



Destruction of alkali chlorides using sulphur and ferric sulphate during grate combustion of corn stover and wood chip blends

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HIGHLIGHTS

- ▶ Corrosive alkali chlorides can be destroyed with ferric sulphate spraying from grate furnaces.
- ▶ Instead, sulphur added to the fuel is much less effective producing high SO₂ emissions.
- ▶ Ferric sulphate spraying can be economic.

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ABSTRACT

Sulphur containing additives were used to destroy alkali chlorides in the furnace of a 100 kW grate reactor during combustion of a blend containing 40 ± 4% (based on energy content) corn stover with wood chips. Ferric sulphate spray, when added to zones where alkali chlorides have already been formed and gas temperature is <1000 °C, can destroy a significant portion of alkali chlorides in the furnace even at dosage S/Cl = 0.4–0.6 and prevent high temperature chlorine corrosion of superheaters. This dosage can increase SO₂ emissions from about 100 (without additives) to 250–350 mg/Nm³ 6% O₂. Additive costs can be estimated at 0.4–1 €/MW h electricity with blends containing 40–100% corn stover, assuming a 30% efficiency in electricity production. Mixing ferric sulphate with fuel feed had little effectiveness compared to spraying it into the upper furnace. Elemental sulphur mixed with the fuel feed was much less effective than the ferric sulphate spray. The minimum dosage of elemental sulphur needed to prevent Cl deposition (S/Cl = 3) lead to high SO₂ formation (≈2000 mg/Nm³ 6% O₂).

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1. Introduction

According to earlier studies using a 100 kW grate reactor with mixtures of wood chips and corn stover (CS), even blends containing small portions of CS raised local Cl concentrations in the deposits to a risky level (>10 wt%) enabling fast metal loss from the superheaters [1]. Therefore, means have to be developed to prevent Cl deposition if CS blends are to be burnt. Co-firing such biomass with coal or lignite might, in principle, provide a solution [2], but blends containing fuels with very different combustion properties (in relation to ignition delay, volatiles vs. fixed carbon formation, etc.) are difficult to burn in grate power plants. In addition, getting permission to use fossil fuels in such power plants and to purchase them at reasonable cost may be difficult or even impossible. Therefore, additives capable of destroying alkali chlorides in the furnace and preventing chlorine deposition on superheater tubes may be the only economical or even possible solution to prevent metal loss

from the superheaters when combusting CS blends in grate power plants. Literature on deposit formation and corrosion was widely referred to in an earlier paper [1].

Aluminium [3], ferric [3] and ammonium [4–6] sulphates, elemental sulphur [5,6] and kaolin [7,8] have been found to destroy alkali chlorides in the furnace. Sulphates when sprayed on the superheater area can be more effective than elemental sulphur mixed with the fuel [5,6] because SO₃ is formed directly from the additive at optimal furnace zones enabling effective sulphation of alkali chlorides and minimising the consumption of SO₃ in other reactions such as calcium sulphate formation or reduction of SO₃ to SO₂ [3]. Temperatures higher than 630 °C are needed for sulphation [9–11]. SO₂ is too slow for alkali chlorides sulphation under furnace conditions [12,13]. Therefore, SO₂ must be oxidised to SO₃ in order to be effective [12–14]. This oxidation is dependent on the available oxygen partial pressure [15].

The ability of ferric sulphate both as a spray and when mixed in the fuel and elemental sulphur mixed in the fuel were studied as methods for destroying alkali chlorides formed at grate combustion conditions. Similar studies have been conducted earlier under

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fluidised bed combustion conditions, but not under grate combustion conditions, where temperature distribution is different and the maximum furnace temperature can be higher than in fluidised bed combustion. In addition, the portion of fly ash is much lower in grate combustion than in fluidised bed combustion which can affect the effectiveness of the additives.

2. Experimental

2.1. Grate reactor, fuel and test description

A 100 kW grate reactor [1] was used for the combustion tests, where a blend containing Spanish wood chips and $40 \pm 4\%$ corn stover (CS) on the basis of energy content was burnt (Fig. 1). The diameter of the rotating grate and the furnace was 0.40 m and total height of the reactor (before flue gas cooler) was 5.00 m. The ratio between primary and secondary air was 1:1 and O_2 in the flue gas was kept at 5 ± 1 vol%. The CO concentration was then usually <50 ppm vol. More details of the reactor have been presented earlier [1]. Selected analysis results of corn stover and wood chips, and blend thereof are shown in Table 1. More detailed results on compositions of the same corn stover and wood chip delivery were presented earlier [1].

2.2. Experiments, with constant fuel loading (89 ± 5 kW = 0.708 ± 0.04 MW/m²)

Based on temperature vs. residence time data, the above loading level was assumed to best simulate the full load of a grate

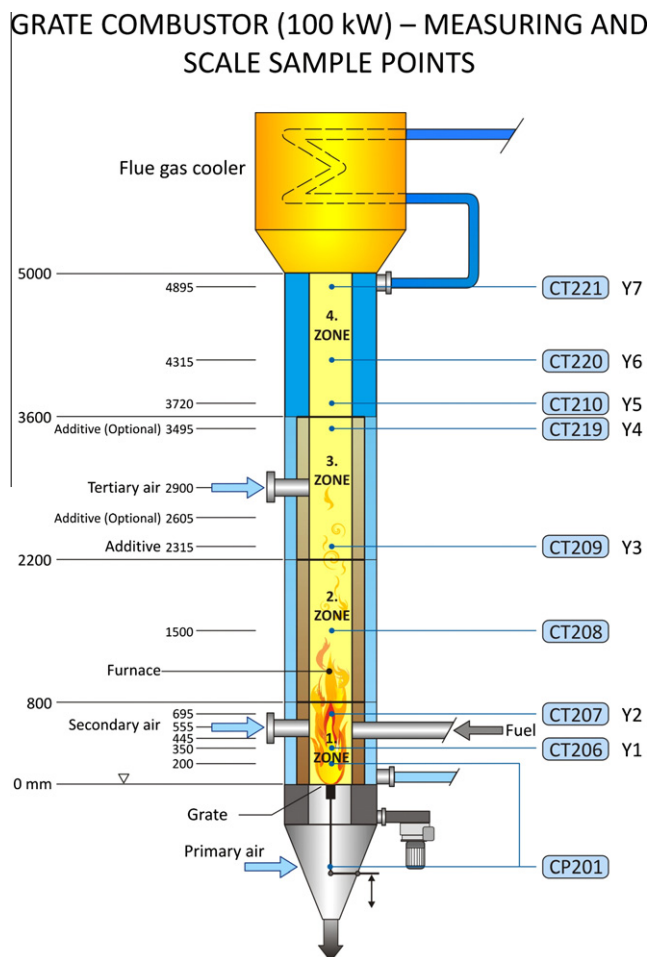


Fig. 1. A schematic of the 100 kW grate reactor.

Table 1
Key fuel analysis results.

	0	40	100
CS% enb.	0	40	100
% water	40	29	12
Ash (wt% dry)	0.6	8	22
S (wt% dry)	<0.02	0.04	0.09
Cl (wt% dry)	0.008	0.24	0.51
LHV (MJ/kg)	19.1	17.0	13.9
As rec. (MJ/kg)	10.5	10.7	11.1
Cl (wt% wet)	0.005	0.17	0.44

CS is corn stover, the residue is wood chips, enb. is energy basis.

power plant fired with such biomass as corn stover and wood chips. Ferric sulphate was sprayed into the furnace via port Y3 depicted in Fig. 1. The corresponding temperature vs. time history is shown in Fig. 3. The flow rate of ferric sulphate solution was kept constant (0.30 g/s) and the dosage was varied by changes in the concentration. More details of the spraying procedure were given earlier [3]. In addition, ferric sulphate (Fig. 4) and elemental sulphur (Fig. 5) were mixed directly in the fuel feed. The dosages were determined as molar ratios $S_{\text{reagent}}/Cl_{\text{fuel}}$. Sulphur content of the fuel was excluded from this ratio. S/Cl was 0.4, 0.6, 0.8 and 1.0 during ferric sulphate spraying tests. S/Cl was adjusted to 0.6, 0.8, 1.0, 1.2 and 1.4 during mixing elemental sulphur and solid ferric sulphate in the fuel feed. In addition, elemental sulphur was added with dosages S/Cl = 2.5 and 3.0.

2.3. Experiments with varied fuel loading

Fuel loading was varied at levels 113 kW (0.90 MW/m²), 89 kW (0.71 MW/m²) and 53 kW (0.43 MW/m²). The highest fuel loading is approximately the maximum for the reactor. The lowest fuel loading illustrates a partial load in a grate combustion power plant. Ferric sulphate was added with a constant dosage (molar S/Cl = 1.0) through port Y3. Fig. 6 shows the temperature distribution vs. residence time for these tests.

Sampling of alkali vapours and small particulates using a low pressure impactor was conducted for all the tests through port Y5 using a method described earlier [1]. This sampling was followed by analysis of key elements from the obtained fractions of the fine fly ash [1]. The Cl found in particulates which were smaller than $0.62 \mu\text{m}$ was assumed to have originated from alkali chlorides present in the furnace as vapours. This portion of the chlorine was labelled as corrosive Cl. In contrast, Cl in HCl was considered as non-corrosive, because Cl in this form cannot be condensed on superheater surfaces due to gas and metal temperatures being too great.

Flue gas analysis, described elsewhere [1], was performed with traditional on-line analysers and FTIR spectroscopy. The results for SO_2 concentrations were the most important in terms of interpreting the effectiveness of the additives. Unfortunately, the SO_3 concentration cannot be known using on-line measurements, but an estimation of the excess of SO_3 may be possible from the composition of the finest particles (based on findings of excess S in relation to cationic elements).

2.4. Deposit collection and analysis

Deposits were collected on removable rings with outer diameter 0.016 m and length 0.03 m. The rings formed components of a superheater tube simulator, whose surface temperature can be adjusted to the desired value. A probe with ring temperature of 540°C was inserted through port Y5 (Fig. 1). In some experiments deposits were also collected at a metal temperature of 470°C through port Y4, where gas temperature is higher than at port Y5

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