Flue gas heat recovery through the acid dew point

Polymer based heat exchange technology enables more heat recovery from flue gas by addressing acid corrosion issues

PIM VAN KEEP and ROBERT SAKKO
HeatMatrix Group

Crude oil refining is an energy intensive process. On average, the thermal energy consumption of a refinery is in the order of 350-400 MJ/bbl, based on 2017 data from environmental agencies in the Netherlands, with some refiners achieving a higher energy efficiency than others. In order to reduce operational expenditure as well as the carbon footprint, refiners engage in projects to improve energy efficiency and process sustainability.

For a 100 000 b/d refinery, the typical thermal energy consumption equates to 400 MW. Of this energy, most is consumed in endothermic processes. Approximately 10% however is lost through the stack as waste heat. Historically, these stack losses of flue gas being emitted at high temperatures were accepted as a given because further heat recovery would lead to acid corrosion and related operational reliability issues. These corrosion and reliability concerns can now be overcome, allowing refiners to recover about a third of the waste heat from their flue gases (14 MW/100 000 b/d) in an economical way. As a result, an improvement of the overall refinery energy efficiency of 3-4% can be achieved.

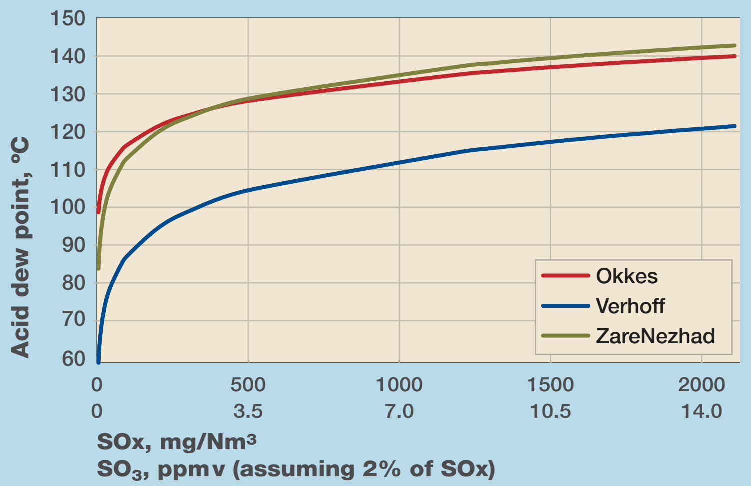
In this article, we look at the issues traditionally linked to recovering heat from flue gases. We review the solution that allows more heat to be recovered by cooling the flue gas down to temperatures below the acid dew point, and we discuss what the implications are for existing downstream equipment.

What is the issue with corrosive flue gas?

In refineries, a wide range of fuels are combusted in thermal processes, ranging from natural gas, off-gases, LPG to naphtha and fuel oil. Most of these fuels contain sulphur components like H_2S, mercaptans and thiophenes, which are readily converted to SOx in the combustion chamber. Mainly SO_2 is formed, but part of this SO_2 (typically about 2-4%) oxidises further to SO_3. This SO_3 reacts with H_2O in a condensing reaction to form sulphuric acid, when the flue gas cools below the acid dew point (ADP):

$$SO_{3\,(g)} + H_2O_{(g)} \rightarrow H_2SO_{4\,(l)} \qquad [1]$$

The acid dew point temperature depends on the levels of reactants present in the flue gas. It generally lies in the range 100-150°C. **Figure 1** shows the relationship between the ADP and the SO_3 level, calculated at a typical H_2O level of 15 vol% by using a number of different approaches proposed in the literature.



Okkes:
$$TDEW\ (°C) = 203.25 + 27.6\log_{10}(pH_2O) + 10.83\log_{10}(pSO_3) + 1.06(\log_{10}(pSO_3) + 8)^{2.19}$$
where,
pH_2O = volume fraction H_2O in m^3/m^3
pSO_3 = volume fraction SO_3 in m^3/m^3

Verhoff:
$$TDEW\ (K) = 1000/[2.276 - 0.02943\ln(pH_2O) - 0.0858\ln(pSO_3) + 0.00626\ln(pH_2O.pSO_3)]$$

ZareNezhad:
$$TDEW\ (°C) = 150 + 8.1328\ln(pH_2O) + 11.664\ln(pSO_3) - 0.38226\ln(pH_2O)\ln(pSO_3)$$
where,
pH_2O = partial pressure H_2O in mm Hg (= [volume fraction] × [pressure in mm Hg])
pSO_3 = partial pressure SO_3 in mm Hg (= [volume fraction] × [pressure in mm Hg])

Figure 1 Acid dew point H_2SO_4

Sulphuric acid is highly corrosive and affects susceptible equipment surfaces. For example, on cold surfaces in metal air preheaters, local temperatures drop below the ADP, leading to sulphuric acid condensation, which results in rapid corrosion and breakdown of plates and

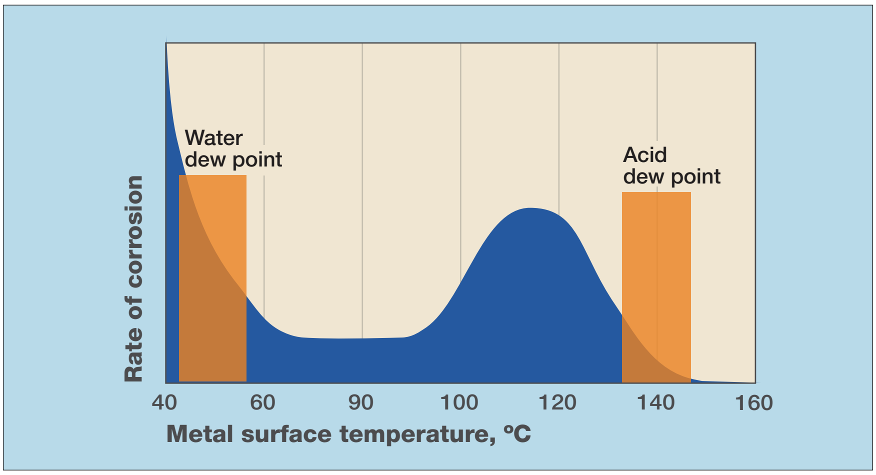


Figure 2 Rate of sulphuric acid corrosion

tubes. This phenomenon is known as cold spot corrosion. The degradation will go unnoticed for a period, but in the end leaks will result in a short cut between combustion air and flue gas and thereby an energy loss through a loss in recovery efficiency as well as an increase in power consumption by the combustion air fan. The leakage can impact the production rate, once the combustion air fan reaches its limitation.

Such cold spots can occur even if the flue gas bulk temperature is still as high as 250°C, because of the cold ambient air at the other side of the air preheater surface. The excessive cooling leads to flue gas side surface temperatures below the acid dew point. Cold spot corrosion can be aggravated by varying levels of sulphur in the fuels. As sulphur levels increase, the acid dew point increases accordingly. Even if the refiner targets to remain 10-20°C above the typical acid dew point, these variations in fuel sulphur content can lead to sulphuric acid condensation during sulphur peaks, resulting in loss of equipment integrity and a reduction in plant performance.

What are the challenges with conventional equipment?

To deal with acid corrosion, the industry has implemented different approaches with mixed success. The first approach is to stay away from the acid dew point by keeping stack temperatures up. But as described above, variations in fuel sulphur levels and localised cold spots can still lead to corrosion. To avoid over-cooling of exchange surfaces by cold air, part of the heated combustion air can be recycled to the inlet of the forced draught air fan which will lift the air temperature in the air preheater and thereby reduce the risk of cold spot corrosion. This however requires extra ducting, demands more power on the air fan and reduces the heat recovery on the air preheater. Alternatively, the combustion air can be first warmed up with a steam air preheater. This approach results in additional costs of steam and reduces the heat recovery. Both of these mitigation approaches still limit the recovery of the heat in the flue gas to approximately 20°C above the acid dew point.

To recover more energy from the flue gas, it has to be cooled down below the original acid dew point. Around the acid dew point, corrosion rates are high, but as the flue gas is cooled further down through the corrosive temperature range (see **Figure 2**), rates of corrosion become manageable again. Below 90-100°C, the corrosiveness of the flue gas is significantly lower compared to the corrosiveness just below the acid dew point temperature.

Under the acid condensing conditions arising from cooling down through the acid dew point, standard metal heat exchangers are not suitable. Special alloys need to be used. The cost of these, however, makes the heat recovery uneconomical. Alternative materials of construction like glass or enamel coated metal have been implemented at times. These solutions are, however, susceptible to flow induced vibrations and thermal shocks, which lead to damaged enamel coatings (allowing the acid to reach the underlying metal surface and corrode it away), tube breakage or rupture. The subsequent short cut between combustion air and flue gas reduces heat recovery and increases the load on the air fan as described before.

Polymer heat exchanging tube bundles

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, to preheat combustion air and thereby improve overall process energy efficiency. This technology allows operators to recover even more heat from the flue gas down to temperatures well below the acid dew point, or replace their existing glass tube or glass lined air preheater or steam air preheater with a reliable, more efficient solution.

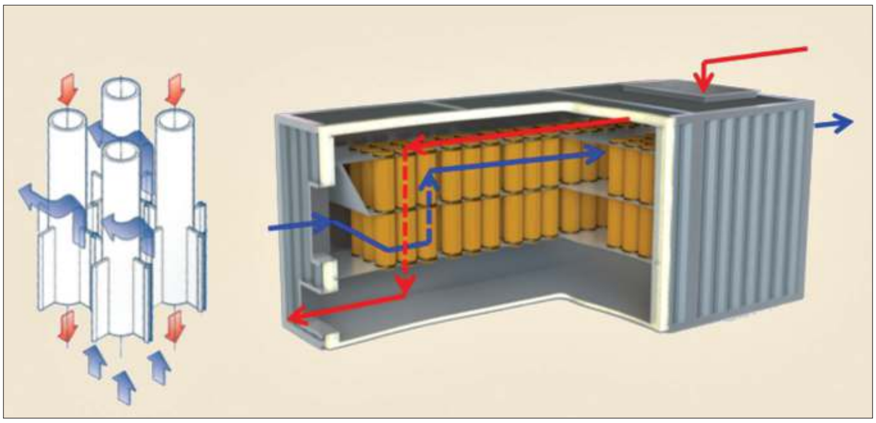


Figure 3 HeatMatrix Polymer Honeycomb technology

The HeatMatrix APH air preheater is based on Polymer Honeycomb technology. In this technology, multiple tubes are connected to each other over a significant length of the tube, forming a honeycomb modular bundle (see **Figure 3**, left). Multiple corrosion resistant polymer tube bundles are mounted into a metal casing (see **Figure 3**, right) to give the required heat exchange area.

Polymer Honeycomb technology provides a strong and rigid heat exchange matrix that is able to resist high gas velocities and thermal shocks. The geometry creates a 100% counter current flow configuration between the flue gas and air streams. This configuration improves the heat transfer by up to 20% compared to cross flow type exchangers. Flue gas flows from top to bottom through the tubes (see **Figure 3**, red arrow) and combustion air flows in the opposite direction around the tubes (see **Figure 3**, blue arrow). Inside the polymer tubes, the flue gas will go through its acid dew point and acid condenses on the tube wall. At the ADP, the concentration of sulphuric acid is high. As the acid travels down the tube, it will absorb water and the resulting condensate is collected in and drained from the bottom section of the air preheater. This bottom section has been designed to disengage condensate from the flue gas. Whereas the top three sections of the exchanger are carbon steel based, the bottom section is specifically designed to withstand the diluted acidic condensate (approximately 1% H_2SO_4 content).

In addition to corrosion resistance, the application of polymer offers benefits in fouling conditions. Polymers have very smooth surfaces and have low affinity for binding with dust, soot, salts and particulates. The positioning of the tubes in a vertical flow direction means that there are no dead zones inside the tubes where fouling can accumulate. As a result, fouling build-up is reduced. In cases of extremely fouling flue gases, each bundle can be equipped with an in-line spraying nozzle, which cleans each bundle in an alternating cleaning sequence during operation. The bundles can be washed with water. The chemical properties of the polymer allow for even more aggressive cleaning with detergents, acids or caustic if the duty requires this.

Figure 4 HeatMatrix APH examples: cylindrical (L) and box (R)

The low weight of the polymer bundles allows flexible installation of the heat exchanger, even at height, when plot space is limited. The lightweight bundles are retractable from the top and can be cleaned or replaced without demounting the complete exchanger.

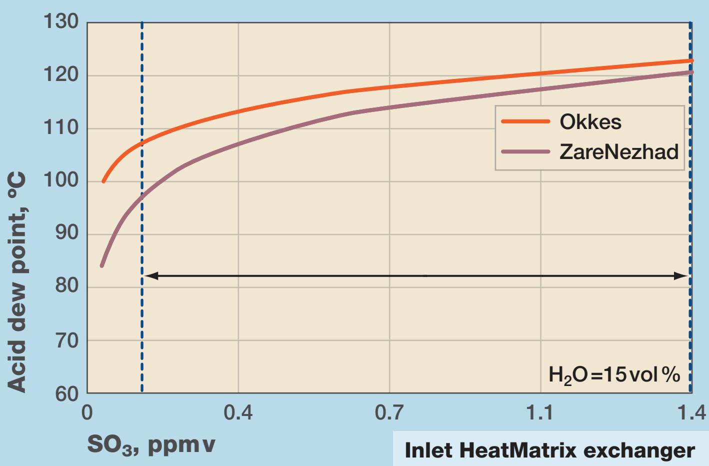
What about downstream?

Acid removal

The HeatMatrix exchanger has been designed to cool the flue gas down through the acid dew point. Sulphuric acid condenses on the tube wall in the polymer heat exchanger. The highly hygroscopic acid absorbs water as it moves down the tube and drops into the bottom basin. It is worth noting that the temperatures remain above the water dew point.

Research

The condensation of sulphuric acid means that SO_3 is selectively removed from the flue gas. Hence the acid dew point of the exit flue gas is reduced accordingly. To confirm that SO_3 is indeed removed and to what extent, a research project was set up in conjunction with the TNO research institute in the



Outlet HeatMatrix exchanger	
SO_3	0.18 to 0.28ppmv
ADP Okkes	108 to 112°C
ADP ZareNezhad	98 to 105°C

Inlet HeatMatrix exchanger	
SOx	200mg/Nm³
SO_2	70ppmv
SO_3	1.4ppmv
ADP Okkes	123°C
ADP ZareNezhad	121°C

Figure 5 ADP reduction in a Polymer Honeycomb

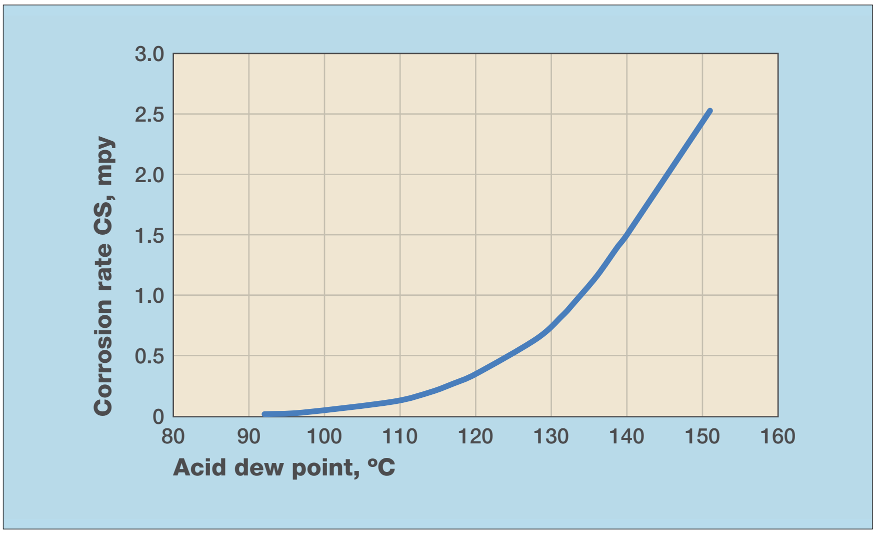


Figure 6 Relationship between rate of corrosion and the acid dew point
Source: HeatMatrix Group B.V.: No rights can be derived from this graph

Netherlands. In the test programme, gas with SO_3 was passed through the polymer tubes at typical gas velocities. The inlet and exit SO_3 levels were measured. The testing showed that 80 to 90% of the SO_3 will be removed in HeatMatrix Polymer Honeycomb technology.

As SO_3 is removed, the acid dew point is lowered accordingly. Taking for example the Okkes equation and starting with a SOx level of 200 mg/Nm^3, an SO_3 level of 1.4 ppmv (assuming 2 vol% SO_3) gives an ADP of 123°C. After 80-90% has condensed out, the SO_3 level in the cooled gas drops to 0.14-0.28 ppmv, which equates to an ADP of 108-112°C, so a drop of 11-15°C (see **Figure 5**).

Impact on corrosion rate

A lower acid dew point corresponds to a lower corrosivity of the flue gas. **Figure 6** shows the corrosion rate of carbon steel as a function of the acid dew point. 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 a typical design corrosion rate. This shows that cooled flue gas is significantly less corrosive and that the corresponding corrosion rates are within the design parameters for the materials of construction used downstream of the air preheater.

Proof from the field

At an operating unit, a carbon steel material coupon was installed in the exit of the HeatMatrix polymer APH. The flue gas SOx level in this unit is 500 mg/Nm^3, corresponding to a SO_3 level of 3.5 ppmv, which means an ADP (Okkes, ZareNezhad) of 130°C. With 80-90% of the SO_3 condensing out, the SO_3 level in the cooled gas is in the range 0.35-0.7 ppmv, which equates to an ADP of 113-118°C (Okkes) or 107-114°C (ZareNezhad). In line with **Figure 6**, a corrosion rate of 0.1-0.3 mm/year would be expected. Over the period of a year, the corrosion coupon was monitored for any signs of corrosion or weight change. No significant impact was discernible. In **Figure 7**, development of the plate thickness and material loss is shown for the carbon steel coupon.

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 of sulphuric acid in the heat exchanger that the corrosion rate has dropped to levels well below the design corrosion rate of 0.1 mm/year.

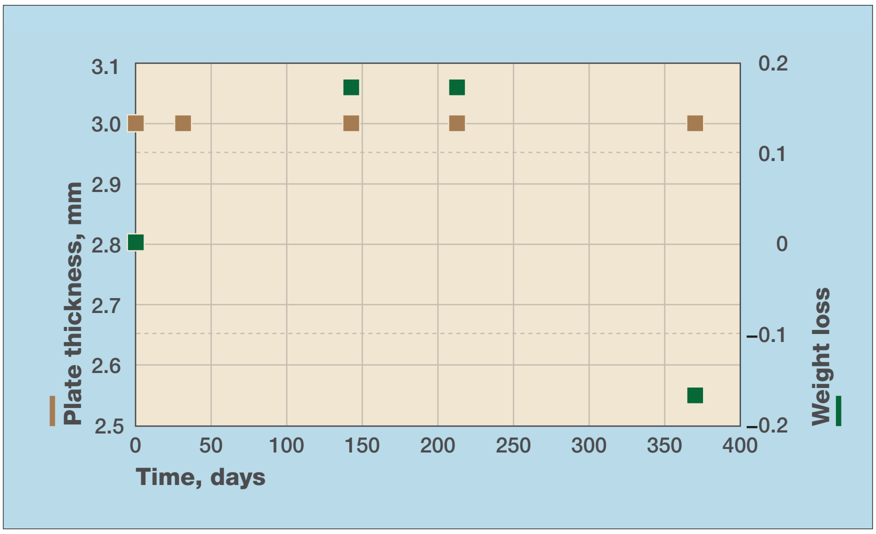


Figure 7 Carbon steel coupon in flue gas below the acid dew point

Case study: CDU furnace

HeatMatrix technology has been proven in a wide range of applications, including methane steam reformer and oil refinery furnaces. Here is a case study in a refinery. On a CDU furnace, an existing metal air preheater (APH) recovered part of the heat in the flue gas. The acid dew point of the flue gas was 129°C (Okkes, ZareNezhad). To protect the existing metal APH against cold spot corrosion and to improve the refinery's energy performance, an additional metal APH in combination with a HeatMatrix polymer APH was installed. The polymer APH protects the metal APH from cold spot corrosion. The combined additional recovery amounted to an energy saving of 9 MW, of which about 30% is recovered in the polymer APH.

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

Conclusion

Crude oil refineries are large consumers of energy in their thermal processes. Of the energy used in combustion, about 10% is lost through the stack. Concerns about acid dew point corrosion have held refiners back in recovering more waste heat from the flue gases. Traditional solutions like glass tubes or enamel coated tubes have caused reliability issues and are therefore less frequently applied. Operators tend to stay well above the acid dew point after their air preheaters. However, variations in fuel sulphur content and low ambient air temperatures in winter can still lead to cold spot corrosion in the existing metal air preheaters. To mitigate against this cold spot corrosion, some operators choose to preheat the combustion air with steam, which implies costs for steam and reduces the overall heat recovery.

Polymer based heat exchange technology allows operators to recover more heat from the flue gas by addressing acid corrosion concerns. Moreover, in the HeatMatrix polymer honeycomb heat exchanger, most of the sulphuric acid is removed from the flue gas, which makes the cooled flue gas much more benign to equipment downstream from the polymer APH.

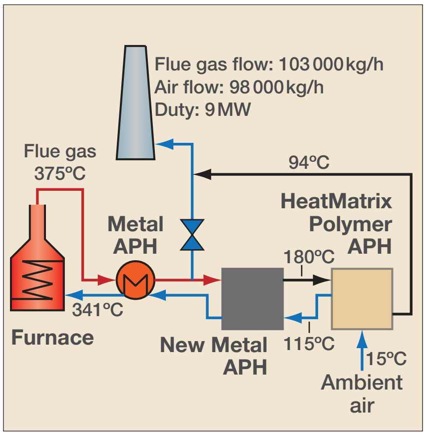


Figure 8 Refinery CDU furnace: revamp case

The extra heat recovered from the flue gas can be used to preheat the combustion air which in turn leads to a reduction in the consumption of combustion fuel. Overall, this solution allows refiners to improve their sites' energy efficiency by up to 4%. The many references of the HeatMatrix technology have proven that concerns around acid dew point should no longer be a showstopper for this kind of energy saving.

References

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

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

3 ZareNezhad B, New correlation predicts flue gas acid dewpoints, *O&G Journal* 107, 35, 2009.

Pim van Keep is Director of Technical Sales at HeatMatrix Group BV. He has an extensive background in catalytic processes in oil refining and the chemical industry. He holds an MSc in Chemical Engineering from Delft University of Technology, The Netherlands and an MSc in Business Management.
Email: pim.vankeep@heatmatrixgroup.com

Robert Sakko is Director of Technology with HeatMatrix Group BV. A co-founder of the company, he has worked for many years in the process industries, before taking on the new adventure of helping industry to become more sustainable. He holds an MSc in chemical engineering from the University of Delft, the Netherlands.
Email: robert.sakko@heatmatrixgroup.com