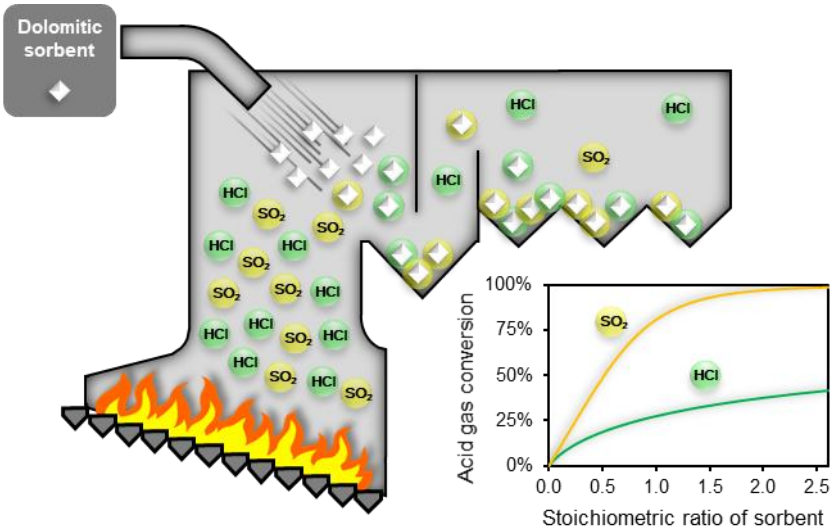
Techno-economic performance of HCl and SO2 removal in waste-to-energy plants by furnace direct sorbent injection

Graphical Abstract



HIGHLIGHTS

Techno-economic performance of HCl and SO_2 removal in waste-to-energy plants by furnace direct sorbent injection

Alessandro Dal Pozzo, Lorenzo Lazazzara, Giacomo Antonioni, Valerio Cozzani *
LISES - Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater Studiorum - Università di Bologna, via Terracini n.28, 40131 Bologna, Italy

* *corresponding author*, Tel. +39-051-2090240, Fax +39-051-2090247, e-mail: valerio.cozzani@unibo.it

- Furnace injection of a dolomitic sorbent in WtE plants was tested
- Full-scale test runs were carried out to assess sorbent performance
- A model of acid gas removal efficiency was calibrated
- The dolomitic sorbent reacts at high temperature with acid gases
- The cost-effectiveness of dolomite sorbent injection was assessed

Abstract

With the impending release of Best Available Techniques (BAT) conclusions on waste incineration, existing European waste-to-energy (WtE) plants will be required to achieve a higher efficiency in the removal of several target pollutants, such as acid gases (above all, HCl and SO_2). The direct injection of a sorbent in the furnace as a primary deacidification stage may be a cost-effective option to achieve the required performances. The present study investigated the furnace injection of a specific dolomitic sorbent, with the aim of identifying the techno-economic optimum for the sorbent feed rate considering different scenarios of flue gas composition. A full-scale test run campaign was carried out on two WtE plants and a phenomenological model linking HCl and SO_2 conversion to reactant feed rate was developed. The model allowed assessing the cost-effectiveness of dolomitic sorbent furnace injection for WtE plants equipped with either a single or a two-stage acid gas treatment system. The addition of dolomitic sorbent resulted particularly suitable for WtE plants equipped with a single stage treatment coping with a high SO_2 concentration in the flue gas, where the injection of dolomitic sorbent can increase the redundancy of flue gas treatment with a reduction of the total operating costs.

Techno-economic performance of HCl and SO_2 removal in waste-to-energy plants by furnace direct sorbent injection

*Alessandro Dal Pozzo, Lorenzo Lazazzara, Giacomo Antonioni, Valerio Cozzani**
LISES - Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater Studiorum - Università di Bologna, via Terracini n.28, 40131 Bologna, Italy

(*) *corresponding author*, Tel. +39-051-2090240, Fax +39-051-2090247, e-mail: valerio.cozzani@unibo.it

Revised Version

Abstract

With the impending release of Best Available Techniques (BAT) conclusions on waste incineration, existing European waste-to-energy (WtE) plants will be required to achieve a higher efficiency in the removal of several target pollutants, such as acid gases (above all, HCl and SO_2). The direct injection of a sorbent in the furnace as a primary deacidification stage may be a cost-effective option to achieve the required performances. The present study investigated the furnace injection of a specific dolomitic sorbent, with the aim of identifying the techno-economic optimum for the sorbent feed rate considering different scenarios of flue gas composition. A full-scale test run campaign was carried out on two WtE plants and a phenomenological model linking HCl and SO_2 conversion to reactant feed rate was developed. The model allowed assessing the cost-effectiveness of dolomitic sorbent furnace injection for WtE plants equipped with either a single or a two-stage acid gas treatment system. The addition of dolomitic sorbent resulted particularly suitable for WtE plants equipped with a single stage treatment coping with a high SO_2 concentration in the flue gas, where the injection of dolomitic sorbent can increase the redundancy of flue gas treatment with a reduction of the total operating costs.

Keywords

Waste-to-energy; Flue gas treatment; Acid gas removal; Sorbent; Furnace injection.

1. Introduction

Acid gases such as HCl and SO_2 are typical pollutants formed in waste combustion, whenever chlorine and sulphur are present in the waste feed [1]. Control of their emission in waste-to-energy (WtE) facilities is performed by reaction with neutralising agents, supplied either as absorbent solutions in wet scrubbing equipment or as powdered alkaline sorbents in dry injection systems [2-6].

Given the recent trends in waste generation and management [7,8], overall Cl and S content in the waste feed of European WtE plants is increasing, due to the increasing amounts of industrial wastes fed to these disposal systems. On the other hand, WtE installations are subject to the strictest emission limits among all combustion facilities [9] and the release of the new Best Available Techniques (BAT) Reference Document for waste incineration [10] will further raise the bar, introducing new, ambitious emission targets.

The adoption of multi-stage treatment systems for the removal of acid gases, *i.e.* the combination of more than one unit for acid gas treatment, will be needed in many situations to obtain the required removal efficiency.

For retrofitting applications, the introduction of an additional acid gas removal stage should ideally require minimal impact on plant layout and limited investment costs. Furnace sorbent injection (FSI), *i.e.* the introduction of a powdered solid reactant for the capture of acid gases directly in the combustion chamber, is a method that meets both criteria [11,12]. The reactant is injected directly in the flow path of the flue gas by pneumatic conveying. Then, the reacted particles are deposited on the surface of the heat exchange equipment, thus a dedicated separation equipment is generally not required [13].

FSI was first introduced as a desulfurisation technique in coal combustion [14,15]. The sorbent, typically limestone, is blended with coal or injected with staged air [16]. Once introduced in the furnace at high temperature, limestone is calcined to calcium oxide (CaO), with the development of a porous structure that increases its reactivity towards acid gases. SO_2 removal efficiencies in the range 40-70% are expected [17,18]. Petrini et al. [19], Mura and Lallai [20] and Partanen et al. [21] demonstrated experimentally the suitability of high temperature reaction with limestone also for HCl capture. However, the reactivity of limestone at high temperature is hindered by pronounced sintering [22]. The onset of sintering for calcium carbonate occurs at T ~ 500 °C [23], whereas the injection near to the combustion area exposes the sorbent at temperatures ranging from 800 to 1200 °C. Upon sintering, the porous structure of the sorbent collapses and the surface area decreases, leading to a reduced sorption activity. Alternative Ca-based sorbents, as organic calcium salts [24,25] or, specifically, calcium magnesium acetate [26,27] have been proposed with the aim of achieving higher acid gas removal efficiency thanks to superior surface areas.

More recently, commercial sorbents derived from dolomite rock have been introduced, with the aim of overcoming the limitations of limestone. The presence of magnesium confers a higher resistance to sintering [28] and reduces the clogging and fouling that the deposition of limestone residues typically causes to boilers [29]. Biganzoli et al. [30] offered a first quantitative assessment of the full-scale acid gas removal performance of a dolomitic sorbent, carrying out a test campaign in four Italian WtE facilities. They observed that a furnace sorbent injection at a feed rate of 6 kg/t_{waste} yielded a reduction of acid gas concentration downstream of the boiler in the range 7–37% for HCl and 34–95% for SO_2.

The aim of the present study is to collect extended and detailed quantitative information on the performance of acid gas removal based on dolomitic sorbent direct furnace injection, quantifying the relationship between reactant feed rate and acid gas removal efficiency. The

effectiveness of reactant injection towards HCl and SO_2 was systematically investigated by full-scale test runs carried out in two Italian WtE facilities. The experimental data were used to develop a specific phenomenological model for removal efficiency with respect to sorbent feed and initial acid gas concentrations. The model was used to assess the economics of the process, also considering the other acid gas treatment stages and the composition of the inlet flue gas stream.

2. Materials and methods

2.1 The dolomitic sorbent

The solid reactant tested in the experimental campaign, commercially known as Depurcal and supplied by Unicalce SpA (Italy), is obtained via the calcination and slaking of dolomite rock. The reactant, referred to as dolomitic sorbent (DS) in the following, is mainly composed of calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH)_2$) and magnesium oxide (MgO). According to patent information [29], an average composition on mass basis of the DS is the following: 58.2% $Ca(OH)_2$, 22.3% $Mg(OH)_2$, 19.2% MgO and 0.3% impurities (SiO_2, Fe_2O_3, Al_2O_3).

2.2. Reference WtE plants

The experimental assessment of DS performance was carried out in two Italian WtE facilities, here referred to as plant A and plant B. The key features of the two plants are summarised in Table 1, while the layout of their acid gas treatment systems is sketched in Figure 1. With respect to acid gas removal, plant A presents a two-stage treatment system (Fig. 1a), consisting in the injection of calcium hydroxide, $Ca(OH)_2$, and sodium bicarbonate, $NaHCO_3$, respectively in two consecutive sections of reaction and filtration. Hence, the introduction of a FSI of the dolomitic sorbent realises a three-stage acid gas removal system. Conversely, plant B is equipped with a single acid gas treatment stage fed with sodium bicarbonate (Fig. 1b). Here, the FSI of the dolomitic sorbent introduces a second stage of acid gas removal.

The acid gas treatment lines of the two selected facilities represent two of the most common configurations for WtE flue gas treatment [31] and are both listed among the best available techniques for waste incineration [10]. The reactions between the solid sorbents and the acid gases are illustrated in section S4 of the Supplementary Material.

Table 1. Main features of the WtE plants considered in the study.

	Plant A	**Plant B**
Nominal capacity (t_{waste}/h)	16	9.5
Average flue gas flow rate (Nm^3/h)	110′000	65′000
Range of HCl concentration in the untreated flue gas (mg/Nm^3)	600-1000	800-1400
Range of SO_2 concentration in the untreated flue gas (mg/Nm^3)	10-100	10-100
Acid gas treatment line	$Ca(OH)_2$ + FF + $NaHCO_3$ + FF	$NaHCO_3$ + FF

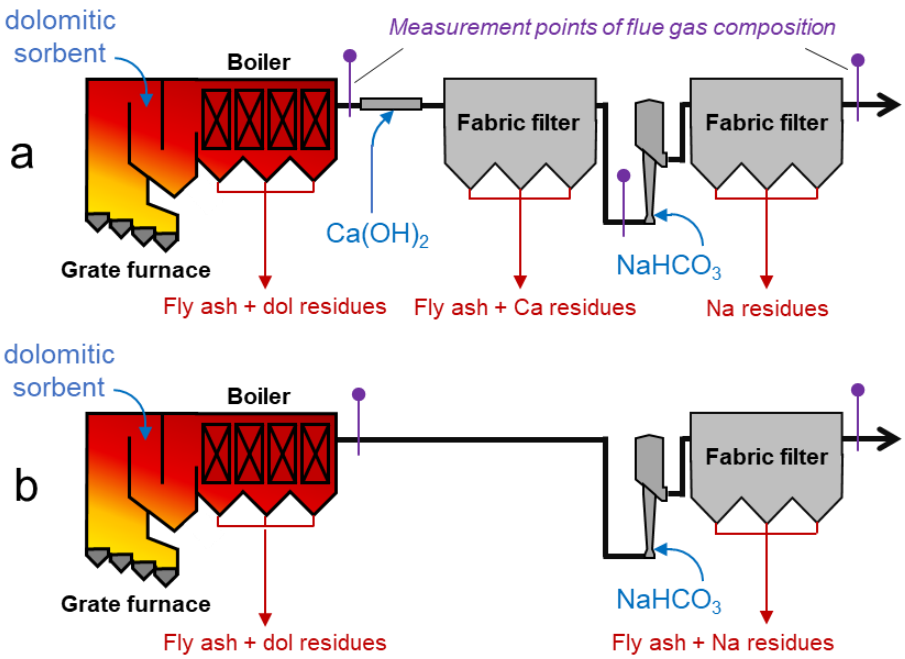


Figure 1. *Configurations of acid gas treatment in the two plants used for the experimental tests: a) two-stage system ($CaOH)_2$ + $NaHCO_3$), which becomes a three-stage system with the furnace injection of dolomitic sorbent, and b) single stage system ($NaHCO_3$), which becomes a two-stage system with the furnace injection of dolomitic sorbent. The points where measurement of flue gas composition is available are highlighted.*

2.3 Test configurations and protocols

Figure 1 shows the feed point of the sorbent in the two plants. The dolomitic sorbent was injected to the top of the combustion chamber by means of a screw feeder that allowed the control of the feed rate. The injected DS reacted with the acid pollutants both while entrained in the flue gas stream and after deposition on the surface of the boiler. The concentration of the acid pollutants (primarily, HCl and SO_2) in the flue gas was measured by Fourier-transform infrared (FTIR) spectrometry at the boiler outlet. In both plants, the FTIR device installed at the boiler outlet was part of a continuous emission monitoring system (CEMS) compliant with the Quality Assurance Level 3 (QAL3, see EN 14181 [32,33]) required by the EU Industrial Emissions Directive [34].

2.3.1 Test runs in specific operating conditions

The relationship between DS feed rate and HCl/SO_2 removal was analysed quantitatively by dedicated test runs. The test runs were carried out injecting the reactant at incremental steps of constant feed rate for defined time intervals. The steps of feed rate tested were: 40, 60, 90, 100 and 200 kg/h for plant A, ranging from to 0.36 to 1.8 kg/10^3 Nm^3; 40, 120 and 200 kg/h for plant B, ranging from 0.62 to 3.1 kg/10^3 Nm^3. The injection of reactant was stopped for 40 min between each feed rate step to allow monitoring the acid gas concentrations in the untreated gas and to avoid any residual effect of the injected DS in the previous step of feed rate on the following step. Table 2 provides the list of all the tests completed.

Data analysis was carried out considering the trend of acid gas concentration at the boiler outlet during the tests. Figure 2 shows the supply of different DS feed rates and the effect on HCl and SO_2 concentrations at the boiler outlet during one of the test runs. The conversion

of HCl or SO_2 related to each step of DS feed rate was calculated from the difference in acid gas concentration before and after the start of DS injection:

(1)

where $C_{acid\ gas,w/o\ DS}$ is the concentration measured in the minute before DS injection and $C_{acid\ gas,w\ DS}$ is the pseudo-stationary concentration measured during DS injection after the transient of concentration decrease was concluded. Similarly, the conversion of acid gases related to each step of DS feed rate was also calculated when DS injection was stopped. In these cases, $C_{acid\ gas,w\ DS}$ was taken as the concentration measured in the minute before the interruption of DS injection, while $C_{acid\ gas,w/o\ DS}$ was the pseudo-stationary concentration measured after DS injection was interrupted and the concentration increase transient was concluded.

A screening protocol was established to accept the experimental data, given the uncertainty due to fluctuations in acid gas concentration formed in combustion flue gas. The exclusion of outliers (i.e. data for which an abrupt variation of HCl and SO_2 generated by waste combustion either covers or magnifies the effect of DS injection) was performed during model fitting by least trimmed squares regression [35], as described in section 3.1.

Table 2. *Test runs performed and steps of reactant feed rate.*

DS feed rate (kg/h)	**Plant A** Test id.								**Plant B** Test id.
	1A	**2A**	**3A**	**4A**	**5A**	**6A**	**7A**	**8A**	**1B**
40	✓	✓	✓	✓	✓	✓	✓	✓	✓
60 [a]	✓	✓	✓	✓	✓	✓	✓	✓	
90						✓	✓	✓	
100	✓	✓	✓	✓	✓				
120									✓
200	✓	✓	✓	✓	✓				✓

[a] the feed rate at 60 kg/h was imposed before and after each test run, as it was the selected constant rate for the 3-month experimental campaign described in section 2.3.2

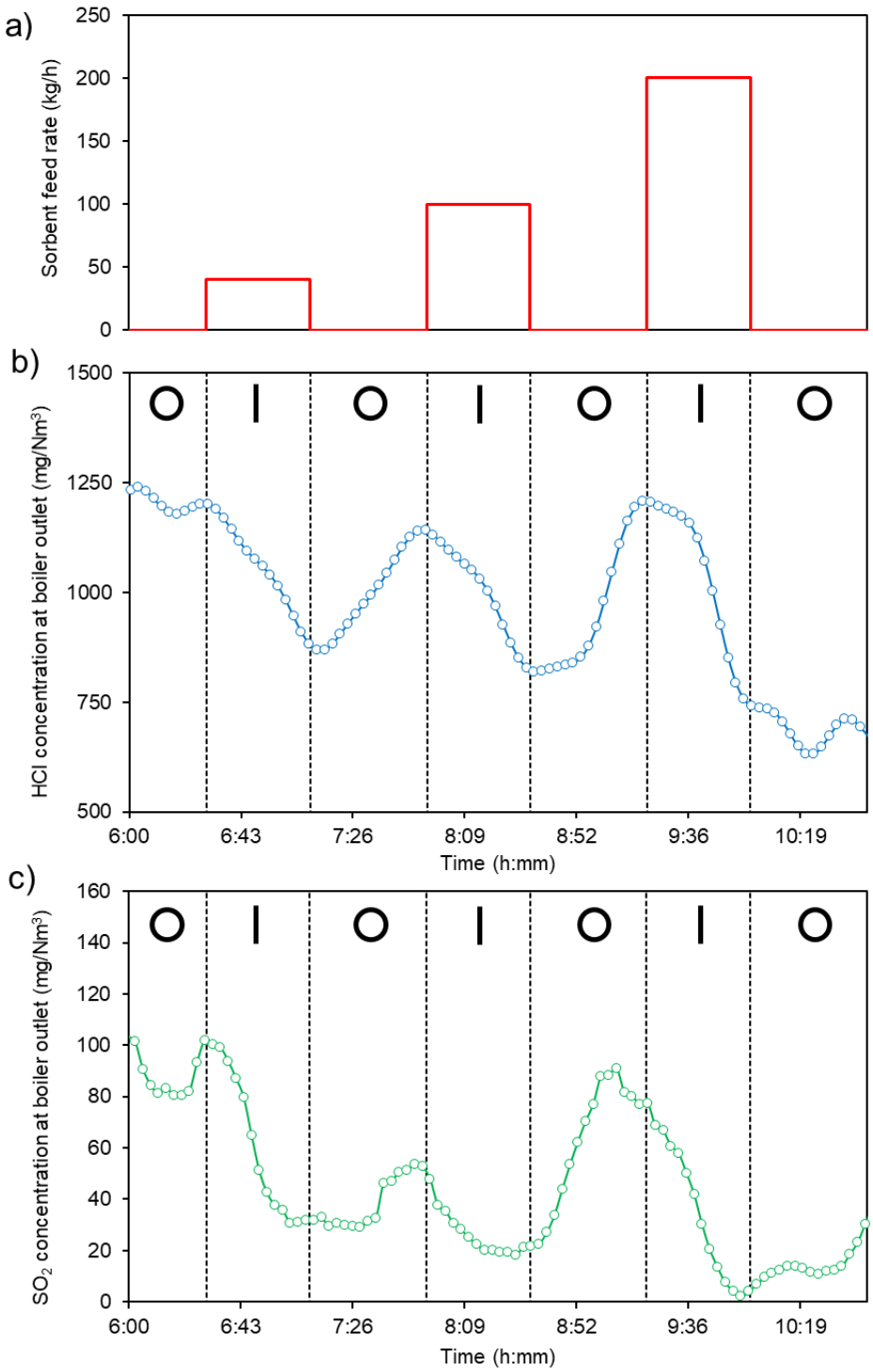


Figure 2. *(a) Feed rate of dolomitic sorbent, and corresponding (b) HCl and (c) SO_2 outlet concentration during test 3A. The symbols I and O indicate respectively the time intervals with and without DS injection. Dots are 5-min moving average values of measured concentration.*

2.3.2 Test run in normal operating conditions

In plant A, the injection of DS was also tested for 3 consecutive months during normal operation of the facility. DS was fed to the flue gas treatment line at a constant feed rate of 60 kg/h (0.55 kg reactant/10^3 Nm^3 of flue gas, considering the average flow rate reported in Table 1). The values of HCl and SO_2 concentration at the boiler outlet, continuously monitored by the FTIR device during the test period, were collected and compared to the same data measured in the previous 3 months of operation without DS injection. The comparison was made considering for the two periods the distribution of the hourly averages of concentration values. The overall 3-month average concentration in the period $\bar{C}_{period}$ and the related standard deviation σ_{period} were calculated starting from the hourly average concentrations, as follows:

(2)

(3)

The total cumulative mass flow of HCl and SO_2 at the boiler outlet over the 3 months was also compared between the two periods.

The main objective of this analysis was to assess the global effect of the dolomitic sorbent in reducing the average concentration of acid gases exiting the combustion chamber. This comparison is based on the underlying assumption that the average concentration of acid pollutants in the raw flue gas upstream of DS injection during the 3 months of DS injection is approximately the same as that measured at the boiler outlet in the previous 3 months without DS injection. This assumption is valid only if there is no significant seasonal effect in waste composition that varies the raw HCl and SO_2 concentration between a 3-month period and the following. The validity of this assumption was checked by comparing the concentration data at boiler outlet for the same two 3-month periods in the previous year (referred to in the following as 'control year'), when no DS testing was carried out. As discussed in section 4.1, no appreciable variation of acid gas concentration at boiler outlet was found between the two 3-month periods of the control year.

3. Models

3.1 Modelling of the performance of dolomitic sorbent

When the sorbent is injected in the combustion chamber of a WtE plant, at temperatures higher than 800 °C, the hydroxides decompose releasing water vapor and forming meso and macropores in the material [30].

(4)

The development of the porous structure promotes the reactivity of the sorbent towards acid gases. The possible reactions with HCl and SO_2 are the following:

(5)

(6)

(7)

(8)

However, it is generally assumed that MgO is chemically inert to acid gases at the temperatures of interest (800-1000 °C), on the basis of experimental findings at laboratory [21] and pilot scale [15]. A wide literature on the high-temperature CO_2 sorption by dolomitic compounds provides similar evidence [23,36]. In addition, a thermodynamic analysis of reactions 5-8, shown in section S1 of the Supplementary Material, confirms that, at temperatures higher than 900°C, only the reactions between acid gases and the Ca-based phase of the sorbent present a negative Gibbs free energy of reaction. Therefore, in the activated dolomitic sorbent after reaction 4, it is considered that CaO is the reactive compound towards acid gases, while MgO acts almost exclusively as structural agent, preventing the collapse of the porous structure developed in reaction 4, as suggested by Biganzoli et al. [30].

A phenomenological model for the description of the acid gas removal process by solid sorbents was used to generalise the information obtained from the test runs. The modelling approach is described comprehensively in a previous study [37]. The model correlates the removal efficiency of an acid pollutant *i* (X_i) to the stoichiometric ratio SR of sorbent *j* at a generic time:

(9)

where SR can be assessed as the ratio of the actual feed rate of the sorbent to the feed rate theoretically required to convert all the acid pollutant *i* in the inlet gas stream over a time interval of interest. The exponent *n* is an empirical parameter that lumps together the effect of all the variables influencing the gas-solid reaction (reactivity of the sorbent, operating conditions such as temperature and humidity, fluid-dynamics of the system). As such, the value of *n* needs to be calculated from the test run data and is specific of the facility.

In the present study, least trimmed squares fitting was used to calculate the values of interest of $n_{i,j}$ using the experimental data from the test runs. The model in Eq. 9 was log-linearised as follows:

(10)

Linear regression was then used to fit the model to the test run data and the least trimmed squares procedure [35] for outlier exclusion was applied until a satisfactorily high value of R^2 was obtained for the fitted model ($R^2 > 0.99$ for HCl, $R^2 > 0.95$ for SO_2).

In order to apply the model to the dolomitic sorbent, it was assumed that its sorption capacity towards acid gases is entirely ascribed to the Ca-based fraction (*i.e.* $Ca(OH)_2$ that decomposes to CaO upon furnace injection), while the Mg-based compounds (MgO, $Mg(OH)_2$) have only the role to avoid the high-temperature sintering of the material and do not participate to the gas-solid reactions, as discussed above. Therefore, the SR was defined on the basis of the Ca content in the sorbent. According to the typical composition of the sorbent reported in section 2.1, the weight fraction of $Ca(OH)_2$ in the DS is 0.58. A weight fraction of 0.42 is obtained when considering the amount of CaO formed from hydroxide dehydration at high temperature after DS injection in the furnace. It was thus

possible to express the data from test runs in terms of SR_{CaO} and the related acid gas conversions $X_{HCl,CaO}$ and $X_{SO2,CaO}$.

In particular, the mass feed rates of sorbent injected in the test , were converted to runs, SR_{CaO} as follows:

(11)

where is the volumetric flue gas rate, and and are the concentrations of the acid gases in the untreated flue gas, measured in the periods without DS injection as described in section 2.3.1.

In order to model the overall performance of the multi-stage acid gas removal process implemented by both plant A and plant B, Eq. 9 was applied as well to the other stages of acid gas removal. Details on the models and on the procedure for model calibration are reported in section S4 of the Supplementary Material.

3.2 Modelling approach for the optimisation of acid gas removal

The cost-effectiveness of the introduction of DS injection in the acid gas removal process can be evaluated estimating the overall operating costs of the process given the initial and final acid gas concentrations. In a multi-stage treatment system, the required overall removal efficiency can be obtained by different distributions of reactants in the removal stages. Therefore, the objective of the optimisation is to assess the share of acid gas removal by DS injection that minimises the overall operating costs of the process.

The performance model of section 3.1 was used to simulate the removal efficiencies of each step in the acid gas abatement line. Simulations were performed for both plant A and plant B. To take into account the variability of acid gas load, six different cases of raw flue gas composition, listed in Table 3, were considered. The six cases cover the typical range of HCl and SO_2 concentrations in the untreated flue gas for the WtE plants that hosted the experimental campaign (see Table 1). The average flue gas flow rate of each plant (see Table 1) and a concentration at stack of 2 mg/Nm^3 of HCl were considered in all the cases.

Table 3. *Cases of raw flue gas composition considered in the optimisation study.*

	C_{HCl} (mg/Nm^3)	C_{SO2} (mg/Nm^3)
Low Cl, low S	600	10
Medium Cl, low S	1000	10
High Cl, low S	1400	10
Low Cl, high S	600	200
Medium Cl, high S	1000	200
High Cl, high S	1400	200

Different configurations of the multi-stage treatment system were explored varying the HCl conversion in the different stages, while keeping equal the overall efficiency of HCl removal in the system:

(12)

where N is the total number of abatement stages (2 for plant B, 3 for plant A), and $X_{HCl,j}$ is HCl conversion in stage j. The value of $X_{SO2,overall}$ could not be kept constant as well, as

different repartitions of abatement between the stages were explored in the simulations, because each sorbent has a different relative reactivity towards HCl and SO_2. Nonetheless, given the significantly lower amount of SO_2 compared to HCl in the raw flue gases considered in Table 3, the concentration of SO_2 at stack resulted similar and lower than 1 mg/Nm^3 in all the simulations.

The consumption of reactants associated to the acid gas conversion in each abatement stage can then be calculated considering the reaction stoichiometry (Eqs. 4-6 for the dolomitic sorbent, Eqs. S5-S9 in section S4 of the Supplementary Material for the other reactants) and the model correlation provided by Eq. 9. Given the acid gas conversion and the required consumption of reactants, the mass rate and composition of the solid process residues generated in each stage can be quantified by means of a mass balance.

The overall operating cost of acid gas treatment was thus estimated as:

(13)

where $C_{reactants}$ and $C_{residues}$ are the costs respectively associated to the purchase of reactant and the management of process residues for each treatment stage. The values adopted for the unit costs are listed in Table 4. These numbers are average values for the Italian context. For a detailed overview on the cost data of dry acid gas treatment operations the reader is referred to Dal Pozzo et al. [37]. Here, it is worth recalling that the management of process residues is associated to two different fates and costs. Streams of residues that are mixed with fly ash coming from the combustion chamber and potentially carrying hazardous materials in traces (heavy metals, organochlorinated compounds) are to be sent to dedicated landfill sites [38,39]. Hence, recalling the schemes in Figure 1, this is the case for the residues of dolomitic sorbent, calcium hydroxide, and sodium bicarbonate, if no upstream dedusting equipment is installed (see Fig. 1b). Conversely, the process residues generated by the reaction between sodium bicarbonate and acid pollutants can be sent to dedicated recycling facilities [40] if a fabric filter is installed upstream of $NaHCO_3$ injection to collect separately the fly ash (see Fig. 1a).

Table 4. *Values of the unit costs adopted in the study for the considered cost entries.*

Cost entry	**Unit cost (€/t)**
Reactants	
Dolomitic sorbent	100
Calcium hydroxide	50
Sodium bicarbonate	240
Management of process residues	
Disposal (residues mixed with fly ash)	200
Recycling (Na residues separated from fly ash)	170

4. Results and discussion

4.1 Test run in normal operating conditions: effect of DS injection on the concentration of HCl and SO_2 leaving the furnace

The test run in normal operating conditions conducted at plant A had the aim of assessing the effect of a fixed feed rate of DS injection on the flue gas composition leaving the

furnace/boiler. The outcome of the test run on plant A in normal operating conditions was evaluated comparing the hourly data of HCl and SO_2 concentrations in the gas at the boiler outlet (first sampling point in Figure 1a) for the two 3-month periods with and without DS injection, as described in the sampling protocol of section 2.3.2.

The hourly concentration data measured at the boiler outlet in each 3-month period were put in ascending order and multiplied with their respective hourly flue gas flowrate data, in order to obtain a curve of cumulative mass flow of the acid pollutants exiting the boiler.

Fig. 3a shows the cumulative mass flow of HCl at the boiler outlet for the two reference periods. The total mass flow of HCl leaving the combustion chamber measured in the 3 months of DS injection amounted to 164.7t, compared to 218.2t for the 3 months without DS injection. A 25% reduction of the HCl mass flow released in the reference period is thus observed as a consequence of DS injection.

More specifically, the cumulated mass flow curves in Fig. 3a trace how the hourly data of HCl concentration measured at the boiler outlet contributed to the total mass flow in the two 3-month periods. The concentration of HCl measured at the sampling point fluctuates over time as a natural consequence of the variable Cl content of the waste burnt in the furnace: in this plant, Fig. 3a shows that during the 3-month period without DS injection the HCl concentration varied mostly from 400 to 1500 mg/Nm^3 with peaks up to 3000 mg/Nm^3. In the 3 months of DS injection this range of variation moved towards lower values (the cumulated mass flow curve with DS injection is shifted leftward compared to that for the period without DS injection). This is further clarified by the distributions of the hourly averages of HCl concentration at the boiler outlet for the two reference periods shown in Fig. 3b. The hourly values of HCl concentration recorded at the boiler outlet during the two 3-month periods were subdivided in the 5 classes of the figure. For each class, the frequency of occurrence of concentration values within that class range is reported as percent of the total hourly concentration data in the 3-month period. The furnace injection of DS clearly resulted in a shift of the distribution of HCl concentration towards lower values. With DS injection, the frequency of concentrations higher than 800 mg/Nm^3 is more than halved, while the occurrence of concentrations in the interval 400-600 mg/Nm^3 is approximately tripled.

The overall 3-month average of the hourly HCl concentration data at the boiler outlet with DS injection resulted of 702 mg/Nm^3, compared to a value of 897 mg/Nm^3 for the 3-month period without DS injection. This corresponds to an average 22% reduction of the HCl load leaving the combustion chamber thanks to the DS effect. Furthermore, also the standard deviation of the hourly HCl concentration data exhibited a noticeable decrease: a value of 287 mg/Nm^3 was obtained during DS injection, with respect to a value of 323 mg/Nm^3 in the period without DS injection. A reduction of the standard deviation means that the hourly HCl concentration values at the sampling point were less dispersed during DS injection and, thus, less peaks at high HCl concentration were present compared to the period without DS injection.

To confirm that all the aforementioned effects were owing to the DS injection and not to a change of other operating conditions between the two 3-month periods, an identical analysis was carried out for the same 3-month periods in the previous year of operation of the plant, when no DS testing was performed. The results are shown in section S2 of the Supplementary Material. No appreciable difference in the mass flow of HCl and in the distribution of HCl concentration was observed between the first and the second period of the control year. A difference lower than 2% is present among the 3-month average HCl concentrations for the two periods. Therefore, it is reasonable to assume that the reduction of the average HCl concentration in the flue gas observed in Fig. 3a and 3b is due to the

addition of DS and not to a variation in the overall average composition of the waste feed between the periods.

The results observed with reference to SO_2 are similar to those obtained for HCl. Fig. 3c shows that the cumulative mass flow of SO_2 in the 3 months of DS injection was equal to 5.3t, a 37% reduction compared to the 8.4 t calculated for the 3-month period without DS injection.

It is evident that during DS injection, as observed for HCl, lower SO_2 concentrations at the sampling point appeared more frequently than in the reference period without DS injection. As shown in Fig. 3d, more than 60% of the hourly SO_2 concentration data measured in the period with DS injection show values lower 15 mg/Nm^3, while the occurrences in all the frequency classes higher than 15 mg/Nm^3 diminish systematically compared to the period without DS injection.

The overall 3-month average of the hourly SO_2 concentration data at the boiler outlet in the 3-month period with DS injection resulted of 22.7 mg/Nm^3, compared to a value of 31.4 mg/Nm^3 without DS injection (a 28% reduction). Again, also the standard deviation of the hourly SO_2 concentration data was noticeably lower during DS injection: 40.6 mg/Nm^3 vs. 52.6 mg/Nm^3.

For the control year (see section S2 in the Supplementary Material), no significant difference in the global 3-month average concentration was recorded: the average SO_2 concentration at the boiler outlet was 32.1 mg/Nm^3 in the first period and 31.0 mg/Nm^3 in the second period. The total mass flow of SO_2 measured in the 3 months varied less than 2% between the two periods. Again, it is confirmed that in normal operation the overall conditions at the boiler outlet remains generally constant between contiguous 3-month periods, thus the observed reduction of HCl and SO_2 mass flow for the 3 months of DS testing can be reasonably ascribed to the effect of DS injection.

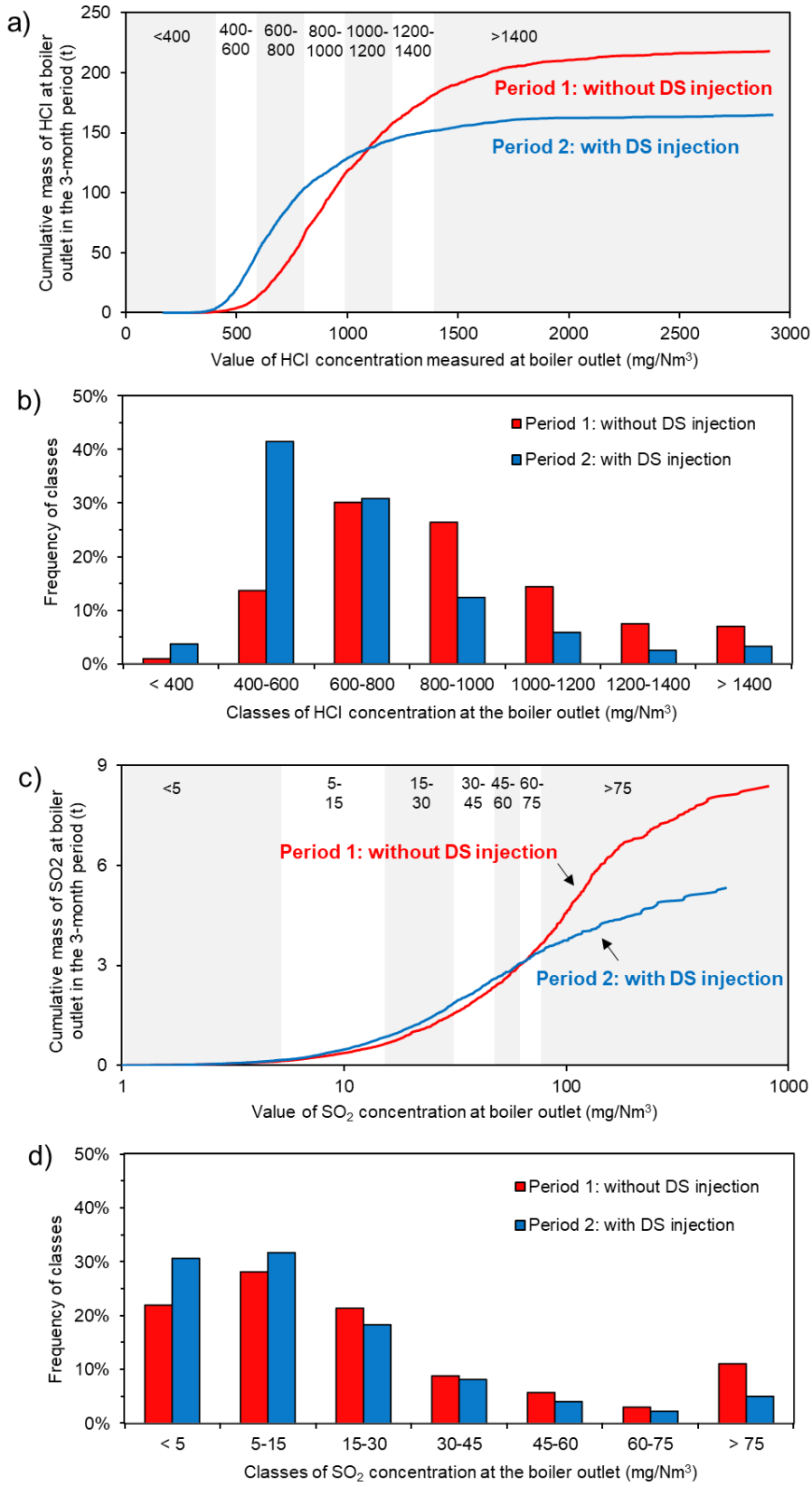


Figure 3. *Analysis of the effect of DS injection: a) cumulative mass flow of HCl at the boiler outlet in period 1 (without DS injection) and in period 2 (with DS injection); b) distribution of the hourly averages of HCl concentration at the boiler outlet in the two periods; c) cumulative mass flow of SO_2 at the boiler outlet in the two periods; d) distribution of the hourly averages of SO_2 concentration at the boiler outlet in the two periods.*

4.2 Test runs in specific operating conditions: effect of DS feed rate

As introduced in section 2.3.1, the test runs at specific operating conditions were carried out varying the feed rate of the DS injected in the furnace. The objective of this specific set of test runs was to collect data with a finer time resolution than the macroscopic analysis of section 4.1 and to provide a quantitative evaluation of the relation between feed rate of reactant and removal efficiency of the acid pollutants. The test runs allowed collecting data on the difference in HCl and SO_2 concentration measured at the sampling point before and after DS injection at different feed rates, hence obtaining a dataset of HCl and SO_2 conversion at different SR of dolomitic sorbent injection. Tables S2 and S3 in section S3 of the Supplementary Material report the complete datasets obtained, which were used to calibrate the phenomenological model developed for acid gas conversion. The detailed results of all the test runs are also provided in section S3 of the Supplementary Material.

4.3 Model results

The datasets related to plant A and plant B obtained from the test runs were used to calibrate the phenomenological model presented in section 3.1 and to determine the values of parameter *n* for the two acid pollutants. As mentioned in section 3.1, the least trimmed squares method was adopted for concurrent outlier exclusion and model fitting. The following values of *n* were obtained for plant A: 1.38 for HCl and 5.26 for SO_2. The corresponding values of *n* obtained for plant B are: 1.36 for HCl and 7.29 for SO_2.

The fitting of calibration data points for plant A is shown in Fig. 4a and 4b, for HCl and SO_2 sorption respectively. Only the sample points after outlier removal are reported, while the complete dataset is presented in section S3 of the Supplementary Material. An additional data point representing the average performance of the dolomitic sorbent during the 3-month campaign analysed in section 4.1 is also reported in the figure, showing a quite good alignment with the data from the test run campaign. Fig. 4c and 4d reports the fitting of data points for plant B.

In relative terms, the dolomitic sorbent shows a markedly higher sorption capacity towards SO_2 than towards HCl. Hence, the DS behaves differently than the reactants injected at low temperatures (calcium hydroxide and sodium bicarbonate), which exhibit a higher reactivity towards HCl (see data in section S4 of the Supplementary Material).

In absolute terms, the reactivity of the DS via furnace injection towards SO_2 is significantly higher than that of calcium hydroxide via low-temperature injection in the flue gas ductwork. Conversely, the DS appears less reactive than calcium hydroxide with respect to HCl.

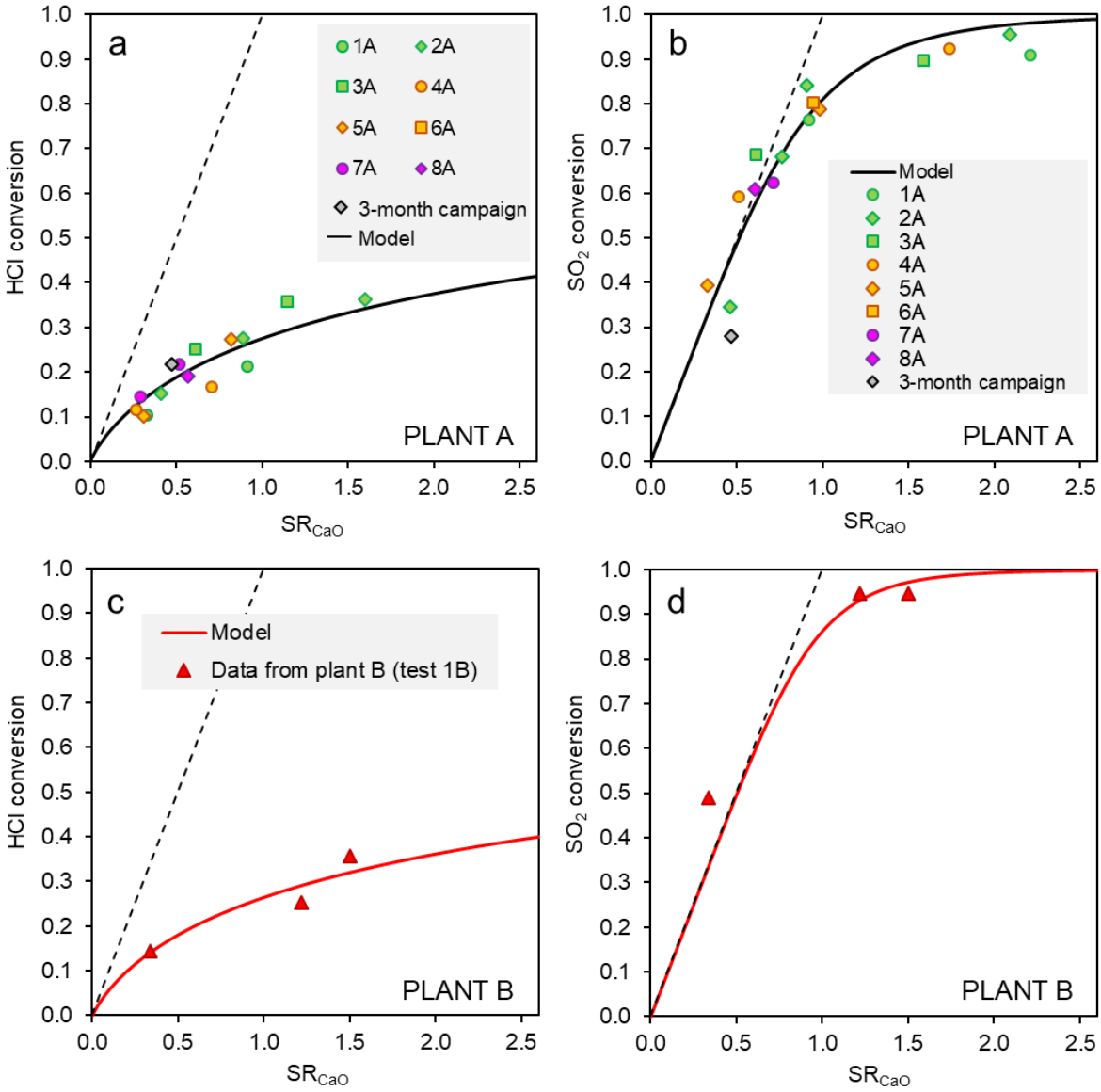


Figure 4. *Phenomenological model results (continuous line) compared to calibration data for plant A: a) HCl removal, b) SO_2 removal; and plant B: c) HCl removal, d) SO_2 removal. The dotted line corresponds to stoichiometric efficiency.*

The model results for plant A and plant B were compared to each other in Fig. 5. The tests on plant B had the main intent to confirm the general trends identified on plant A. Indeed, the model curve obtained fitting the data points available for plant B appears quite similar to the model curve obtained for plant A. Clearly enough, the semi-empirical nature of the model implies that its calibration parameter, *n*, is site-specific, thus valid only for the description of the performance of the plant where the model was calibrated via test runs. However, the results in Fig. 5 confirm that the model has the potential to fit (after a specific tuning) experimental results across different WtE facilities, with different capacity, layout and average acid gas loads.

Fig. 5 also compares the model results of this study with data of DS performance collected in four WtE plants by Biganzoli et al. [30], the only other report on DS furnace injection available in the literature, to the best of our knowledge. The data of ref. [30] were obtained

by calculating the SR of DS injection from the information on reactant feed rate and acid gas concentrations given by the authors, under the assumptions of section 3.1.

At least for HCl, there is a fairly good agreement between the model results and the experimental data set by Biganzoli et al. [30], even if no specific tuning of the model was made. This further supports the comparability of HCl removal efficiency data by DS furnace injection across different WtE facilities.

With respect to SO_2, the data by Biganzoli et al. [30] exhibit a much wider scatter than those presented in Fig. 4b, arguably owing to the uncertainty associated to the lower and more variable loads of this pollutant formed in waste combustion across different WtE plants. In that regard, a merit of the test runs of the present study is to offer a robust and ample set of homogeneous data on SO_2 removal by DS injection obtained in a single WtE plant (Fig. 4b).

In general, the analysis of the results in Fig. 5 support the robustness of the experimental and modelling approach adopted in the present study.

In addition, the data of Fig. 4 are of clear interest for WtE operators, because only full-scale testing can assess the performance of sorbent in presence of specific process conditions (e.g. fluid-dynamics of the process in the furnace/boiler environment, interference between gas species, morphological evolution of sorbent particles injected in the furnace) that are not easily reproducible at laboratory scale. For instance, laboratory data available for the dolomitic sorbent [29], collected in a fixed bed reactor at 900 °C, showed a conversion of SO_2 in the range 78-82% (tests in SO_2/N_2 atmosphere, SO_2 inlet concentration of 1070 mg/Nm^3, SR_{CaO} = 2) and a conversion of HCl in the range 67-72% (tests in HCl/N_2 atmosphere, HCl inlet concentration of 1430 mg/Nm^3, SR_{CaO} = 2). The present full-scale results demonstrated that the conversion of HCl that should be expected in a real furnace is lower than the laboratory results (here, a SR_{CaO} = 2 corresponds to a HCl conversion slightly lower than 40%; see Fig. 4). Conversely, the conversion of SO_2 registered at full-scale is higher than that observed at laboratory scale (here, a SR_{CaO} = 2 corresponds to a SO_2 conversion higher than 90%; see Fig. 4), presumably owing to the significantly lower concentration of SO_2 typically measured at plant (< 200 mg/Nm^3) compared to the value adopted in laboratory, and a possible synergic effect on SO_2 sorption given by the presence of HCl or its product of reaction $CaCl_2$ [41,42]. It is thus clear that the quantification of removal efficiencies at full scale is necessary to obtain reliable data for the economic assessment.

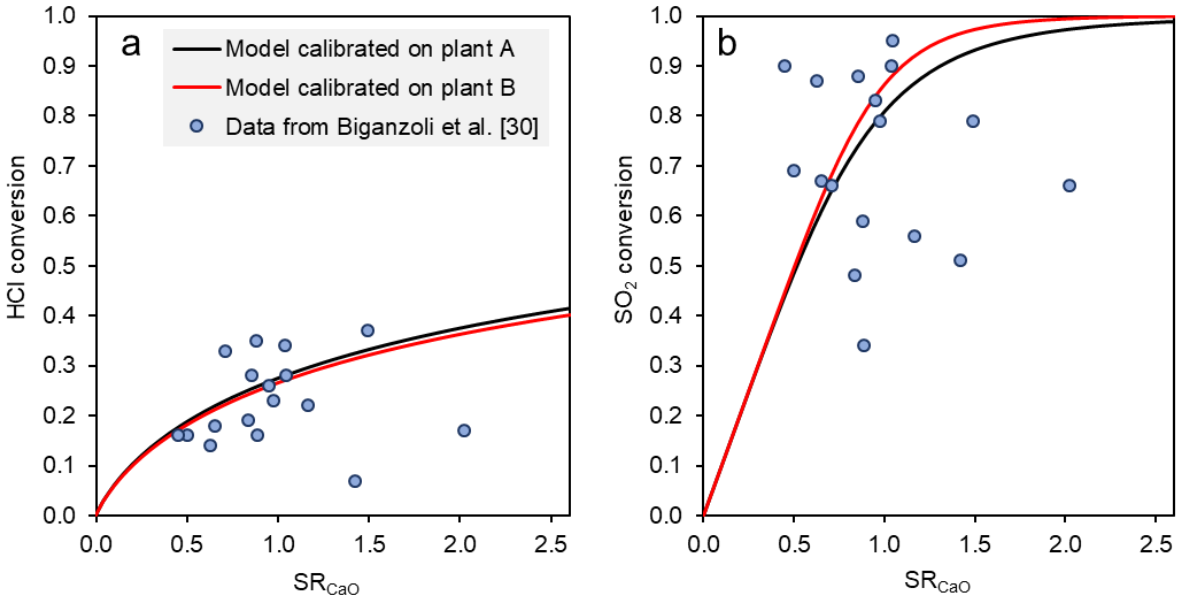


Figure 5. *Results of phenomenological models for plant A and plant B compared to literature data for: a) HCl, b) SO_2. The models were used without calibration to the specific operating conditions of plants where literature data were obtained.*

4.4 Optimisation of multi-stage acid gas removal processes

The developed phenomenological model allows addressing the minimisation of the operating costs of multi-stage acid gas removal processes. In the following, the cost-effectiveness of introducing a FSI of dolomitic sorbent was preliminarily assessed for both plants A and B, given the process constraints of section 3.2 and using the specific calibration data obtained for the model. In the economic assessment, only the costs for the procurement of sorbents and the management of residues were considered, being the most important operating cost entries in determining process economics [37,43].

4.4.1 Two-stage optimisation: dolomitic sorbent + $NaHCO_3$ (plant B)

The search for the optimal repartition of acid gas abatement between DS and sodium bicarbonate feed for a plant equipped with a furnace injection of dolomitic sorbent and a subsequent in-duct injection of $NaHCO_3$ (see the scheme of plant B, in Fig. 1b) was performed varying the conversion of HCl at the DS stage, while keeping constant the HCl concentration at stack. The results are shown in Fig. 6 in terms of overall operating cost (€ per Nm^3 of treated flue gas) as a function of HCl conversion by the dolomitic sorbent, for the different cases of flue gas composition introduced in Table 3. The minimum of each curve represents the optimal operating point for the corresponding inlet flue gas composition. Clearly enough, the cost associated to the operation of the acid gas removal system without DS injection is that corresponding to $X_{HCl,dolomitic\ sorb}$ = 0%.

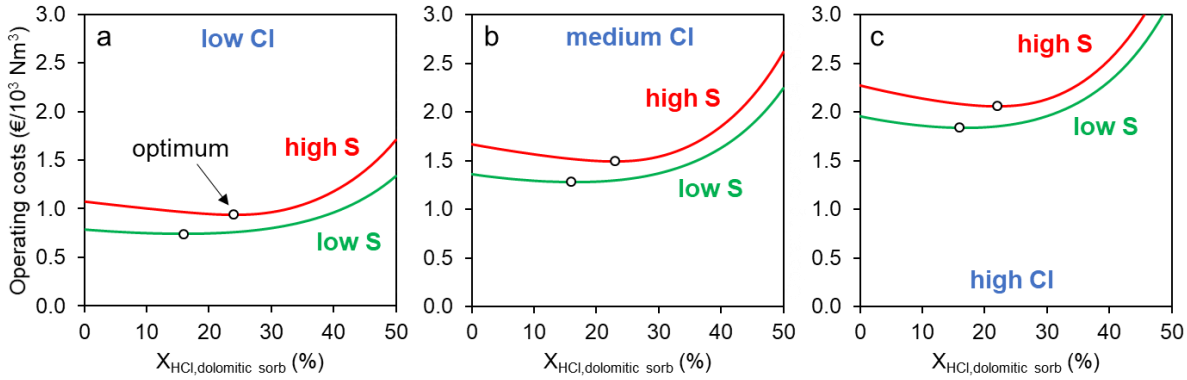


Figure 6. *Operating costs of the dolomitic sorbent + $NaHCO_3$ two-stage system as a function of HCl conversion in the DS stage for the six cases of flue gas composition in Table 3: a) low content of Cl; b) medium content of Cl; c) high content of Cl. Open circles: minimum cost.*

The curves for the six scenarios considered for flue gas composition exhibit a common behaviour. There is a region where variation of costs is limited ($X_{HCl,dolomitic\ sorb}$ < 30%), while costs start increasing steeply at higher $X_{HCl,dolomitic\ sorb}$ values. As shown by the open circles, an optimum is always present and it corresponds to a $X_{HCl,dolomitic\ sorb}$ value of 16 and 23%, respectively for the low S and high S scenarios. The cost savings of the optimal operating point of the DS + $NaHCO_3$ configuration with respect to the single stage $NaHCO_3$ injection are of about 6% for the low S cases. For the high S cases, instead, the savings range from 10% to 13%. The cost-effectiveness of the DS injection at higher SO_2 concentration and higher S/Cl ratio in the inlet flue gas stems from the higher relative reactivity of the dolomitic sorbent towards SO_2 compared to sodium bicarbonate.

Figure 7 details the contribution of the different entries to the overall operating cost for the scenarios of medium Cl and low or high S in the flue gas. The single stage $NaHCO_3$ system and the DS + $NaHCO_3$ configuration at the optimal operating point are compared. The addition of DS reduces the total cost related to reactant procurement, as the expense for DS and $NaHCO_3$ in the two-stage system is 11 and 20% lower than the expense for $NaHCO_3$ alone in the single stage configuration, respectively for the low and high S cases. Conversely, when DS injection is present, the cost associated to the management of process residues increases of 5 and 10% for the low and high S cases. This is due to the combined effect of a higher unit cost for the management route of DS residues (see Table 4) and the weight gain associated with acid gas capture: considering the sorption of HCl, a mole of dolomitic sorbent, upon dehydration and chloridisation (Eqs. 1 and 2), exhibits a 22% mass increase, while a mole of sodium bicarbonate, after thermal activation and chloridisation, undergoes a 69.5% net weight loss. On the whole, the net effect of DS injection at the optimal feed rate is the slight reduction of operating costs shown in Fig. 6, resulting from lower costs for reactants and higher costs for residues handling.

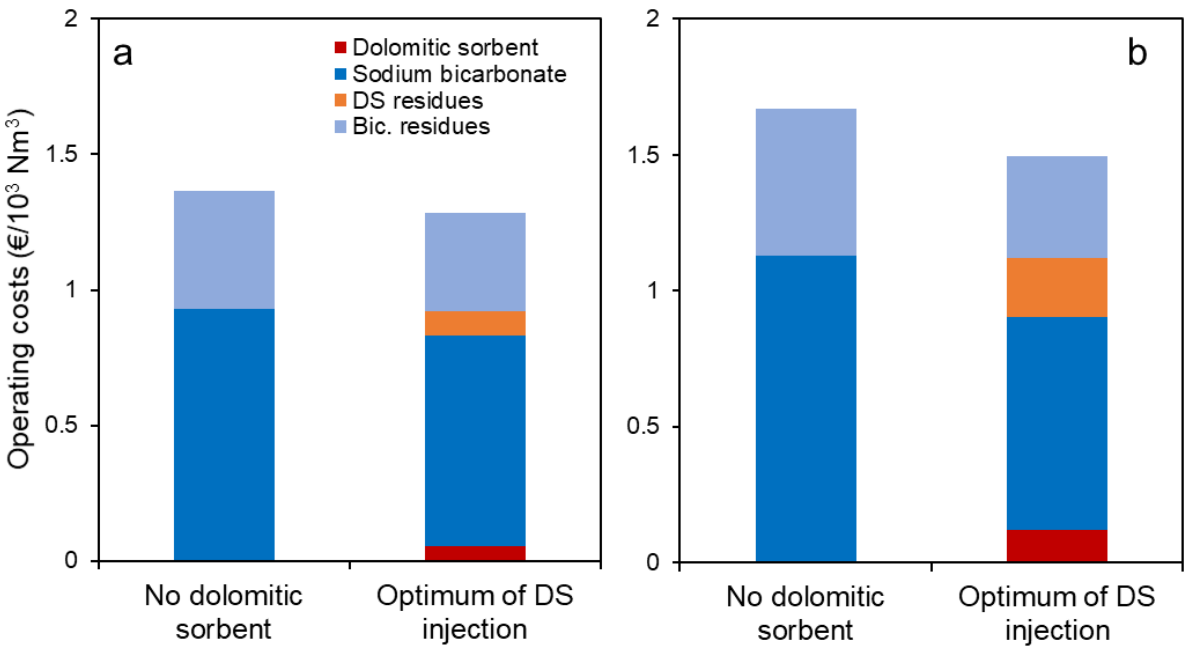


Figure 7. *Contribution of the different cost entries to the overall operating costs of acid gas removal for the single stage bicarbonate system (no furnace injection) and for the two-stage system with DS injection at the optimal operating point (optimum). Medium Cl and: a) low S, b) high S compositions were considered for flue gas.*

4.4.2 Three-stage optimisation: dolomitic sorbent + $Ca(OH)_2$ + $NaHCO_3$ (plant A)

For an acid gas treatment line as that of plant A, already presenting two stages of sorbent injection (calcium hydroxide and sodium bicarbonate), the introduction of DS injection forms a three-stage system. As such, the system exhibits two degrees of freedom in the selection of acid gas removal repartition between the stages, at a fixed overall HCl removal efficiency. Therefore, the evolution of the overall operating cost (€ per Nm^3 of treated flue gas) was explored as a function of HCl conversion in both the DS injection stage and the $Ca(OH)_2$ injection stage, as shown in the contour plots of Fig. 8.

As for the two-stage system, the optimal operating point of the three-stage system, pinpointed by a circle dot in the panels of Fig. 8, includes an injection of dolomitic sorbent, corresponding to 9-10% $X_{HCl,dolomitic\ sorb}$ for the low S cases and to 16-20% $X_{HCl,dolomitic\ sorb}$ for the high S cases. However, the cost savings associated to the three-stage optimum are in all scenarios lower than 10%, compared to the two-stage optimum of the $Ca(OH)_2/NaHCO_3$ system, which corresponds to values in the range 47-50% $X_{HCl,Ca(OH)2}$ when $X_{HCl,dolomitic\ sorb}$ is set to zero. Actually, a properly operated $Ca(OH)_2/NaHCO_3$ two-stage system is already an optimised system compared to the single stage injection of sodium bicarbonate [37], thanks to the use of cheaper calcium hydroxide (see again table 4) for the reduction of the acid gas concentration entering the bicarbonate stage. Thus, the margin for further cost reduction is lower.

Nonetheless, in operational terms, maintaining the optimal operating point of the $Ca(OH)_2/NaHCO_3$ two-stage system is not an easy task for the control system of a flue gas treatment line, as the concentration of inlet acid pollutants fluctuates widely and frequently. Therefore, DS injection can help because it enlarges the operational region where costs are within +10% of the optimum. As an example, focusing on panel 8b, the window of operating

costs within +10% of the optimum, without DS injection, is comprised between $X_{HCl,Ca(OH)2}$ ranging from 35 to 55%, while for a DS injection corresponding to $X_{HCl,dolomitic\ sorb}$ = 20%, it is possible to remain within +10% of the minimum operating costs even for $X_{HCl,Ca(OH)2}$ ranging from 20 to 65%. Therefore, the addition of a dolomitic sorbent stage flattens the cost variation related to the repartition of acid gas removal between the treatment stages, possibly limiting the deviation from optimal operation.

Table 5 summarises the findings of sections 4.4.1 and 4.4.2, listing the specific feed rates of dolomitic sorbent that correspond to the optimal $X_{HCl,dolomitic\ sorb}$ identified for the configurations of plant A and plant B in the six cases of flue gas composition. It is recalled that the conversion of HCl is linked to the SR of sorbent by the model of Fig. 4, calibrated on the plant-specific test runs, and the SR of sorbent is linked to the mass feed rate of sorbent by Eq. 11.

Table 5. *Specific feed rate of dolomitic sorbent (kg/10^3 Nm^3 of flue gas) corresponding to the optimal $X_{HCl,dolomitic\ sorb}$ shown in Fig. 6 and 8.*

Cases of flue gas composition		**System**	
		DS + $Ca(OH)_2$	**DS + $Ca(OH)_2$ + $NaHCO_3$**
		Optimal DS feed rate (kg/10^3 Nm^3)	**Optimal DS feed rate (kg/10^3 Nm^3)**
Low Cl	Low S	0.39	0.20
	High S	1.04	0.53
Medium Cl	Low S	0.65	0.33
	High S	1.43	0.79
High Cl	Low S	0.90	0.46
	High S	1.75	1.05

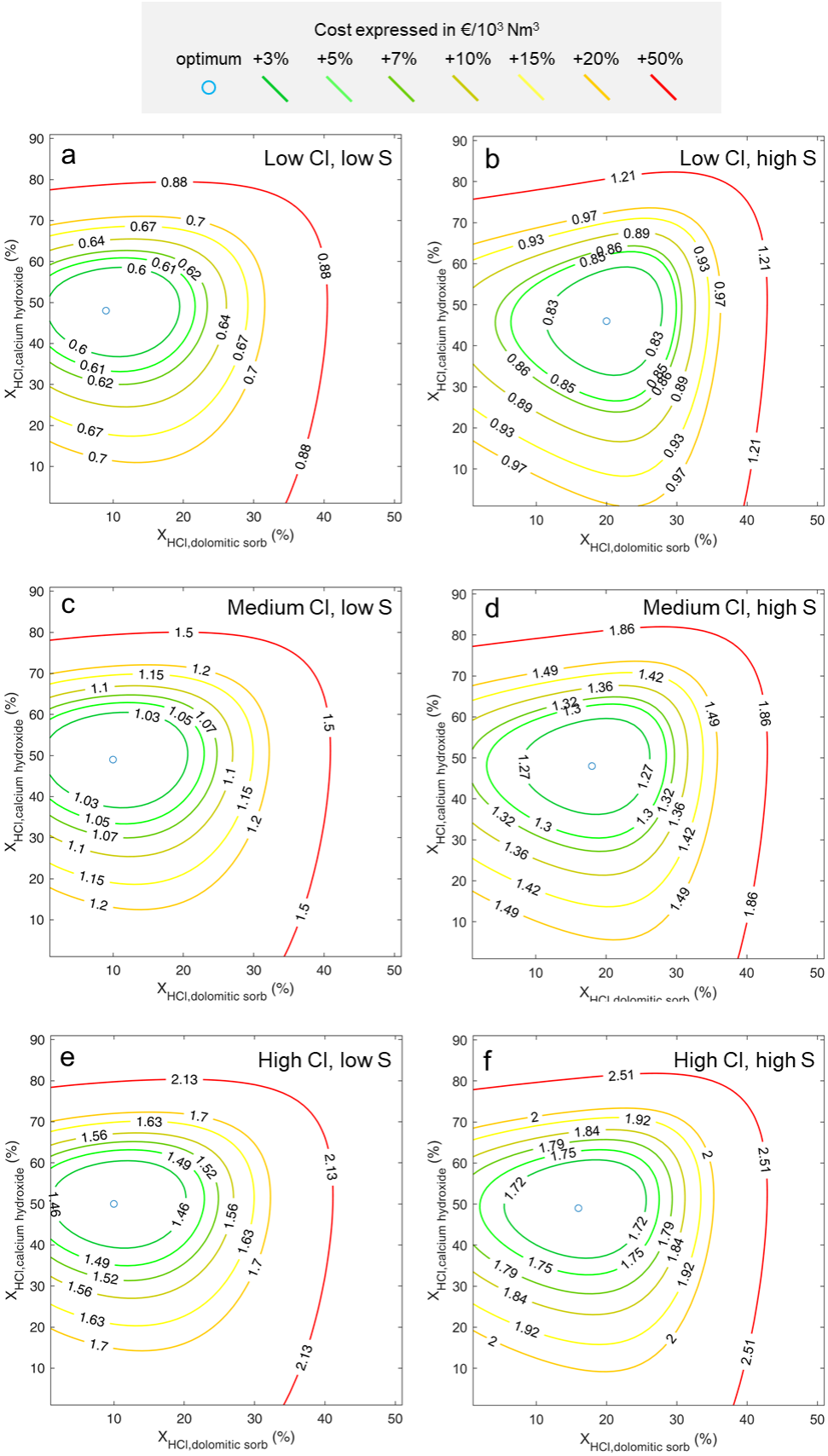


Figure 8. *Operating costs of the dolomitic sorbent + $Ca(OH)_2$ + $NaHCO_3$ three-stage system as a function of HCl conversion in the DS and $Ca(OH)_2$ stages, for the six cases of flue gas composition in Table 3.*

4.4.3 Effect of unit cost variability

The economic analysis in sections 4.4.1 and 4.4.2 is clearly influenced by the adopted unit cost values for the considered cost entries. To assess the effect of different unit costs than those listed in Table 4 on the economic optimisation, two scenarios were explored:

- an unfavourable scenario for the DS, named '*costly DS, cheap $NaHCO_3$*', in which the costs for the procurement of DS and the disposal of process residues are 20% higher than the values in Table 4, while the costs for the procurement of sodium bicarbonate and the costs for the recycling of Na-based process residues are 20% lower than the values in Table 4;
- a favourable scenario for the DS, named '*cheap DS, costly $NaHCO_3$*', in which – vice versa – the costs for the procurement of DS and the disposal of process residues are 20% lower than the values in Table 4, while the costs for the procurement of sodium bicarbonate and the costs for the recycling of Na-based process residues are 20% higher than the values in Table 4.

The ±20% range assumed is a conservative interval of variation, considering the relatively low differences in unit costs reported by several technical and scientific sources (see the overview of cost data by Dal Pozzo et al. [37]).

The overall operating costs estimated for the systems without DS injection and for the systems with DS injection at the optimal operating point were compared for the different cost scenarios, as shown in Fig. 9. The comparison was carried out for both the two-stage and the three-stage system, with reference to medium Cl and high or low S flue gas composition cases.

The first evidence is that the 'costly DS, cheap $NaHCO_3$' scenario always generates lower overall operating costs, while the upper end of the operating costs range corresponds to the the 'cheap DS, costly $NaHCO_3$' scenario. This finding is obvious for the cases with no DS injection. For the cases with optimal DS injection, it results from the much higher $NaHCO_3$ feed with respect to the DS feed rate in the optimal repartition of feed rate between stages, that results in a higher fraction of the total costs (as shown in Fig. 7).

In the 'costly DS, cheap $NaHCO_3$' scenario, the slight cost savings ensured by DS injection, discussed in sections 4.4.1 e 4.4.2, are further reduced, and the operating costs of the systems with and without DS injection are almost equivalent. The exception is the case of the DS + $NaHCO_3$ system in presence of a flue gas composition with high S, for which the injection of DS still results in a 7% cost reduction.

Vice versa, in the 'cheap DS, costly $NaHCO_3$' scenario the gap between the operating costs with and without DS injection is enlarged. The addition of DS results in savings, ranging from 9 to 16% for the $NaHCO_3$ system and from 5 to 12% for the $Ca(OH)_2/NaHCO_3$ system (lower and upper end of the range are for the flue gas compositions with low and high S, respectively).

Overall, these results clarify that, even in presence of uncertainty in the unit costs, the introduction of a DS injection stage reduces the variation of the total operating costs, as evident from the reduction of the cost brackets in Fig. 9. In the cost scenario that is unfavourable for DS, the overall costs of the system with or without DS injection are the same, while in the cost scenario that is favourable for DS, its injection generates appreciable savings. Therefore, from the viewpoint of WtE operators, adding a furnace injection of DS can increase the robustness of the entire acid gas treatment line.

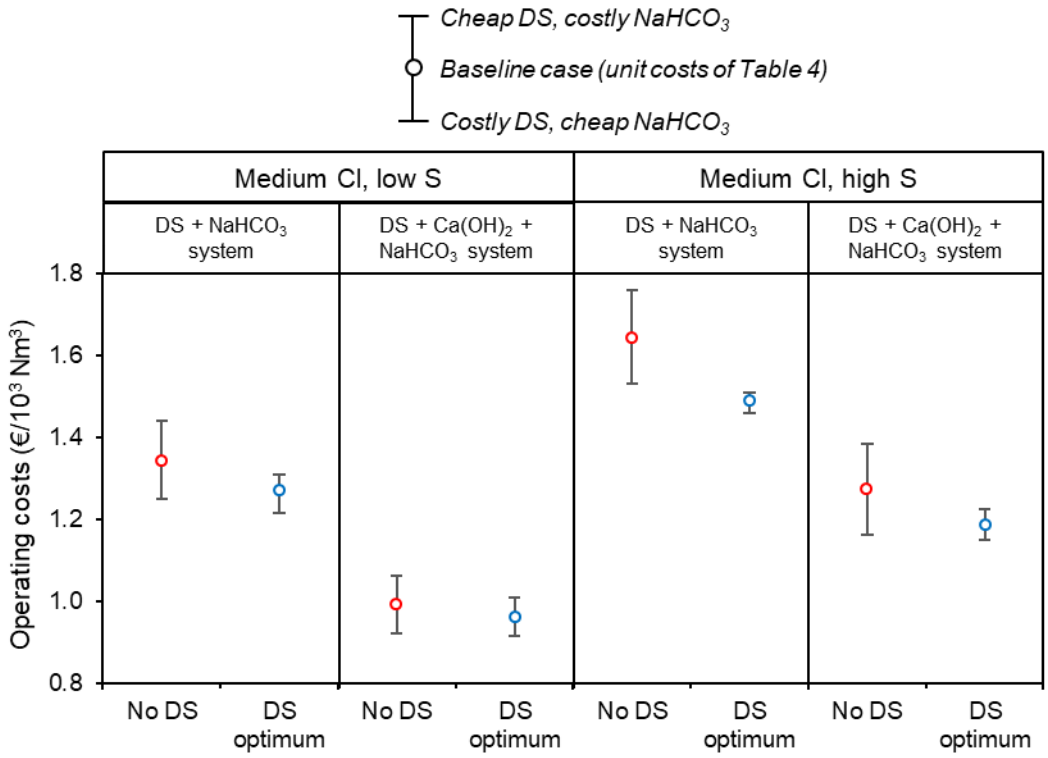


Figure 9. *Operating costs of acid gas removal in the different cost scenarios indicated in the legend. Comparison between no DS injection and DS injection at the optimum, for the DS + $NaHCO_3$ two-stage system and for the DS + $Ca(OH)_2$ + $NaHCO_3$ three-stage system with DS injection at the optimal operating point (optimum). Medium Cl and: a) low S, b) high S compositions were considered for flue gas.*

5. Conclusions

A quantitative analysis of the HCl and SO_2 removal performance of a dolomitic sorbent injected in the combustion chamber of WtE plants was carried out. Data obtained via dedicated test runs at full plant scale and their interpretation by means of a phenomenological model allowed deriving a non-linear relationship between the stoichiometric ratio of sorbent feed rate and the resulting conversion of acid pollutants. At the typical concentrations of HCl and SO_2 expected in WtE flue gas, a SR of sorbent equal to 1 was found to achieve a mean 27% HCl conversion and 83% SO_2 conversion, while a SR of 2 resulted in conversions of HCl and SO_2 respectively equal to 37% and 98%.

Since the introduction of a furnace injection of DS can be considered as an additional deacidification stage to the existing acid gas treatment line of a WtE facility, the developed model was used to identify the optimal feed rate of DS, *i.e.* the feed rate that minimises the overall operating costs of the line, for a WtE plant already equipped with a single or a two-stage acid gas treatment system. An optimum is generally present because the DS injected at high temperature, as opposed to calcium hydroxide or sodium bicarbonate injected at low temperature, has a higher relative reactivity towards SO_2 than HCl, hence it is complementary to the low-temperature sorbents, and it is cheaper than sodium bicarbonate, hence it is suitable as a pre-treatment step to limit the consumption of the more expensive reactant.

In particular, for WtE plants operating with furnace DS injection plus a single downstream acid gas removal stage, the optimal operating point consists in demanding a conversion of HCl in the range 16-23% from DS injection. Such an optimised feed rate of DS can achieve a reduction of operating costs, which was estimated as high as 13% when the concentration of SO_2 in the raw flue gas is relevant.

For WtE plants operating with furnace DS injection plus a downstream two-stage acid gas treatment system, the optimal feed rate of DS corresponds to a conversion of HCl in the range 9-20%, depending on the SO_2 concentration in the flue gas. The savings that may be obtained thanks to the use of DS were estimated to be limited (less than 10% reduction of operating costs even for flue gas with high SO_2 concentration). However, the DS injection can still be a valid addition in order to stabilise the operation of the multi-stage acid gas removal process, smoothing the variability of acid gas load coming from the combustion chamber.

The advantages of DS injection are confirmed even in the presence of uncertainties in the unit costs considered in the economic analysis. Overall, the dolomitic sorbent injection emerges as a useful technology to control acid gas emissions, particularly as a cost-effective retrofitting option to single-stage removal processes.

Acknowledgments

Plant operators involved in test runs at the two WtE facilities are gratefully acknowledged for the support in the execution of the test run campaign.

References

[1] P. Lu, Q. Huang, A.C. Bourtsalas, N.J. Themelis, Y. Chi, J. Yan, Review on fate of chlorine during thermal processing of solid wastes, J. Environ. Sci. 78 (2019) 13-28.

[2] M. Bal, T.T. Reddy, B.C. Maikap, Removal of HCl gas from off gases using self-priming venturi scrubber, J. Haz. Mat. 364 (2019) 406-418.

[3] A. Dal Pozzo, R. Moricone, A. Tugnoli, V. Cozzani, Experimental Investigation of the Reactivity of Sodium Bicarbonate toward Hydrogen Chloride and Sulfur Dioxide at Low Temperatures, Ind. Eng. Chem. Res. 58 (2019) 6316-6324.

[4] K.-D. Kim, S.-M. Jeon, N. Hasolli, K.-S. Lee, J.-R. Lee, J.-W. Han, H.-T. Kim, Y.-O. Park, HCl removal characteristics of calcium hydroxide at the dry-type sorbent reaction accelerator using municipal waste incinerator flue gas at a real site, Korean J. Chem. Eng. 34 (2017) 747-756.

[5] C. Li, Z. Jia, X. Ye, S. Yin, Simulation on deacidification performance of waste incinerator flue gas by rotating spray drying, Energy 152 (2018) 652-665.

[6] J. Vehlow, Air pollution control systems in WtE units: An overview, Waste Manage. 37 (2015) 58-74.

[7] A.L. Brooks, S. Wang, J.R. Jambeck, The Chinese import ban and its impact on global plastic waste trade, Sci. Adv. 4 (2018) eaat0131.

[8] W. Wang, N.J. Themelis, K. Sun, A.C. Bourtsalas, Q. Huang, Y. Zhang, Z. Wu, Current influence of China's ban on plastic waste imports, Waste Disposal Sust. Energy 1 (2019) 67-78.

[9] J. Van Caneghem, K. Van Acker, J. De Greef, G. Wauters, C. Vandecasteele, Waste-to-energy is compatible and complementary with recycling in the circular economy, Clean Technol. Environ. Policy 21 (2019) 925-939.

[10] European IPPC Bureau, Best Available Techniques (BAT) Reference Document for Waste Incineration. Technical draft, 2018. Available at: eippcb.jrc.ec.europa.eu/reference/BREF/WI/WI_BREF_FD_Black_Watermark.pdf (last accessed: 18/11/2019).

[11] S. Belosevic, I. Tomanovic, N. Crnomarkovic, A. Milicevic, D. Tucakovic, Numerical study of pulverized coal-fired utility boiler over a wide range of operating conditions for in-furnace SO_2/NO_x reduction, Appl. Thermal Eng. 94 (2016) 657-669.

[12] L. Shi, G. Liu, B.S. Higgins, L. Benson, Computational modeling of furnace sorbent injection for SO_2 removal from coal-fired utility boilers, Fuel Proc. Technol. 92 (2011) 372-378.

[13] B.G. Miller, Formation and Control of Sulfur Oxides, in: Clean Coal Engineering Technology. 2nd ed. Oxford: Butterworth-Heinemann, 2017, pp 467-506.

[14] M.J. Miller, Retrofit SO_2 and NO_X control technologies for coal-fired power plants. Environ. Prog. 5 (1986) 171-177.

[15] L.J. Muzio, G.R. Often, Assessment of Dry Sorbent Emission Control Technologies Part I. Fundamental Processes, JAPCA 37 (1987) 642-654.

[16] J. Cheng, J. Zhou, J. Liu, Z. Zhou, Z. Huang, X. Cao, X. Zhao, K. Cen, Sulfur removal at high temperature during coal combustion in furnaces: a review, Prog. Energy Combust. Sci. 29 (2003) 381-405.

[17] W.Z. Khan, B.M. Gibes, SOx emissions from a fluidized-bed combustor with and without limestone addition, Energy 21 (1996) 105-113.

[18] J. Zhou, J. Cheng, X. Cao, J. Liu, X. Zhao, Z. Huang, K. Cen, Experimental research on two-stage desulfurization technology in traveling grate boilers, Energy 26 (2001) 759-774.

[19] S. Petrini, H. Eklund, I. Bjerle, HCl-Absorption durch Kalkstein (in German), Aufbereitungstechnik 6 (1979) 309–311.

[20] G. Mura, A. Lallai, Reaction kinetics of gas hydrogen chloride and limestone, Chem. Eng. Sci. 49 (1994) 4491-4500.

[21] J. Partanen, P. Backman, R. Backman, M. Hupa, Absorption of HCl by limestone in hot flue gases. Part I: the effects of temperature, gas atmosphere and absorbent quality, Fuel 84 (2005) 1664-1673.

[22] R.H. Borgwardt, Sintering of nascent calcium oxide, Chem. Eng. Sci. 44 (1989) 53-60.

[23] A.M. Kierzkowska, R. Pacciani, C.R. Müller, CaO-Based CO_2 Sorbents: From Fundamentals to the Development of New, Highly Effective Materials, ChemSusChem 6 (2013) 1130-1148.

[24] B. Shemwell, Y.A. Levendis, G.A. Simons, Laboratory study on the high-temperature capture of HCl gas by dry-injection of calcium-based sorbents, Chemosphere 42 (2001) 785-796.

[25] A.A. Patsias, W. Nimmo, B.M. Gibbs, P.T. Williams, Calcium-based sorbents for simultaneous NOx /SOx reduction in a down-fired furnace, Fuel 84 (2005) 1864-1873.

[26] B. Courtemanche, Y.A. Levendis, Control of the HCl Emissions from the Combustion of PVC by In-Furnace Injection of Calcium-Magnesium-Based Sorbents, Environ. Eng. Sci. 15 (1998) 123-135.

[27] Y.A. Levendis, W. Zhu, D.L. Wise, G.A. Simons, Effectiveness of calcium magnesium acetate as an SO_X sorbent in coal combustion, AIChE J. 35 (1993) 30-36.

[28] J.M. Valverde, P.E. Sanchez-Jimenez, L.A. Perez-Maqueda, Ca-looping for postcombustion CO_2 capture: A comparative analysis on the performances of dolomite and limestone, Appl. Energy 138 (2015) 202-215.

[29] R. Moreschi, R. Marras, International patent n° WO/2014/080373, 2014. Available at: https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2014080373&tab=PCTBIBLIO (accessed 03/09/2019).

[30] L. Biganzoli, G. Racanella, L. Rigamonti, R. Marras, M. Grosso, High temperature abatement of acid gases from waste incineration. Part I: Experimental tests in full scale plants, Waste Manage. 36 (2015) 98-105.

[31] A. Dal Pozzo, D. Guglielmi, G. Antonioni, A. Tugnoli, Environmental and economic performance assessment of alternative acid gas removal technologies for waste-to-energy plants, Sustainable Prod. Consumption 16 (2018) 202-215.

[32] CEN, EN 14181:2014—Stationary source emissions—quality assurance of automated measuring systems, Brussels (2014).

[33] T.O.M. Smith, R.A. Robinson, M.D. Coleman, Modelling European quality assurance procedures for analysers monitoring emissions under the EU's Industrial Emissions Directive, Accreditation and Quality Assurance 24 (2019) 443-449.

[34] European Parliament, Directive 2010/75/EU on industrial emissions (integrated pollution prevention and control), Off J Eur Union L 334 (2010) 17–119.

[35] P.J. Rousseeuw, Least Median of Squares Regression, J. Am. Stat. Assoc. 79 (1984) 871–880.

[36] R. Filitz, A.M. Kierzkowska, C.R. Müller, Highly Efficient CO_2 Sorbents: Development of Synthetic, Calcium-Rich Dolomites, Environ. Sci. Technol. 46 (2012) 559-565.

[37] A. Dal Pozzo, G. Antonioni, D. Guglielmi, C. Stramigioli, V. Cozzani, Comparison of alternative flue gas dry treatment technologies in waste-to-energy processes, Waste Manage. 51 (2016) 81-90.

[38] A. Dal Pozzo, A. Armutlulu, M. Rekhtina, C.R. Müller, V. Cozzani, CO_2 Uptake Potential of Ca-Based Air Pollution Control Residues over Repeated Carbonation–Calcination Cycles, Energy Fuels 32 (2018) 5386-5395.

[39] M. Margallo, M.B.M. Taddei, A. Hernandez-Pellon, R. Aldaco, A. Irabien, Environmental sustainability assessment of the management of municipal solid waste incineration residues: a review of the current situation, Clean Technol. Environ. Policy 17 (2015) 1333-1353.

[40] L. Ninane, J.F. Adam, C. Humblot, Method for Producing an Aqueous Industrial Sodium Chloride Solution, U.S. Patent 5478447, 1995.

[41] T. Chin, R. Yan, D. T. Liang, J.H. Tay, Hydrated Lime Reaction with HCl under Simulated Flue Gas Conditions, Ind. Eng. Chem. Res. 44 (2005) 3742-3748.

[42] R. Han, F. Sun, J. Gao, S. Wei, Y. Su, Y. Qin, Trace Na_2CO_3 Addition to Limestone Inducing High-Capacity SO_2 Capture, Environ. Sci. Technol. 51 (2017) 12692-12698.

[43] P. Quicker, M. Rotheut, Y. Noel, M. Schulten, U. Athmann, Treating WTE Plant Flue Gases with Sodium Bicarbonate, Power 158 (2014) 59-63.

Supplementary Material

Click here to download Supplementary Material: SupplementaryMaterial_Depurcal_JHM.docx

*Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CREDIT AUTHOR STATEMENT

Techno-economic performance of HCl and SO_2 removal in waste-to-energy plants by furnace direct sorbent injection

Alessandro Dal Pozzo, Lorenzo Lazazzara, Giacomo Antonioni, Valerio Cozzani *
LISES - Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater Studiorum - Università di Bologna, via Terracini n.28, 40131 Bologna, Italy

* *corresponding author*, Tel. +39-051-2090240, Fax +39-051-2090247, e-mail: valerio.cozzani@unibo.it

Alessandro Dal Pozzo: conceptualization, methodology, investigation, formal analysis, writing - original draft.
Lorenzo Lazazzara: investigation, formal analysis
Giacomo Antonioni: methodology, formal analysis
Valerio Cozzani: conceptualization, methodology, supervision, writing - review and editing

*Novelty Statement (maximum limit:100 words)

STATEMENT OF NOVELTY

Techno-economic performance HCl and SO_2 removal in waste-to-energy plants by furnace direct sorbent injection

Alessandro Dal Pozzo, Lorenzo Lazazzara, Giacomo Antonioni, Valerio Cozzani *

LISES - Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater Studiorum - Università di Bologna, via Terracini n.28, 40131 Bologna, Italy

* *corresponding author*, Tel. +39-051-2090240, Fax +39-051-2090247, e-mail: valerio.cozzani@unibo.it

Direct furnace injection of a dolomitic sorbent may be a viable cost-effective technique to improve removal of acid gases in waste-to-energy plants, required by the oncoming new release of Best Available Techniques conclusions. However, apart from laboratory-scale results, no full-scale data is reported in the literature to assess the actual performance of such technology and optimal operational parameters. The present study, based on a full-scale campaign, carried out a first, systematic assessment of the effectiveness of adding furnace sorbent injection to different flue gas treatment processes, establishing a quantitative correlation between feed rate of reactant and resulting HCl/SO_2 conversion.