

Criteria for Selection of Coal Additives

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INTRODUCTION

Ash deposits are a major concern for coal users. They can reduce boiler availability, reliability, performance and efficiency.

The problems will become more acute in the near future. The energy crisis demands increased use of coal, and problems may be expected to grow at a faster rate than that of coal use. This is because disruption of normal coal supplies may be expected as increased demand puts a strain on the supply and transportation systems. Ash concentration will become less predictable. Cooperation will be needed among boiler manufacturers, coal users and coal suppliers.

Chemical treatment offers a means of alleviating the problems caused by coal ash deposits. Treatment of oil has been accepted for a number of years(1), but only occasional successes have been reported for coal (2-6).

This paper presents a rational approach to the choice of chemicals for treatment of ash from direct combustion of coal. It is hoped that application of the results of this study will advance the art, to the benefit of boiler owners and operators.

DEPOSIT PROBLEMS

There are two basic types of deposit problems, furnace slag and fouling of convection sections and superheaters. Corrosion of superheaters and supports is associated with the latter type of deposits. This study is addressed to alleviation of the fouling and corrosion of superheaters.

The key components in superheater corrosion by coal ash are the alkali iron sulfates. They are molten at superheater metal temperatures and participate in corrosive reactions, destroying the protective metal oxide coating and causing rapid corrosion. These compounds and their melting points are shown in Table 1.

TABLE 1. Alkali iron sulfates

<u>Compound</u>	<u>Melting points °F</u>
$\text{Na}_3\text{Fe}(\text{SO}_4)_3$	1155
$\text{NaFe}(\text{SO}_4)_2$	1274
$\text{K}_3\text{Fe}(\text{SO}_4)_3$	1145
$\text{KFe}(\text{SO}_4)_2$	1281

In addition to corrosion, the alkali iron sulfates may contribute significantly to the fouling of superheaters and the hotter parts of

convection sections. The molten sulfates can trap other ash particles and bond them.

CHEMICAL TREATMENT

There are two common mechanisms in direct chemical treatment of ash deposits. One is chemical reaction of the additive with the injurious deposit components or their precursors to form less harmful products. In the case of oil ash, for example, magnesium oxide reacts with vanadium pentoxide or sodium vanadyl vanadates to form magnesium vanadate, $3\text{MgO}\cdot\text{V}_2\text{O}_5$, which melts at 2179°F .

Treatment by chemical reaction has been suggested by Borio (7) and by Rahmel (8). Treatment with alkaline earth metal compounds was proposed to form compounds such as $\text{K}_2\text{Ca}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ at the expense of the alkali iron sulfates.

The second mechanism is physical. Dilution, formation of a barrier layer, or absorption of melts can prevent molten deposits from contacting tube surfaces, and hence prevent corrosion. All of these phenomena can also reduce the formation of bonded deposits. Certain types of successful oil additives are thought to work in this manner (1).

It appears from experience that the best method of application is to feed additives intermittently and to coordinate feed with the sootblower cycle. The treatment is fed immediately after the sootblowers have swept the target area, so as to allow maximum contact with inner deposit layers. Great care must be exercised in choosing the points and methods of addition to assure that the maximum amount of additive reaches the target surfaces. Success has been reported for intermittent feed (3, 6). To prevent corrosion and bonding, the alkali iron sulfates in the inner deposit layers must be affected. Attacking these compounds with additives is feasible, since they constitute a relatively small fraction of the total ash. Even with intermittent, directed feed, however, the major barrier to successful treatment is dilution or blocking of the additive by the bulk of the deposits. It is this effect of the matrix which chiefly distinguishes coal treatment from oil treatment.

Successful treatment with additives fed with the fuel is unlikely due to dilution by the bulk of the coal ash.

PRESENT INVESTIGATION

This paper reports a laboratory investigation of the effect of additives on synthetic superheater deposits which takes into account the effect of the matrix. The effect of additives on alkali iron sulfates was first determined. The experiments were then repeated with the addition of a third component: a matrix of bulk coal ash.

The criteria for success were the formation of solid, friable reaction products with the alkali iron trisulfates at 1100°F and maintenance of a solid, friable product with the addition of the ash matrix up to 1800°F , a representative gas temperature at superheater banks.

Friability of the mixture at the higher temperature was required since reaction of the additives with inner, sulfate-rich deposit layers will require periodic removal of outer layers by sootblowers. In

practice, if the additive and the outer parts of the deposit do not form friable products, attempts at treatment will simply powder the top of growing deposits.

EXPERIMENTAL

Additives were heated for two hours with alkali iron sulfates under a high-sulfur trioxide atmosphere to promote the stability of the sulfates. They were examined after heating at 1100°F and 1800°F. Appearance was noted visually and friability was tested with a spatula. It was noted whether the heated materials had wet the containers. Selected products were characterized by X-ray diffraction. The investigations were repeated with the addition of the ash matrix materials.

The equipment is shown in Figure 1. A commercial SO₂-air mixture was catalytically oxidized to SO₃ over a V₂O₅ catalyst.

ADDITIVES AND SYNTHETIC DEPOSITS

The alkali iron sulfates were prepared by the wet method of Corey and Sidhu (9). The synthesis and the stability of the materials at 1100°F under the experimental atmosphere were checked by X-ray diffraction. One simulated ash matrix had an elemental composition typical of Eastern coals. It was the following mixture: SiO₂ (40.1 weight %), Al₂O₃ (16.7), Fe₂O₃ (22.4), CaO (7.7), MgO (0.8), Na₂SO₄ (6.6), and K₂SO₄ (5.9). The other simulated Western coal ash and contained SiO₂ (25 weight %), Al₂O₃ (11), Fe₂O₃ (9), CaO (23), MgO (8) and Na₂SO₄ (25).

A mixture of K₃Fe(SO₄)₃ and Na₃Fe(SO₄)₃ by weight was used because the mixture melted below 1100°F. This allowed studies at 1100°F. Higher temperatures would have increased the instability of the sulfates and made the atmosphere more critical.

The additives in Table 2 are available in commercial grades. The rare earth oxide mixture contained 48% CeO₂ and 34% La₂O₃. The additives were applied at a ratio of 1:1 by weight to the alkali iron sulfate mixture. Matrix material was added as 1 part by weight to 1 part additive to 1 part sulfates.

RESULTS AND DISCUSSION

Without Matrix

Table 2 shows that effective deposit conditioning was achieved with a wide range of materials including both acidic and basic oxides. Mixtures contained the weight ratios shown.

TABLE 2. Additive evaluation, no matrix

Additive	Product at 1100°F	1800°F
Control	melt	melt
MgO	powder	melt
CaO	fusion, sticking	-
Rare earth oxide	powder	melt

TABLE 2. Additive evaluation, no matrix

Additive	Product at 1100°F	1800°F
TiO ₂	powder	melt
MnO	fusion, no sticking	fusion, melt
CuO	melt	
ZnO	melt	
Al ₂ O ₃	powder	fusion, slight melt
SiO ₂	powder	melt
MgO 66.7/Al ₂ O ₃ 33.3	powder	melt
MgO 28.3/Al ₂ O ₃ 71.7	powder	slight fusion
MgO 50.0/SiO ₂ 50.0	powder	melt
CaSiO ₃	slight fusion	melt

Of the transition and post-transition metals only titania, the rare earth oxides, and perhaps manganous oxide were satisfactory. Ti⁺⁴, La⁺³ and Ce⁺⁴ give a formal octet at the metal, as do the formal oxidation states in magnesia, alumina, and silica. The noble electronic configuration appears to be a favorable factor.

It is noteworthy that calcium and magnesium were not equivalent. A recent correlation of coal ash composition with melting behavior (10) distinguished elements on the basis of ionic radii and ionic potential. Magnesium fell with Si, Ti, and Al, while Ca fell with Na and K. The same trend appears to hold for reaction with alkali iron sulfates.

Another trend is that with the stability of the sulfate of the additive. Satisfactory additives with sulfates unstable at 1100°F were TiO₂, SiO₂ and Al₂O₃. Poor performers with stable sulfates at 1100°F included CuO, ZnO, CaO and MnO. MgSO₄ is stable, but less so than CaSO₄. Generally materials with unstable sulfates were more effective.

Since some of the heavier elements performed poorly, a study was conducted to assure that the results in Table 2 were not biased by unequal additive: sulfate mole ratios. It was determined that one mole of MgO per 0.23 moles of trisulfates was needed for a satisfactory product. All of the other oxides were then reacted with the sulfates at that mole ratio and their performance relative to MgO was not changed from that shown in Table 2.

The addition of a second component increased effectiveness in some cases. Calcium silicate performed better than CaO, and one MgO-Al₂O₃ mixture was superior to magnesia or alumina alone. The latter may have been due to spinel formation as shown in Table 3.

TABLE 3. Crystalline Reaction Products

<u>Additives</u>	<u>Temperature</u>	<u>Products</u>
MgO	1100°F	MgSO ₄ , K ₂ Mg ₂ (SO ₄) ₃ , (K, Na) ₃ Fe(SO ₄) ₃ *
MgO	1800°F	MgO, K ₂ Mg ₂ (SO ₄) ₃ , MgFe ₂ O ₄ *
Al ₂ O ₃	1100°F	Al ₂ O ₃ , (K, Na) ₃ Fe(SO ₄) ₃
Al ₂ O ₃	1800°F	Al ₂ O ₃ , Unidentified*
Al ₂ O ₃ 71.7 MgO 28.3	1100°F	K ₂ Mg ₂ (SO ₄) ₃ , Al ₂ O ₃ , Unidentified*
Al ₂ O ₃ 71.7 MgO 28.3	1800°F	MgAl ₂ O ₄ , K ₂ Mg ₂ (SO ₄) ₃ , Unidentified*

* Minor

The identification of the reaction products showed that magnesia reacted to form K₂Mg₂(SO₄)₃. No reaction was apparent for alumina. Its beneficial effects were due to dilution and absorption. At 1800°F magnesia and alumina reacted to form the spinel MgAl₂O₄. Alumina has been shown to be an effective adjunct to magnesia for conditioning oil ash deposits (11), and spinel has been identified in those deposits. The same beneficial effect is apparent here.

With Matrix

The results in Table 4 are cautionary and provide no simple trend to allow one to predict the relative performance of the additives.

TABLE 4. Additive Evaluation with Matrix

<u>Additive</u>	<u>Matrix</u>	<u>Product at 1800°F</u>
Control	Eastern or Western	melt
MgO	Eastern or Western	sl. fusion, sticking
Al ₂ O ₃	Eastern or Western	sl. fusion, sticking
SiO ₂	Eastern or Western	melt
MgO 28.3 Al ₂ O ₃ 71.7	Eastern or Western	powder, some sticking
MgO 50 SiO ₂ 50	Eastern or Western	powder, some sticking
CaSiO ₃	Eastern Western	melt powder, some sticking

Magnesia, alumina, their combination and the magnesia-silica combination showed satisfactory performance. Beneficial effects of mixtures were again seen for these materials, as the combinations were superior to MgO or Al₂O₃ alone.

However, silica, which performed well in the absence of the matrix, was unsatisfactory. The formation of the melt with the Eastern matrix was not predictable by standard composition-behavior correlations (12). The extreme difference for the two matrices with CaSiO_3 was also surprising. This unpredictability is a reflection of the complex chemical system involved. The complexity may be seen in mechanistic studies which have been reported (13). An empirical approach is suggested.

CONCLUSIONS

The corrosive components of superheater deposits may be chemically treated by a wide range of materials, both acidic and basic. They include magnesia, alumina, titania, silica and rare earth oxides and their combinations.

Only those additives which form high-melting friable products with the alkali iron sulfates in the presence of a matrix of bulk ash should be used. It is not possible to predict suitability from composition at this time.

Suitable additives may be selected empirically by studies such as the present one using samples of the appropriate deposits. The studies may be conducted by reputable chemical treatment suppliers.

Suppliers and boiler operators must then work in close cooperation to apply the additives in such a way that maximum benefits may be achieved. Only with such cooperation may the difficulties inherent in a high-ash fuel be overcome.

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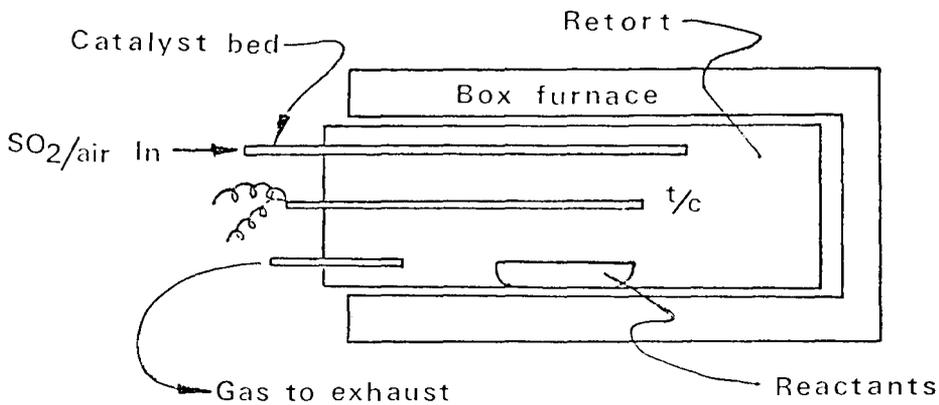


Figure 1 Furnace & Retort