

Acid Dewpoint Temperature Measurement

Introduction

Measurements of the Acid Dewpoint Temperature (ADT) are important for combustion efficiency, environmental compliance and process optimization on a variety of coal- and oil-fired processes. The Lancom 200 Portable Analyser and ADM440, a continuous monitoring device, provide valuable tools for ADT measurement.

Sulfuric Acid Formation

It is commonly known that sulfur dioxide (SO_2) emissions from process plants contribute to acid rain, and that many sites have to monitor or control such emissions. Problems associated with sulfur trioxide (SO_3) and sulfuric acid (H_2SO_4) emissions, however, are less widely recognized, and sulfuric acid in stack gases contributes to serious and expensive maintenance problems as well.

Most solid and liquid fuels contain some sulfur – most coals, heavy oil, petroleum coke (petcoke) and Orimulsion® bitumen-based fuels typically contain between 0.5% and 3% sulfur by weight. When these fuels are burned, the sulfur is oxidized to SO_2 and typical flue gases contain between 300 ppm and 3000 ppm SO_2 . If sufficient oxygen is available, some of that SO_2 oxidizes further to SO_3 . In most cases, the SO_3 forms a small, but significant, fraction of the oxidized sulfur - typically a few percent of the total. Water in the flue gas reacts with the SO_3 to form H_2SO_4 in a reversible reaction, so that there is an equilibrium between the SO_3 and H_2SO_4 concentrations. The reaction between SO_3 and H_2O is exothermic, so the dissociation reaction is favored at higher temperatures.

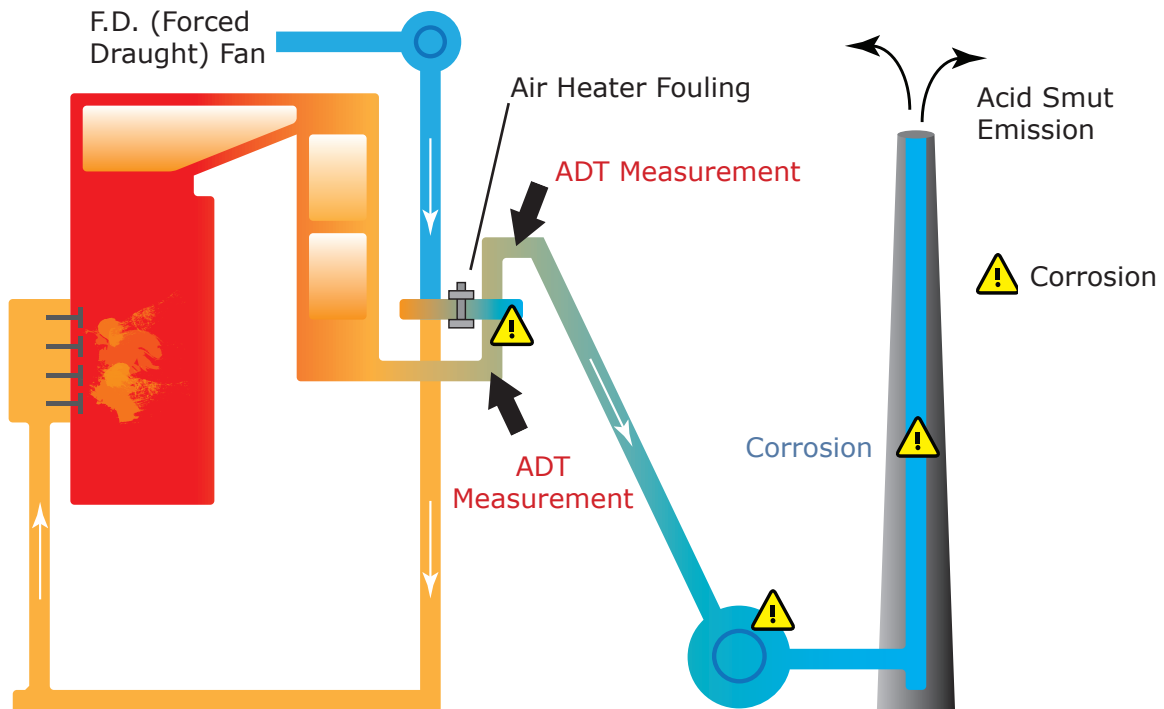
SO_3 also adsorbs onto fly ash. Ash is generally basic and so the acidic SO_3 binds easily to the surface, resulting in low levels of free SO_3 . The ash is removed from the gas stream by the precipitators or the baghouse along with the adsorbed SO_3 . This can make it difficult to measure the ADT in a coal-fired process.

Effects of Sulfuric Acid in Flue Gases

The presence of sulfuric acid in stack gases can lead to a number of undesirable consequences. Sulfuric acid condenses at temperatures well above 100°C / 212°F . If the gas temperature drops below the acid dewpoint, sulfuric acid aerosol is formed, and a film of sulfuric acid also will form on any exposed surface with a temperature below the dewpoint.

Sulfuric acid aerosols contribute to PM2.5 emissions that can affect human health. The aerosol droplets are very small, typically around $1\ \mu\text{m}$ in diameter, so they also scatter light very effectively. If sulfuric acid is present in the gases at the stack exit, the condensing aerosol forms a so-called "blue plume". The blue color comes from the preferential scattering of blue light by the aerosol. Once formed, such plumes are very persistent and can negatively impact visibility a long distance from the source. Air quality managers increasingly are concerned about visibility issues resulting from sulfate aerosol emissions. In addition, blue plume problems have been linked to selective catalytic reduction (SCR) systems used to reduce NO_x concentrations. The catalyst apparently helps promote the SO_2 to SO_3 reaction, leading to the formation of large amounts of sulfuric acid in the stack exhaust.

When particulate matter is allowed to build up in the ductwork, agglomerations of particles can form, and the SO_3 adsorbs onto these particles as noted previously. When such agglomerations become detached, they may be emitted from the stack as acid smuts – highly corrosive pieces of dust that attack the surfaces they land on, including nearby cars, homes and vegetation. In addition, the ammonia used in SCR systems can combine with the sulfuric acid to form ammonium bisulfate, which is an especially difficult material since it precipitates directly from a gas to a solid at temperatures below 260°C , leaving sticky deposits on ductwork and cooler surfaces such as heat exchangers. Ammonium bisulfate deposited on the air preheater has a big impact on the heat transfer efficiency, which in turn affects the operating costs of the process.



I.D. (Induced Draft) Fan

Schematic showing corrosion and optimum ADT measurement points

For plant operators, the most serious consequences occur when the gases drop below the dewpoint within the process. Corrosion is an inevitable consequence whenever hot sulfuric acid is deposited on a metal surface. Glass-coated surfaces are an option but are very expensive to install. In general, it is better to maintain the temperature above the dewpoint. This is no trivial matter, since increasing the stack exit temperature decreases the thermal efficiency of the plant and increases fuel costs. Clearly, there is an optimum operating temperature – safely above the dewpoint but as close to it as can practically be arranged. Cold-end corrosion can occur anywhere the gas temperature drops, or where ambient conditions can lead to surface cooling. Heat exchangers, exposed ducts and stacks are especially vulnerable, see diagram above.

Summary

A number of strategies can be used to minimize SO_3 formation and related emissions. Wet scrubbers, such as those used to remove SO_2 , tend to be ineffective in removing sulfuric acid aerosols because the droplets are too small to be entrained in the scrubbers' slurry. One solution is to use fuel additives such as magnesium oxide (MgO) or magnesium hydroxide (MgOH). These react with sulfur from the fuel in the combustion zone, forming solid salts that precipitate from the gas stream. Along with the removal on the fly-ash, this is the principal mitigation strategy for both SO_3 formation and sulfate aerosol emissions. Another approach is to use a wet precipitator that effectively collects the sulfate aerosol. However, any strategy for dealing with SO_3 and H_2SO_4 requires a method for measuring their concentration in stack gases. This may be rather difficult, especially if continuous measurement is required.

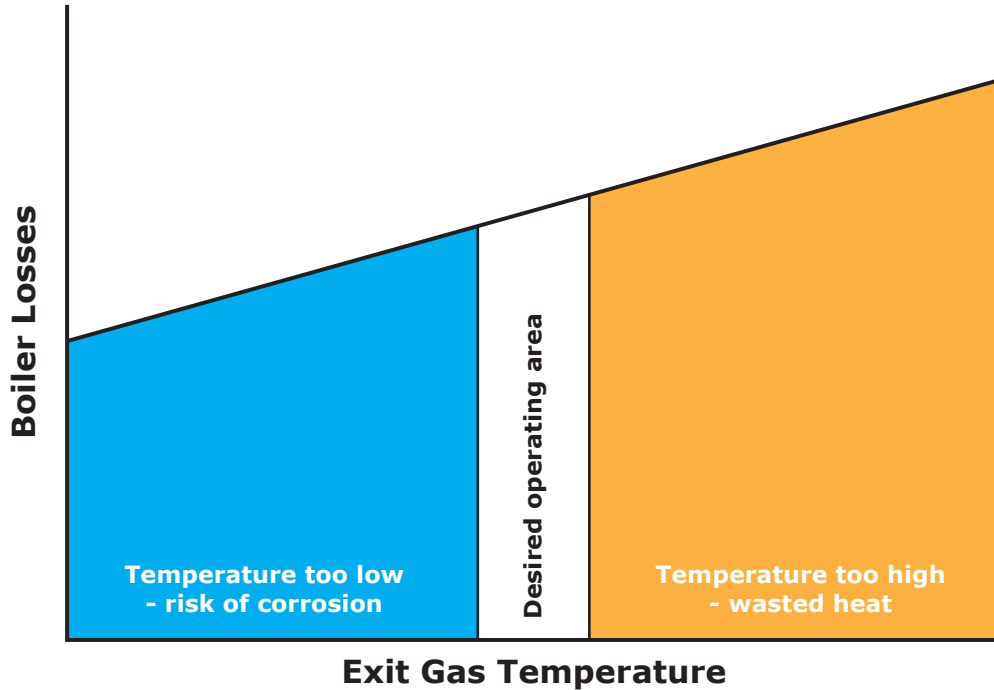
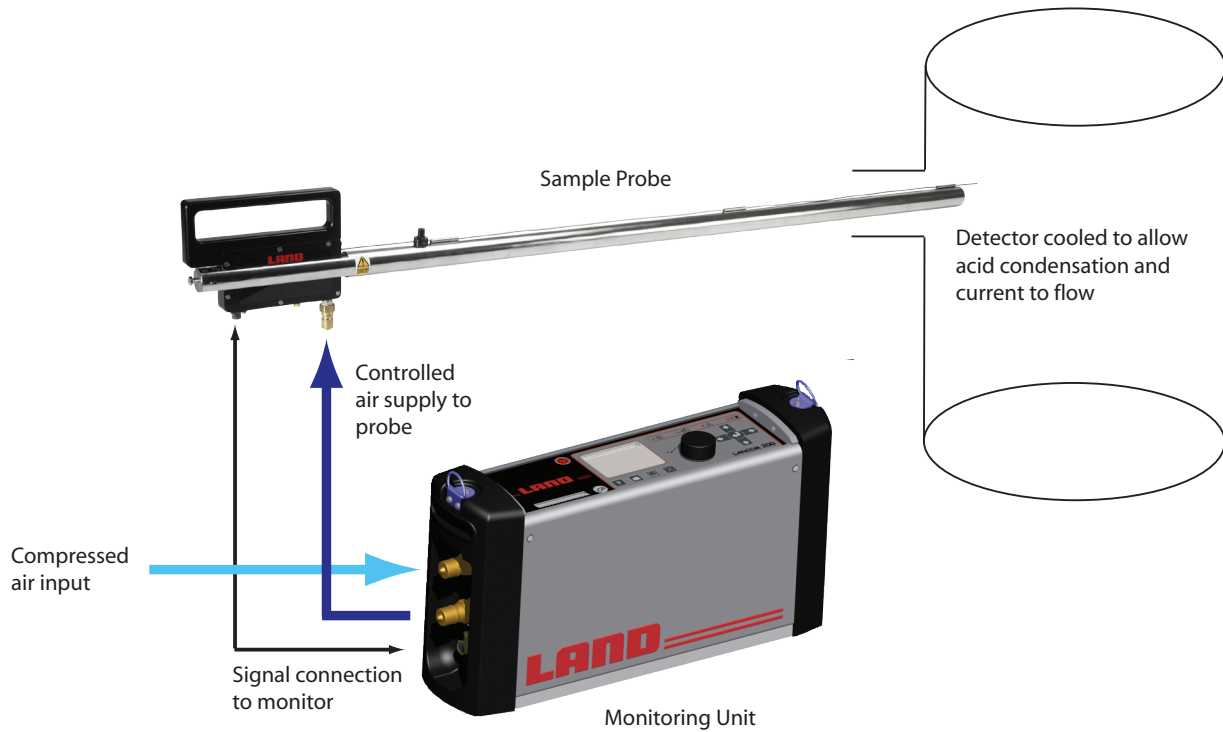


Chart showing Boiler Losses vs. Exit Gas Temperature

How the Lancom 200 Portable Sulfuric Acid Dewpoint Monitor Works

Lancom 200 consists of a probe with sensor mounted in the tip and a portable control unit that includes an air flow regulator and electronics to measure the conductivity and thermocouple temperature. Data logging and printing allow successive measurements to be stored for subsequent analysis. This configuration is very practical because it allows the operator to survey of a number of different points on a process plant, logging the data in real-time, before downloading it to a PC for subsequent analysis.



Schematic showing the Lancom 200 in use

The sensor consists of two platinum electrodes embedded in a borosilicate glass thimble. As the sensor cools, sulfuric acid condenses on the sensor and this can be detected by measuring the conductivity between the two electrodes. The ring electrode is made of pure platinum but the linear electrode is actually a Type R thermocouple, and this allows the Lancom 200 to measure the temperature of the acid film. When the rate of condensation is equal to the rate of evaporation, the acid film is in equilibrium and the conductivity is constant. The equilibrium point is the acid dewpoint temperature.

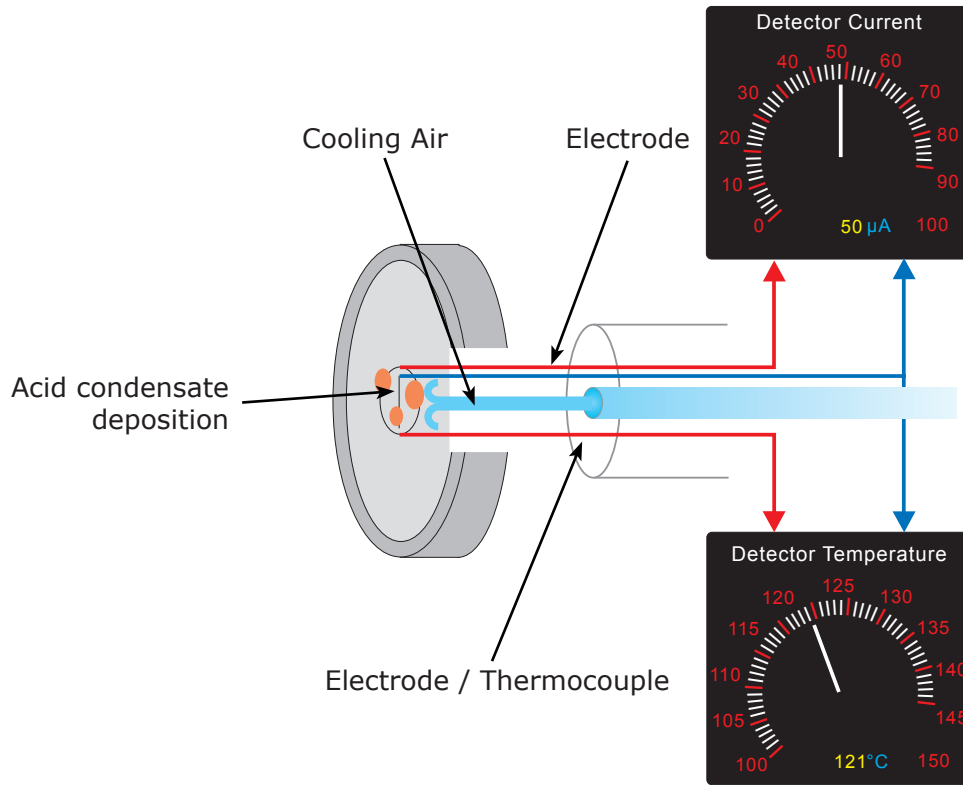
The operating principle of the ADM440 is very similar, but the temperature control is automatic and the system includes an automatic sensor cleaning mechanism which allows the unit to operate unattended for many weeks or months.



Acid Dewpoint Sensor

Using the Lancom 200 to Measure the ADT

The operation of the Lancom 200 is very straightforward.



1. Close the air valve on the Lancom 200 Portable Control Unit (PCU) by turning the knob on the front panel fully clockwise. Turn it gently until it comes to a stop. Do not screw it down tight.
2. Ensure that the PCU is connected to a supply of clean compressed air.
3. Switch on the PCU by pressing the red power button.
4. When the red message screen appears, press the Enter key. The display should show two large dials.
5. Insert the probe into the stack or duct. It needs a hole that is at least 50mm (2in) in diameter. Block any gaps around the probe with cotton cloth to reduce tramp air. Use the small knob in front of the probe handle to slide the flue gas thermocouple out beyond the end of the probe.
6. Allow the probe to heat up to the flue gas temperature. The detector temperature is shown on the right hand dial. The flue gas temperature is in the bottom right corner of the screen. The left hand dial shows the sensor current measurement. It may increase briefly as some acid condenses on the sensor; then it should return to less than 5 μA . Wait until the readings are stable.
7. Increase the air supply slowly by turning the knob anti-clockwise. The air flow rate is shown by the blue bar below the dials. This will get longer as the air flow increases.
8. Increase the air supply until the detector temperature is dropping steadily. Watch the left dial until its reading starts to increase. Reduce the air slightly to slow down the rate of

cooling. As the current reading increases, reduce the air further. The objective is to hold the current reading at around 50µA.

Note: If you know the approximate ADT, you can set the sensor temperature to a few degrees above this value before making the final adjustments. If you reduce the sensor temperature too far below the ADT, the acid film may form very slowly, giving the impression that the sensor is still above the dewpoint.

9. When the current reading has been stable between 40 and 60µA for about five seconds, press the Enter button to record the Acid Dewpoint Temperature (ADT). The message ADT Stored appears on screen.

You should wipe the sensor tip with a soft cloth to remove dust deposits each time you remove the probe from the flue (CAREFUL – IT IS HOT!). This will prevent the accumulation of dust and other contaminants which can affect the dewpoint reading.

Practical Considerations and Limitations of ADT Measurement

It is important to recognize that the Lancom 200 and ADM440 cannot measure the acid dewpoint in every application. Some considerations for successful dewpoint measurement include

- Sulfuric acid concentration. The detection limit of an ADT sensor is set by the time taken to form a measurable film of sulfuric acid on the sensor. At very low concentrations, the film forms so slowly that it is not practical to measure it. This problem is even more acute with the ADM440 because the instrument indicates a fault if it cannot measure an ADT within a reasonable time. A lot of patience is needed when measuring ADT below 130°C (266°F), and the minimum measurable ADT is around 125°C (257°F). That sets the detection limit for H₂SO₄ at approximately 5 ppm.
- Sulfuric acid concentration. Although it is not possible to make an exact calculation of the H₂SO₄ concentration based on the SO₂ content of the flue gas, the concentration is usually between 1% and 1.5% of the SO₂ concentration for a standard application, and may be twice as much after an SCR. Therefore, it is unlikely that an ADT could be measured on a process containing 100 ppm SO₂ but it should be relatively easy to measure on a process with an SCR where the SO₂ concentration is 800 ppm.
- Flue gas temperature. The cooling air must be capable of reducing the sensor temperature below the ADT. The minimum ADT that can be measured (ADT_{min}) depends on the temperatures of the flue gas (T_{flue}) and the cooling air, which is usually at ambient temperature (T_{amb}). Measuring a low ADT in a hot stack can be very difficult; the minimum measurable dewpoint temperature can be estimated using this equation

$$ADT_{min} = 0.65 T_{amb} + 0.35 T_{flue}$$

- It is usually quite easy to measure the ADT in the stack, but temperatures before the air preheater are often too high to allow for an ADT measurement.
- One of the largest uncertainties is the proportion of the H₂SO₄ which is adsorbed onto the fly ash. As noted previously, fly ash has a high affinity for H₂SO₄ and so there may not be enough free H₂SO₄ to measure if the fly ash concentration is high. In the past, this has been a significant problem when using ADT to estimate the SO₃ and H₂SO₄ concentrations in coal-fired power plant, but the combination of high-sulfur coal and SCR has increased the amount of free H₂SO₄ in many modern plants, so that the measurement is feasible in many more places than in the past.

- Gas velocity may have an influence at low H₂SO₄ concentrations – users have reported difficulty in measuring the ADT when the velocity of flue gas is very high, but there are no definite figures available.

Although the ADT measurement depends only on the concentration of H₂SO₄ at the sensor surface, the reaction between SO₃ and H₂SO₄ is so fast that any SO₃ present in the flue gas is converted to H₂SO₄ on the sensor. It is important to remember that the calculations giving the SO₃ and H₂SO₄ concentrations depend on the stack temperature and water content, as well as the ADT, so these calculations will not be accurate unless the flue gas thermocouple is reading a representative gas temperature, and the water concentration parameter is set correctly.

Conclusions

Acid Dewpoint temperature measurement gives valuable information on the combustion process. It can be used to estimate the concentration of SO₃ and H₂SO₄ in the stack, as well as giving valuable data on process efficiency.

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