



## Sulfur recirculation for increased electricity production in Waste-to-Energy plants <sup>☆</sup>



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### ABSTRACT

Sulfur recirculation is a new technology for reducing boiler corrosion and dioxin formation. It was demonstrated in full-scale tests at a Waste to Energy plant in Göteborg (Sweden) during nearly two months of operation. Sulfur was recirculated as sulfuric acid from the flue gas cleaning back to the boiler, thus creating a sulfur loop.

The new technology was evaluated by extensive measurement campaigns during operation under normal conditions (reference case) and operation with sulfur recirculation. The chlorine content of both fly ash and boiler ash decreased and the sulfur content increased during the sulfur recirculation tests. The deposit growth and the particle concentration decreased with sulfur recirculation and the dioxin concentration (I-TEQ) of the flue gas was reduced by approximately 25%. Sulfuric acid dew point measurements showed that the sulfuric acid dosage did not lead to elevated SO<sub>3</sub> concentrations, which may otherwise induce low temperature corrosion.

In the sulfur recirculation corrosion probe exposures, the corrosion rate decreased for all tested materials (16Mo3, Sanicro 28 and Inconel 625) and material temperatures (450 °C and 525 °C) compared to the reference exposure. The corrosion rates were reduced by 60–90%. Sulfur recirculation prevented the formation of transition metal chlorides at the metal/oxide interface, formation of chromate and reduced the presence of zinc in the corrosion products. Furthermore, measured corrosion rates at 525 °C with sulfur recirculation in operation were similar or lower compared to those measured at 450 °C material temperature in reference conditions, which corresponds to normal operation at normal steam temperatures. This implies that sulfur recirculation allows for higher steam data and electricity production without increasing corrosion.

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### 1. Introduction

Today, electricity production in waste to energy plants is limited by the maximum achievable temperature in the superheaters, above which the corrosion rate becomes impractically high.

*Abbreviations:* A, Alkali = Na and K; Cl/S, Chlorine/sulfur molar ratio; DLPI, Dekati Low-Pressure Impactor; EDX, Energy Dispersive X-rays; ICP-AES, (Inductively Coupled Plasma-Atomic Emission Spectrometry); ICP-OES, (Inductively Coupled Plasma-Optical Emission Spectrometry); I-TEQ, International Toxic Equivalents; PCDD, Polychlorinated dibenzo-p-dioxins; PCDF, Polychlorinated dibenzofurans; SEM, Scanning Electron Microscopy; TEF, Toxic Equivalent Factor; XRD, X-Ray Diffraction.

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Usually a steam temperature of 400 °C, corresponding to a material temperature of 425–450 °C, is used, but some newer plants are designed for slightly higher temperatures. This paper aims at increasing the steam temperature to 500 °C. The purpose of the novel sulfur recirculation process, described in Section 1.1, is to reduce the corrosion rate of the superheaters in waste to energy plants by recirculating sulfur from the wet flue gas cleaning back to the boiler. The recirculated SO<sub>2</sub> reacts with the chloride containing ashes and deposits as described in Section 1.2, creating sulfates, which are less sticky than chlorides. Ashes with less chlorides produce less dioxins and less superheater corrosion (Sections 1.3 and 1.4). The long-term aim is higher electricity efficiencies in biomass and waste fired boilers using sulfur recirculation.

#### 1.1. Sulfur recirculation

The purpose of this study is to demonstrate how the sulfur in the fuel can be recirculated in a full scale plant in order to achieve

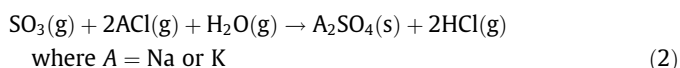
less corrosive deposits in Waste-to-Energy plants. The recirculated sulfur will increase the gas concentration of SO<sub>2</sub> in the boiler and decrease the Cl/S ratio of the deposits and ashes, thus producing a less corrosive environment for the superheaters (Hunsinger et al., 2006, 2007). The innovative, patented sulfur recirculation process, for which Götaverken Miljö AB has a world-wide exclusive license, was invented by Hans Hunsinger at Karlsruhe Institute of Technology (KIT) and has previously been tested in the 0.5 MW waste incineration pilot plant “TAMARA” at KIT. The proposed technology is unique in the way that it, contrary to other methods, only uses the existing sulfur in the fuel and does not increase the amount of residues produced.

### 1.2. The influence of sulfur on ashes and deposits

The formation of deposits is more pronounced in waste incineration compared to combustion of most other fuel. One reason is the high content of chlorine, alkali (sodium and/or potassium) and ash in waste. During incineration, most of the chlorine enters the gas phase (Bøjer et al., 2008; Lang et al., 2006). Some of it reacts with alkali to form volatile alkali chlorides (Miles et al., 1996; Olsson et al., 1997) and the rest is HCl(g). In the furnace, alkali chlorides are mainly gaseous, but form submicron particles (size < 1 μm) when the gas is cooled in the boiler. The gaseous and particulate alkali chlorides are deposited on the heat transfer surfaces where they may cause corrosion. Sulfur may react with alkali chlorides to form alkali sulfates by so called sulfation. Addition of sulfate and sulfur has been shown to decrease the chlorine content in the deposits during co-firing of straw pellets and wood pellets in a fluidised bed (Davidsson et al., 2008). During co-firing of bark and peat, an increase in deposits was found at Cl/S > 0.15 (Theis et al., 2006). By increasing the sulfur content in the fuel, the chlorine content of the deposits may be reduced (Robinson et al., 2002). In flue gases from incineration, sulfur is mainly present as SO<sub>2</sub> and a minor fraction (typically a few percent) as SO<sub>3</sub> which is described by the equilibrium and reaction rate of:



Alkali chlorides react readily with SO<sub>3</sub> according to:



(Iisa et al., 1999; Glarborg and Marshall, 2005)

According to Hunsinger et al. (2007), alkali chlorides also react with SO<sub>2</sub>. Hindiyarti et al. (2008) have studied the reaction of alkali chlorides with SO<sub>2</sub> in an entrained flow reactor and propose the following reactions based on detailed kinetic modeling:



### 1.3. The influence of sulfur on dioxins

It has been shown in numerous laboratory, pilot- and full-scale studies that the presence of sulfur in the flue gas reduces the amount of dioxins (I-TEQ) emitted (Chang et al., 2006; Gullett et al., 1992, 2000; Hunsinger et al., 2003, 2006, 2007; Lindbauer and Wurst, 1992; Ogawa et al., 1996). Two possible theories behind the phenomena are often discussed viz.:

- (1) Due to the presence of SO<sub>2</sub> in the flue gas the equilibrium between Cl<sub>2</sub> and HCl is shifted towards the inactive form (HCl) (Griffin, 1986; Wikström et al., 2003)
- (2) Metal chlorides, especially CuCl<sub>2</sub>, which promote the reaction rate of the de novo synthesis of dioxins, react with sulfur to form inactive metal sulfates (Ryan et al., 2006; Gullett et al., 1992).

Experiments in full scale have shown that the inhibition effect of sulfur lasts for several hours (Hunsinger et al., 2007); a finding that indicates that the role of metal chlorides and the de novo synthesis (theory 2 above) is important.

### 1.4. The influence of sulfur on corrosion

It is well known that waste-fired plants are affected by more serious corrosion problems compared to coal-fired boilers. The higher corrosion rate can be related to differences in the combustion environment: less sulfur-containing compounds, higher concentrations of water vapor and HCl in addition to an increased amount of alkali compounds, especially alkali chlorides. Laboratory investigations of the initial corrosion attack have shown the following:

- Water vapor and oxygen react with chromium oxide to form a compound which evaporates so that chromium is depleted from the metal surface. Since chromium is necessary to form a protective oxide layer on FeCr steels this protection is inhibited and the metal surface is subject to rapid corrosion (Asteman et al., 1999; Halvarsson et al., 2006; Segerdahl et al., 2002; Froitzheim et al., 2010).
- The breakdown of the protective oxide on FeCr steels does also occur in the presence of alkali chlorides. In this case, the chromium rich and protective oxide is converted into alkali chromate (e.g. K<sub>2</sub>CrO<sub>4</sub>) and poorly protecting Fe<sub>2</sub>O<sub>3</sub>, resembling the corrosion properties of low alloyed steels (Pettersson et al., 2005; C. Pettersson et al., 2006; Segerdahl et al., 2004; Jonsson et al., 2009)
- On low alloyed steels, the presence of alkali chlorides increases the corrosion rate by the formation subscale transition metal chlorides, causing an increased ionic transport through the oxide and poor scale adhesion (Folkesson et al., 2011; Jonsson et al., 2011).

The good resistance towards high temperature corrosion which characterizes high temperature materials is due to the ability to form oxides which inhibits further oxidation and corrosion. Stainless steels are a group of materials which are often used in the more corrosive parts of the boiler. These steels will at high temperatures form a protective oxide, consisting of both iron and chromium, on the form (Fe<sub>x</sub>Cr<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> (i.e. a solid solution of chromium (III) oxide (Cr<sub>2</sub>O<sub>3</sub>) and iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>)). The protective properties of this oxide depend on the chromia content, where oxides with a high Cr/Fe ratio are more protective. Hence, processes that deplete the oxide in chromium tend to be harmful, leading to an iron rich oxide with poor protective properties. With biomass or waste as fuel, such processes are related to the high concentrations of alkali compounds and water vapor, forming alkali chromate and gaseous chromic acid, respectively, and a poorly protective oxide layer.

It has been shown that the corrosive effect of alkali chlorides and water vapor can be suppressed by increasing the presence of sulfur-containing compounds in the corrosive environment. Pettersson et al. (2011) have shown how the protective chromium rich oxide layer of the austenitic stainless steel 304L can react with KCl and K<sub>2</sub>CO<sub>3</sub> to form K<sub>2</sub>CrO<sub>4</sub> which is non-protective. K<sub>2</sub>SO<sub>4</sub>,

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