

## **IAPWS Certified Research Need - ICRN**

### **Dew Point for Flue Gas of Power-Plant Exhaust**

The IAPWS Working Group Industrial Requirements and Solutions has examined the published work in the area of dew-point prediction for power-plant exhaust and recognizes that there is a requirement for work to be pursued in this field and has prepared this document to assist potential investigators in obtaining sponsorship.

This ICRN specifies the main questions that must be answered for the development of this technology.

Although encouraging this work, IAPWS is not able under its statutes to provide financial support. The IAPWS contact can provide any further development information and will act as a liaison between research groups.

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Water and Steam**

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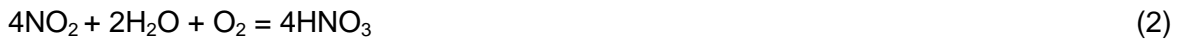
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### Dew Point for Flue Gas of Power-Plant Exhaust

#### Background

Coal is the fuel used in the majority of power-generation plants over the world. Also, there are significantly more reserves of coal than other fossil fuels. However, on a global level, coal use accounts for a significant proportion of greenhouse gas emissions, particularly carbon dioxide (CO<sub>2</sub>).

When sulfur-bearing fuel is burned, sulfur is converted to sulfur dioxide (SO<sub>2</sub>) and sulfur trioxide (SO<sub>3</sub>). The sulfur trioxide combines with moisture to form sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) [See eq.(1)]. During combustion, some nitrogen is oxidized to form nitrogen dioxide (NO<sub>2</sub>). Nitrogen dioxide in the flue also reacts with water to give nitric acid [eq.(2)] and with sulfur dioxide and water to form more sulfuric acid [eq.(3)].



If the flue gas is cooled sufficiently, condensation will occur and liquid will appear on surfaces at temperatures below the dew point. The liquid phase will contain highly corrosive sulfuric acid. This causes sulfuric acid corrosion, so called low-temperature corrosion.

Low-temperature corrosion needs to be taken into consideration for optimum system design of exhaust gas treatment, oxy-combustion capture of CO<sub>2</sub> and advanced power plants such as IGCC (Integrated Gasification Combined Cycle), IGFC (Integrated Gasification Fuel Cell), etc., which contribute to CO<sub>2</sub> emission reduction.

Problems with regard to the prediction of low-temperature corrosion result from the fact that the dew point of flue gases depends not only on the partial pressure of water, but also on the partial pressure of H<sub>2</sub>SO<sub>4</sub>. Existing prediction methods for dew points of flue gases are not comprehensive.

The main issues with regard to the dew point may be summarized as follows:

- Dew-point equations with experimental data for several flue gas compositions exist, but there are significant discrepancies among the results.
- Concentration of H<sub>2</sub>SO<sub>4</sub> depends on the SO<sub>3</sub> conversion rate and on the surface temperature of the wall. Therefore, it is important to attempt to control SO<sub>3</sub> content and to predict precisely local surface temperatures.

- Reliability of dew-point estimation depends not only on the equation but also on the temperature measurement uncertainty such as an accuracy of duct surface temperature distribution. A precise measuring method is necessary.

A proper prediction of exhaust gas temperatures is required to ensure optimized overall performance and to minimize the potential for low-temperature corrosion. For example, an exhaust temperature that is 10 K higher than necessary will cause approximately a 0.3% reduction in overall efficiency, and an increase of 12000-tonne/year CO<sub>2</sub> emissions for a 1000-MW-class coal-fired power plant.

Several empirical equations for dew point of flue gas with SO<sub>2</sub> from combustion plants have been obtained by fitting experimental data [1]-[7]. The curves shown in Figure 1 are based on a condition with SO<sub>3</sub> conversion rate of 6%. Large discrepancies, as much as 20 K, can be seen between these formulations. The curves in Figure 2 show the deviation of the Ohtsuka equation [7] from the Verhoff and Banchemo (V&B in Figure 1) equation [1], having the larger difference (up to 10 K) at lower moisture and higher SO<sub>3</sub> concentration. These two equations are commonly utilized in Japan and within major boiler suppliers over the world, respectively.

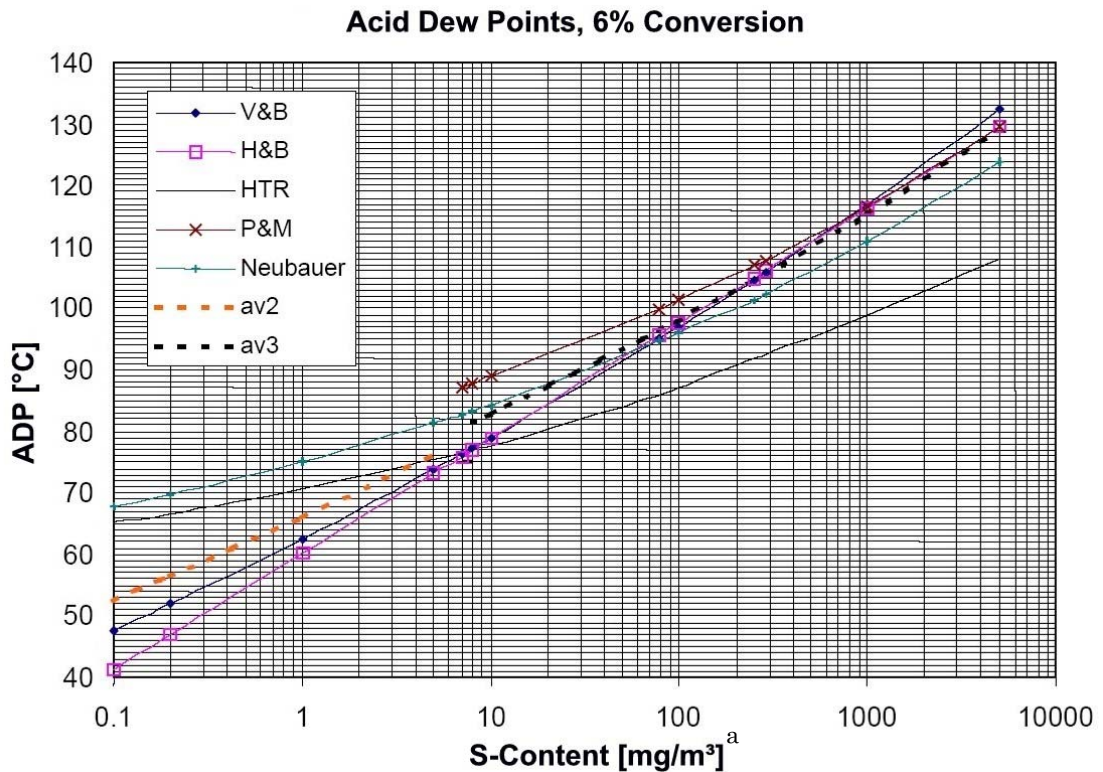


Figure 1: Comparisons of dew-point formulations<sup>b</sup>

Footnotes to Figure 1:

<sup>a</sup> Volume in cubic meters at the normal state of 101.325 kPa and 0 °C (273.15 K)

<sup>b</sup> V&B: Verhoff and Banchemo (1974), see [1]; H&B: Haase and Borgmann (1981), see [2]; HTR: Siemens AG Energy Sector internal document; P&M: Pierce and Mueller (1977), see [3],[4]; Neubauer (1962), see [5]; av2, av3: Curves averaged over the different equations valid in the respective range

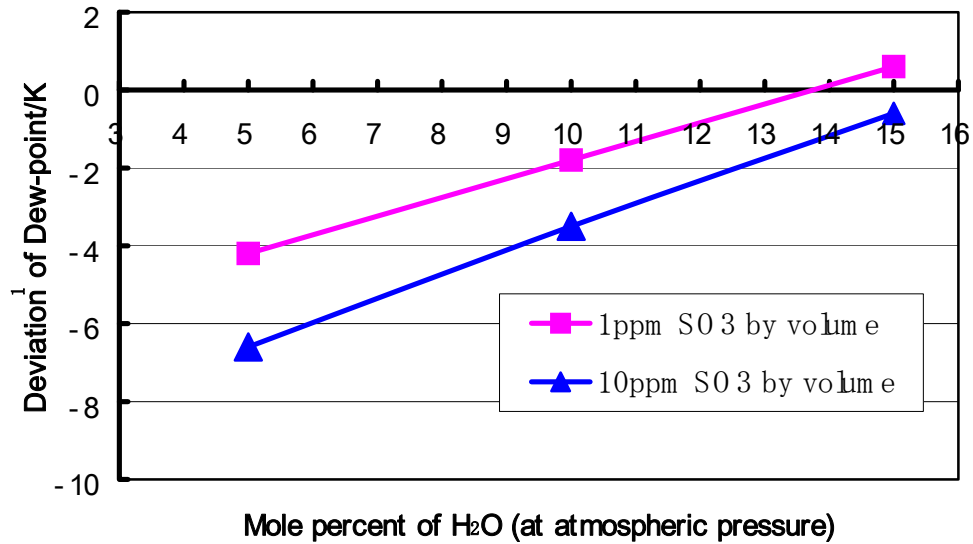


Figure 2: Comparison between Ohtsuka equation and Verhoff & Banchero equation  
 (<sup>1</sup> Deviation = Ohtsuka equation – V & B equation at atmospheric pressure)

Reasons for the discrepancies above may include non-ideal behavior of the flue gas, non-equilibrium states, and impurities including fly ash reducing the SO<sub>3</sub> precipitation [8].

The SO<sub>3</sub> conversion rate is important for predicting the dew point; however, it is outside the scope of IAPWS because it is a function of chemical reaction mechanisms.

In addition, impurity effects including fly ash as well as wall temperature influence on heat and mass transfer should be investigated experimentally and theoretically, so that dew-point formulations become more comprehensive. These could be applied with advantage to future design of new power plant systems, such as oxy-combustion capture, IGCC and IGFC, etc.

In summary,

- For design of air preheaters for coal-fired boilers, there is a need for accurate data and/or formulations for dew point for a range of actual flue gas compositions, including the effect of fly ash and wall temperature distribution, in order to reduce and keep proper design margins.
- For extensive applications in future design of new power-plant systems, adequate predictive methods of dew point considering effects of impurity and wall temperature profile are necessary from empirical and theoretical points of view, so that dew-point phenomena become more comprehensively understood.

## Range of Compositions for Dew-Point Predictions

The required range of concentration of each component of flue gas for data and formulations up to relatively high sulfur content is shown in Table 1. This takes into consideration several kinds of fuel, including heavy fuel oil which is also used when starting a coal-fired power plant and bringing it up to its initial load.

Future application may be highlighted for system designs of oxy-combustion CO<sub>2</sub> capture, IGCC, IGFC, etc. For an oxy-combustion capture with wet-cooled flue gas, there will be a need to consider low-temperature corrosion by the acidic water leaving the cooling section (See Figure 3), but the SO<sub>x</sub> and NO<sub>x</sub> levels will be within the levels in the flue gas of existing coal-fired power plants. In a current design of IGCC (IGFC), called the EAGLE project in Japan, target SO<sub>x</sub> is 8 ppm with 5 ppm NO<sub>x</sub> at 16% O<sub>2</sub> condition, which is a very small level compared to those of existing coal-fired plants.

Table 1: Required Range of Exhaust Gas Compositions<sup>1</sup>

Component	Range
N <sub>2</sub>	0 – 80 mol %
CO <sub>2</sub>	2 – 100 mol %
O <sub>2</sub>	0 – 20 mol %
H <sub>2</sub> O	0.1 – 90 mol %
CO	0 – 5 mol %
Ar	0 – 5 mol %
SO <sub>2</sub>	0 – 1 mol %
SO <sub>3</sub>	0 – 0.1 mol %
NO <sub>2</sub>	0 – 300 ppm
NO	0 – 100 ppm

<sup>1</sup> 1 ppm = 10<sup>-4</sup> vol % = 10<sup>-6</sup> mole fraction

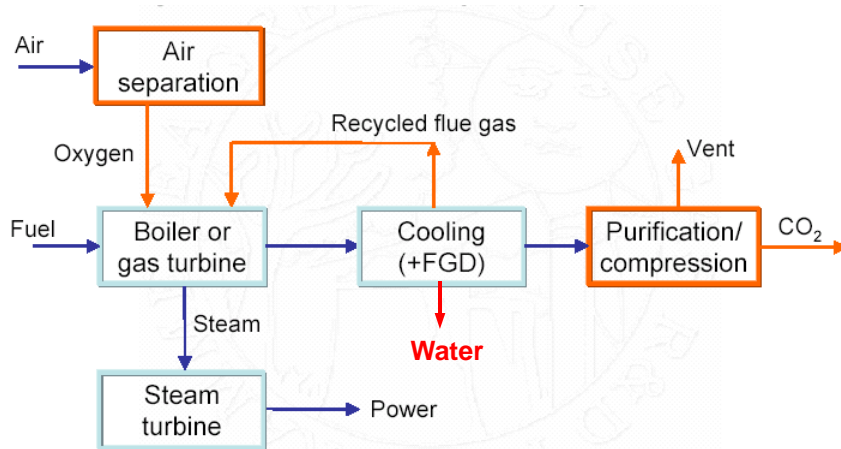


Figure 3: Oxy-combustion CO<sub>2</sub> capture process [9]

A common application in the future may be in the design of post-combustion exhaust gas treatment systems.

Therefore, the values given in Table 1 will be sufficient, even in the future. Note that most systems may cover a much smaller range.

### Previous Work and Current Studies

Since the 1950's when oil-fired power plants were a large part of power-generation capacity, dew point formulations have been obtained, especially for high sulfur-content oil fuels, by fitting experimental data. The data were provided using model equipment and/or actual plant data. These formulations were compared in Figures 1 and 2 using the equations listed below. Additionally, every HRSG (Heat Recovery Steam Generator of combined-cycle power plant) supplier has its own method for calculation. All values are dependent on boundary conditions like the conversion rate from SO<sub>2</sub> to SO<sub>3</sub> or the water content.

#### Nomenclatures:

$T_D$  : Dew-point temperature (K)

$t_D$  : Dew-point temperature (°C)

$t_S$  : Saturation temperature of water at total pressure of exhaust flue gas (°C)

$C$  : Conversion rate of SO<sub>3</sub> from SO<sub>2</sub> by volume

$p_{SO_2}$  : mole fraction of SO<sub>2</sub>, equivalent to partial pressure (in atm) with the mixture of gases at standard atmospheric pressure (101.325 kPa)

$p_{H_2O}$  : mole fraction of water, equivalent to partial pressure (in atm) with the mixture of gases at standard atmospheric pressure (101.325 kPa)

$V$  : H<sub>2</sub>SO<sub>4</sub> concentration (vol %)

#### Verhoff / Banchero (1974)[1]

$$T_D = 10000 /$$

$$[15.13 - 0.2943 \ln(p_{H_2O}) - 0.858 \ln(C p_{SO_2}) + 0.062 \{6.633 - \ln(C p_{SO_2})\} \{6.633 - \ln(p_{H_2O})\}]$$

#### Haase / Borgmann (1981)[2]

$$t_D = [255 + 27.6 \lg(p_{H_2O}) + 18.7 \lg(C p_{SO_2})]$$

#### Neubauer (1962)[5]

$$t_D = t_S + (290.54 - 30.79 p_{H_2O}) p_{SO_2}^{(0.0959 + 0.1430 p_{H_2O} - 0.1669 p_{H_2O}^2)}$$

**Pierce (1977)[3] / Mueller (1959)[4] / Okkes(1987)[6]**

$$t_D = 203.25 + 27.6 \lg(p_{H_2O}) + 10.83 \lg(C p_{SO_2}) + 1.06 \{ \lg(C p_{SO_2}) + 8 \}^{2.19}$$

**Ohtsuka (1961)[7]**

$$t_D = 20 \lg V + A$$

A : a constant depending on moisture content (°C)

: ex. 184 for 5%, 194 for 10%, 201 for 15%

As for the measuring tool itself for dew point of several kinds of gas, accurate instruments have been developed and the current accuracy level within  $\pm 1$  K is enough [10].

Methods for a precise prediction of surface temperatures considering different thermal conductivities of wall materials have been developed [11], but may still need more attention for application to system design by simple calculations.

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