

Cold end corrosion: causes and cures

Calculating dew points of various acid gases and options for reducing cold end corrosion of heat recovery exchangers are

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WHENEVER FOSSIL FUELS containing sulfur are fired in heaters or boilers, sulfur dioxide, and to a small extent sulfur trioxide, are formed in addition to CO₂ and water vapor. The SO₃ combines with water vapor in the flue gas to form sulfuric acid and condenses on heat transfer surfaces, which could lead to corrosion and destruction of the surfaces. This condensation occurs on surfaces that are at or below the dew point of the acid gas. Also, when cooled below the water vapor dew point, CO₂ can combine with water vapor to form carbonic acid, which though weak, can attack mild steel.

While thermal efficiency of the equipment is increased with reduction in exit gas temperature (or enthalpy), lower temperatures than the acid gas dew point are not advisable for metallic surfaces in contact with the gas.

In municipal solid waste fired plants, in addition to sulfuric acid, one has to deal with hydrochloric and hydrobromic acid formation.

This article deals with methods for solving cold, or back end corrosion as it is called, with the most commonly used heat recovery equipment, namely economizers or water heaters. These are used to preheat feed water entering the system (Fig. 1) and operate at low metal temperatures, thereby increasing their susceptibility to corrosion by sulfuric, hydrochloric, hydrobromic and carbonic acid.

Estimating the dew point of these acid gases is the starting point in understanding the problem of back end corrosion. Appendix 1 gives the dew points of the various acid gases as a function of their partial pressures in the flue gas.¹ Fig. 2 gives the dew point for sulfuric acid.²

CO₂ = 87%, H₂O = 12%, N₂ = 73%, SO₂ = 0.02%,
HCL = 0.015%. 02 = 6 % . HBR = 0.01%. all by volume.
To compute the sulfuric acid dew point, one should know the amount of SO₃ in the flue gases. The formation of SO₃ is primarily derived from two sources.

1. Reaction of SO₂ with atomic oxygen in the flame zone. It depends on the excess air used and the sulfur content.
 2. Catalytic oxidation of SO₂ with the oxides of vanadium and iron, which are formed from the vanadium in the fuel oil.
- It is widely agreed that 1 to 5 % of SO₂ converts to SO₃. Hence the % volume in our case would be 4 ppm, assuming a 2 % conversion.

Using these numbers and after proper conversion and

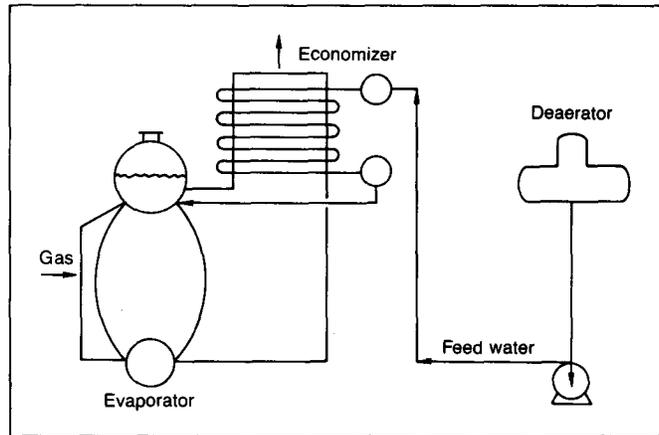


Fig. 1—Economizer in a heat recovery boiler system.

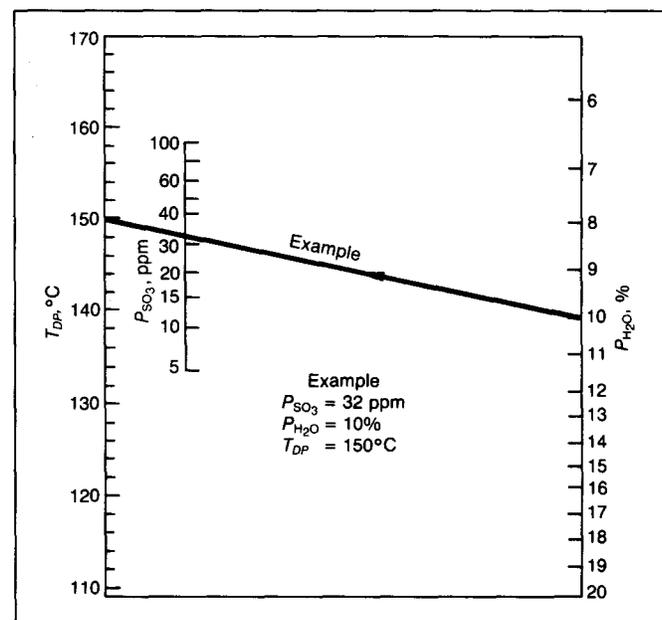


Fig. 2—Dew point of sulfuric acid as a function of partial pressures of SO₃ and water vapor.

substitution in the equations in Appendix 1, we have: dew point of sulfuric acid = 267° F, dew point of hydrochloric acid = 128° F, dew point of hydrobromic acid = 134° F and dew point of water vapor = 121° F.

Hence, it is apparent the limiting dew point is that due to sulfuric acid and any heat transfer surface should be above this temperature (267° F) if condensation is to be avoided. There is a misconception even among experienced engineers that the gas temperature dictates the metal temperature of surfaces such as economizers. It is not so. To explain this, an example will be worked to show the metal temperature of an economizer with two different gas temperatures. Appendix 2 shows this calculation.

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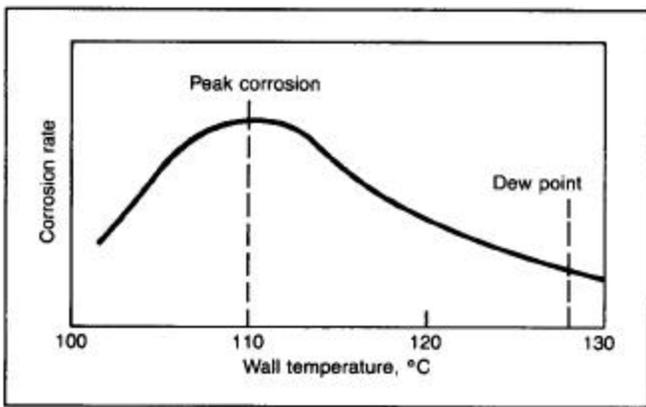


Fig. 3—Corrosion rate as a function of wall temperature.

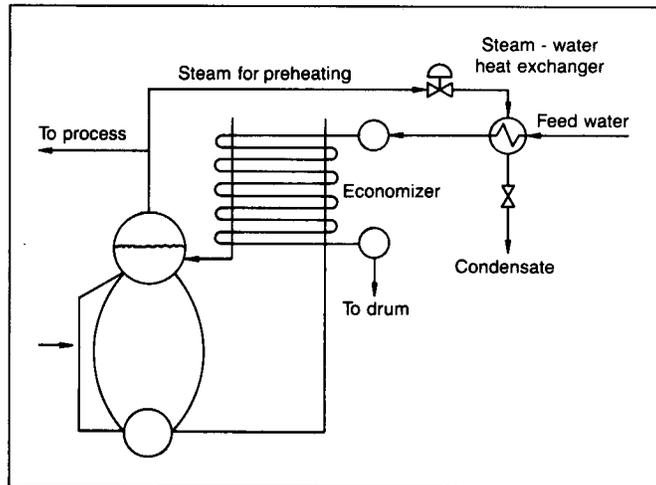


Fig. 4—Steam-water exchanger preheats feed water.

It can be seen that the water side coefficient is so high that the tube wall temperature runs very close to the water temperature in spite of a large difference in the gas temperatures. Thus, the tube wall temperature will be close to the water temperature and the water temperature fixes the wall temperature and hence, the dew point. Some engineers think that by increasing the flue gas temperature the economizer corrosion can be solved; not so.

It should be noted also that the maximum corrosion rate occurs at a temperature much below the dew point (Fig. 3).

Methods of dealing with cold end corrosion. Basically there are two approaches used by engineers to combat the problem of cold end corrosion:

A. Avoid it by using protective measures such as maintaining a high cold end temperature so that condensation of any vapor does not occur.

B. Permit condensation of acid vapor or both acid and water vapor, thereby increasing the duty of the heat transfer surface, and use corrosion resistant materials such as glass, teflon, etc.

Methods of avoiding cold end corrosion:

1. Maintain a reasonably high feed water inlet temperature. If the computed dew point is say 250°F, a feed water of 250°F should keep the minimum tube wall temperature above the dew point. With finned heat transfer surfaces, the wall temperature will be slightly higher than with bare tubes.

The simplest way would be to operate the deaerator at a slightly higher pressure, if the feed water enters the economizer from a deaerator (Fig.1).

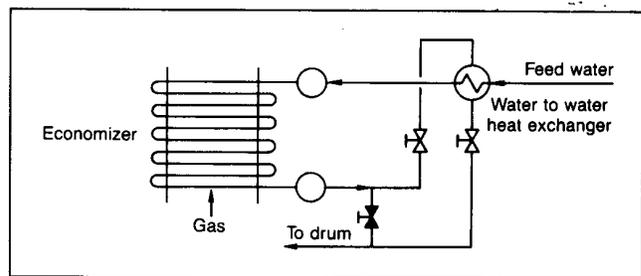


Fig. 5—Water-to-water exchanger preheats feed water.

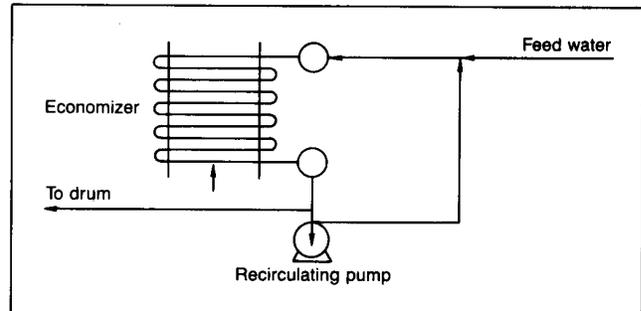


Fig. 6—Recirculation pump mixes hot water with feed water.

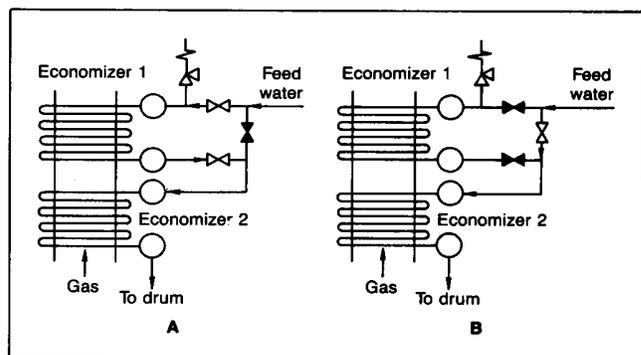


Fig. 7—Bypass arrangement for economizer. In "b" economizer one is bypassed. This increases exit gas temperature and avoids steaming but does not solve dew point corrosion in economizer two.

At 5 psig the saturation is 228°F and at 10 psig it is 240°F. In case the deaerator pressure cannot be raised, a heat exchanger may be used ahead of the economizer (Fig. 4) to increase the feed water temperature. It may be steam or water heated.

3. Fig. 5 shows a method for using an exchanger to pre heat the water. The same amount of water from the economizer exit preheats the incoming water. By controlling the flow of the hotter water, one can adjust the water temperature to the economizer so that a balance between corrosion criterion and efficiency of operation can be maintained.

4. Hot water from either the economizer exit or the steam drum (Fig. 6), can be recirculated and mixed with the incoming water. The economizer has to handle a higher flow, but the exchanger is eliminated and a pump is added. Note that some engineers have the misconception that bypassing a portion of the economizer (Fig. 7) would solve the problem; not so. While bypassing, the heat transfer surface reduces the duty on the economizer and increases the exit gas temperature; it does not help to increase the wall temperature of the tubes, which is the most important variable. A higher exit gas temperature probably helps the downstream ductwork and equipment, but not the economizer. One benefit, however, from bypassing is



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Permitting condensation on surfaces. By using proper materials one can protect the heating surfaces from corrosion attack, if condensation is likely. This concept has now been extended to recovering the sensible and latent heat from the flue gases, thereby increasing the thermal efficiency of the system by several percentage points in what are called condensing heat exchangers. If flue gases contain say 10% by volume water vapor, by condensing even half of it, approximately 30 Btu/lb of flue gas can be recovered. This is nearly equivalent to a 120°F drop in gas temperature if sensible heat alone is transferred.

A large amount of sensible and latent heat in the flue gas can be recovered if the gas is cooled below the water dew point. This implies that sulfuric acid, if present in the gas stream, will condense on the heat transfer surfaces as its dew point is much higher than that of water vapor.

Borosilicate glass and teflon coated tubes have been widely used as heat transfer surfaces for this service. Glass is suitable for low pressures and temperatures (less than 450°F and 20 to 100 psig). However, presence of fluorides and alkalis is harmful to the glass tubes.

One manufacturer of condensing heat exchangers uses teflon coated tubes. A thin film (about 0.015 in.) is extruded onto carbon or alloy steel tubes, and the surface is resistant to corrosion of sulfuric acid. Finned tubes cannot be used as teflon cannot be extruded onto these surfaces. Hence, these exchangers will be larger than those with extended surfaces, however, the higher heat transfer rates with condensation process improves the overall heat transfer coefficients and partly compensates for the lower surface area per linear foot of bare tubes.

The high initial investment associated with condensing heat exchangers has to be carefully reviewed along with the energy recovered, fuel costs, etc. If the fuel cost is not high, then the payback period for this type of equipment may be long.

Materials such as cast iron and stainless steels probably have better corrosion resistance than carbon steel, but still they are not

Conclusion The article outlined the importance of the dew point of acid gas and methods for dealing with the problem of condensation on heating surfaces such as economizers. Similar methods could be used for air heaters. The basic difference lies in the fact that the back end temperature is a function of both the gas and air temperatures. Steam air heating or air bypassing have been used to combat the problem of corrosion. Replaceable matrices and corrosion resistant materials such as enamels have been used at the cold end of regenerative air heaters

APPENDIX 1-Dew points of acid gases'

HCl, HBr, HNO₃ and SO₂ correlations were derived from vapor-liquid equilibrium data.⁴ The H₂SO₄ correlation is from reference 5.

Hydrobromic acid:
 $1,000/T_{DP} = 3.5639 - 0.1350 \ln(P_{H_2O}) + 0.0398 \ln(P_{HBr}) + 0.00235 \ln(P_{H_2O}) \ln(P_{HBr})$

Hydrochloric acid:
 $1,000/T_{DP} = 3.7368 - 0.1591 \ln(P_{H_2O}) - 0.0326 \ln(P_{HCl}) + 0.00269 \ln(P_{H_2O}) \ln(P_{HCl})$

Nitric acid:
 $1,000/T_{DP} = 3.6614 - 0.1446 \ln(P_H)$

Sulfurous acid:
 $1,000/T_{DP} = 3.9526 - 0.1863 \ln(P_{H_2O}) + 0.000867 \ln(P_{SO_2}) - 0.000913 \ln(P_{H_2O}) \ln(P_{SO_2})$

Sulfuric acid:
 $1,000/T_{DP} = 2.276 - 0.0294 \ln(P_{H_2O}) - 0.0858 \ln(P_{H_2SO_4}) + 0.0062 \ln(P_{H_2O}) \ln(P_{H_2SO_4})$

Where: T_{DP} is dew point temperature (K) and P is partial pressure (mmHg).

Compared with published data, the predicted dew points are within about 6K of actual values except for H₂SO₄ which is within about 9K.

REFERENCES

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- ⁴ Perry, R. H., and Chilton C. H., ed., "Chemical Engineers' Handbook," 5th ed., McGraw-Hill, New York, 1973.
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APPENDIX 2-Determining tube wall temperatures of economizers

The average wall temperature of a bare tube economizer is given by the simple equation:

$$t_w = 0.5[t_i + t_g - U(t_g - t_i) (1/h_a - 1/h_i)]$$

Where:

h_i = heat transfer coefficient inside tubes, Btu/ft²h °F
 It = heat transfer coefficient outside tubes, Btu/ft²h °F
 t_i = temperature of water inside tubes, °F t_g = temperature of gas outside tubes, °F
 t_w = average tube wall temperature, °F
 U = overall heat transfer coefficient, Btu/ft²h °F $1/U = 1/h_i + 1/h_o$, neglecting fouling and metal resistance, which are much smaller.

Typically h_i = 1,000, h_a = 15 and hence U = 4.77

Case 1: Determine t_w when t_g = 750°F and t_i = 50°F $t_w = 0.5 [250 + 750 - 14.77 (750 - 250) (0.066 - 0.001)] = 260°F$

Case 2: t_g = 350°F, t_i = 250°F
 $t_w = 0.5 [250 + 350 - 14.77 (350 - 250) (0.066 - 0.001)] = 252°F$

Thus, for a variation of 400°F gas temperature, the tube wall temperature hardly changes by 8°F Thus, the water temperature fixes the tube wall temperature.

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