (2009)
Typical SO$_3$ levels are in the range of 2 to 4% of the SO$_2$ level measured. The corresponding graph for the acid dew point related to the SO$_x$ level (in mg/Nm$^3$) in the gas, assuming a 2% SO$_3$ content is as shown in Figure 12.