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Effective new chemicals to prevent corrosion due to chlorine in power plant superheaters

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Abstract

Firing or co-firing of biomass in efficient power plants can lead to high-temperature corrosion of superheaters due to condensation of alkali chlorides into superheater deposits. Corrosion can be prevented if a significant portion of the alkali chlorides present in the flue gases is destroyed before reaching the superheaters. The alkali capturing power of aluminium and ferric sulphates was determined in a pilot-scale fluidised bed (FB) reactor. The reagents were added in solution, through a spraying nozzle, to the upper part of the freeboard. Both reagents, at economical dosages, fast and effectively destroyed the alkali chlorides by producing sufficient SO_3 for the sulphation. Both the mass flow rate and type of sulphate affected the sulphation ability. Thus, the cation, too, plays a role in the reaction. The required chemical dosage is not directly proportional to the $S_{reagent}/Cl_{2fuel}$ ratio because alkali chlorides must compete with calcium and magnesium oxides and probably also with alkali oxides for the available SO_3.

Keywords: Combustion; Fluidised bed; Corrosion; Chlorine

1. Introduction

High-temperature superheater corrosion during combustion of fuels containing biomass is due to chlorine deposition and subsequent reactions between chlorine and metal [1–3]. Problematic corrosion is possible at steam temperatures higher than 420 °C [4]. Superheater corrosion due to sulphur is also possible. This occurs at very high SO_3 concentrations such as produced from coals with very high sulphur content (several weight percentages) [5].

Cl deposition in the form of alkali chlorides dominates strongly over the deposition of Cl in other compounds, in the form of $CaCl_2$, for example [6]. The risk for superheater corrosion can be removed through the destruction of alkali chlorides before their deposition. A side benefit is the lower rate of mass deposition since alkali chlorides tend to act as a glue, giving rise to sticky deposits that cannot be cleaned in the normal way.

Sulphur trioxide react with alkali chlorides, binding the alkali and liberating HCl (Eq. (1)):

$$2MCl + SO_2 + 1/2O_2 + H_2O \rightarrow M_2SO_4 + 2HCl \qquad (1)$$

where M is K or Na.

Reaction (1) is called sulphation. Attempts have been made to prevent Cl deposition by mixing sulphur-rich fuels with Cl-rich fuels [7]. However, the improved availability of SO_2 can be ensured in this way only if the Ca/S ratio in the feedstock is low. The reaction between SO_2 and alkali chlorides is slow, and fast sulphation requires the oxidation of SO_2 to SO_3 [2] (Eq. (1)). The rate of oxidation is proportional to $[SO_2] \times [O_2]^{1/2}$ [8]. Probably only a minor part of the SO_2 will be oxidised, and the flow rate of sulphur in the fuel needed to destroy a given flow rate of alkali chlorides is clearly higher than the theoretical S flow rate required for complete alkali conversion. Limits for a safe S/Cl ratio in the feedstock have been suggested [7].

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Another, probably more effective way to apply sulphation is to add chemicals that directly form SO_3 under conditions prevailing near by the superheaters. Solubility in water will enable them to be added as a spray. Evaporation of water from the small droplets can be presumed to produce a huge number of nanometer-size particles before thermal destruction of the chemicals, so that a uniform zone of fresh SO_3 is formed against the alkali chlorides. Vattenfall AB has applied for a patent based on this idea [9]. Several reagents are protected in that application ($(NH_4)_2SO_4$, NH_4HSO_4, H_2SO_4 and $FeSO_4$), but it is usually the results of trials with ammonium sulphate $(NH_4)_2SO_4$ that have been presented. An equation for the thermal destruction of ammonium sulphate in the furnace can be written as follows:

$$(NH_4)_2SO_4 \rightarrow SO_3 + 2NH_3 + H_2O \qquad (2)$$

Alternative reagents to those mentioned in the patent are possible, as we show in this paper.

If the conversion of the reagent S to SO_3 were 100% in the furnace independent of the cation in the sulphate, and if the SO_3 that formed had equal lifetimes under constant conditions, and if the cation did not play a role in the alkali capture process, then the power of different sulphates to destroy alkali chlorides would depend solely on the molar flow rate of SO_4^{2-} in the reagent. In fact, water soluble sulphates decompose at widely different temperatures [10]. Moreover, catalytic or inhibiting effects may be present, and competing alkali capture reactions may be occurring, varying with the type of cation in the sulphate. In that case, variation could be expected in the sulphation power.

In addition to possible differences in the sulphation power of reagents, still other factors may complicate the estimation of the sulphate dosage needed to reduce the alkali concentrations to a safe level. Fig. 1 illustrates a case where the addition of SO_3 does not decrease the concentration of alkali chloride at all: CaO consumes the SO_3 to produce calcium sulphate. Alkali hydroxides (as basic compounds) can consume SO_3 as well and convert HCl (a product of sulphation, Eq. (1)) back to alkali chlorides.

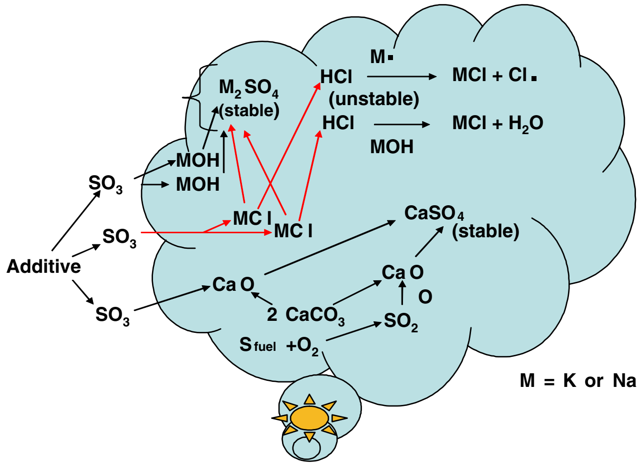

Fig. 1. Example of a situation where an addition of SO_3 does not decrease the concentration of alkali chlorides in the furnace.

The complexity of the reactions makes it difficult to select a suitable parameter for the chemical dosage. One option is S [mol]/2 × Cl [mol], where S is the flow rate of sulphur in the chemical and Cl is the flow rate of chlorine in the fuel (coefficient 2 comes from Eq. (1)). A second option might be S [mol]/2(K [mol] + Na [mol]), where Na and K are the flow rates of these elements in the fuel.

Optimisation of the type and dosage of reagent requires knowledge of the concentrations of the alkali chlorides in the flue gases and the amount of Cl deposition at different sites. HCl can be measured, if required, by FTIR spectroscopy. The best method to determine alkali chlorides is not so obvious, but one effective approach could be to separate the fine fly ash into various size fractions with a low pressure impactor for determination of the key elements of sulphation (Cl, K, Na and S) [11]. Sampling of alkali vapours and fine fly ash particles with impactors at furnace temperatures is a demanding task and must be conducted carefully to avoid altering the form of the sample too much and to minimise losses on the walls of the sampling line [11]. In this study the sulphation power of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ was tested in a pilot-scale FB reactor. The reagents were added as a spray to the upper part of the freeboard. Concentrations of Cl, K, Na and S were determined in the fine fly ash, concentrations of HCL and SO_2 in the flue gas and concentrations of Cl were measured at various locations in deposits.

2. Experimental

2.1. Reagents

Both ferric and aluminium sulphate are soluble in water, but the solubility of ferric sulphate (440 g in the form of $Fe_2(SO_4)_3 \cdot 9H_2O$) clearly exceeds that of aluminium sulphate (87 g in the form of $Al_2(SO_4)_3 \cdot 18H_2O$) (unit: per 100 cm^3 water at 0 °C) [12]. The strongest solutions contained about 12 g metal sulphate in 100 cm^3 water. Ferric sulphate decomposes at lower temperature (480 °C) than aluminium sulphate (770 °C) [10]. There might be an optimal residence time for SO_3 formation, enabling a best possible distribution of SO_3 to the cross-sectional area of the furnace. Fe^{3+} has been reported to catalyse the oxidation of SO_2 to SO_3 [2], so if the thermal decomposition of ferric sulphate were also to produce SO_2 as a result of reducing reactions, the presence of Fe^{3+} could promote the re-oxidation of SO_2 to SO_3. Al_2O_3 may not be capable of reacting with SiO_2 to produce aluminium silicates $Al_2O_3 \cdot 2SiO_2$ in the furnace. Aluminum silicates have been found to capture alkalies from alkali chlorides under furnace conditions (Eq. (3)) [13,14]. Therefore, in addition to SO_3, the presence of Al_2O_3 (the other product of thermal destruction of $Al_2(SO_4)_3$, Eq. (4)) might play a role in alkali capture from alkali chlorides where aluminium sulphate is used as reagent. The differences noted above could lead to differ-