



CHALMERS
UNIVERSITY OF TECHNOLOGY

Recirculation of NO_x and SO_x Scrubber Effluent to an Industrial Grate Fired MSW Boiler - Influence on Combustion Performance, Deposition

Downloaded from: <https://research.chalmers.se>, 2022-10-11 19:49 UTC

Citation for the original published paper (version of record):

Gall, D., Allgurén, T., Johansson, J. et al (2022). Recirculation of NO_x and SO_x Scrubber Effluent to an Industrial Grate Fired MSW Boiler - Influence on Combustion Performance, Deposition Behavior, and Flue Gas Composition. *Energy & Fuels*, 36(11): 5868-5877. <http://dx.doi.org/10.1021/acs.energyfuels.2c00293>

N.B. When citing this work, cite the original published paper.

Recirculation of NO_x and SO_x Scrubber Effluent to an Industrial Grate Fired MSW Boiler—Influence on Combustion Performance, Deposition Behavior, and Flue Gas Composition

Dan Gall,* Thomas Allgurén, Jakob Johansson, Fredrik Normann, Anette Heijnesson Hultén, Adrian Gunnarsson, and Klas Andersson



Cite This: *Energy Fuels* 2022, 36, 5868–5877



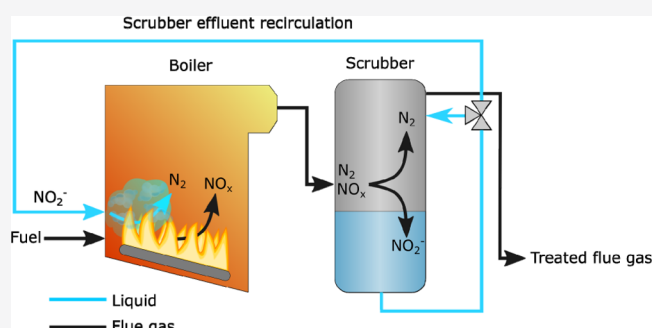
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The concept of scrubber effluent recirculation has recently received attention in connection to NO_x emission control. Here, we present data from an industrial-scale MSW-fired plant, where effluent from a combined NO_x and SO_x scrubber was recirculated and injected into a grate-fired boiler. The combustion characteristics were carefully studied during the injections to observe the potential effects on burnout and flue gas composition. In addition, deposition measurements were performed to observe effects on growth rate and chemical composition of deposits, which are critical factors for any solid fuel-fired heat and power plant. The recirculation of the nitrogen-rich waste streams was performed via pre-existing liquid injection equipment, and the results show that the N-containing compounds in the scrubber effluent were efficaciously reduced to inert nitrogen gas. Furthermore, the recirculation of the scrubber effluent may reduce ammonia demand for selective non-catalytic reduction systems by inhibiting the formation of ammonium chloride. Sulfur and alkali components in the effluent increased the deposition growth rate and also changed the chemical composition of the deposits. Understanding how the local conditions at the injection point influence the distribution and speciation of the injected compounds is essential for a successful recirculation strategy.



1. INTRODUCTION

Multi-pollutant emission control has received increased attention in recent years due to the increased simplicity, minimized area requirement, and reduced operational cost.¹ In our recent work,² simultaneous removal of SO_x and NO_x by wet absorption in a scrubber has been demonstrated in a commercial-scale waste-to-heat plant. The technology showed promising results in terms of removal rates: $\sim 90\%$ of NO_x and $>99\%$ of SO_x , which is comparable to the removal rates of technologies listed by the EU as the best available technology.³ However, treatment of the scrubber effluent was identified as key to the process economics² due to high disposal costs. Discharge of the scrubber effluent has been questioned recently, in particular, open discharge of untreated effluent, which represents only a shift of burden between air and water.^{4,5} Typically, the scrubber effluent from a waste-to-energy plant is managed by physiochemical treatment, evaporation, or valorization, depending on the plant size and market conditions.⁶ For large facilities, such as pulp and paper plants, the scrubber effluent can be proficiently treated by the existing wastewater infrastructure.⁷ However, for small- and medium-scale plants, it is difficult to justify the large installation cost associated with wastewater treatment.

One solution investigated in this work is to recirculate the scrubber effluent to the boiler. Recirculation of the effluent is commonly used to reduce discharge costs and water consumption as well as for combustion control purposes, but has, to our knowledge, not yet been widely implemented for scrubber effluents. The most important factor to consider with effluent recirculation is the impact on the process equipment and boiler environment. Multi-pollutant scrubber effluents typically contain alkali, which is known to cause deposition and corrosion problems. This relates to corrosion damage on heating surfaces, which is generally the main concern during heat and power generation.⁸ On the other hand, the injection of sulfur-rich liquids may reduce corrosion caused by chloride deposits as sulfur may react with the alkali to form alkali sulfates, which are less problematic than alkali chlorides

Received: January 28, 2022

Revised: May 4, 2022

Published: May 13, 2022



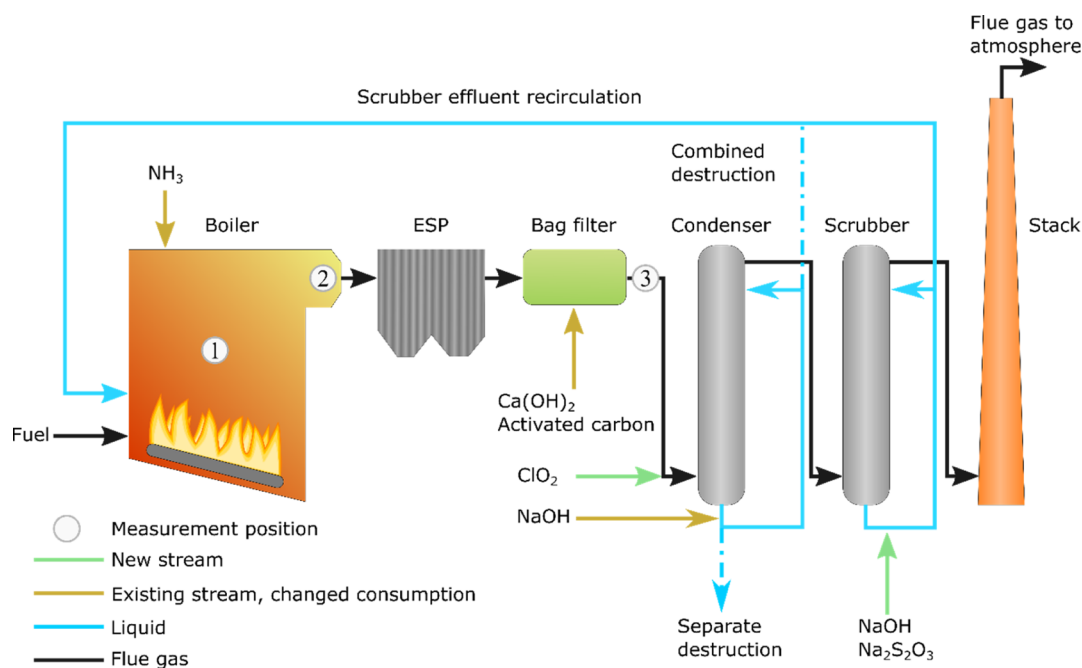


Figure 1. Schematic of the 25 MW_{th} waste-to-energy plant, including the recirculation streams from the scrubber and condenser. Measurement positions 1–3 are used for the gas composition and position 2 for deposition analysis. Ca(OH)₂ and activated carbon are added to the bag filter to remove acid gases and mercury, respectively.

regarding corrosion.^{9,10} Such systems have been implemented at commercial-scale facilities (for example, the sulfur circulation concept was recently demonstrated at full scale by¹¹). However, the recirculation of the scrubber effluent at commercial-scale incineration plants is uncommon due to the potentially malign effects by the inorganic constituents and the large capital value of the industrial equipment. The conceivable corrosion and fouling damage overshadow any possible beneficial factors of nitrogen reduction, and an improved understanding of the transformation and partitioning of the inorganic constituents is required to improve the industrial uptake of the proposed recirculation scheme.

There have been numerous studies investigating individual interactions between alkali, N, and S during combustion of solid fuels, with a focus on the influence of volatile matter released from the fuel itself.^{12–17} It has been shown that these species can not only interact with each other but might also influence fuel oxidation.¹⁸ However, most of the available literature is based on results from single additives, and the combined effect of adding a multicomponent liquid to the primary reactive zone is not known. Injecting a scrubber effluent containing alkali, N, and S components would create an additional source of active species and introduce a different type of interaction. Vaporization of the injected liquid and potential transformation to gaseous species might differ from the release pattern of the fuel, which could also result in a different impact on the combustion. There are some studies available on the influence of liquid injection on combustion and emission formation. It has, for example, been shown that the injection of KCl (aq) in a propane flame can both influence fuel oxidation and depress the formation of NO. It was also shown that the effect of injection could change from inhibiting to promoting, depending on the combustion conditions.^{19,20} Another study focused on the recirculation of a liquid containing H₂SO₄ in a full-scale waste-to-energy plant.²¹ It was found that it had a clear effect on the aerosol and

deposition formation in terms of reduced corrosion and the deposition growth rate. The results from these studies on liquid injection have not provided enough information to conclude on the influence of liquid injection in general. However, they do show that the effect of injecting a spent liquid containing alkali, N, and S, such as the one obtained from the combined SO_x and NO_x scrubbing process, can be assumed to impact the combustion, emission, and deposition formation. The possible influence on NO_x formation is of particular interest as it opens up possibilities to explore thermal treatment of nitrogen-rich waste streams. In addition to experimental studies, numerical simulations on NO_x behavior may also be useful to find an optimum strategy for thermal treatment of the scrubber effluent.^{22–24}

This work describes the first of its kind, large-scale recirculation tests by injecting the scrubber effluent containing high levels of sulfate, nitrite, and sodium into a municipal solid waste (MSW)-fired boiler. The proposed scheme, if successful, will eliminate the need for additional treatment of scrubber effluents by converting NO_x to N₂ and the sulfur components to form either SO₂, which would have a positive effect on the consumption of scrubber chemicals^{2,25} or alkali salts, which in the best case could reduce deposits of chlorides in the boiler. The aim of this work is to decide on the feasibility of the proposed concept and to identify eventual detrimental effects by the recirculated effluent by assessing the influence on combustion, the fate of nitrogen and sulfur compounds, and the effect on depositions.

2. METHODOLOGY

The recirculation experiments were performed at a commercial waste-to-heat plant located in Avesta, Sweden. The plant operates on a grate-fired hot water boiler with a flue gas condenser and has an installed capacity of 25 MW_{th}. A schematic outline of the plant flue gas pass, including a combined NO_x and SO_x scrubber installed during a previous

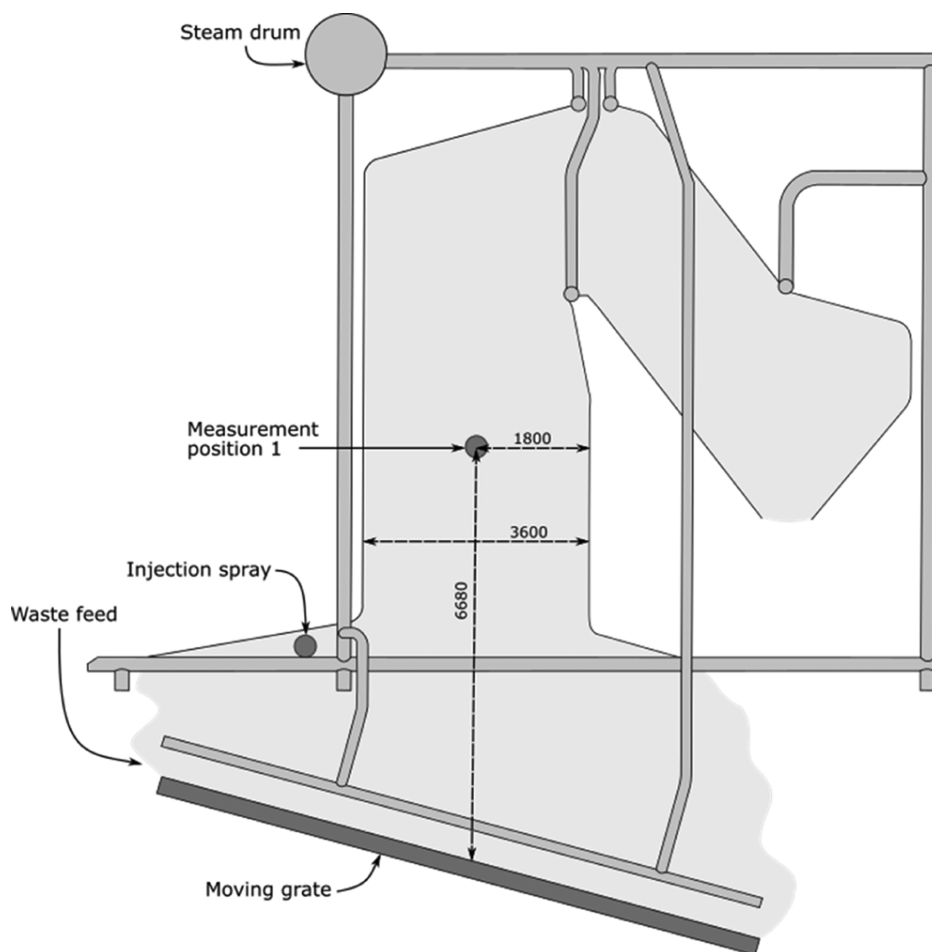


Figure 2. Schematic illustration of the grate boiler showing the injection point, measurement position, and boiler dimension.

slipstream campaign, is shown in Figure 1. The schematic outline is based on the scrubber concept with NO oxidation by chlorine dioxide (ClO_2) as demonstrated in our previous work.² This work, however, is focused on the injection of the scrubber effluent and should also be applicable to other scrubber concepts or nitrogen-rich waste streams.

During normal operation, the plant operates with recirculation of flue gas condensate. The liquid recirculation system injects the liquid into the boiler using three lances and is used for both the disposal of flue gas condensate and boiler temperature control. The fuel mainly consists of household waste, together with a smaller share of industrial waste. There are multiple suppliers of household waste from different countries, and the composition varies depending on the source. This leads to large variations in fuel composition both in terms of minutes and days. It was not possible to obtain a representative fuel analysis during the measurements. However, according to the specification of acceptable waste, the heating value can range from 9 to 15 MJ/kg and have a maximum moisture, ash, and nitrogen content of 40, 20, and 1% (by weight), respectively. The measurements were performed during a two day period of normal boiler operation, meaning that the boiler had to adjust its load following the demand for heat. However, during the recirculation of the scrubber effluent and the transition between different cases, the plant operators used the thermal capacity of the district heating grid to keep load variations at a minimum (<1 MW).

The spray injection system installed 3 m above the grate is used to inject the recirculated flue gas condensate under normal process conditions. The injection point and boiler dimensions are illustrated in Figure 2. The estimated gas residence time, assuming plug flow, is grate, 0 s; spray injection point, 1.4 s for measurement position 1 and 2.3 and 6.6 s for measurement positions 2 and 3, respectively. The estimated residence time is based on plug flow calculations using the entire cross-section throughout the boiler. Such a flow pattern is not in absolute agreement with reality, especially the volume immediately above the grate, where we expect the least uniform flow profile.

During the test campaign, the scrubber effluent from the pilot scrubber was recirculated using this existing spray injection system by simply switching between the liquid supplies. Thus, it was possible to promptly change the liquid injection back and forth between the conventional operation with the condensate and the operation with the recirculated scrubber effluent. Seven operational conditions were investigated, and these are referred to as cases 1–7, with the details given in Table 1. Due to environmental regulations, it was not possible to operate without active SNCR for extensive time periods. Thus, the results and discussion are emphasized for cases 1–4.

As mentioned, the scrubber effluents were collected during a previous campaign where a slip stream of the flue gas passed through a mobile pilot plant for NO oxidation with ClO_2 and subsequent scrubbing of NO_x and SO_x .² Around 3 m³ of the

Table 1. Investigated Operational Conditions

case	recirculation	SNCR	test (measurement position)
1	none	yes	gas composition (1,2), plant performance
2	condensate	yes	gas composition (1–3), plant performance, deposition (2)
3	scrubber effluent 1	yes	gas composition (1–3), plant performance
4	scrubber effluent 2	yes	gas composition (3), plant performance, deposition (2)
5	none	no	gas composition (2), plant performance
6	condensate	no	gas composition (2), plant performance, deposition (2)
7	scrubber effluent 1	no	gas composition (2), plant performance

scrubber effluent was accumulated from each campaign. The batches have different compositions due to the differences in scrubber operation. Scrubber effluent 1 was used during gas composition measurements and the assessment of combustion performance, whereas scrubber effluent 2 was used during the deposition measurements. During conventional operation, the condensate is recirculated at a volume flow of $\sim 1 \text{ m}^3 \text{ h}^{-1}$, which would also be the required flow of the effluent during a full-scale installation of the scrubber system. Therefore, the flow rate was kept at $1 \text{ m}^3 \text{ h}^{-1}$ during the recirculation campaign, which grants 6 h of operation with the scrubber effluent. The enthalpy of evaporation of $1 \text{ m}^3 \text{ h}^{-1}$ is 0.63 MW, which corresponds to approximately 3% of the thermal load. Both the scrubber effluents and the condensate were analyzed with ion chromatography (Dionex ICS-1000), and the chemical compositions are given in Table 2. For clarity, the

Table 2. Liquid Concentration of Major Chemical Species in the Condensate and Scrubber Effluent 1 and 2^a

species	condensate	scrubber effluent 1	scrubber effluent 2
K (mg/L)	120	130	33
Na (mg/L)	540	16,000	17,000
Cl (mg/L)	2,100	9,200	420
total S (mg/L)	170	7,500	9,100
SO ₄ ²⁻ (mg/L)	510	12,000	27,000
NO ₃ ⁻ (mg/L)	0.3	210	26
NO ₂ ⁻ (mg/L)	0.3	2,030	99
corresponding gas concentration^b (Nwg)			
SO ₂ (ppm)	3	126	152
NO (ppm)	<1	86	5
Na + K (ppm)	16	395	416

^aThe corresponding gas species is calculated using the average flue gas flow rate to display the theoretical maximum increase in the flue gas concentration by each species. ^bAssuming a complete conversion of S and N to SO₂ and NO.

hypothetical maximum contribution from each species in the liquid is calculated using the average flue gas flow rate, assuming full conversion to the corresponding gas species listed in the table; that is, all nitrates and nitrites in the scrubber effluent are converted to NO in the flue gas.

2.1. Analytical Techniques. Gas sampling was performed using a probe inserted at measurement positions 1 and 2 through available ports in the furnace wall and flue gas path, respectively. The sampling probe used in position 1 was

constructed in stainless steel with an opening in the tip of 6 mm. The probe was used to sample the gas at a distance of 60 cm from the furnace wall. A thermocouple was placed at the tip of the probe to monitor temperature variations in the sampling position. Position 2 allowed for a longer probe, which made it possible to penetrate into the center of the flue gas path. This probe was also wider, with an inner diameter of 18 mm. The temperature of the probes was not actively controlled but monitored at the back end of the probe to ensure that low temperatures were avoided. From the probes, the gas sample is led through electrically heated tubes to ensure gas temperatures above 160 °C and avoid condensation. The gas sample is cleaned from the particles by two heated filters, with a size cut-off of 1 and 0.01 μm , respectively, before being split into two separate lines. The first line is kept at 160 °C, and the sample passes through a second heated 0.01 μm particle filter before the gas is heated up to 190 °C and analyzed by Fourier-transform infrared spectroscopy, which is used to detect H₂O, CO, HCN, and NO, among others. The gas sample of the second line passes through a condenser and is analyzed using a paramagnetic analyzer (O₂) and electrochemical sensors (NO and NO₂).

Deposition measurements were carried out using a temperature-controlled deposition probe in position 2. Three measurements were performed for each case, with different sampling times (35, 40, and 70 min). For each measurement, a metal ring (253 MA steel) was used to collect the deposition positioned at the tip of the probe. The temperature of the ring was set to 450 °C and was controlled by three thermocouples spread out over the perimeter of the ring and an adjustable flow of pressurized air for cooling. A small fraction of the deposits (1–3 mg) was collected, pretreated, and analyzed with XRD, ICP–MS (ICP-iCAP 7400 Duo), and ion chromatography (Dionex ICS-1000). For ICP–MS analysis, the solid samples were dissolved in HNO₃ at 175 °C and thereafter diluted with Milli-Q water prior to elemental analysis. In addition, solid samples were leached in 50 mL of Milli-Q water at 80 °C for 24 h, followed by sulfate and chloride analysis of the liquid.

3. RESULTS

The results from the scrubber effluent recirculation tests are presented in three parts: combustion performance, flue gas composition, and deposit formation.

3.1. Combustion Performance. Figure 3 presents the boiler load, total combustion air flow (primary and secondary), and the furnace temperature in positions 1 and 2 over 2 h of condensate and scrubber effluent recirculation. The temperature–time profile at position 2 showed a lower variation (± 20 °C) during the liquid injections. During case 1 (without liquid injection), the temperature at position 1 was about 50 °C lower compared to operation with liquid injection as expected. The variations in the boiler load (adjusted to heat demand) and fuel composition cause the conditions to change over time, and therefore, a direct comparison of averages is not meaningful. There is also relatively large variance within the investigated cases, which is expected for a heat-generating waste incineration plant and should be kept in mind when evaluating the results. The differences in variance between the investigated cases are, however, relatively small for the process parameters, suggesting that factors other than the injected liquids are causing the effect.

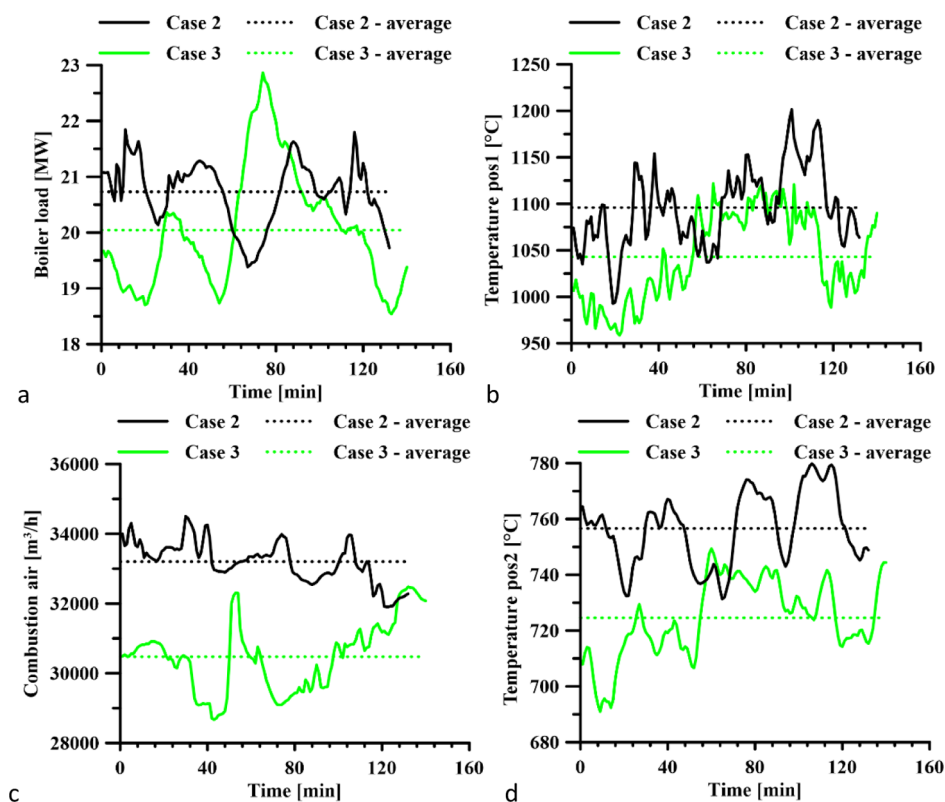


Figure 3. Time series of boiler load (a), boiler temperature in position 1 (b), total combustion air flow (c), and boiler temperature in position 2 (d) during injection of the condensate (black line) and scrubber effluent (green line). The mean value for each case is indicated by the dotted line.

3.2. Flue Gas Composition. The detailed gas composition measurement from position 1 inside the boiler is shown in Figure 4a–f during the transition between cases 1 and 2 as well as between cases 1 and 3. Time “0”—marked by a dashed vertical line in the figure—represents the change between cases. The second dashed line, at around 29 min, denotes the change back to the starting case. A clear increase in H_2O concentration is visible when changing from case 1, without injection, to either condensate (case 2) or scrubber effluent (case 3). The observed increase is found to be around 4%—units independent of injection liquid, which corresponds well with the amount of water added. The analyzing equipment operates at 1 Hz resulting in high temporal resolution data. The time delay due to gas transport in the sampling line and the rise time of the instrument was never >50 s, which is sufficient to identify any major influence on gas composition caused by the injected liquid. The increased variance as well as the absolute concentrations of CO and CH_4 are apparent during recirculation of both liquids, whereas the concentrations are close to zero without recirculation. Regarding NO_x , no significant increase is visible when the scrubber effluent is injected, whereas the condensate recirculation appears to increase both NO and NO_2 formation. A clear increase in the HCN concentration can be observed for both liquids, which indicates increased activity in nitrogen chemistry during the injection of both liquids. Note that even though the scrubber effluent contains nitrogen while the condensate does not, there is no significant difference regarding the concentration of nitrogen compounds in the flue gas.

Some of the flue gas composition from position 2, measured downstream of the SNCR, is presented in Figure 4g–i. The cases with and without the SNCR in operation (cases 1–3 and

5–7, respectively) behaved similarly; only two data sets are therefore presented. The transition from case 2 to 1 reveals that the changes are relatively small and in the same order of magnitude as the occurring time-dependent variation. It should also be noted that the CO concentration is low, and even though the relative variation seems to be large, it is still within 10 ppm in absolute variation. The transition from case 3 to 7 represents the effect of turning off the SNCR. As expected, this results in an increased NO concentration. It is known from operational experience that suspension of the SNCR induces a pulse of NH_3 before the injection is suspended. The notable decrease in NO at the same time as an increase in CO and N_2O during the transition from case 3 to 7 is an effect of the NH_3 pulse prior to suspension.

Another observed effect when switching from condensate (case 4) to effluent (case 2) was the decreased amount of NH_3 required by the SNCR system to maintain a stable NO output. A similar trend is observed for both scrubber effluents, even though they have a widely different nitrogen content. The time profile of the added NH_3 is illustrated in Figure 5 together with the NO concentration in position 3 and the recirculation feed rate. When the liquid is changed from scrubber effluent to condensate, a significant increase in NH_3 consumption is visible. The NH_3 injection is controlled to maintain a constant NO concentration in the chimney by measuring the NH_3 slip, and the difference in NH_3 consumption is likely an effect of either the reduced NO formation or the increased efficiency of the SNCR; that is, the recirculated condensate, rich in chlorine, is consuming some of the NH_3 .

3.3. Deposit Formation. The deposition growth rate during the injection of the condensate (case 2) and scrubber effluent (case 4) is shown in Figure 6 for three different

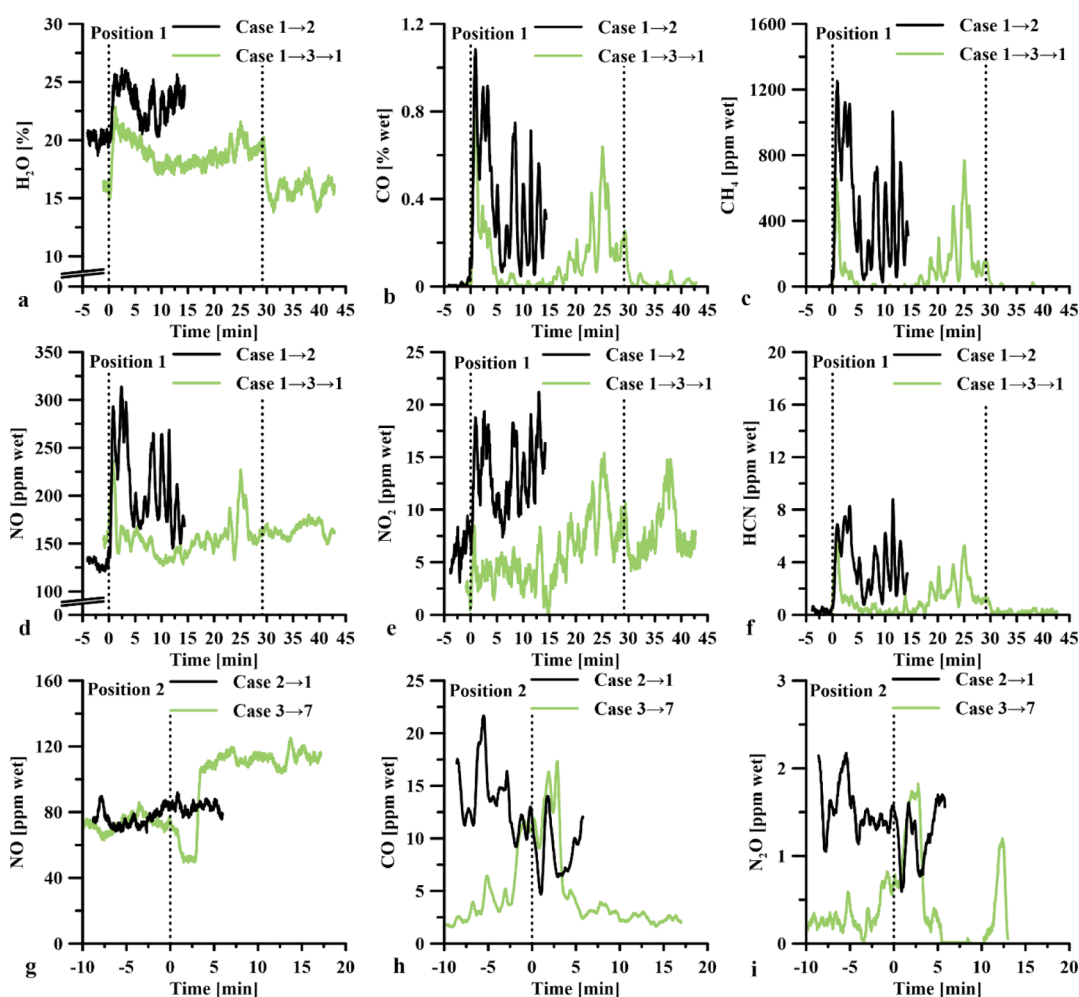


Figure 4. Time series of selected gas components at the onset of injection of the scrubber effluent and condensate. Dashed vertical lines indicate the switch between cases. Parts (a–f) show measurements in position 1, while parts (g–i) show measurements in position 2.

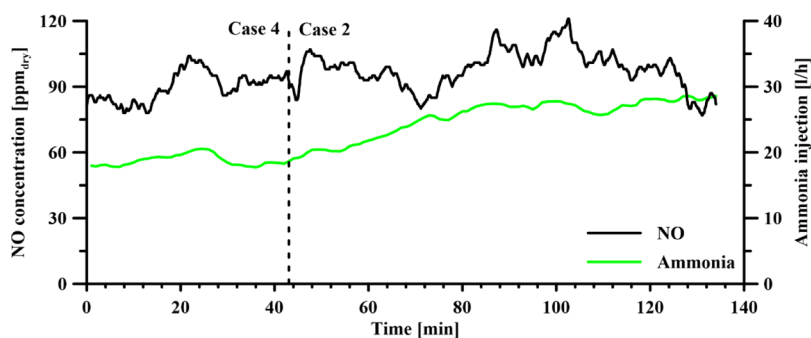


Figure 5. Time series of NO (position 3) and NH_3 addition during transition from the scrubber effluent (case 4) to the condensate (case 2). The dashed vertical line indicates the time when the liquid injected was changed from the scrubber effluent to the condensate.

sampling time lengths (35, 40, and 70 min). A significant increase in the growth rate was detected with injection of the scrubber effluent relative to the reference case with injection of the condensate. During condensate recirculation, the deposition growth rate is 3.0 mg min^{-1} with no significant differences in the deposition rate over time. During scrubber effluent injections, the deposition growth rate was about doubled to 6.3 mg min^{-1} based on the 35 and 75 min measurements. The 40 min measurement during injection of the scrubber effluent coincided with a soot-blowing event, which explains why the

deposition rate seems lower. Apart from that, no significant differences were observed for different sampling periods.

The chemical composition of the depositions is given in Table 3. During recirculation of the condensate, the depositions mainly consist of Ca, followed by S, K, and Na. During scrubber effluent recirculation, Na and S are the main components, likely as Na_2SO_4 , followed by Ca and K. The XRD analysis provides only qualitative data due to the presence of complex and amorphous compounds. Nevertheless, the XRD analysis identified both CaSO_4 and CaCl_2 in the depositions created during the injection of the condensate.

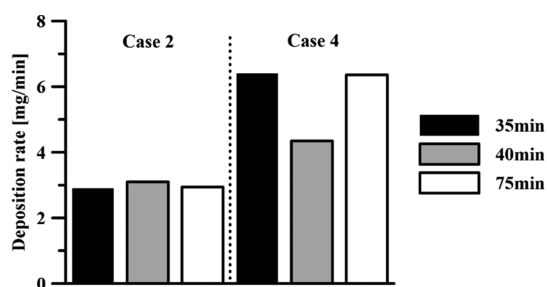


Figure 6. Deposition growth rates during the recirculation of the condensate (case 2) and scrubber effluent (case 4). The times represent different sampling lengths. A soot-cleaning event was performed during the 40 min measurement of case 4.

Table 3. ICP–MS Analysis of Collected Solid Depositions During Recirculation of the Condensate (Case 2) and Scrubber Effluent (Case 4)

	case 2	case 4	case 2	case 4
	%	%	growth rate (mg h ⁻¹)	growth rate (mg h ⁻¹)
Ca	12.5	6.9	23	25
S	5.7	12	10	43
K	3.8	4	7	14
Na	5.8	17	10	61
Zn	2	0.9	4	3
Al	1	0.9	2	3
Si	0.6	0.4	1	1
Fe	1	0.9	2	3
Mg	0.8	0.5	1	2
Pb	0.3	0.1	1	0
Ti	0.4	0.3	1	1
Cl	12.5	8,1	23	29
SO ₄	13.3	29	24	104

During the recirculation of the scrubber effluent, Na₂SO₄, KCl, NaCl, and CaCl₂ were identified in the deposition, which agrees with the ICP–MS and ion chromatography analysis of the deposits as well as the elements present in the recirculated liquids (Table 2).

4. DISCUSSION

For most MSW-fired power plants, fuel heterogeneity gives rise to large fluctuations in plant performance metrics during operation, which obviously interfere with the evaluation. Therefore, the transients and step responses in the change between operational modes (cases) are analyzed instead of comparing the parameter mean values. In addition, the clear increase in variance between certain cases was also used to support the assessment, for example, CH₄ and CO during both condensate and effluent recirculation. Although the changes introduced with the addition of the scrubber effluent in most cases were of a lower magnitude than what is seen in daily operation, the 6 h of effluent recirculation, including multiple transitions, did not indicate an increase in NO_x emissions.

NO_x formation from the introduction of nitrite salts with liquid recirculation is a major concern as the conventional flue gas condensate does not include nitrogen compounds. The gas composition measurements in position 1 during the transition between injection and no injection of the scrubber effluent did not show any increased NO formation. The injection of the condensate did however result in a higher concentration of NO as well as NO₂, compared to operation without recirculated

liquid. Reduced nitrogen species, for example, HCN, were detected in the furnace in both case 2 and case 3, which indicates that the nitrogen chemistry is still active in this location. Therefore, any difference in the NO_x concentration at this point does not necessarily remain. Measurement position 2 is located in the flue gas path where neither the combustion nor the nitrogen chemistry is active. At this point, there is no noticeable difference in the NO concentration between cases 2 and 3 (Figure 4g). The same results were also seen in position 3 (Figure 5). Both positions 2 and 3 are however located downstream of the SNCR. However, with the switch to scrubber effluent injection from condensate injection, the ammonia consumption in the SNCR decreased as shown in Figure 5. This indicates that the nitrites in the scrubber effluent are reduced to nitrogen gas, and/or the chemicals in the scrubber effluent are active in the reduction of NO_x formed from the primary combustion process. The high ammonia consumption during condensate recirculation is likely due to the formation of ammonium chloride, which is a critical problem of the SNCR process in the presence of HCl.²⁶ In general, the amount of nitrogen added in the form of nitrite and nitrate with scrubber effluents 1 and 2 is relatively modest compared to the observed changes in the process conditions. Also, the location of the scrubber injection corresponds to conditions that can effectively reduce all nitrogen oxides to nitrogen, both with respect to the residence time and temperature conditions; the kinetics are fast in the transformation of nitrogen oxides to nitrogen-containing volatiles.²⁷ From this, it can be concluded that the location of the injection is critical to the transformation of nitrogen species and that the chosen location in this work allows for sufficient time in a fuel-rich zone for the nitrogen contained in the scrubber effluents to be reduced rather than oxidized.

The injection of the condensate and scrubber effluent not only influences the nitrogen chemistry but also the combustion chemistry and hydrocarbon oxidation, as indicated by the increased concentrations of CO and CH₄ in position 1 (Figure 4b,c). The effect is visible as an increase in both the mean and variance during the injection of both liquids. Burnout is, however, complete in position 2, where the CO levels are below 20 ppm and no CH₄ was detected. This suggests that the injection of liquids to the boiler prolongs the combustion zone but does not result in a less efficient burnout. The condensate lacks nitrogen and has a much lower sulfur content compared to the scrubber effluent, yet the two liquids show similar results regarding hydrocarbon oxidation. It is well known that the introduction of inorganic elements such as chlorides and alkali affects the radical chemistry,^{18–20,28,29} and the added amount of inorganics is sufficient to cause the observed effect. However, the injected liquid reduces the local temperature above the grate, which also influences the combustion, and the effect of temperature and inorganic additions cannot be fully untangled by the present study.

The injected scrubber effluent also contains considerably higher amounts of sulfur (~10 gL⁻¹) than the conventional condensate as sulfur is added to the scrubber by means of Na₂SO₃ and/or Na₂S₂O₃ to enhance the NO₂ adsorption efficiency.² Most of the SO₃²⁻ is oxidized to SO₄²⁻ in the wet scrubber process and neutralized with sodium hydroxide. Depending on the heating rate, temperature, and the reducing character of the environment, the alkali sulfates may decompose in the boiler to form SO₂,³⁰ which can subsequently be absorbed by the scrubber. The presence of

SO₂ in the flue gas is favorable for the scrubber as less sulfite needs to be added to enhance NO₂ absorption. The reducing character and temperature at the injection point (<950 °C) seem insufficient to decompose the alkali sulfates that form during the initial stage of the injection,³¹ and we did not observe any increased levels of SO₂ during scrubber effluent recirculation. However, alkali sulfates may form alkali chlorides in the presence of chlorine by the reversed sulfation reaction. The chemistry is described in^{32,33} and experimentally shown in a recent injection study.³⁴

The increased level of sulfur seen in the depositions is benign from corrosion aspects if chloride is substituted by sulfates.^{10,14} Further tests with injections at different temperatures and compositions would be interesting to explore as options to recirculate sulfur to the scrubber process and reduce the chemical costs for the gas scrubber. However, increasing the vapor pressure of SO₂ may also increase problems related to alkali chlorides; thus, the injection point must be selected carefully.

As the amount of alkali (mainly sodium) and sulfur recirculated to the boiler was considerably higher during scrubber effluent recirculation (relative to the condensate), the main concern is the risk of deposition, fouling, and corrosion. The total deposition growth rate was approximately doubled during operation with the scrubber effluent compared to that with the condensate, and the SO₄ deposition growth rate was increased by a factor of almost 5. The increased degree of sulfation is expected to reduce the deposition growth rate by increasing the melting point, thus forming less sticky alkali compounds.^{14,21} In general, the deposition growth rate varies with the fuel composition, and the distribution of trace elements released from MSW incineration is strongly influenced by the feedstock composition, temperature, and reducing character.¹² Since the injection point is located above the grate, the added elements do not influence the fuel inorganic constituent's transformation and release pattern. However, at the given temperature, several gas phase reactions are possible, which may influence the gas-to-particle partitioning and aerosol formation. The deposition growth rate of the fuel released elements (Zn, Al, Si, Fe, Mg, Pb, and Ti) was relatively stable during all six measurements. It is possible that the inorganic compounds released by the fuel form a sticky surface, which increases the deposition growth by particle impaction;³⁵ however, further tests are required to conclude how the added effluent influences the deposition growth rate. Furthermore, the soot blowing that occurred during one of the deposition measurements, shown in Figure 6, drastically reduced the deposition rate. The stickiness of deposits is a vital aspect, as loosely bound deposits that can be easily cleaned are less problematic. A longer operational time including at least a couple of soot-blowing cycles is needed to conclude the possible long-term effects of scrubber effluent recirculation.

The chemical analysis of the deposits, given in Table 3, suggests that the added sulfur mainly forms SO₄ depositions based on the clear increase in sulfur and sodium during effluent circulation. Increasing the S/Cl ratio in a combustion system may reduce alkali chlorides in the deposits and thereby the corrosivity. However, the extent of sulfation depends not only on the gas composition but also on the temperature. Understanding the transformation and distribution of the inorganic species is critical to reduce corrosion damage and avoid unwanted depositions in the recirculation process. The

same applies to the formation of the atmospheric pollutants investigated in this case study. Fundamental knowledge of how these species behave and can be controlled is the key to establishing a successful recirculation strategy.

The results from this study show that thermal treatment of the scrubber effluent by injection to the boiler is possible without any major influence on thermal performance or emissions. For a hot water boiler system equipped with a flue gas condenser, such as the one described herein, the energy required to evaporate the injected liquid will be recovered. The potential effect of the liquid injection on the thermal performance would have to be considered if applied to a boiler with another configuration.

CONCLUSIONS

This work discussed thermal treatment of liquid waste streams in commercial boilers with a focus on the injected liquids' influence on the combustion process, emission formation, and deposition parameters. A full-scale test of the injection of the scrubber effluent from a combined NO_x and SO_x scrubber into an MSW-fired grate boiler has been performed. From the performed measurements, it is possible to conclude that the thermal reduction of nitrite by recirculation of scrubber effluents to the boiler is efficient—no significant increase in NO_x occurs; if anything, the effluent seems to reduce NO_x formation. Furthermore, the injection of sulfates does not increase the flue gas SO₂ concentration. Sulfur recirculation may be beneficial to the process by either reducing the corrosiveness of depositions and/or decreasing the required chemical consumption in the scrubber. The distribution and partitioning of injected sulfate species are believed to be dependent on the temperature at the injection point. Finally, the injection of alkali increased the deposition rate. The composition of the deposits looks favorable due to the increased sulfur and decreased chloride content, but long-term deposition tests are required.

AUTHOR INFORMATION

Corresponding Author

Dan Gall — Department of Space, Earth and Environment, Gothenburg, Chalmers University of Technology, Goteborg SE 412 96, Sweden; orcid.org/0000-0003-3130-8377; Email: dan.gall@chalmers.se

Authors

Thomas Allguren — Department of Space, Earth and Environment, Gothenburg, Chalmers University of Technology, Goteborg SE 412 96, Sweden

Jakob Johansson — Department of Space, Earth and Environment, Gothenburg, Chalmers University of Technology, Goteborg SE 412 96, Sweden; orcid.org/0000-0001-8011-7783

Fredrik Normann — Department of Space, Earth and Environment, Gothenburg, Chalmers University of Technology, Goteborg SE 412 96, Sweden

Anette Heijnesson Hultén — Nouryon Pulp and Performance Chemicals AB, Bohus SE 445 80, Sweden

Adrian Gunnarsson — Department of Space, Earth and Environment, Gothenburg, Chalmers University of Technology, Goteborg SE 412 96, Sweden

Klas Andersson — Department of Space, Earth and Environment, Gothenburg, Chalmers University of

Technology, Goteborg SE 412 96, Sweden; orcid.org/0000-0001-5968-9082

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.energyfuels.2c00293>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the personnel at Källhagsverket in Avesta for their technical support and assistance during the measurements. We thank Johan Boström for technical support and helpful discussions during the measurements. The personnel at Nouryon are gratefully acknowledged for their analysis of deposition samples and liquids. This work was supported by the Swedish Energy Agency under grant no. 50368-1.

REFERENCES

- (1) Hultén, A. H.; Nilsson, P.; Samuelsson, M.; Ajdari, S.; Normann, F.; Andersson, K. First Evaluation of a Multicomponent Flue Gas Cleaning Concept Using Chlorine Dioxide Gas – Experiments on Chemistry and Process Performance. *Fuel* **2017**, *210*, 885–891.
- (2) Johansson, J.; Heijnesson Hultén, A.; Normann, F.; Andersson, K. Simultaneous Removal of NO_x and SO_x from Flue Gases Using CLO₂: Process Scaling and Modeling Simulations. *Ind. Eng. Chem. Res.* **2021**, *60*, 1774–1783.
- (3) European Commission. *Best Available Techniques (BAT) Reference Document for Waste Incineration*; Sevilla, 2019.
- (4) Teuchies, J.; Cox, T. J. S.; Van Itterbeeck, K.; Meysman, F. J. R.; Blust, R. The Impact of Scrubber Discharge on the Water Quality in Estuaries and Ports. *Environ. Sci. Eur.* **2020**, *32*, 103.
- (5) Thor, P.; Granberg, M. E.; Winnes, H.; Magnusson, K. Severe Toxic Effects on Pelagic Copepods from Maritime Exhaust Gas Scrubber Effluents. *Environ. Sci. Technol.* **2021**, *55*, 5826–5835.
- (6) Dal Pozzo, A.; Cozzani, V. Wastewater Management of Wet Scrubbers in Waste-to-Energy Facilities: A Life Cycle Analysis. *Chem. Eng. Trans.* **2021**, *86*, 619–624. SE-Research Articles
- (7) Pokhrel, D.; Viraraghavan, T. Treatment of Pulp and Paper Mill Wastewater—A Review. *Sci. Total Environ.* **2004**, *333*, 37–58.
- (8) Lee, S.-H.; Themelis, N. J.; Castaldi, M. J. High-Temperature Corrosion in Waste-to-Energy Boilers. *J. Therm. Spray Technol.* **2007**, *16*, 104–110.
- (9) Pettersson, J.; Asteman, H.; Svensson, J.-E.; Johansson, L.-G. KCl Induced Corrosion of a 304-Type Austenitic Stainless Steel at 600°C; the Role of Potassium. *Oxid. Met.* **2005**, *64*, 23–41.
- (10) Pettersson, J.; Folkesson, N.; Johansson, L.-G.; Svensson, J.-E. The Effects of KCl, K₂SO₄ and K₂CO₃ on the High Temperature Corrosion of a 304-Type Austenitic Stainless Steel. *Oxid. Met.* **2011**, *76*, 93–109.
- (11) Andersson, S.; Jonsson, T.; Photer-Simon, J.; Dolores, M. High temperature corrosion and dioxin abatement using sulfur recirculation in a waste-to-energy plant. *Detritus* **2018**, *5*, 92–98.
- (12) Pedersen, A. J.; Van Lith, S. C.; Frandsen, F. J.; Steinsen, S. D.; Holgersen, L. B. Release to the Gas Phase of Metals, S and Cl during Combustion of Dedicated Waste Fractions. *Fuel Process. Technol.* **2010**, *91*, 1062–1072.
- (13) Pedersen, A. J.; Frandsen, F. J.; Riber, C.; Astrup, T.; Thomsen, S. N.; Lundtorp, K.; Mortensen, L. F. A Full-Scale Study on the Partitioning of Trace Elements in Municipal Solid Waste Incineration—Effects of Firing Different Waste Types. *Energy Fuels* **2009**, *23*, 3475–3489.
- (14) Ma, W.; Wenga, T.; Frandsen, F. J.; Yan, B.; Chen, G. The Fate of Chlorine during MSW Incineration: Vaporization, Transformation, Deposition, Corrosion and Remedies. *Prog. Energy Combust. Sci.* **2020**, *76*, 100789.
- (15) Arena, U.; Di Gregorio, F. Element Partitioning in Combustion- and Gasification-Based Waste-to-Energy Units. *Waste Manag.* **2013**, *33*, 1142–1150.
- (16) Arvelakis, S.; Frandsen, F. J.; Koukios, E. G. Study of the Composition and Gas-Phase Release Characteristics of Salt Material Extracted from MSW Ash Particles Using STA. *J. Therm. Anal. Calorim.* **2007**, *88*, 769–774.
- (17) Quina, M. J.; Bordado, J. C. M.; Quinta-Ferreira, R. M. Percolation and Batch Leaching Tests to Assess Release of Inorganic Pollutants from Municipal Solid Waste Incinerator Residues. *Waste Manag.* **2011**, *31*, 236–245.
- (18) Glarborg, P. Hidden Interactions-Trace Species Governing Combustion and Emissions. *Proc. Combust. Inst.* **2007**, *31*, 77–98.
- (19) Allgurén, T.; Andersson, K. Chemical Interactions between Potassium, Sulfur, Chlorine, and Carbon Monoxide in Air and Oxy-Fuel Atmospheres. *Energy Fuels* **2020**, *34*, 900–906.
- (20) Allgurén, T.; Andersson, K. Influence of KCl and SO₂ on NO Formation in C₃H₈ Flames. *Energy Fuels* **2017**, *31*, 11413–11423.
- (21) Andersson, S.; Blomqvist, E. W.; Bäfver, L.; Jones, F.; Davidsson, K.; Froitzheim, J.; Karlsson, M.; Larsson, E.; Liske, J. Sulfur Recirculation for Increased Electricity Production in Waste-to-Energy Plants. *Waste Manag.* **2014**, *34*, 67–78.
- (22) Al-Abbas, A. H.; Naser, J. Effect of Chemical Reaction Mechanisms and NO_x Modeling on Air-Fired and Oxy-Fuel Combustion of Lignite in a 100-kW Furnace. *Energy Fuels* **2012**, *26*, 3329–3348.
- (23) Karim, M. R.; Naser, J. CFD Modelling of Combustion and Associated Emission of Wet Woody Biomass in a 4 MW Moving Grate Boiler. *Fuel* **2018**, *222*, 656–674.
- (24) Hu, Z.; Jiang, E.; Ma, X. Numerical Simulation on NO_x Emissions in a Municipal Solid Waste Incinerator. *J. Clean. Prod.* **2019**, *233*, 650–664.
- (25) Johansson, J.; Normann, F.; Sarajlic, N.; Andersson, K. Technical-Scale Evaluation of Scrubber-Based, Co-Removal of NO_x and SO_x Species from Flue Gases via Gas-Phase Oxidation. *Ind. Eng. Chem. Res.* **2019**, *58*, 21904–21912.
- (26) Hwang, I.-H.; Minoya, H.; Matsuto, T.; Matsuo, T.; Matsumoto, A.; Sameshima, R. Removal of Ammonium Chloride Generated by Ammonia Slip from the SNCR Process in Municipal Solid Waste Incinerators. *Chemosphere* **2009**, *74*, 1379–1384.
- (27) Glarborg, P.; Miller, J. A.; Ruscic, B.; Klippenstein, S. J. Modeling Nitrogen Chemistry in Combustion. *Prog. Energy Combust. Sci.* **2018**, *67*, 31–68.
- (28) Lissianski, V. V.; Zamansky, V. M.; Maly, P. M. Effect of metal-containing additives on nox reduction in combustion and reburning. *Combust. Flame* **2001**, *125*, 1118–1127.
- (29) Berdugo Vilches, T.; Weng, W.; Glarborg, P.; Li, Z.; Thunman, H.; Seemann, M. Shedding Light on the Governing Mechanisms for Insufficient CO and H₂ Burnout in the Presence of Potassium, Chlorine and Sulfur. *Fuel* **2020**, *273*, 117762.
- (30) Ficalora, P. J.; Uy, O. M.; Muenow, D. W.; Margrave, J. L. Mass Spectrometric Studies at High Temperatures: XXIX, Thermal Decomposition and Sublimation of Alkali Metal Sulfates. *J. Am. Ceram. Soc.* **1968**, *51*, 574–576.
- (31) Gall, D.; Pushp, M.; Davidsson, K. O.; Pettersson, J. B. C. Online Measurements of Alkali and Heavy Tar Components in Biomass Gasification. *Energy Fuel* **2017**, *31*, 8152–8161.
- (32) Allgurén, T.; Viljanen, J.; Li, X.; Wang, Y.; Andersson, K.; Wendt, J. O. L. Alkali Sulfation during Combustion of Coal in a Pilot Scale Facility Using Additives to Alter the Global Sulfur to Potassium and Chlorine to Potassium Ratios. *Proc. Combust. Inst.* **2021**, *38*, 4171–4178.
- (33) Hindiyarti, L.; Frandsen, F.; Livbjerg, H.; Glarborg, P.; Marshall, P. An Exploratory Study of Alkali Sulfate Aerosol Formation during Biomass Combustion. *Fuel* **2008**, *87*, 1591–1600.
- (34) Gall, D.; Viljanen, J.; Gogolev, I.; Allgurén, T.; Andersson, K. Alkali Monitoring of Industrial Process Gas by Surface Ionization—Calibration, Assessment, and Comparison to In Situ Laser Diagnostics. *Energy Fuels* **2021**, *35*, 20160–20171.

(35) Mueller, C.; Selenius, M.; Theis, M.; Skrifvars, B.-J.; Backman, R.; Hupa, M.; Tran, H. Deposition Behaviour of Molten Alkali-Rich Fly Ashes—Development of a Submodel for CFD Applications. *Proc. Combust. Inst.* **2005**, *30*, 2991–2998.

Recommended by ACS

Characteristics of Leakage and Diffusion for a Chlorine Storage Tank Based on Simulation

Wenhe Wang, Hongfu Mi, *et al.*

AUGUST 05, 2021
ACS CHEMICAL HEALTH & SAFETY

READ 

Chemical Looping Combustion of a Biomass Char in Fe₂O₃-, CuO-, and SrFeO_{3-δ}-Based Oxygen Carriers

K. Y. Kwong, E. J. Marek, *et al.*

JUNE 14, 2022
ENERGY & FUELS

READ 

Enhanced Mitigation of Fire and Explosion Risks due to Hydrogen Leakage Using Targeted Nitrogen Nozzle Spray Approach

Wei Jian Tan, Kok Keong Lau, *et al.*

APRIL 29, 2022
ACS CHEMICAL HEALTH & SAFETY

READ 

Industrial Experiment on NO_x Reduction by Urea Solution Injection in the Fuel-Rich Zone of a 330 MW Tangentially Pulverized Coal-Fired Boiler

Hao Bai, Degui Bi, *et al.*

MARCH 31, 2022
ACS OMEGA

READ 

Get More Suggestions >