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DISCUSSION

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Summarized in these few pages is a tremendous amount of information on external corrosion in boiler furnaces. Although the paper treats the general problem of advanced thermal cycles and particularly of one system involving temperatures far in advance of present experience, the authors direct most of their attention to the problems of metal wastage. Some of the points raised about external corrosion are worth further consideration.

It is inevitable that encompassing this huge field with such brevity should lead to possible misinterpretation by those to

whom external corrosion is still a mysterious phenomenon. For example, the mechanism described by the authors by which alkali iron trisulfates cause metal loss is only one of those that have been proposed. A much earlier concept was described by Corey, Cross, and Reid in 1945³ from their studies when these complex sulfates were first identified in external corrosion reactions. Based on laboratory experiments involving the scale present on metal surfaces, that work proved that the alkali iron trisulfates could be formed by reaction of alkali sulfates and sulfur trioxide with the oxide film on the tube. Oxidation of the tube metal to reestablish the usual layer of FeO, Fe₃O₄, and Fe₂O₃ on the surface then is the direct cause of metal loss.

The mechanism described in this paper, in which the ash deposit provides the iron oxides, ignores the point that the resultant trisulfates are prevented from reaching the tube itself by the oxide film always present between the tube metal and the overlying deposit. This oxide film presents a physical and chemical barrier to the trisulfates so that the reaction listed in the paper between metallic iron and the sulfate radical cannot occur. The earlier mechanism in which this oxide film is specifically involved in forming trisulfates faces no such limitations. Both mechanisms may well lead to the formation of the alkali iron trisulfates, and it is important in evaluating the total process to recognize that it may proceed by more than one path. Certainly the oxide-film mechanism explains the facts satisfactorily.

Another point worthy of discussion is the effect of chlorine. It is unusual for a coal in the United States to contain more than 0.3 percent chlorine, yet it is only at appreciably higher levels that chlorine adds to the external corrosion problem. Hence, chlorine may accentuate metal wastage in England, but the same serious corrosion problems occur in the United States without chlorine being present. In this country, chlorine largely can be ignored as a significant contributor to external corrosion in coal-fired boiler furnaces. Chlorine certainly was not responsible for the large amount of trisulfates found in the authors' Trial III. It seems more reasonable to attribute the occurrence of the largest quantity of trisulfates to the Na₂O content of the coal, which was the highest by a factor of at least three of any of the coals tested. The authors clarify this point later in part by pointing out that chlorides themselves are of minor importance in the corrosion mechanism.

That the authors' test rig produces combustion gases containing only 2 ppm SO₃ should be of some concern, since, in practice, the SO₃ level generally is about one percent of the SO₂ concentration, or normally 20 to 40 ppm SO₃. If the SO₃ in the flue gas here is so low, there can be serious questions about the utility of this combustor for reproducing field conditions.

A final point has to do with the authors' conclusions that avoidance of ash "is no guarantee of freedom from nongaseous corrosion." Experience has shown that serious external corrosion occurs *only* under deposits, and indeed the corrosion mechanism assumed by the authors is based on reactions occurring within the deposit. Another way in which deposits establish corrosion conditions is their provision of an environment in which SO₃ can attain levels essentially at equilibrium with SO₂, possibly by shielding the interface between the tube and deposit to increase the residence time of flue gas in contact with active catalytic surfaces. Laboratory experiments at Battelle in the studies for ASME demonstrated that near equilibrium levels of SO₃ can be reached in the boundary layer of slowly moving flue gas in contact with Fe₂O₃-coated surfaces. Deposits may well provide these conditions, thereby leading to the high levels of SO₃ necessary to form the alkali iron trisulfates.

Despite these comments, the intent of CEGB to investigate the problem of increasing steam temperatures by 400 deg F over present practice is certainly well worthwhile and should be applauded. Only by such imaginative engineering will the gigan-

³ Corey, R. C., Cross, B. J., and Reid, W. T., "External Corrosion of Furnace-Wall Tubes—II. Significance of Sulphate Deposits and Sulphur Trioxide in Corrosion Mechanism," *TRANS. ASME*, Vol. 67, No. 4, 1945, pp. 289-302.

tic steps be taken to allow fuel-burning steam generators to keep their lead in the race with nuclear power, to the benefit of all consumers of electricity.

Authors' Closure

In discussing mechanisms of corrosion it was our aim to review briefly the possible alternatives and to mention in particular the species which were most likely to contribute to tube wastage. Space considerations have inevitably led to omissions and we are grateful to Mr. Reid for elaborating on the possible mechanism of attack of trisulphate species.

Chlorine and the chlorides of the coal are terms which are usually used synonymously. When we speak of a high chlorine coal this is taken to infer a coal of high chloride content and for British coals a coal of high alkali chloride content. Alkali chlorides and sulfur together are an index of a coal's potential corrosiveness, the sulfur combining with the alkali to form highly aggressive constituents. Alkali chlorides are decomposed in the flame and the sulfation of the resulting hydroxides or oxides takes place mainly at the tube surface.

It is known that chlorides can act as accelerators in sulfate corrosion and, it has been suggested, may directly contribute to tube wastage. However, our experience in the high temperature trials, both from the amount and the time of the persistence of chloride in the tube deposits, leads us to believe they were in themselves of minor importance in the corrosion mechanism. Alkali content rather than chloride content may be more important, but in British coals these are generally inseparable.

The SO_3 contents recorded in the trials were measured only at port level 6, that is only part way along the flame which occupied most of the chamber down to port level 12. The higher values quoted by Mr. Reid presumably refer to the economizer inlet of conventional boilers and are not strictly comparable. Our

measurements were primarily intended to test the reliability of the automatic analyzer under operating conditions. However, although the values recorded would not be typical of conventional boilers, they may be relevant to conditions in a full scale multicell-boiler of the novel design proposed in the paper, our prototype representing one cell of such an arrangement. In such a configuration it may be significant that the gas residence time is lower than in conventional boilers and so a shorter time for SO_3 formation is available—but this is largely conjecture as there may be interdependence on other factors.

In any event, from Mr. Reid's own work, it is likely that the SO_3 content of combustion gas is no true indication of the concentration existing within the deposits.

We should make clear our philosophy regarding nongaseous corrosion. Initially we had hoped to minimize corrosion by placing tubes in the boundary layer of flowing gas thus limiting ash deposition. Experience showed, however, that even when we succeeded in preventing thick layers of ash from forming (and we were not always successful) the more easily volatilized and often aggressive constituents of the coal mineral matter could deposit independently. We wish to make a distinction between the latter constituents which probably reach the tube surface by a process of molecular diffusion or even eddy diffusion, and the larger particles, often of high melting point, which are less corrosive, which deposit by inertial impaction. In our chamber, deposit layers less than $\frac{1}{2}$ in. thick and with a high water soluble content were shown to be very corrosive.

We did not assume any particular corrosion mechanism although it is true we thought the alkali complex trisulfates method of attack best explained our results. Invoking the mechanism that Mr. Reid proposed in the first part of his comments on our paper, namely the reaction of alkali sulphates and sulphur trioxide with the oxide film on the tube, it would appear feasible for alkali complex trisulfates to promote wastage without the presence of large quantities of coal ash iron oxide.