

Measures to reduce chlorine in deposits: Application in a large-scale circulating fluidised bed boiler firing biomass

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ABSTRACT

Combustion of biomass with a high content of alkali (mainly potassium, K) and chlorine (Cl) can result in operational problems including deposit formation and superheater corrosion. Among the measures applied to decrease such problems are co-combustion and the use of additives. The positive effects of these measures are to a large extent either sulphation of the alkali chlorides (KCl) to less corrosive alkali sulphates or capture of alkali from KCl during release of HCl. A test campaign was carried out in a large-scale circulating fluidised boiler fired with biomass where the measures applied were sulphation by ammonium sulphate and co-combustion with peat. Their performance was evaluated by means of several advanced measurement tools including: IACM (on-line measurements of gaseous KCl); a low-pressure impactor (size distribution and chemical composition of extracted fly ash particles) and deposit measurements (chemical composition in collected deposits). The overall performance was better for ammonium sulphate, which significantly lowered KCl in the flue gas. Meanwhile no chlorine was found in the deposits. Only a minor reduction of gaseous KCl was obtained during co-combustion with peat although the chlorine content in the deposits was greatly reduced. These findings were supported by the results from the impactor measurements.

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1. Introduction

Increasing energy consumption and global warming are a serious concern. Energy produced from biomass is not considered to contribute to the net CO₂ emissions to the atmosphere. Political actions have therefore been taken to increase the share of biomass utilisation as an alternative to the use of fossil fuels. The content of alkali (potassium, K and sodium, Na) is generally high in biomass, and the chlorine (Cl) content is also rather high in some biomass fuels, such as straw. However, the content of sulphur (S), which has an important role in combustion, is relatively low. Combustion of such fuels in a fluidised bed boiler can result in various operational problems including bed agglomeration, deposit formation and superheater corrosion [1–3]. The dominant mechanism for bed agglomeration is melt formation and it has been suggested that coating layers formed on bed particles play an important role [3,4]. Potassium (K) released [5] during combustion can condense on heat transferring surfaces as chlorides (KCl) or aerosol particles containing sulphates (K₂SO₄) can deposit as particles. High levels of

KCl in the flue gas can cause enhanced deposit formation, and in turn high content of chlorine in deposits may cause accelerated superheater corrosion [1,6].

Mechanisms for deposit formation were reviewed by Zbogor et al. [7]. An increased concentration of ash particles in the flue gas can cause increased deposit growth rate from impaction. Another important factor is the composition of the deposits. Sticky deposits can capture fly ash particles, which increase the deposit growth rate. Increasing deposition rates corresponded to higher levels of Cl and lower levels of S in the deposits for mixtures of peat and bark in an investigation by Theis et al. [8].

Deposit formation and superheater corrosion can be reduced by either co-combustion or the use of additives. Coal, peat and municipal sewage sludge are among the fuels suitable for co-combustion with biomass containing high amounts of alkali and chlorine. These measures also have an impact on bed agglomeration. The reduction could be due to both capture of K in ash components from the additional fuel and/or to sulphation of KCl due to its sulphur content.

Formation of alkali aluminosilicates was, according to Aho and Ferrer [9], the dominant path to capture alkali during co-combustion of coal and Meat and Bone Meal (MBM). This investigation found sulphur in the different coals to be less relevant in preventing alkali chlorides in the deposits.

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Co-combustion with peat can prevent bed agglomeration and reduce deposit formation [10,11]. It was proposed by Pommer et al. [11] that co-combustion of peat transferred alkali from the bed material and the fine particle fractions to the coarser ones by sorption and/or reaction with the increased amount of residual ash particles.

The content of chlorine in deposits was eliminated during co-combustion of a chlorine-rich biomass with municipal sewage sludge (MSS), whereas it decreased for potassium [12]. The KCl concentration in the flue gas was partly limited by sulphation, and partly by capture of K by the sludge ash. K captured was found in species mainly composed of silicon (Si), aluminium (Al), calcium (Ca), iron (Fe), and phosphorus (P). Especially important is the formation of potassium aluminium silicates, although the presence of Ca, Fe and P was also found to influence the alkali capture chemistry [13].

Additives can prevent the release of gaseous KCl by capturing K in compounds such as potassium aluminium silicates. Additives used for the capture of K are for instance various clay minerals, where the performance of kaolin especially has been investigated [14–16]. Most of these additives have also been considered as sorbent materials for alkali for cleaning high temperature flue gases from pressurised fluidised-bed combustors or for alkali removal in a biomass gasifier combined cycle application [17].

Elemental sulphur or other sulphur/sulphate-containing additives can be used for sulphation of alkali chlorides. Here the additive reacts with KCl, converting it to a less corrosive alkali sulphate. In [18–20] results are presented using elemental sulphur or other sulphur/sulphate-containing additives such as ammonium sulphate ((NH₄)₂SO₄).

In a previous paper by Kassman et al. [20], several advanced measurement tools were applied to evaluate two sulphur containing additives for sulphation of gaseous KCl: elemental sulphur and ammonium sulphate ((NH₄)₂SO₄). Ammonium sulphate lowered gaseous KCl and also reduced the chlorine content in the deposits significantly better than sulphur.

The tests were carried out in a 12 MW circulating fluidised bed (CFB) boiler at Chalmers University of Technology. The boiler is specially equipped for research purposes and in it a multitude of projects concerning various research fields has been carried out. An advantage with this boiler is the possibility to perform measurement campaigns in a real boiler, while maintaining control over important operation parameters such as load, air supply and composition of the fuel mix. Alkali related issues have been investigated in the Chalmers boiler in for instance [12,13,20–24]. However, results from such well-controlled research tests should also be verified in larger commercial boilers.

The performance and evaluation of measurement campaigns in full-scale boilers pose a real challenge. Identical operating conditions can often not be achieved from one day to the next rendering the interpretation of the results more difficult. There may also be restrictions in available openings for the measurement equipment at positions relevant for research purposes, such as in the combustion chamber or in the superheater region of the boiler. Full-scale measurements focusing on operational problems during biomass combustion have often been carried out involving researchers from Sweden, Denmark and Finland [18,19,25–34].

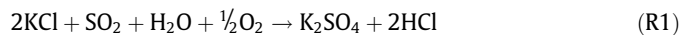
The scope of this paper is to demonstrate measures to reduce alkali related problems in a large-scale boiler, which is approximately ten times larger than in the Chalmers boiler used in Kassman et al. [20]. The measures applied were sulphation of KCl by ammonium sulphate and co-combustion with peat. Additionally, an attempt is made to explain the results with the present knowledge concerning sulphation of alkali chlorides and capture of K. These tests were included in a larger project and some of the results have previously been presented [19].

2. Theory

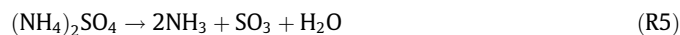
The measures to reduce alkali related problems such as deposit formation and superheater corrosion during biomass combustion are mainly either sulphation of the alkali chlorides or capture of alkali (mainly K) from alkali chlorides during release of HCl. During co-combustion of peat both sulphation and alkali capture can be of great importance.

2.1. Sulphation of alkali chlorides

Both homogeneous and heterogeneous mechanisms have been proposed for formation of alkali sulphates from alkali chlorides found in either deposits or ash particles [35]. The overall sulphation reaction, R1, as well as other reactions of particular interest for this paper, are presented below. The required sulphur in R1 can both originate from a fuel such as peat or from sulphur/sulphate-containing additives such as sulphur or ammonium sulphate. Potassium can be released as KCl or as potassium hydroxide (KOH) according to R2, when the concentration of water is high and of chlorine low [5].



The homogeneous mechanism includes formation of an alkali sulphate aerosol from an alkali chloride in the gas phase [36]. The sulphation rate in the gas phase is limited by the presence of sulphur trioxide (SO₃) (R4) [37–41], and oxidation of SO₂ to SO₃ (R3) is the rate-limiting step according to Glarborg and Marshall [40]. Meanwhile, the reactions between alkali and SO₃ in gas phase have only been investigated to a certain extent [39].



SO₃ is formed according to R5 during decomposition of ammonium sulphate [42]. The sulphur in elemental sulphur must be oxidised from SO₂ to SO₃ (R3). Below 900 °C the oxidation of SO₂ in R3 is slow. It can, however, be enhanced by radicals or be catalysed by components in fly ash particles [39]. According to these reactions, sulphation of gaseous KCl is more efficient if SO₃ is formed directly instead of being oxidised from SO₂. Elemental sulphur and ammonium sulphate were evaluated for sulphation of gaseous KCl, and ammonium sulphate performed significantly better than sulphur [20]. Thus the presence of SO₃ was of greater importance than that of SO₂ for the sulphation of gaseous KCl.

In a proposed heterogeneous mechanism, a gas phase alkali-containing precursor is transported to a surface where it is then sulphated by reactions in condensed or solid phases [35]. There is an efficient and fast heterogeneous formation mechanism for condensed phase alkali sulphates in flames that occurs on any surface including fly ash particles [43]. The literature available concerning heterogeneous sulphation of alkali chlorides (R1) has to a large extent not been updated [37,43,44].

The rate of sulphation of KCl in gas phase and in condensed phases was investigated in [37], and found to be considerably slower in the condensed phase. Heterogeneous sulphation of KCl is of greater importance in deposits compared to particles in the flue gas, due to its longer reaction time. The heterogeneous sulphation is, however, not as important as homogeneous sulphation for formation of alkali sulphate aerosols according to Jiménez and Bal- lester [39].

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