

Burning Sulfur Compounds

Sulfur compounds such as hydrogen sulfide (H_2S), methyl mercaptan (CH_4S) and sulfur (S) burn in the presence of oxygen to produce sulfur oxides (SO_2 and SO_3) in the flue gas. Flue gas always (almost) contains substantial water vapor (hydrogen in the combustibles combines with oxygen in the combustion air to form H_2O).

Neither of the sulfur oxides presents much of a problem with normal materials of construction UNLESS the flue gas temperature falls below the gas dewpoint temperature.

The gas dewpoint temperature is where the first liquid droplets begin forming in the gas. Above the dewpoint there is no liquid. As the temperature falls below the dewpoint for the flue gas, more and more liquid forms. Room air can reach the dewpoint temperature on the outside of an ice water pitcher, and the water which condenses collects and forms a puddle under the pitcher. If the same pitcher was placed in a flue gas containing sulfur oxides, the condensed liquid would be sulfurous acid (H_2SO_3 from the SO_2) and/or sulfuric acid (H_2SO_4 from the SO_3). The puddle would be corrosive.

Either SO_2 or SO_3 in flue gas results in a much higher gas dewpoint temperature than what you would see with water vapor alone. For instance, flue gas with 5% water vapor and no sulfur oxides has a dewpoint of about 90°F. The same flue gas with just 0.01% SO_3 added has a dewpoint of about 245°F! If this gas reaches 245°F, sulfuric acid will begin to condense out of the gas. Adding the same amount of SO_2 presents much less of a problem, because the dewpoint change is not nearly as severe, plus sulfurous acid is much less corrosive than sulfuric acid.

The two graphs below can be used to calculate the dewpoint of flue gas containing varying amounts of SO_3 . One graph shows very low SO_3 concentrations and the other plots higher concentrations. In the high concentration graph, the line at the lower right with numbers running from 5 to 160 is the H_2O Partial Pressure in the flue gas (air pressure at sea level is 760 MM Mercury). Thus 40 PP MM Mercury of water amounts to $40/760=0.0526$ fraction (=5.26% by volume) of water in the flue gas. With no SO_3 in this flue gas, the first liquid will condense out when the temperature reaches about 95°F (the axis on the left). Starting with 40 PP MM Mercury of H_2O , add enough SO_3 to amount to 0.01% in the flue gas – on the graph, starting at 40 on the lower line, follow the diagonal line up and to the left to the line marked 0.01 along the top of the lines. Then look to the left axis of the graph to read about 250°F as the dewpoint temperature. The low concentration graph works in a similar way.

This is the easy part. The uncertainty begins when we try to predict the fraction of sulfur which will oxidize to form SO_3 instead of SO_2 . This chemical reaction would reach a specific end point if enough time elapsed (maybe an hour). But no combustor holds flue gas for longer than a few seconds, so the “equilibrium” level of SO_3 is never reached. In practice, when burning sulfur-containing compounds, somewhere between 1% and 10% of the sulfur ends up as SO_3 in combustor flue gas. Most designers use 3% conversion to SO_3 but some use 7% conversion. Attempts at exact calculation of the conversion have not been

successful. The most conservative estimate would be 10%. This is important because if any portion of the equipment in contact with the flue gas cools to the SO₃ dewpoint temperature, sulfuric acid will form. If this portion of the equipment will not tolerate sulfuric acid, corrosion problems will result.

In the real world, furnaces with excessive refractory (conserving heat but cooling the vessel shell) are often “holed” by condensing sulfuric acid. Flue gas / air preheat exchangers have been damaged when the metal temperature near the cold air entry point could not be kept above the SO₃ dewpoint temperature. Careful designs avoid problems like these. If condensation cannot be avoided, any metals should be able to resist concentrated sulfuric acid, which is the liquid that condenses!

For high concentrations of SO₃ in flue gas, use this graph:

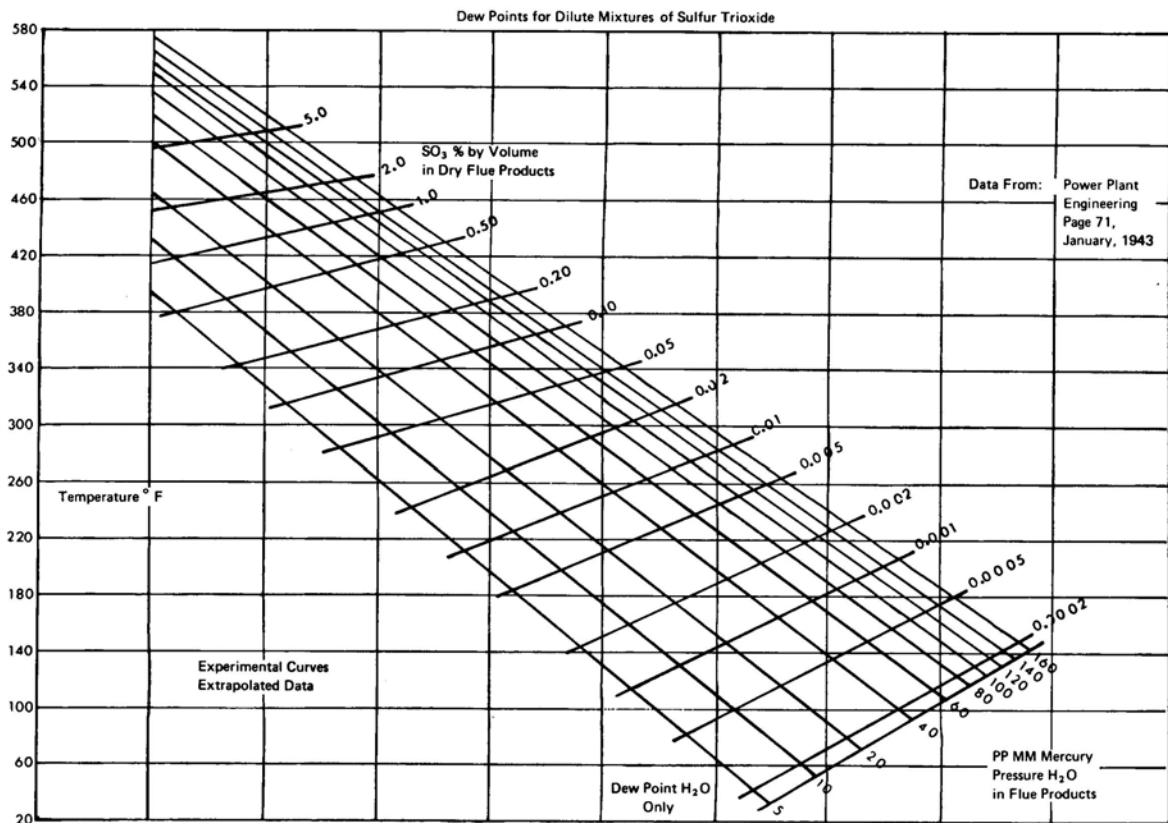


Figure 3-7. Dew points for dilute mixtures of sulfur trioxide. (Data from Power Plant Engineering, Jan. 1943, p. 71.)

For low concentrations of SO_3 , use the graph below instead. Notice that the dewpoint temperature does not fall off as quickly when concentrations are low.

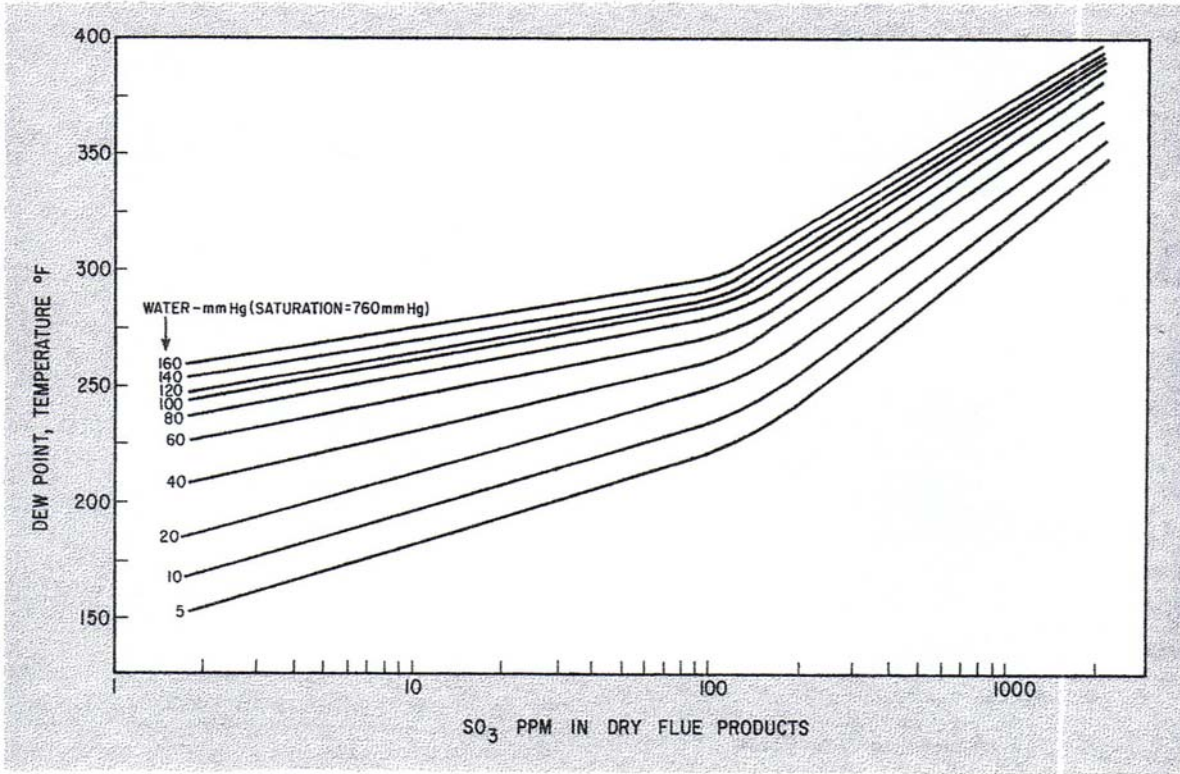


Fig. 1—Dew points for dilute mixtures of sulfur trioxide in stack gases with various water contents.

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