



Experimental study of the kinetics of sulfation of alkali chloride deposits



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ABSTRACT

The composition of ash deposits formed in biomass combustion systems can be significantly modified by the sulfation of alkali salts. In order to assess the efficiency of this process, the conversion of alkali chlorides into alkali sulfates occurring in deposits at surface temperatures representative of those in biomass boilers (350–650 °C) was quantified by means of specific short-term experiments with realistic deposits. The influence of operating conditions (reaction time, surface temperature and sulfur concentration) was characterized and the results were used to derive a kinetic expression for the in-deposit sulfation of KCl. This kinetics was compared with those proposed by other authors for solid NaCl and molten KCl. Contrary to previous results for solid NaCl, but in agreement with observations for solid KCl and calculations for molten KCl, the proposed kinetics predicts a relevant effect of sulfation on the properties of deposits formed in biomass-firing boilers even in the short-term scale.

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1. Introduction

The combustion of biomass for the production of electricity and heat represents an attractive option to efficiently use this renewable energy source. However, there are still some unresolved technical issues such as the formation of alkali salt deposits on boiler surfaces, which leads to a decline in its efficiency and capacity and possibly to significant corrosion rates [1–5]. The severity of these effects varies with both the mass and the chemical composition of the ash deposits.

Among other variables, the presence of sulfur may cause significant modifications in the properties of ash deposits by replacing the chlorine in alkali salts. Alkali sulfates in deposits can originate from alkali chlorides either through homogeneous reactions in the gas flow and subsequent deposition on the heat transfer surfaces, or by heterogeneous sulfation of chlorides previously captured in the deposit. Both routes are not mutually exclusive and sulfation of alkali chlorides may occur simultaneously in the gas stream and in the deposit. The (gaseous) homogeneous formation of alkali sulfate was previously addressed in several works by the authors' research group. Those studies concluded that vaporized alkalis can be partially or totally bound as sulfates, which determines the composition of the aerosols formed by nucleation and condensation [6,7]. The limiting step was shown to be the oxidation of SO₂ to SO₃ [8,9]. This issue has been specifically studied in other published works (e.g. [10–13]) with similar conclusions. The impact of homogeneous sulfation can be further analyzed with the help of detailed reaction mechanisms provided in

some of those works. Nevertheless, gas-phase processes will not be analyzed in this work, which is focused on heterogeneous sulfation.

In principle, the substitution of alkali chlorides by sulfates is expected to reduce operational problems in biomass-fired plants, although some authors (e.g. [14]) indicate that in-deposit sulfation can enhance corrosion due to the HCl released in the vicinity of the wall). In any case, there is no general agreement on the actual relevance of in-deposit sulfation on the composition of alkali deposits.

On the one hand, many authors propose that in-deposit sulfation occurs on the tube after deposition of potassium chloride, based on the observation that the chlorine content decreases and sulfur content increases along the time in ash deposits [3,15–19]. Also, Hansen et al. [19] observed more sulfur in the inner part than in the outer layers in deposits from straw burning and ascribed this effect to a longer exposition of the inner layers to sulfur-containing compounds in the surrounding gases. Furthermore, some authors [20–23] compared the composition of fly ashes and deposits obtained at surface temperatures around 550 °C and gases at 800–900 °C and found lower chlorine content in the deposits (and higher sulfur content) than in the fly ashes in “short-term” (1–4 h) experiments; therefore, they concluded that the decrease of chlorine (and increase of sulfur) in the deposit had to be due to a relatively fast in-deposit sulfation.

On the other hand, other authors like Boonsongsup et al. [24] consider the in-deposit sulfation too slow to play a significant role in short-term deposits. This is one of the few works in which the sulfation rate is quantified in terms of a kinetic law from experimental data, which was derived for the sulfation of solid NaCl particles (125–250 μm).

In the authors' opinion, there is disagreement among previous works regarding sulfation kinetics and, in any case, a great uncertainty remains on the rates of in-deposit sulfation at industrial conditions.

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Moreover, as highlighted by Kassman [21], the investigations available concerning heterogeneous sulfation of alkali chlorides are rather old and more quantitative efforts would be needed to derive kinetic expressions valid for the conditions prevailing in real boilers.

The main objectives of the experiments described here were to evaluate the relevance of in-deposit sulfation of potassium chloride in short-term deposits for a range of realistic conditions (including variations of surface temperature, exposure time and sulfur dioxide concentration) as well as to determine the kinetic parameters governing this reaction. The kinetics found in this study was finally compared with those found in previous works, including that of Boonsongsup et al. [24] (for solid NaCl) and Pyykönen and Jokiniemi [25] (from the data of Iisa and coworkers [26] for molten KCl).

2. Method and tests

A set of 'sulfation tests' were performed to study the sulfation of potassium chloride deposits under well-controlled conditions. The procedure comprised two steps. First (Step 1), the KCl deposit was formed by simulating the process actually taking place in a boiler, as a means to obtain deposits that are as realistic as possible. With that purpose, cylindrical coupons were inserted into the flue gases generated in the combustion of a biomass resulting in the formation of a deposit of nearly pure KCl. Four adjacent, stainless steel tubes (o.d. 15 mm, length 14.5 mm) were simultaneously mounted on the head of a cylindrical deposition probe (internally cooled), as shown in Fig. 1. The probe was placed at the exit of a down-fired Entrained Flow Reactor (EFR, see e.g. [6] for a detailed description of this facility). Sawdust doped with KCl (3.2% in a mass basis) was used as a fuel. The sawdust particles were sieved below 300 μm and had a low ash content (0.24% in a wet mass basis). Six identical deposits were generated, all of them at gas temperature $T_g = 1300^\circ\text{C}$, surface temperature $T_w = 550^\circ\text{C}$, and with a duration of 90 min. These conditions were selected from previous experience to produce the thickest KCl deposits for this exposure time [27]. The deposits generated had a dendritic structure and a thickness around 150 μm , as shown in Fig. 2. The molar fraction of alkali sulfates with respect to the total salts (sulfate and chloride) of these deposits, given in terms of $R_{s,d}$ ($2S/(2S + Cl)$ molar ratio), is ~ 0.02 , thus confirming that they are mostly composed of KCl. Under the assumption that S and Cl exist only as alkali sulfate or chloride in the

deposits, the ratio $R_{s,d}$ will be used throughout this work to express the molar fraction of alkali sulfates with respect to the total amount of alkali salts (chlorides and sulfates), with 0 and 1 indicating, respectively, that only chlorides or sulfates are present. Since, as shown later, the alkali chlorides may gradually be transformed into sulfates, this ratio constitutes also a convenient index to characterize the progress of the sulfation reaction.

In a second step, heterogeneous sulfation was induced by re-inserting these KCl deposits into a hot gas stream (with 5% oxygen by volume, in a dry basis) doped with SO_2 . These experiments were repeatedly interrupted to extract one of the fouled rings and replacing it by a clean one. So, four samples were finally obtained in Step 2, corresponding to four exposure times in the same hot, SO_2 -containing atmosphere (0, 30, 90 and 180 min, 0 meaning no exposure, since one of the original four tubes from Step 1 was kept for reference of the original deposit). Six experiments with different SO_2 concentrations and probe surface temperatures were carried out in order to obtain sufficient data as for deriving reaction order, activation energy and pre-exponential factor of the sulfation reaction. Table 1 summarizes the conditions ($[\text{SO}_2]$ and T_w) used in each experiment. In all cases, the reactor temperature was 1300°C and the probe was located at a point where the gas temperature was 850°C . Since there is no alkali in the reactor to 'accelerate' SO_2 oxidation towards SO_3 , the concentration of the latter is expected to be small ($< 10\%$ of the initial SO_2 concentration), according to Jiménez and Ballester [9] (and references therein).

Different surface temperatures, in the usual range for heat exchanger surfaces in combustion plants, were selected for these sulfation experiments: 350°C , 450°C , 550°C and 650°C (identified as Sulf1 to Sulf4, respectively). Surface temperature was regulated by modifying the air flow rate used to cool the probe. At $T_w = 450^\circ\text{C}$, the influence of SO_2 concentration in combustion gases was studied by performing additional experiments with 100 and 220 ppmv of SO_2 in the gas stream (tests Sulf3-s1 and Sulf3-s2, respectively). The sulfation rate at this temperature was expected to be high enough as to obtain measurable changes in the conversion of potassium chloride to sulfate after variations of the SO_2 concentration.

Additionally, selected samples from a different set of experiments (*deposit formation tests*), performed in the same facility with the aim of studying the properties of deposits formed in the combustion of different biomasses and pure materials, were also analyzed in order to extract information on the sulfation process. Specifically, results for three different 'fuels' were considered: cardoon ($< 300\ \mu\text{m}$), sawdust ($< 300\ \mu\text{m}$, doped with 3.2% KCl) and silica particles ($43\text{--}63\ \mu\text{m}$, again doped with 1.2% KCl). The experimental procedure for these is the same as described for the "Step 1" above. The concentration of SO_2 at the reactor inlet was set at 170 ppm, and that of the oxygen at 5% at the deposition section. The duration of the tests was again 90 min. The probe shown in Fig. 1 was used in those tests with a single steel coupon. In the absence of extra SO_2 , pure alkali chloride deposits were formed.

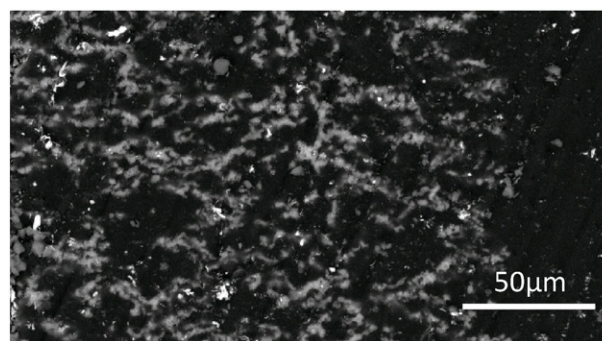
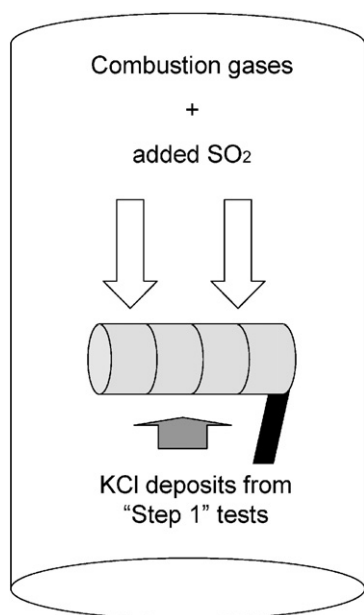


Fig. 1. Scheme of the setup for the sulfation tests (Step 2). Four adjacent, stainless steel coupons with a previously-formed KCl deposit are placed on the same probe head.

Fig. 2. SEM image of a typical deposit formed in step 1 of the method described in the text (i.e. deposition of KCl carried by sawdust particles into the EFR). $T_{\text{reactor}} = T_{\text{gas}} = 1300^\circ\text{C}$, $T_{\text{surface}} = 550^\circ\text{C}$, 90 min.

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