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Fume generation in kraft recovery boilers

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Fume in a kraft recovery furnace originates from the vaporization and condensation of inorganic salts. It consists of fine dustlike particles, typically .25 to 1.0 μm in diameter. Figure 1 is a scanning electron micrograph of typical fume particles within a kraft recovery furnace.

Recent work indicates that fume generation in a kraft furnace depends on gas phase reactions and mass transfer considerations. This suggests that fume is more than an equilibrium phenomenon and that fume is a process that can be manipulated.

EFFECTS OF FUME ON RECOVERY BOILERS

Sodium-based fume has both good and bad effects on a kraft recovery furnace. Fume forms deposits on the heat transfer surfaces in the recovery boiler. These deposits reduce the heat transfer rates and may eventually plug gas passages in the superheater and boiler bank. To remove these deposits requires the use of soot-blowing steam, with as much as 3% to 8% of the total steam production used for soot-blowing.[1]

The reduction in heat transfer rates may significantly reduce the capacity of a kraft recovery boiler. In situations where the pulp mill is recovery boiler limited, this reduction in heat transfer coefficients also reduces the capacity of the pulp mill. Fume particles are eventually collected in the precipitator and recycled into the black liquor.

Not all aspects of sodium-based fume are detrimental, however. Fume also serves as a collector for sulfur dioxide in the furnace, reducing the level of sulfur dioxide emitted from the furnace.

Deposits in the kraft recovery furnace result from two distinct types of particles. One type of particle results from the entrainment of black liquor droplets in the furnace gases. These droplets burn and leave a residual of inorganic salts forming a relatively large particle. The other type of particles found within the kraft recovery furnace is true fume formed through the evaporation and condensation of inorganic salts. As noted, these are relatively small, dustlike particles.

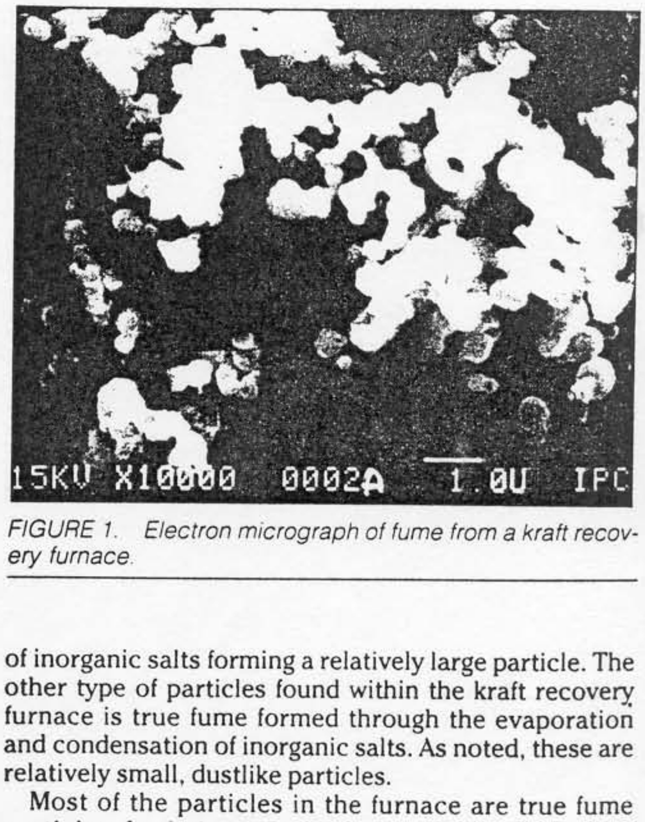

FIGURE 1. Electron micrograph of fume from a kraft recovery furnace.

Most of the particles in the furnace are true fume particles. In their study on the origins of sulfur and sodium emissions in a kraft recovery boiler, Borg, *et al.*[2] identified both types of particles. The percentage of actual carryover particles was found to be very small compared to the true fume particles. Rizhinshvili[3] also conducted a study on sodium emissions and reported that true fume comprised most (95% to 97%) of the precipitator dust.

A relatively high level (9% to 15%) of the sodium entering the furnace in black liquor vaporizes and forms fume. The sodium vapor can react with oxygen and carbon dioxide in the furnace to form sodium carbonate:

$$2\,Na + \tfrac{1}{2}O_2 + CO_2 \rightarrow Na_2CO_3(S)$$

The beneficial aspect of sodium based fume is that it serves as a collector for sulfur dioxide. Sulfur dioxide can be captured through the reaction with sodium carbonate and oxygen:

$$Na_2CO_3(S) + \tfrac{1}{2}O_2 + SO_2 \rightarrow Na_2SO_4(S) + CO_2$$

This capture of sulfur dioxide not only reduces the sulfur dioxide emissions from the furnace, but also reduces the formation of sticky deposits in the upper boiler or in the precipitator.

The precipitator dust is a mixture of sodium sulfate and sodium carbonate. If the quantity of sodium-based fume generated is insufficient to capture all the sulfur dioxide present, the precipitator dust will be entirely sodium sulfate. If excess sodium-based fume is generated, the precipitator dust will contain a relatively high level of sodium carbonate. To ensure that sulfur dioxide is maintained at a minimal level without excess fume, the precipitator dust should consist of about 90% sodium sulfate and 10% sodium carbonate. The optimal level of fume in a kraft recovery boiler is that required to maintain an acceptable sulfur dioxide level. Fume generation rates above this level have only a detrimental effect on boiler operation.

FUME GENERATION MECHANISM

Fume generation within the kraft recovery furnace usually has been considered the result of sodium volatilization resulting from the high temperature and reducing conditions present in the char bed.

Equilibrium[4] diagrams predict that sodium volatilization becomes significant at temperatures above 1,700°F and increases with temperature and the strength of the reducing environment. By including sodium hydroxide vapor in the equilibrium calculations, Warnqvist[5] developed a rationale for fuming under oxidizing conditions. These treatments of fume generation as an equilbrium process suggest that there is little that can be done to control fuming other than manipulating furnace temperature.

Recently, Cameron, *et al.*[6] demonstrated the importance of gas phase reactions and mass transfer considerations in fume generation. It is well established that the vaporization of many substances is significantly enhanced due to the reaction of the volatile species in the gas phase.[7] This is especially evident with molten metals where fume generation is increased many orders of magnitude during oxidation of the molten metal. In these systems, the metal vapor is oxidized in the gas phase to form a metal oxide fume. This oxidation reaction creates a sink for the metal vapor which significantly enhances the metal vaporization rate.

Cameron, *et al.*[6] demonstrated that a similar phenomenon occurs with smelt. During the oxidation of the sulfide in the smelt, the fume generation rate can increase significantly. The enhanced fume generation is the result of the sodium evolving from the smelt reacting

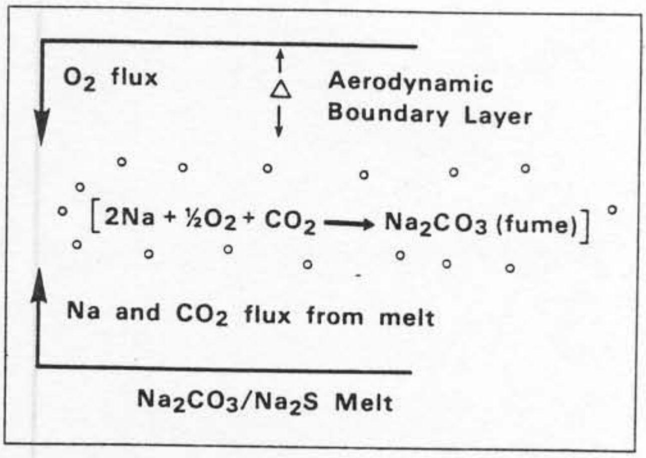

FIGURE 2. Oxidation-enhanced fume generation.

with oxygen to form sodium oxide, which then react further with carbon dioxide to form sodium carbonate fume. (Figure 2.)

The rate of sodium evolution is dependent on the difference between the vapor pressure of sodium at the smelt's surface and the partial pressure of sodium in the gas phase. Because the oxidation reaction reduces the partial pressure of sodium in the gas phase, the rate of sodium evolution is increased and fume production increases.

The most significant aspect of this mechanism is that fuming is controlled not by an equilibrium process, but by a rate process. The fume generation rate depends not only on temperature, but also on how the black liquor is burned.

POTASSIUM, CHLORIDE BEHAVIOR

A major concern with fume generation in the kraft recovery furnace is the behavior of potassium and chloride. Deposits in the upper stages of the furnace become enriched with these elements, which significantly alters the nature of these deposits.

Potassium and chloride lower the melting point of the deposits, which may lead to harder and thicker deposits or to a corrosive environment.

Reeve, *et al.*[8] have reported that precipitator dust is much richer in potassium and chloride than the smelt. By comparing the molar ration of chloride/sodium in the precipitator dust to their ration in the smelt, Reeve, *et al.*[8] found an average enrichment of 1.4 for three West Coast mills. For potassium, the comparison of the molar ratio of potassium/sodium in the precipitator dust to the ratio in the smelt showed an average enrichment ratio of 2.0.

The chloride enrichment is due to the relatively great volatilities of sodium and potassium chloride compared to the carbonates. The potassium enrichment is the result of the higher volatility of potassium chloride to sodium chloride.

MODERATE TEMPERATURE DEPENDENCE

Cameron, *et al.*[6] reported that the maximum fume generation rates occurred during smelt oxidation under turbulent conditions (smelt well mixed during oxidation) and that fume generation under these conditions depends exponentially on temperature with an activation energy of about 20,000 cal/mole. In the recovery furnace, the fume generation rate should increase as the combustion process becomes more intense.

Fume generation has a moderate temperature dependence. At a furnace temperature of 1,700°F, the fume generation rate should increase by 10% for every 20°F increase in furnace temperature. Black liquor particles burning in flight and the char bed are both sources of fume. An increase in bed surface temperature would increase the fume being generated from the bed.

If, however, the operational changes that were made to increase bed temperature resulted in less combustion of black liquor particles in flight, the fume production rate from these particles would decrease and the overall fume generation rate might actually drop. An increase in bed temprature, therefore, may not always increase the fume generation rate.

The sulfur reduced in the furnace is captured through the reaction of sulfur dioxide with the sodium-based fume (Equation 2). Sulfur is released in the furnace primarily as hydrogen sulfide. This hydrogen sulfide is oxidized in the furnaces gases to sulfur dioxide, which is then captured by the sodium carbonate fume. If insufficient oxygen is available to oxidize the hydrogen sulfide, the emissions from the furnace will contain both hydrogen sulfide and sodium carbonate.

CONCLUSION

Progress has been made in understanding the processes responsible for fume generation in a kraft recovery furnace. The concept that the fume generation rate is dependent on gas phase reactions and mass transfer effects implies that fume is more than an equilibrium phenomenon and that fume generation is a process that can be manipulated. Research using these fundamental fume generation concepts is now required to define how black liquor burning can be varied to optimize fume generation in a kraft recovery furnace. □

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