

ACID DEWPOINT TEMPERATURE MEASUREMENT AND ITS USE IN ESTIMATING SULFUR TRIOXIDE CONCENTRATION

Derek D Stuart
AMETEK Process & Analytical Instruments
150 Freeport Rd, Pittsburgh PA 15238

KEYWORDS

Acid Dewpoint, Sulfuric Acid, Sulfur Trioxide, Combustion Efficiency

ABSTRACT

Knowledge of the sulfuric acid dewpoint temperature (ADT) is important in many combustion processes. An effective ADT sensor can be made by cooling a glass surface and measuring its surface conductivity and temperature with a pair of precious metal electrodes, one of which is a Pt-PtRh thermocouple. The main purpose is to prevent ductwork corrosion whilst maintaining good thermal efficiency, but a knowledge of the relevant physical chemistry allows the sulfur trioxide and sulfuric acid concentrations in the flue gases to be derived from the ADT.

INTRODUCTION

It's commonly known that sulfur dioxide (SO₂) emissions from process plants contribute to acid rain, and that many sites have to monitor or control such emissions [1]. Problems associated with sulfur trioxide (SO₃) and sulfuric acid (H₂SO₄) emissions, however, are less widely recognized. It is also less well known that sulfuric acid in stack gases contributes to serious and expensive maintenance problems.

When sulfur-containing fuels are burned, the sulfur is oxidized to SO₂. If sufficient oxygen is available, some of that SO₂ oxidizes further to SO₃. In most cases, the SO₃ forms a small, but significant, fraction of the oxidized sulfur. Typically this is a few percent of the total. Most solid and liquid fuels contain some sulfur – coals typically contain between 0.5% and 5% sulfur by weight [2].

If water is present, it may react with the SO₃ to form H₂SO₄ in a reversible reaction. The dissociation reaction [eq.1] in which H₂SO₄ is broken down to H₂O and SO₃, is favored at higher temperatures. This is shown in Figure 1. At low temperatures, below 200°C, all of the SO₃ is present as H₂SO₄. Above 500°C, it is almost entirely free SO₃. The equilibrium point also depends on the concentration of water vapor at a given temperature. More of the initial SO₃ will be present as H₂SO₄ when the water concentration is high.

Where sulfuric acid forms, a number of factors affect the amount of free SO₃ and H₂SO₄ present in the stack gases. This proportion increases if the fuel contains substances such as vanadium, which acts as a catalyst encouraging the formation of SO₃. Petroleum-based fuels typically contain more vanadium than coal, so the SO₃ concentration is generally higher when burning oil than coal.

PHYSICAL CHEMISTRY

Measuring and interpreting the acid dewpoint and its measurement requires some understanding of the chemistry of the gas-phase reaction



GAS CONCENTRATIONS

An empirical formula relating the acid dewpoint temperature (T_{dew}) to the partial pressures (P_x) of the various constituents was established by Verhoff & Banchemo [3].

$$T_{dew} = 1000 / \{2.276 - 0.0294 \ln(p_{H_2O}) - 0.0858 \ln(p_{SO_3}) + 0.0062 \ln(p_{H_2O} p_{SO_3})\} \quad (2)$$

For this equation partial pressures are expressed as mmHg. This equation is very useful because it allows the partial pressure, and hence concentration, of SO₃ to be determined from the acid dewpoint temperature provided the equilibrium point is known.

EQUILIBRIUM

Reaction (1) is reversible and so the products and reactants will both be present to some extent. For an arbitrary chemical reaction



the equilibrium point is described by the equation

$$K = \frac{p_C^c p_D^d}{p_A^a p_B^b} \quad (4)$$

where a, b c & d are the number of moles of components A, B, C and D required by stoichiometry, K is the equilibrium constant and p_A , p_B , p_C and p_D are the partial pressures of these components, expressed in atmospheres [4].

For reaction (1), this gives

$$K = \frac{P_{H_2SO_4}}{P_{SO_3} P_{H_2O}} \quad (5)$$

The equilibrium constant depends on the temperature and the Gibbs free energy of the reaction according to the equation

$$RT \ln K = -\Delta_r G^0 \quad (6)$$

R is the universal gas constant, T is the absolute temperature and $\Delta_r G^0$ is the standard Gibbs free energy for the reaction at that temperature. The NIST-JANAF tables [5] give values of $\Delta_r G^0$ and $\log_{10} K$ for temperatures from 0 K to 6000 K.

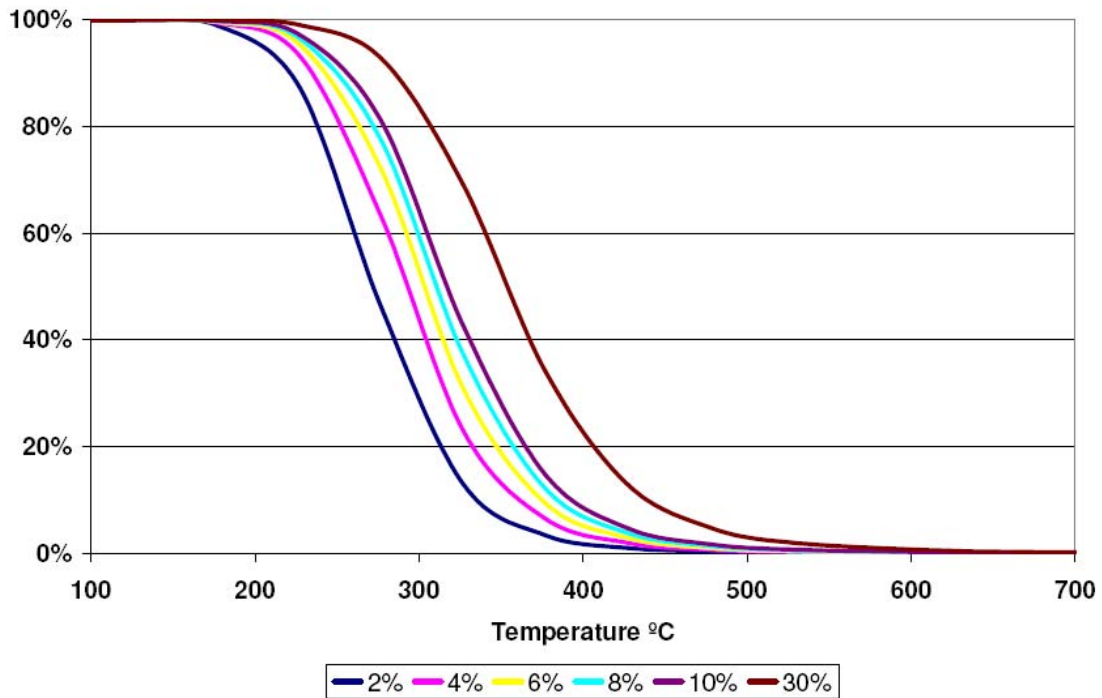


FIGURE 1: FRACTION OF INITIAL SO₃ PRESENT AS H₂SO₄ WITH WATER CONTENT FROM 2% TO 30% BY VOLUME

Applying this data to (5) and (6) allows us to calculate the ratio Q of H₂SO₄ to SO₃ for any given temperature and H₂O content. The fraction F of initial SO₃ present as H₂SO₄ can be calculated as

$$F = 100 \times \frac{Q}{Q+1} \quad (7)$$

Figure 1 shows how F varies with temperature for a range of different water concentrations. Each line shows the equilibrium position as a function of temperature at a fixed water concentration. These are consistent with the graph given by Hardman [6].

REACTION RATE

The acid dewpoint sensor works by cooling the gas immediately in contact with it to the acid dewpoint, and then measuring this temperature. This assumes that all of the SO₃ has been converted to H₂SO₄ at the cooled surface of the sensor. This will only be true if the reaction is fast enough for the equilibrium point to be reached while the gas sample is in contact with the sensor surface.

Reaction (1) is a second-order reaction. This means that its rate has the form

$$\frac{d}{dt}[H_2SO_4] = k[SO_3][H_2O] \quad (8)$$

where [H₂SO₄], [SO₃] and [H₂O] denote the concentrations of the respective components and k is the reaction rate constant.

The NIST chemical kinetics database [7, 8] gives a reaction rate of $1.2 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ at 298K. In the case where [SO₃] = 1 ppm and [H₂O] = 10%, this means that H₂SO₄ is formed at a rate of 1000 ppm.s⁻¹. Put another way, if the reaction continues at the initial rate then it will approach equilibrium in 1 ms at 298 K. Most chemical reactions proceed very much faster as the temperature increases, so the reaction will be very much faster at typical process temperatures.

If we assume a gas flow rate of 20 m.s⁻¹ and a sensor diameter of 20 mm then the interaction time between the stack gas and the cooled surface of the dewpoint sensor will be approximately 1 ms. This is comparable with the time taken for the SO₃ and H₂SO₄ to react at room temperature, but probably much longer than the reaction time at typical process temperatures.

More recent work [9, 10] has shown that the actual reaction rate is many orders of magnitude faster, and a theoretical explanation by Loerting & Liedel [11] suggests that several water molecules are involved in the reaction.

All of the above leads to the conclusion that the reaction time is unlikely to influence the dewpoint measurement in any practical application.

ACID DEWPOINT TEMPERATURE MEASUREMENT

PRACTICAL CONSIDERATIONS

Where sulfuric acid forms, a number of factors affect the amount of free SO_3 and H_2SO_4 present in the stack gases [12]. This ratio of SO_3 to SO_2 increases if the fuel contains substances such as vanadium, which acts as a catalyst encouraging the formation of SO_3 . Petroleum-based fuels typically contain more vanadium than coal, so the SO_3 concentration is generally higher when burning oil than coal [13].

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 .

The presence of SO_3 in stack gases can lead to a number of undesirable consequences. Sulfuric acid condenses at temperatures well above 100°C . If the gas temperature drops below the acid dewpoint, sulfuric acid aerosol is formed, and a film of sulfuric acid also will be deposited on any exposed surface with a temperature below the dewpoint.

The aerosol droplets are very small, typically around $1\ \mu\text{m}$, so they 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”. Once formed, such plumes are very persistent and can negatively impact visibility a long distance from the source.

Air quality managers are increasingly 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 [14].

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.

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 (shown schematically in Figure 2).

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. A number of strategies can be used to minimize SO₃ formation and related emissions. Wet scrubbers, such as those used to remove SO₂, 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 SO₃ 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 SO₃ and H₂SO₄ requires a method for measuring their concentration in stack gases. This may be rather difficult, especially if continuous measurement is required.

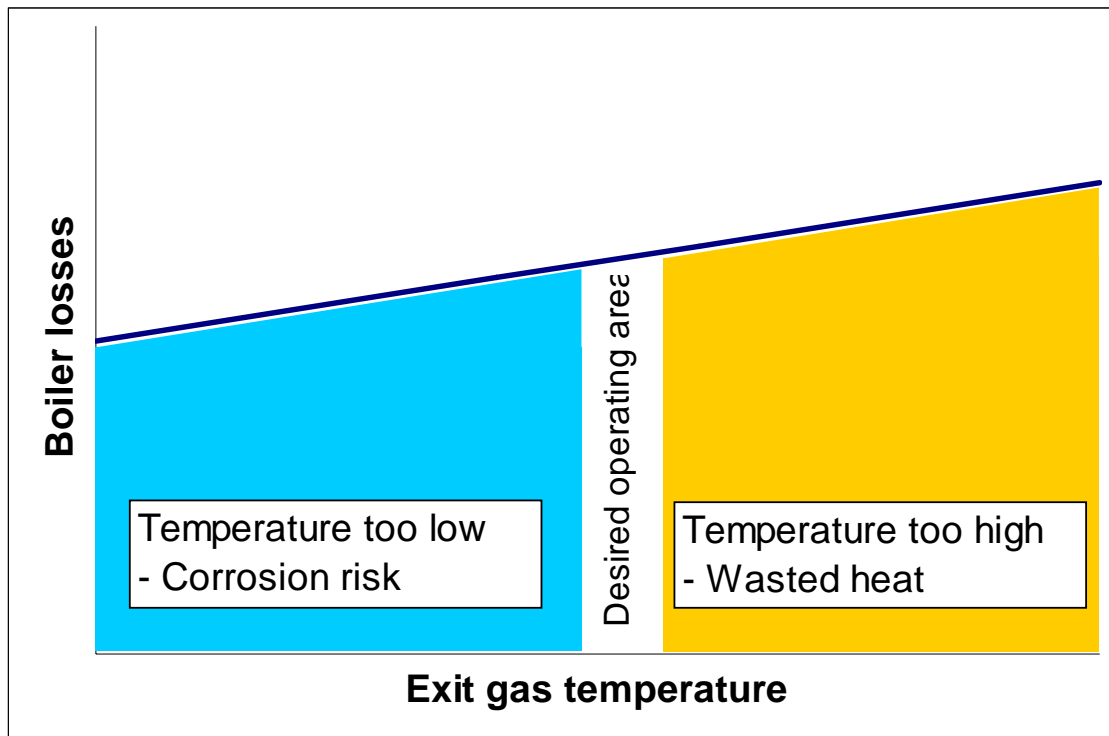


FIGURE 2: OPTIMUM OPERATING CONDITIONS FOR MAXIMUM BOILER EFFICIENCY

ACID DEWPOINT TEMPERATURE MEASUREMENT

The above means little without a practical and reliable method for measuring the SO₃ concentration. The US Environmental Protection Agency's Method 8 - Determination of Sulfuric Acid and Sulfuric Dioxide Emissions from Stationary Sources [15] has long been the method used. In some circumstances, the Controlled Condensation Method for condensable particulate

matter gives a more meaningful result [16]. As a wet-chemical method, it is rather cumbersome, and it is not suited to either rapid or continuous measurements.

An acid dewpoint temperature (ADT) sensor, on the other hand, can be used to effectively monitor sulfuric acid concentration either continuously or periodically. The method was originally developed by Land [17]. The sensor consists of a precious-metal thermocouple and a ring electrode embedded in a glass thimble, as shown in Figure 3.



FIGURE 3: ACID DEWPOINT TEMPERATURE SENSOR

Figure 4 shows a schematic view of the sensor. The inside of the thimble can be cooled by a flow of air. The linear electrode is a Pt-PtRh thermocouple which measures the surface temperature, whilst the ring electrode which surrounds it is a simple platinum wire. A sulfuric acid film forms on the sensor when the sensor is cooled below the acid dewpoint. The acid is very conductive so that the conductivity between the ring electrode and the thermocouple gives an indication of the film's thickness. When the sensor is at the acid dewpoint temperature, the rates of evaporation and deposition are equal, so the film thickness and, hence, its conductivity are constant.

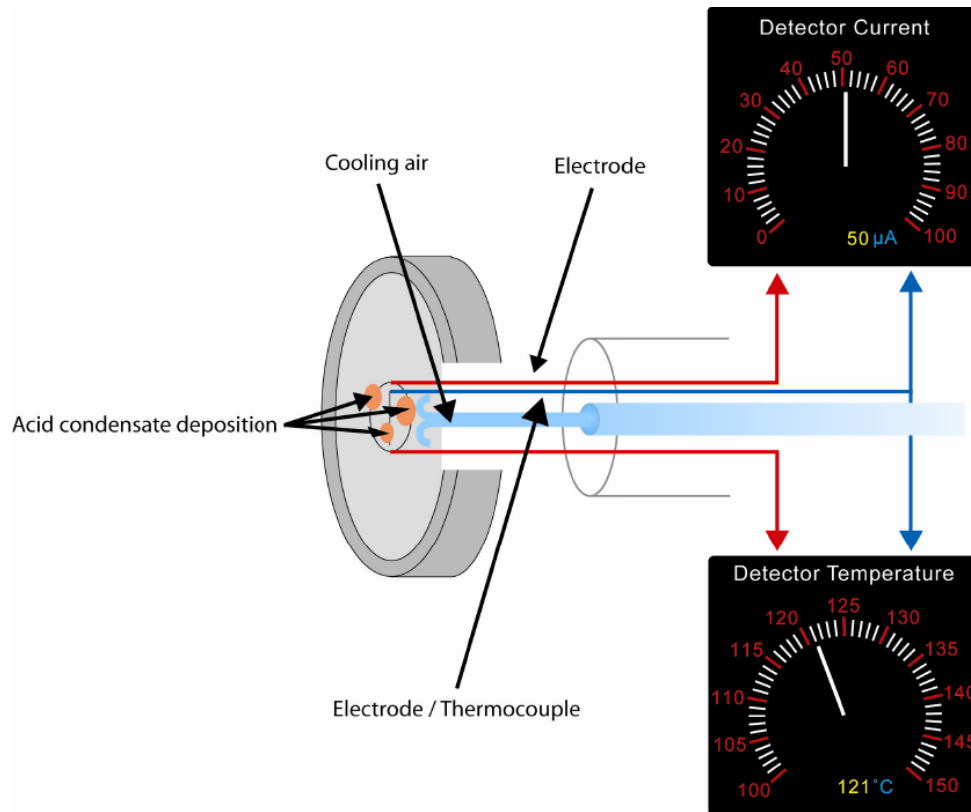


FIGURE 4: ACID DEWPOINT SENSOR

PORTABLE ACID DEWPOINT TEMPERATURE MONITOR

The first ADT monitor based on this sensor design appeared in 1965 [18]. Although improvements in electronics and modern pneumatic controls over the years have resulted in greater efficiency and usability, the measuring principle behind the analyzer has remained essentially the same.

A modern, portable ADT monitor, such as the Lancom 200 shown in Figure 5, 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 a number of different points on a process plant, logging the data in real-time, before downloading it to a PC for subsequent analysis.

The unit is lightweight (10 kg) but robust enough for regular use in an industrial environment. All that's required is a local compressed air supply and a suitable probe access point for sampling.

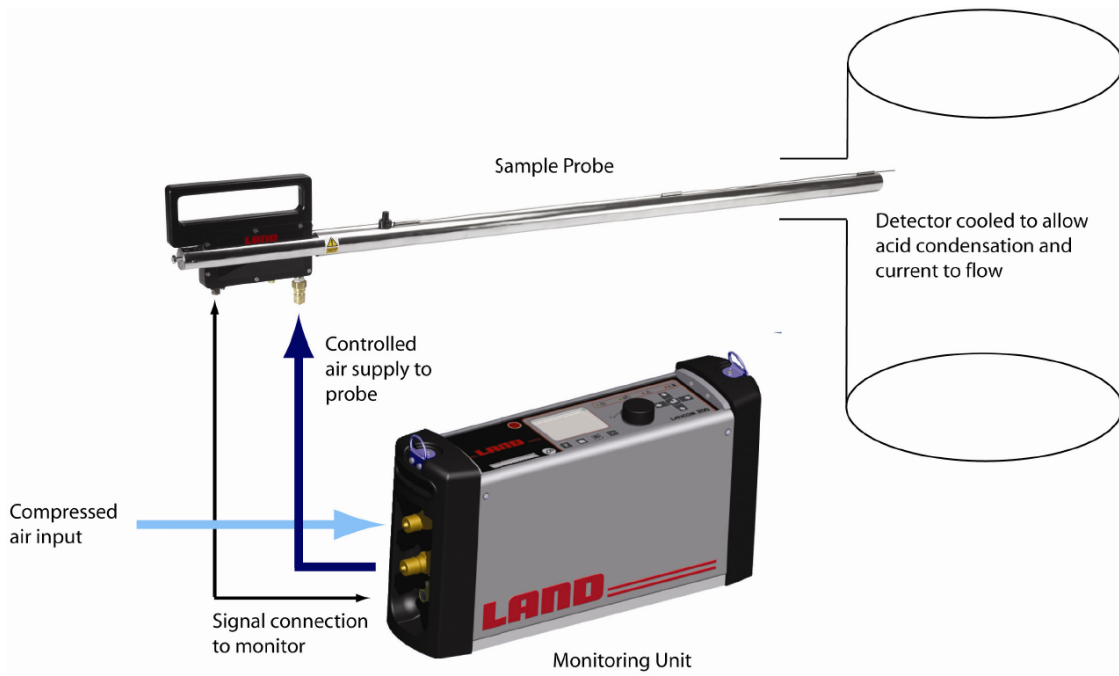


FIGURE 5: PORTABLE ACID DEWPOINT MONITOR

CONTINUOUS ACID DEWPOINT TEMPERATURE MONITOR

Dewpoint sensor cleanliness is very important. Particulate matter and salt deposits on the face of the sensor will alter the conductivity measurement, making it impossible to determine when the ADT has been reached. With a portable analyzer, this isn't a problem: an operator can simply wipe the sensor after each measurement. On a continuous ADT monitor, it is much more difficult to keep the sensor clean. A water-wash system may be employed. However, without careful control, there is a possibility that the thermal shock of the cold water contacting the hot glass will crack the sensor. Only a small amount of water is used, so there is no need to demineralize the water – ordinary potable water has been found to work well.

The following scheme has been found to work well:

1. Cool the sensor using the maximum available flow of cooling air
2. Cool the sensor further using a low-pressure mist of air and water
3. Clean the sensor using a high-pressure jet of air and water

Using this cooling technique, the practical installation time for an ADT monitor can be increased from a few hours to many months before manual cleaning is required.

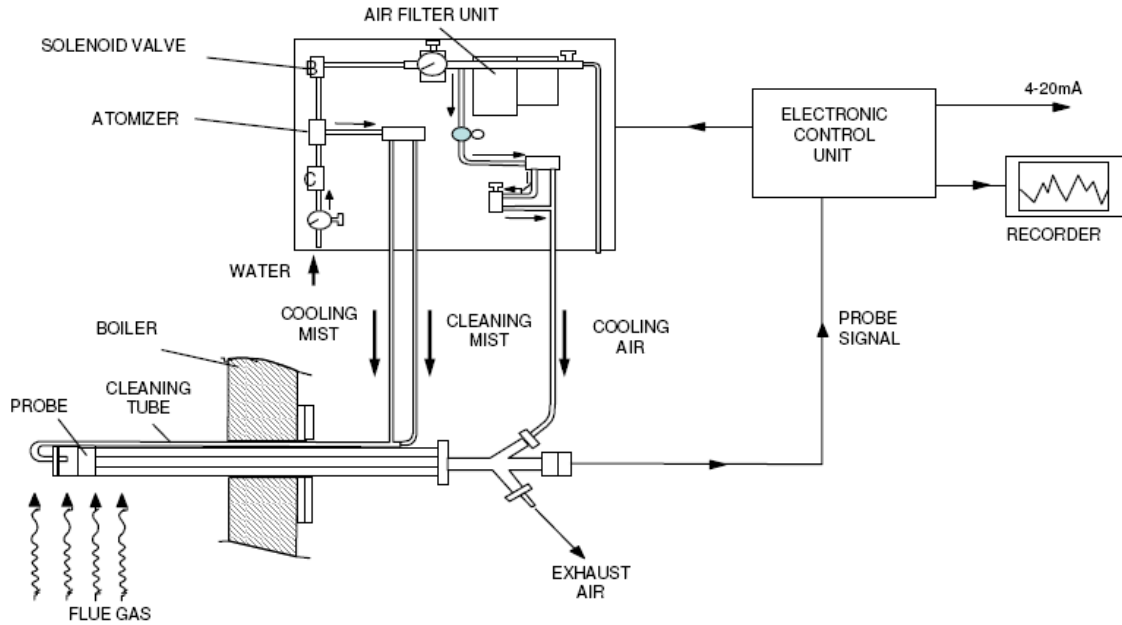


FIGURE 6: FIXED ADT MONITOR SHOWING CLEANING SYSTEM

RESULTS

Figure 7 shows data taken at an oil-burning power station during the course of a working day.

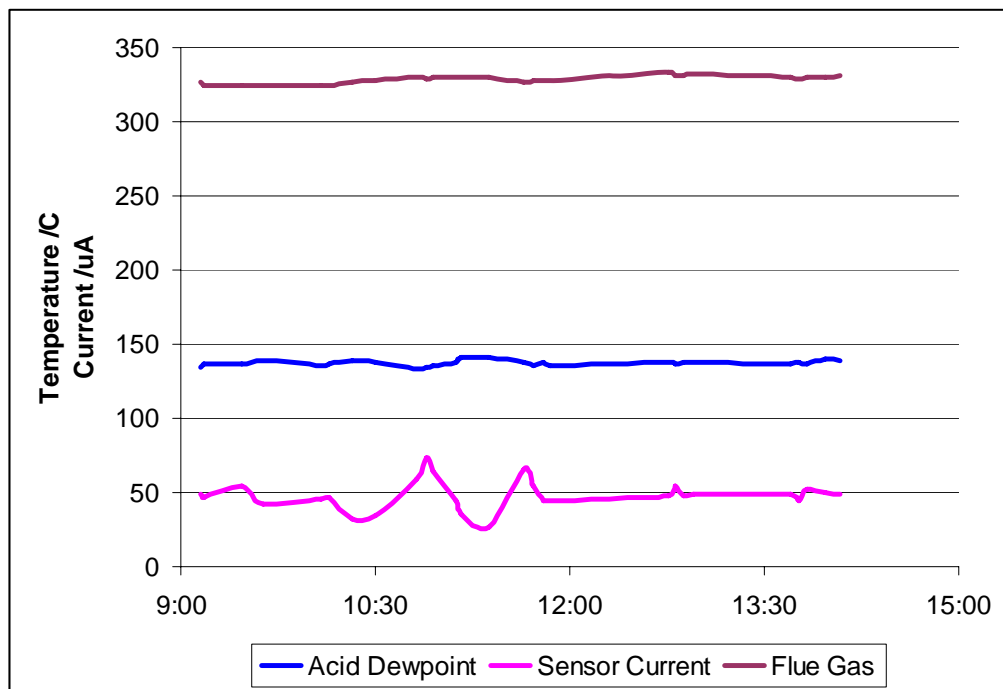


FIGURE 7: ACID DEWPOINT MEASUREMENTS

Even though the boiler load was constant, the measured dewpoint varied from 133°C to 141°C. The stack temperature is very much higher than this, so there is very clear potential for cost savings to be made by increasing the amount of heat transfer between the outgoing stack gas and the incoming combustion air before there is any possibility of acid deposition on the air heater and other ductwork.

CONCLUSIONS

Acid dewpoint monitoring is a powerful tool for improving combustion efficiency and measuring acid emissions. A continuous acid dewpoint monitor can be used to estimate the concentrations of H₂SO₄ and SO₃ in stack gases, but its design requires a proper understanding of the chemical and physical processes involved.

ACKNOWLEDGEMENTS

I would like to thank Richard Whiteside for the field data which is included.

REFERENCES

1. <http://www.epa.gov/air/peg/acidrain.html>
2. Miller, J; Drinka, TP; O'Riley, CW; Baumel CP "Effects Of Coal Blending On The Utilization Of High-Sulfur Iowa Coal And Low-Sulfur Western Coal" <http://purl.umn.edu/32441>
3. Verhoff, FH; Banchero, J "Predicting dewpoints of flue gases", *J Chem. Eng. Prog.*, 70, 1974, pp 71-72.
4. Atkins, P; de Paula, J *Physical Chemistry*, 7th edition, Oxford University Press, Oxford, UK, 2002.
5. MW Chase Jr (ed), *NIST-JANAF Thermochemical Tables*, 4th Edition, American Institute of Physics Phys Chem Ref Data Monograph 9, 1998
6. Hardman, R; Stacy, R; Dismukes, E "Estimating Sulfuric Acid Aerosol Emissions from Coal-Fired Power Plants", US DoE-FETC Conference on Formation, Distribution, Impact and Fate of Sulfur Trioxide in Utility Flue Gas Streams 1998
<http://www.netl.doe.gov/publications/proceedings/98/98fg/hardman.pdf>
7. NIST Chemical Kinetics Database <http://kinetics.nist.gov/>
8. Reiner, T; Arnold, F "Laboratory investigations of gaseous sulfuric acid formation via SO₃ + H₂O + M -> H₂SO₄ + M: Measurement of the rate constant and product identification", *J Chem Phys* 1994 101, pp 7399–7407
9. Jayne, JT; Pöschl, U; Chen, Y-M; Dai, D; Molina, LT; Worsnop, DR; Kolb, CE & Molina, MJ "The Gas Phase Reaction of Sulfur Trioxide with Water Vapor", *J Phys Chem A* 1997 101, pp 10000–10011.
10. Lovejoy, ER; Hanson, DR & Huey, LG "Kinetics and products of the gas-phase reaction of SO₃ with Water", *J Phys Chem* 1996, 100, pp 19911–19916

11. Loerting T, Liedl KR "Toward elimination of discrepancies between theory and experiment: The rate constant of the atmospheric conversion of SO₃ to H₂SO₄", Proc. Nat. Acad. Sci. USA 2000, 97, pp 8874 – 8878
12. Adams, B; Senior, C "Curbing the blue plume: SO₃ formation and mitigation", Power 2006 pp 39-41
13. <http://www.speclab.com/elements/vanadium.htm>
14. Wright, TL; DeLallo, MR "Increased SO₃ and Ammonia Slip from SCR: Balancing Air Heater Deposits, Ammonia in Effluent Discharge and SO₃ Plume"
<http://www.netl.doe.gov/publications/proceedings/02/scr-sncr/wrightsummary.pdf>
15. <http://www.epa.gov/ttn/emc/promgate/m-08.pdf>
16. <http://www.epa.gov/ttn/emc/promgate/m-202.pdf>
17. Land, T "The Theory of Acid Deposition and its Application to the Dew-Point Meter", J Inst Fuel 1977 pp 68-75
18. Land Model 200 Dewpoint Meter, Land Instruments, Chesterfield UK, 1965