

of the two layers. This is in contrast with the 30 percent or more trisulfate found in certain spots when the Fe_2O_3 was intimately mixed with the alkali sulfate indicates that, in these short tests, migration was not a significant factor.

Conclusions

There does not appear to be a simple relationship between the catalytic activity of fly ash and the composition of the ash. Tests with three fly ashes containing 17 to 30 percent Fe_2O_3 did not show a correlation between catalysis and Fe_2O_3 content. Although each of the fly ashes was catalytic, all three ashes were much less catalytic than Fe_2O_3 . Results of tests with Fe_2O_3 -kaolin mixtures showed that mixtures containing only $1/3$ or $2/3$ Fe_2O_3 were as catalytic as Fe_2O_3 itself. Preheating of the Fe_2O_3 -kaolin mixtures at 2000 F for 16 hr significantly reduced the catalytic activity of the mixtures, showing that the thermal history of the fly ash is a factor in determining how catalytic it is. Varying the alkali content of the synthetic ash did not affect the catalytic activity.

Probably the most significant result of these tests is the demonstration that trisulfates can form in only a few hours in an atmosphere not unlike that found in a boiler furnace. It was not always necessary to have thick deposits to form the trisulfates. In fact, trisulfates formed on tubular specimens where the total deposit thickness was about $1/16$ inch. Trisulfates tended to form more readily at specimen temperatures below 1100 F with both the tubular specimens and with the thicker deposits, possibly as a result of the increasing partial pressure of SO_3 necessary for trisulfates to be stable at higher temperatures. Within boiler tube deposits, where gas may be stagnant, SO_3 concentrations even higher than reported here are possible and trisulfates could be stable at higher temperatures.

Potassium appears to be more reactive than sodium in forming trisulfates. Adding small quantities of kaolin, MgSO_4 , CaSO_4 , and CaCO_3 to the deposit reduced the quantity of trisulfate formed in these tests.

Fused deposits, apparently sodium vanadyl vanadate, formed readily in tests when both vanadium and alkalis were present. Addition of MgO to a deposit containing both vanadium and alkalis significantly reduced the degree of fusing, apparently by increasing the melting temperature.

Although these results are not conclusive in defining the exact corrosion mechanism, they represent one more step in the effort to develop an understanding of the reactions leading to corrosion and deposits.

Acknowledgments

The author wishes to thank the ASME Research Committee on Corrosion and Deposits from Combustion Gases for granting permission to present this material. The author also thanks the other members of the Battelle team participating in this study—William T. Reid, Arthur Levy, Horatio H. Krause, Paul D. Miller, and James J. Tabor—for their advice and assistance in carrying out the research. Special recognition is due H. H. Krause for his development of the optical microscopy technique for identifying trisulfates.

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DISCUSSION

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This paper demonstrates considerable ingenuity in adapting laboratory apparatus to provide a realistic simulation of conditions that lead to formation of corrosive deposits in boiler furnaces. That the trisulfates were formed in some cases demonstrates that field conditions were duplicated, and the development of the optical microscopy technique for identifying small quantities of the trisulfates represents a real contribution to the state of the art.

As the author states, the corrosion and deposit mechanism is extremely complicated, and developing an understanding of the many reactions involved will proceed a step at a time. While this paper does add much to our increased knowledge, it seems that one opportunity to add still more was not fully exploited. In describing the "B" series of tests, the comment is made, that "the analysis was not entirely satisfactory because relatively large amounts of a substance were present that could not be identified positively." Identifying this elusive substance would make a significant contribution to understanding the series of reactions leading to trisulfate formation. Would the author care to surmise what the composition of this substance might be? Has any of it been preserved so that further efforts might be made to identify it positively?

Author's Closure

Mr. Wiedersum's comments are particularly apt because of his close connection with this study as chairman of the sponsoring committee. In answer to his question, the object of the "B" series of tests was to investigate trisulfate formation. This necessitated establishing conditions which would promote formation of trisulfate in quantities sufficient to identify. As the optical microscopy technique had not been developed at that time, a minimum of about 5 percent trisulfate was required to enable identification by X-ray diffraction. Therefore, the X-ray dif-

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fraction examination was made to determine if trisulfate was present in at least that concentration. No attempt was made to identify other compounds present. The report of the analyst indicated that trisulfate could not be positively identified in the deposit from this test. He further reported the presence of Fe_2O_3 and an isotropic material but did not positively identify this material. Therefore, this experiment was considered unsuccessful as far as producing a significant quantity of trisulfate. Hence,

other techniques had to be tried, such as two-layer and thicker deposits.

Possibilities for the unidentified material include normal sulfates and pyrosulfates. As Fe_2O_3 remained in what was initially a stoichiometric mixture to form trisulfates, it is reasonable to assume that normal sulfates might have been present. The temperature, 1030 F, was probably too high for pyrosulfates to be stable at the SO_3 concentrations measured in the gas stream. Because such test deposits tend to be unstable, none of the samples was retained.