

essentially agrees with previous work [1-6]³ on SO₃ formation in flames, which showed the importance of atomic oxygen in the reaction. The authors observed that when air was added downstream from flames, SO₃ formation still took place, a phenomenon also reported by Glaubitz [7], but they were uncertain as to why this happened. I would therefore offer the following explanation [2] for their consideration.

It is known [8] that carbon monoxide flames tend to produce more oxygen atoms than hydrocarbon flames, and therefore the formation of SO₃ in them is enhanced. It is possible that this is due to activated CO₂* molecules losing their energy by colliding with oxygen molecules to produce oxygen atoms, as follows:



It is also known that active CO₂* molecules can often exist for appreciable times in combustion gases before losing their energy by subsequent collisions. If additional oxygen is added after the end of a flame, but before the concentration of activated CO₂* molecules has fallen to zero, then it is possible for equation (1) to take place, followed by the reaction (2) resulting in further SO₃ formation



In Glaubitz' work [7] he demonstrated that air added up to a distance of one quarter of the flame length beyond the flame resulted in further SO₃ formation but if air was added beyond this point this did not happen. It is possible that the above explanation could be applied to his results also but it may well have been an aerodynamic effect due to the fact that he worked on a jet flame.

It would be most interesting if the authors could investigate the partial combustion of the fuel to produce combustion products containing carbon monoxide, and then to add further air to burn the CO, and see if a greater amount of SO₃ resulted.

References

- 1 A. B. Hedley, "Formation of SO₃ in Flames," PhD thesis, Sheffield University, 1961.
- 2 A. B. Hedley, Paper 11, *The Mechanism of Corrosion by Fuel Impurities*, Butterworths, London, 1963, p. 204.
- 3 A. G. Gaydon and G. Whittingham, *Proc. Royal Soc. (A)*, vol. 189, 1947, p. 313.
- 4 G. Whittingham and A. Dooley, *Trans. Faraday Soc.*, vol. 42, 1946, p. 354.
- 5 G. Whittingham, 3rd Internat. Comb. Symp., 1949, p. 453.
- 6 G. Whittingham, *Trans. Faraday Soc.* vol. 44, 1948, p. 141.
- 7 F. Glaubitz, *Mitt. Ver. Grosskesselbesitzer*, N.73, August, 1962.
- 8 A. G. Gaydon, *Proc. Royal Soc. (A)*, vol. 183, 1945, p. 111.

Authors' Closure

Dr Hedley's suggestion as to the source of SO₃ when downstream air is added is appreciated, but the short lifetime of activated CO₂* molecules would seem to eliminate them as the source of this SO₃. The additional air was injected 9 in. downstream of the burner plate while the flame length was reported at about 3 in. With the reported gas velocity of 2.5 fps, the residence time of the flue gas from the time it left the flame until the air was injected was about 0.2 sec. Gaydon,⁴ as noted by Hedley, states that the probable life of activated CO₂* is between 10⁻⁸ and 10⁻⁵ sec, or considerably less than 0.2 sec. The source of this SO₃ may not be too important from a practical standpoint as most modern boilers are designed to operate with a positive pressure in the furnace.

Stage burning, where, as he suggests, the total air for combustion might be added in several steps cannot be investigated readily in the present Battelle apparatus. The deliberate forma-

³ Numbers in brackets designate References at end of this discussion.

⁴ A. O. Gaydon, *Proc. Royal Soc.*, Series A, vol. 183, 1945, p. 111.

tion of CO followed by its eventual oxidation to SO₂ might have considerable merit in determining if activated CO₂* molecules indeed are responsible for part of the SO₃. As a practical scheme, however, operation of large boiler furnaces with low excess air to limit the production of oxygen atoms appears simpler and economically more attractive.

Slag-Coal Interface Phenomena¹

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Although the relationships between viscosity, composition, and temperature for coal-ash slags worked out in this country more than two decades ago have been confirmed and extended through more recent work by the Babcock and Wilcox Company and by BCURA for the Central Electricity Generating Board, there are still problems in slag behavior worth additional study. This paper by Mr. Raask is a good case in point. In it he treats the special case of the wetting of different surfaces by molten slag, an important characteristic in the attack of refractories, the interaction between coal and slag in cyclone furnaces, and the burning out of the last traces of carbon in suspended slag particles in a pulverized-coal flame.

Aimed primarily at the behavior of ash in a cyclone furnace, these studies can be applied also to conventional slag-tap furnaces. Less troublesome today than in earlier times, reduction of the iron oxides in slags to metallic iron which then can accumulate at the bottom of the mass of molten slag has caused serious problems in some installations. Most of this trouble usually can be traced to the larger particles of pulverized coal reaching the slag bed unburned. Even in an iron-oxide-rich slag containing 40 percent equivalent Fe₂O₃, only 6.3 lb of carbon per 100 lb of slag is sufficient to reduce all the FeO and Fe₂O₃ in the slag to metallic iron. Hence it is evident that very small amounts of carbon trapped in slag can have serious effects.

The author is quite right in attributing the evolution of gas from molten slag to carbon monoxide released by reaction with carbon, and to the decomposition of sulfates in the original ash. Another factor he does not mention is the thermal dissociation of Fe₂O₃. As shown by Ralston,³ pure Fe₂O₃ begins to dissociate with the release of oxygen at temperatures as low as 2000 deg F, and is converted entirely into Fe₃O₄ at 2458 deg F in air. Even in oxygen, Fe₂O₃ dissociates to Fe₃O₄ at only 2606 deg F. These temperatures might be somewhat higher when the Fe₂O₃ occurs in a silicate melt, but the magnitude would be comparable. Hence, gas evolution by the spontaneous release of oxygen from Fe₂O₃ can be a contributory factor in the "boiling" of molten coal-ash slags. This is a serious problem in the laboratory when coal ash is being melted to form slag; how important it might be in a furnace where the iron oxides are reduced quickly by combustion is less certain.

As to flow of slag, the novel scheme used by the author of supporting a pellet of sintered ash on a platinum or a graphite pin and then observing its tendency to move when heated has the same shortcomings as the conventional ASTM cone fusion test—it relates flow to an arbitrary set of conditions. Presence of a solid phase in the slag, so that the slag does not behave as a Newtonian fluid, vastly complicates the whole picture. This pseudo-plastic behavior can be attributed to suspended, finely divided solids in the slag. And so any attempt at analyzing flow behavior of slags must take into account the nature and the quantity of solid phase present in the slag. It seems unlikely that carbon itself could

¹ By E. Raask, published in the JOURNAL OF ENGINEERING FOR POWER, TRANS. ASME, Series A, vol. 88, 1966, pp. 40-44.

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³ O. C. Ralston, "Iron Oxide Reduction Equilibria," Bull. 296, U. S. Bureau of Mines, 1929, 326 pages.

contribute to this effect, but because over-reduction of the iron oxides by carbon might lead to finely divided particles of metallic iron in the slag, this point might be worth further checking. Certainly the author is quite correct in pointing out the effect of changing the nature of the surface with which the slag is in contact. If he could further relate this with the rheological properties of the slag, he would do all of us a great service.

Author's Closure

The author thanks Dr. Reid for his stimulating comments on his paper.

Dr. Reid rightly points out that on heating the ash prepared in laboratory would lead to the evolution oxygen due to the thermal dissociation of Fe_2O_3 . However, it is unlikely to be a major factor in the evolution of gas from molten slag in a cyclone or slag-tap furnace. There are negligible amounts of free or combined Fe_2O_3 present in coal minerals and the other iron com-

pounds (pyrite, siderite, and ferrous silicates) would not be oxidized to Fe_2O_3 in the flame. The author has examined a number of slag samples from a boiler but failed to find any correlation between the ratio of Fe_2O_3 to FeO in slag and the amount of gas involved judging from the porosity of the slag. Further work on the evolution of gases from coal minerals is in progress and the results would be published at a later date.

The author realizes that his scheme of observing the flow of molten droplets on a platinum or a graphite pin does not give a complete picture of the behavior of slag on furnace walls. As the discussor points out, the presence of solid particles in the slag would alter its flow characteristics. Dissolution of solid particles, such as SiO_2 , or precipitation of iron would have a marked effect on the viscosity of slag as the silica ratio of the melt is changing. Some work on the rheological properties of silicate melts is in progress but it is too early to say whether or not these measurements have any relevance to the behavior of slag in the cyclone or slag-tap boilers.