Watch for elevated
dew points in
SO$_3$-bearing stack gases

Corrosion can eat up savings from heat
recovery before you expect it to happen

R. R. Martin, F. S. Manning and E. D. Reed,
The University of Tulsa, Tulsa, Okla.

The dew point of combustion gases is elevated when sulfur trioxide (SO$_3$) is present even when the SO$_2$ concentration is small. This condition becomes critical with efforts to raise heater efficiencies by recovering stack gas heat since the SO$_3$ combines with water to form sulfuric acid. If dew point occurs within the furnace structure or prior to emergence from the stack, severe sulfuric acid corrosion occurs. If dew point occurs after departure from the stack, a plume of blue-gray sulfuric acid vapor trails from the stack. Furthermore, this danger of dew point effects begins typically to be significant when one weight-percent sulfur is present in the fuel whether the fuel is liquid or gas.

An interesting finding$^{4}$ shows that there is quite an appreciable effect of relative humidity on the reoxidation of SO$_2$ to SO$_3$. Normally, the production of SO$_3$ results from catalysis involving vanadium pentoxide or platinum-black as used for sulfuric acid manufacture. But evidence shows that vapor-phase water can serve a like purpose to a degree such that at high humidities there is a greater SO$_3$ concentration in combustion gases.

One approach to more efficient heater operation is utilization of hot stack gases to preheat combustion air. However, the low flue gas temperature created by the air preheater can cause severe loss of money and production time due to corrosion of the heater components. Therefore, the object is to extract the most energy possible from the flue gases without reducing the flue gas temperature to the point where dew point occurs and corrosion begins. The difficulty in accomplishing this objective is intensified because of the considerable variation that exists between reported dew points and those realized when SO$_3$ is present in combustion gases.

Considerable variations exist even between reported SO$_3$ dew points although they have been measured many times since Thomas and Barker$^2$ in 1925 and Johnstone$^5$ in 1929. The variations may have resulted from the techniques used in the determination. Many early attempts used an electric conductivity method, initially developed by Johnstone, in which the hot gas is drawn over a glass bulb. The glass bulb is cooled by circulating cold air inside the bulb until a conductivity path is observed between two electrodes mounted on the outside surface. A thermocouple measures the temperature at which the condensation of H$_2$SO$_4$ occurs.

Condensation methods were used by Goksoyr and Ross$^6$. Here the gas sample of known SO$_3$ content is drawn through a condenser at a measured temperature. The condensed SO$_3$ trapped in the condenser is measured by washing the condenser with an isopropyl alcohol solution and titrating the H$_2$SO$_4$ with NaOH. Then the exit, equilibrium SO$_3$ concentration is readily computed thus providing the SO$_3$ gas dew point.

Unfortunately, the SO$_3$ dew point measured by these two methods can differ by 125°F at low SO$_3$ concentra-
ELEVATED DEW POINTS

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

Taylor\(^2\) using the conductivity method reported a 126°F dew point for a gas containing 2 ppm SO\(_3\) while Lisle and Sensenbaugh\(^3\) obtained a 250°F dew point with a condensing apparatus for the same SO\(_3\) concentration. In both cases the water dew point was approximately 110°F.

Johnstone\(^8\) suggested one of the most extensively used SO\(_3\) dew point correlations based primarily on data taken using the electrical conductivity method. A similar correlation presented by Yeaw and Shnidman\(^8\) is most reliable at SO\(_3\) concentration above 100 ppm\(^6\); however, recent data\(^9\) indicate that the Yeaw and Shnidman correlation is in error at low SO\(_3\) concentrations.

A corrected correlation (Fig. 1) is based on the Yeaw and Shnidman correlation for high SO\(_3\) concentrations and Martin's research\(^4\) at lower SO\(_3\) contents. Martin's data were collected using a condenser patterned after Ross\(^1\).

Low SO\(_3\) concentrations, which occur even when SO\(_2\) concentrations are below federal guidelines, can be a source of corrosions at temperatures much higher than indicated in previous literature. As SO\(_3\) concentrations fall below 100 ppm the dew point of the combustion gases gets progressively higher than the dew points earlier reported in the literature. Therefore, it is of utmost importance when low sulfur fuels are being burned, which in turn gives low SO\(_3\) concentrations, that the designer be very careful in his choice of flue gas temperatures across the air preheater section and temperature of gases exiting the stack.

LITERATURE CITED

6. The John Zink Co., Tulsa, Okla., privileged communication.

June 1974  HYDROCARBON PROCESSING
The following illustration is a reproduction of the graph presented in the preceding article using the water dew point temperature instead of the water partial pressure at saturation.

This new graph also shows the extension of the upper portion of the curves as a dotted line down to 2 ppm SO3. The upper portion of the curves is a plot of earlier data, as indicated in the article, than presented in the article collected by a different method. There is about 100° F. difference in the predicted dew point temperatures at 2 ppm SO3. However, it should be noted that most of the earlier data were collected for higher SO3 levels and graphs were prepared by extrapolating to the lower SO3 levels. It should also be noted, that if the lines are extrapolated down to 1 ppm the predicted SO3 dew points are less than the water vapor dew points. Therefore, the SO3 dew points must be greater than the dotted lines would indicate at low SO3 concentrations.

The data used to plot the curves with the higher dew point values was used in the Aztec Combustion Calculator that can be downloaded of the site.