

Heat recovery solves carbon capture issues

Flue gas heat recovery at the fired heater overcomes major drawbacks to the successful operation of an amine based carbon capture plant

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The refining sector is facing a major transformation in the next three decades. Driven by more stringent regulation towards CO₂ abatement and increasing pressure from consumers and investors, refiners are exploring options to significantly reduce CO₂ emissions. A broad range of technologies are available to reach a zero emission goal by 2050. Each technology, whether it is heat recovery, electrification, alternative feedstocks, or carbon capture and storage (CCS), is at a different stage of maturity and applicability. Of these four technologies, heat recovery and carbon capture are the most mature and ready for implementation. This article covers the apparent advantages of these two technologies when they are applied simultaneously.

Carbon capture and storage

Post combustion carbon capture technology goes back as far as the 1930s and basically consists of a two-step process. In the first step CO₂ is absorbed into a solvent and in the second step it is thermally released from the solvent, resulting in a concentrated CO₂ stream. The concentrated stream can be further processed for transportation or underground storage. Typically, an aqueous amine solution is used for the reactive absorption of CO₂. The original amine based process has been further developed in order to optimise three major drawbacks. The first is the high energy consumption of the solvent regeneration step. According to the Global CCS Institute, the energy cost of a CO₂ capture unit downstream of a refinery fired heater could be as high as 20-30% of the fired heater duty. The second draw-

back is degradation of the amine solution, and the third drawback is entrained amine emissions. The main challenge of amine emissions is that amine aerosols are difficult to remove from the depleted flue gas stream with standard techniques.

When flue gas contains a high concentration of acidic contaminants (NO_x and SO_x), pretreatment steps prior to CO₂ capture are required to reduce their concentration. Otherwise, these acidic components lead to loss of amine activity due to the formation of heat stable salts. A stable salt bleed and fresh amine make-up will be necessary to compensate for the loss of amine efficiency. A standard selective catalytic reduction (SCR) and wet flue gas desulphurisation column are the appropriate technologies to achieve this.

Another required pretreatment step is the reduction of flue gas temperature to 30-50°C, which is the optimal operating temperature for most carbon capture technologies. Especially in refineries, the flue gas temperature can be as high as 350°C depending on the degree of heat integration between flue gas and combustion air. Typically, the flue gas is cooled using a water quench prior to a CO₂ absorber, either in a separated quench step or integrated in the wet flue gas desulphurisation column (DESOX). A quench step

is a quick and low cost option for reducing flue gas temperatures but has several disadvantages which are explained in the following.

Figure 1 shows a typical lay-out for a post-combustion CO₂ capture system for a typical combustion process. The SCR, ESP, APH and DESOX steps are optional and can switch order depending on local circumstances.

Amine aerosol formation

Since the last decade, it has been established that amine emissions from the CO₂ absorber could significantly exceed regulatory limits. The root cause was tracked down to the formation of sulphuric acid aerosols and subsequent amine entrainment. These aerosols are created when acidic flue gas is fed to the CO₂ absorption column. Very small sulphuric acid aerosols (d <0.02 µm) are too small to be absorbed or knocked out and remain in the gas phase throughout the absorption column. However, amine vapour present in the absorption column can condense on these aerosols, leading to excessive growth of particles. As a result, small particles grow to micron-size particles which are difficult to remove using a standard washing section or demister. Relatively expensive techniques, such as a wet electrostatic precipitator or a Brownian demister,

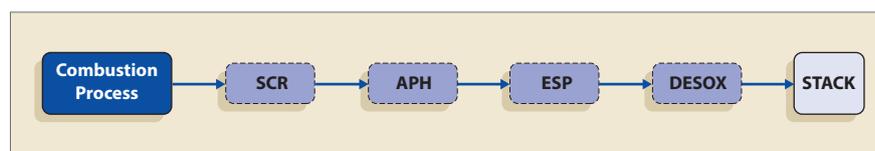


Figure 1 Typical layout of a flue gas condition system prior to a CCS unit. The dashed boxes are optional depending on the flue gas quality and can be placed in a different order: SCR or DESOX, APH (air preheater), ESP (electrical static precipitator), DESOX or WFGD (wet flue gas desulphurisation)

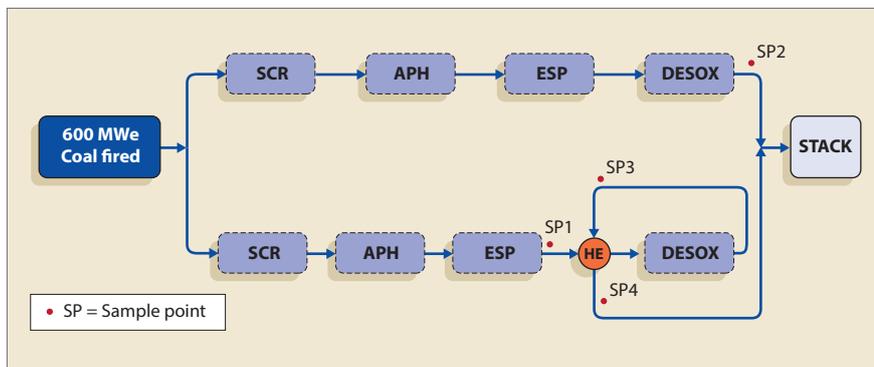


Figure 2 Flue gas conditioning system of a 600 MWe coal fired power plant in Nijmegen, The Netherlands. The lower flue gas conditioning train comprises a heat exchanger for cooling and reheating the flue gas streams around the DESOX column

are required to capture these aerosol particles.

The Dutch research institute TNO has a long track record of improving amine based CCS technology. TNO, as part of a large European consortium, will demonstrate CO₂ capture at a refinery in Ireland. This facility will incorporate the latest developments for amine based CO₂ capture technology in a refinery setting. One of the attention points, next to demonstrating low energy consuming amine solvent systems, will be to further study amine based aerosol formation and countermeasures.

Research case power plant

One of the important steps which TNO took was to identify the root cause of aerosol entrained amine emission. Together with the energy production sector, the relationship between flue gas composition and amine emission have been identified and quantified. To study this in depth, a 600 MWe coal fired power plant in the Netherlands was selected for an extensive flue gas sampling trial. The power plant has two parallel flue gas treatment sections downstream of the boiler, one with heat integration around the wet flue gas desulphurisation column and one without heat integration (see **Figure 2**). The heat integration step consists of a rotating heat exchanger which cools flue gas upstream of the wet flue gas desulphurisation column while reheating the saturated flue gas stream downstream of this column. In this way, flue gas exiting the stack remains above water dew point conditions.

This unique situation allowed for comparing the effect of a sharp temperature reduction in the wet flue gas desulphurisation step (quench) to a slower temperature reduction in the rotating exchanger. Without a rotating heat exchanger, the temperature of the flue gas is instantly reduced from 122°C to 52°C in the desulphurisation column by quenching. In the rotating exchanger, the flue gas temperature is reduced from 122°C to 80°C followed by a moderate quench in the desulphurisation column to 52°C.

TNO researchers measured the flue gas sulphur content around the rotating exchanger and the desulphurisation column. They also measured the particle size distribution (PSD) of the samples with an electrical low pressure impactor (ELPI). Finally, flue gas from sample points was taken to a small amine absorption column in order to visualise the amine based aerosol growth.

The results give a clear picture of the sulphuric acid aerosol formation mechanism.

First flue gas train with quench

With a quench as cooling step, the sulphuric acid concentration upstream and downstream of the column remained the same (SP1: 5.2, SP2: 5.8 mgNm³). Apparently, no sulphuric acid is absorbed in the desulphurisation column. However, downstream of the desulphurisation column a high number of small particles were measured (SP2: 6E7 cm³), which is 100 times higher compared to the sample upstream the desulphurisation column (SP1:

6E5 cm³). The formation of aerosols inside this column can explain why there is no absorption of sulphuric acid since aerosols pass through the column in the gas phase, unaffected by the absorption solution.

The high particle concentration downstream of the desulphurisation column also leads to clear mist formation in the small amine absorber installed downstream of the desulphurisation column due to further growth by amine deposition. This effect has significant consequences for the design of a potential CO₂ capture facility because, without additional measures, amine emission permit levels will be exceeded.

Second flue gas train with heat exchanger

The samples from the second train with a rotating exchanger gave different results. Here, a 70% reduction in sulphuric acid in the flue gas was measured downstream of the exchanger and desulphurisation column. The sample downstream of the desulphurisation column showed no increase in the number of particles compared to the upstream sample (SP1: 6E5, SP3: 6E5 cm³) and no mist formation was seen in the small amine absorber. Although the sulphuric acid concentration downstream of the rotating exchanger is reduced by 70% (SP1: 5.2, SP3: 1.6 mgNm³), the sulphuric acid concentration is still above the acid dewpoint saturation curve. It is assumed that not all sulphuric acid precipitates on the exchanger surface, but that a portion precipitates on fly ash particles. However, these particles are large in size and do not entrain much amine in the absorption column.

TNO explains the observations with a homogenous nucleation model for the fast temperature reduction during the quench step and a heterogeneous nucleation model for the slower temperature reduction in the heat exchanger. Cooling acidic flue gas to 80°C with a heat exchanger clearly prevents aerosol entrained amine loss. It remains unknown whether aerosol formation is prevented due to the smaller temperature drop in the desulphurisation column (80°C to

52°C) or the lower sulphuric acid content of flue gas entering the column at 80°C. Probably both phenomena have a positive effect on preventing aerosol formation.

Other literature sources referred to in TNO's paper showed that aerosol formation can occur with sulphuric acid concentrations as low as 1-2 mgNm³. This corresponds to an SO₃ concentration of 0.2-0.4 volppm and acid dewpoint temperatures of 100-110°C. Reducing the flue gas temperature to 80°C with an exchanger prior to any absorption column (sulphur or amine absorber) will prevent aerosol entrained amine loss to the environment (see **Figure 3**). As a rule of thumb, the submicron particle concentration should be below 1E5 particles per cm³, otherwise aerosol reduction countermeasures will be required.

Solving a problem with benefits

When the acidic flue gas temperature is cooled to 80°C, the acid dewpoint will be crossed. A standard heat exchanger will not suffice because of severe corrosion problems. In the above-mentioned coal fired power plant, corrosion resistant enamelled plates were used in the rotating heat exchanger. As an alternative, a corrosion resistant polymer heat exchanger as an air preheater cold end section can be used to achieve 80°C. Several combined metal-polymer air preheaters are already in operation at refineries throughout Europe. An air preheater solution for cooling flue gas to 80°C prior to a CCS plant has many benefits other than solely preventing amine aerosol emissions.

The following benefits (see **Figure 4**) will be discussed in more detail:

1. Increased heat recovery at a fired heater
2. Less flue gas resulting in a smaller CCS plant and lower energy requirement
3. Fewer corrosion issues due to reduced acid dew point temperature
4. Smaller flue gas duct size to CCS plant
5. No flue gas conditioning step prior to CCS plant
6. No aerosol entrained amine emission

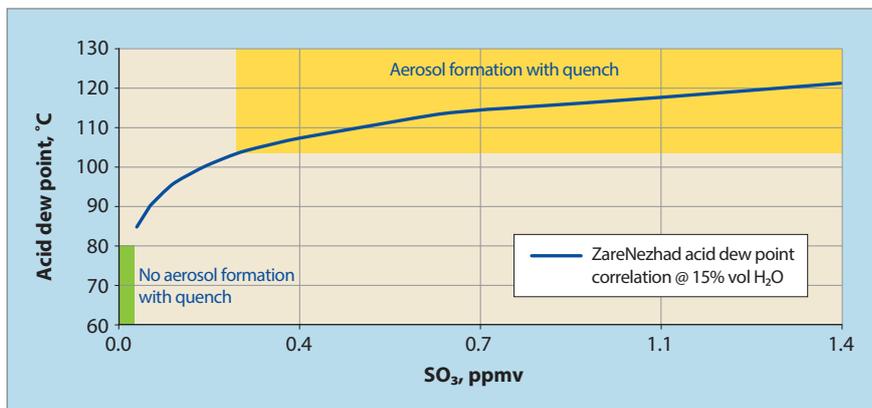


Figure 3 Acid dew point curve indicating areas with high and low risk of sulphuric acid aerosol formation when quenched with water to lower temperatures

Energy saving fired heater

Depending on the current degree of heat integration and acid dew point, the flue gas temperature leaving the fired heater will be between 150°C and 250°C. Implementing an air preheater is the first thing to do to increase energy savings. Among all heat integration options, implementing an air preheater will be the lowest hanging fruit. Extra heat can be recovered with the addition of a corrosion resistant polymer air preheater. When flue gas is cooled through the acid dew point from 150°C to 80°C (which is beneficial for carbon capture), an additional energy saving of 3.5% is achieved for the fired heater. This is a significant additional saving compared

to the required 20-30% extra energy required for a CCS plant.

Less flue gas

The improved energy efficiency of the fired heater results in reduced fuel consumption and a subsequent lower amount of flue gas. This results in a one-on-one smaller CCS plant capacity and CCS energy requirement.

Fewer corrosion issues

The one thing engineers are concerned about with respect to heat integration around fired heaters is the acid dew point. Different measures are taken in order to cool as close as possible to the acid dew point without compromising the

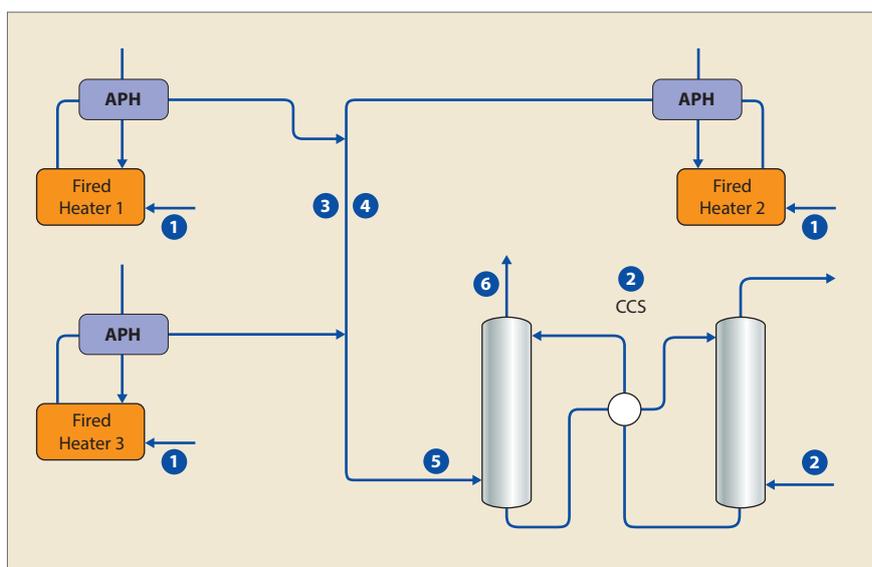


Figure 4 Advantages of heat recovery prior to CCS at a refinery complex:

- 1 Increased fired heater energy efficiency
- 2 Reduced CCS plant size and energy requirement
- 3 Fewer corrosion issues at lower acid dew point temperatures
- 4 Smaller duct size
- 5 No pre-cooling step prior to CCS plant
- 6 No aerosol entrained amine loss

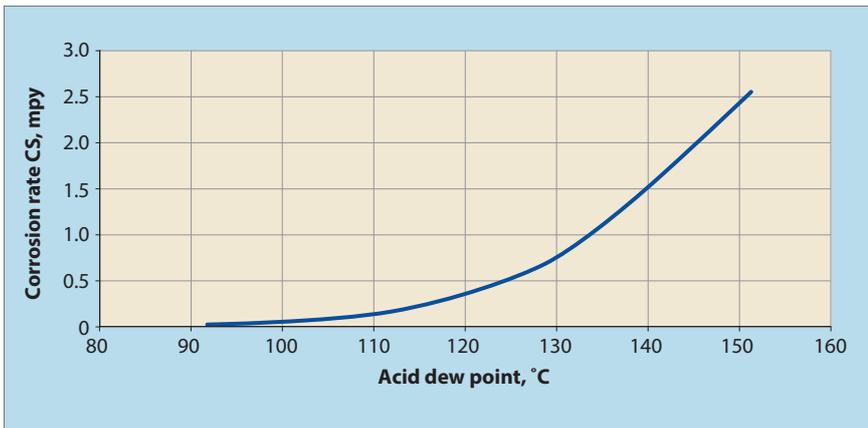


Figure 5 Corrosion rate of carbon steel as a function of acid dew point temperature
 Source: HeatMatrix Group B.V.: no rights can be derived from this graph

integrity of the downstream system. It will not be feasible to add a CCS system for every fired heater individually, due to limited plot space in existing refineries. Instead, a centralised CCS plant will be connected to multiple fired heaters. The consequence will be longer flue gas ducting throughout the site to collect all flue gas. In this case the flue gas exit temperature needs to be increased to prevent crossing the acid dew point during transportation, leading to reduced energy efficiency. Cooling through the acid dew point at the fired heater with an appropriate polymer air preheater reduces the flue gas temperature and sulphuric acid concentration. Hence, the corrosiveness of acidic flue gas downstream of the polymer air preheater is significantly reduced. See **Figure 5** for the corrosion rate as a function of acid dew point temperature.

Smaller flue gas duct size

The improved energy efficiency at the fired heater already results in a reduced amount of flue gas. Moreover, the reduction in flue gas temperature contributes to a lower volumetric flow rate because of an increased density. The combined effect on the volumetric flow rate of cooling flue gas to 80°C with an air preheater is a 20% reduction.

No flue gas conditioning at CO₂ capture plant

Flue gas fed to a CO₂ capture plant needs to be cooled prior to the amine absorption column. Flue gas at elevated temperatures

(150°C) require an additional unit operation, like a quench, water-based absorption column or heat exchanger. Locating this cooling step at the fired heaters could prevent additional flue gas conditioning. The small additional cooling step from 80°C to approximately 50°C could be integrated in the amine absorption column since this quench will not generate sulphuric acid aerosols.

No aerosol formation

TNO research shows that cooling flue gas prior to a CCS system with an exchanger instead of a quench



Figure 6 HeatMatrix air preheater in a fired heater

prevents the formation of sulphuric acid aerosols. This prevents aerosol entrained amine loss and hence has a positive impact on the overall amine efficiency and the environment.

Polymer air preheater

Cooling acidic flue gas through the acid dew point can only be done with the appropriate air preheater. While the corrosiveness of acidic condensate declines with temperature, severe corrosion will still occur at the actual acid dew point. The polymer tubes of the HeatMatrix honeycomb technology are well suited for this type of cooling. The acidic flue gas enters the polymer tube above the acid dew point and is cooled in an enclosed corrosion resistant space. The polymer tube is resistant to acid dew point temperatures up to 180°C. Once cooled through the acid dew point to 80°C, the flue gas and condensate exit the polymer tube. The corrosiveness of this mixture is significantly less, with a corrosion rate for carbon steel below 0.1 mm/y. The sulphuric acid condensate will be separated from the cooled flue gas in the bottom of the exchanger. The flue gas can be subsequently transported to the CCS unit.

The HeatMatrix polymer heat exchanger consist of multiple identical polymer tube bundles. Such a tube bundle is an assembly of connected polymer tubes which are not susceptible to flow-induced vibrations due to connections between the tubes. Heat transfer is optimised inside the tube bundle due to a countercurrent flow arrangement and an optimum ratio between pressure drop and heat transfer coefficient. Multiple tube bundles are placed inside a shell to separate flue gas and combustion air streams. This shell can be tailored to the local situation with respect to plot space, for instance when an existing metal air preheater needs to be replaced (see **Figure 6**).

The best arrangement for cooling flue gas to 80°C is a combination of a metal heat exchanger for the high temperature end and a polymer heat exchanger for cooling through the acid dew point. The

polymer exchanger preheats (cold) combustion air in order to prevent cold spots at the flue gas side of the metal heat exchanger. The polymer exchanger also allows for a further reduction in flue gas temperature without any corrosion problems. Typically, the exit temperature of the metal exchanger will be 165-180°C.

Case study crude distiller

HeatMatrix polymer heat exchangers have been proven in a wide range of applications, including a methane steam reformer, crude distillers, and other fired heaters. In a particular crude distiller, an existing air preheater was extended with an extra combined metal and polymer heat exchanger section. The original flue gas exit temperature was thereby further reduced from 180°C to 94°C, resulting in a further 4% efficiency gain. In the case of a downstream CCS unit, the flue gas temperature can be reduced further by increasing the metal heat exchanger's surface area. The overall payback time for this particular project was less than five years.

Conclusion

The changes needed for the refinery industry are quite challeng-

ing. The ambition to implement these changes within three decades are even more challenging with a zero-carbon emission goal at 2050 set by one of the big oil companies. Fortunately, the technology to meet these goals has been progressing significantly over the past 10 years. From the options available, heat recovery and carbon capture are the most mature and ready for short term implementation. The two major drawbacks of amine based carbon capture technology are the aerosols amine entrainment and the high energy requirement of the solvent recovery column. Both issues can be addressed with extended flue gas heat recovery at the fired heater prior to the CO₂ capture plant. A corrosion resistant cold end section that can cool through the acid dew point is a prerequisite. Cooling through the acid dew point to 80°C has six advantages for CCS operation of which the main three are: additional energy efficiency, preventing aerosol formation during a water quench, and reduced corrosiveness of the pre-cooled flue gas.

Further reading

1 Global CCS Institute, CO₂ capture

technologies, post combustion capture (PCC), 2012.

2 Horizon 2020 project REALISE; <https://realiseccus.eu>

3 Mertens J, Bruns R, Goetheer E, *et al*, Effect of a gas-gas-heater on H₂SO₄ aerosol formation: implications for mist formation in amine based carbon capture, *International Journal of Greenhouse Gas Control* 39, 2015, 470-477.

4 van Keep P, Sakko R, Flue gas heat recovery through the acid dew point, *PTQ*, Q2 2019, 93-97.

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