



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

ARCHIVIO ISTITUZIONALE
DELLA RICERCA

Alma Mater Studiorum Università di Bologna Archivio istituzionale della ricerca

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

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Dal Pozzo A., Lazazzara L., Antonioni G., Cozzani V. (2020). Techno-economic performance of HCl and SO₂ removal in waste-to-energy plants by furnace direct sorbent injection. JOURNAL OF HAZARDOUS MATERIALS, 394, 1-13 [10.1016/j.jhazmat.2020.122518].

Availability:

This version is available at: <https://hdl.handle.net/11585/790984> since: 2021-01-24

Published:

DOI: <http://doi.org/10.1016/j.jhazmat.2020.122518>

Terms of use:

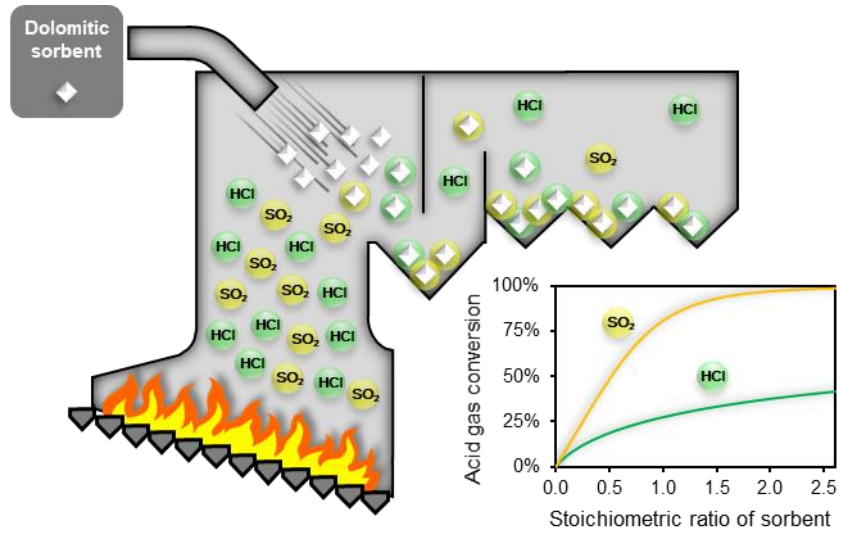
Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

1
2
3
4
5

Graphical Abstract



6
7
8

HIGHLIGHTS

Techno-economic performance of HCl and SO₂ 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

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

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 SO₂). 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 SO₂ 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 SO₂ 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.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

Techno-economic performance of HCl and SO₂ 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 SO₂). 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 SO₂ 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 SO₂ 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.

35 1. Introduction

36 Acid gases such as HCl and SO₂ are typical pollutants formed in waste combustion,
37 whenever chlorine and sulphur are present in the waste feed [1]. Control of their emission in
38 waste-to-energy (WtE) facilities is performed by reaction with neutralising agents, supplied
39 either as absorbent solutions in wet scrubbing equipment or as powdered alkaline sorbents
40 in dry injection systems [2-6].

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

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

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

57 FSI was first introduced as a desulfurisation technique in coal combustion [14,15]. The
58 sorbent, typically limestone, is blended with coal or injected with staged air [16]. Once
59 introduced in the furnace at high temperature, limestone is calcined to calcium oxide (CaO),
60 with the development of a porous structure that increases its reactivity towards acid gases.
61 SO₂ removal efficiencies in the range 40-70% are expected [17,18]. Petrini et al. [19], Mura
62 and Lallai [20] and Partanen et al. [21] demonstrated experimentally the suitability of high
63 temperature reaction with limestone also for HCl capture. However, the reactivity of
64 limestone at high temperature is hindered by pronounced sintering [22]. The onset of
65 sintering for calcium carbonate occurs at $T \sim 500$ °C [23], whereas the injection near to the
66 combustion area exposes the sorbent at temperatures ranging from 800 to 1200 °C. Upon
67 sintering, the porous structure of the sorbent collapses and the surface area decreases,
68 leading to a reduced sorption activity. Alternative Ca-based sorbents, as organic calcium
69 salts [24,25] or, specifically, calcium magnesium acetate [26,27] have been proposed with
70 the aim of achieving higher acid gas removal efficiency thanks to superior surface areas.

71 More recently, commercial sorbents derived from dolomite rock have been introduced, with
72 the aim of overcoming the limitations of limestone. The presence of magnesium confers a
73 higher resistance to sintering [28] and reduces the clogging and fouling that the deposition of
74 limestone residues typically causes to boilers [29]. Biganzoli et al. [30] offered a first
75 quantitative assessment of the full-scale acid gas removal performance of a dolomitic
76 sorbent, carrying out a test campaign in four Italian WtE facilities. They observed that a
77 furnace sorbent injection at a feed rate of 6 kg/t_{waste} yielded a reduction of acid gas
78 concentration downstream of the boiler in the range 7–37% for HCl and 34–95% for SO₂.

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

82 effectiveness of reactant injection towards HCl and SO₂ was systematically investigated by
 83 full-scale test runs carried out in two Italian WtE facilities. The experimental data were used
 84 to develop a specific phenomenological model for removal efficiency with respect to sorbent
 85 feed and initial acid gas concentrations. The model was used to assess the economics of the
 86 process, also considering the other acid gas treatment stages and the composition of the
 87 inlet flue gas stream.

88
 89

90 **2. Materials and methods**

91

92 **2.1 The dolomitic sorbent**

93 The solid reactant tested in the experimental campaign, commercially known as Depurcal
 94 and supplied by Unicalce SpA (Italy), is obtained via the calcination and slaking of dolomite
 95 rock. The reactant, referred to as dolomitic sorbent (DS) in the following, is mainly composed
 96 of calcium hydroxide (Ca(OH)₂), magnesium hydroxide (Mg(OH)₂) and magnesium oxide
 97 (MgO). According to patent information [29], an average composition on mass basis of the
 98 DS is the following: 58.2% Ca(OH)₂, 22.3% Mg(OH)₂, 19.2% MgO and 0.3% impurities
 99 (SiO₂, Fe₂O₃, Al₂O₃).

100

101 **2.2. Reference WtE plants**

102 The experimental assessment of DS performance was carried out in two Italian WtE
 103 facilities, here referred to as plant A and plant B. The key features of the two plants are
 104 summarised in Table 1, while the layout of their acid gas treatment systems is sketched in
 105 Figure 1. With respect to acid gas removal, plant A presents a two-stage treatment system
 106 (Fig. 1a), consisting in the injection of calcium hydroxide, Ca(OH)₂, and sodium bicarbonate,
 107 NaHCO₃, respectively in two consecutive sections of reaction and filtration. Hence, the
 108 introduction of a FSI of the dolomitic sorbent realises a three-stage acid gas removal system.
 109 Conversely, plant B is equipped with a single acid gas treatment stage fed with sodium
 110 bicarbonate (Fig. 1b). Here, the FSI of the dolomitic sorbent introduces a second stage of
 111 acid gas removal.

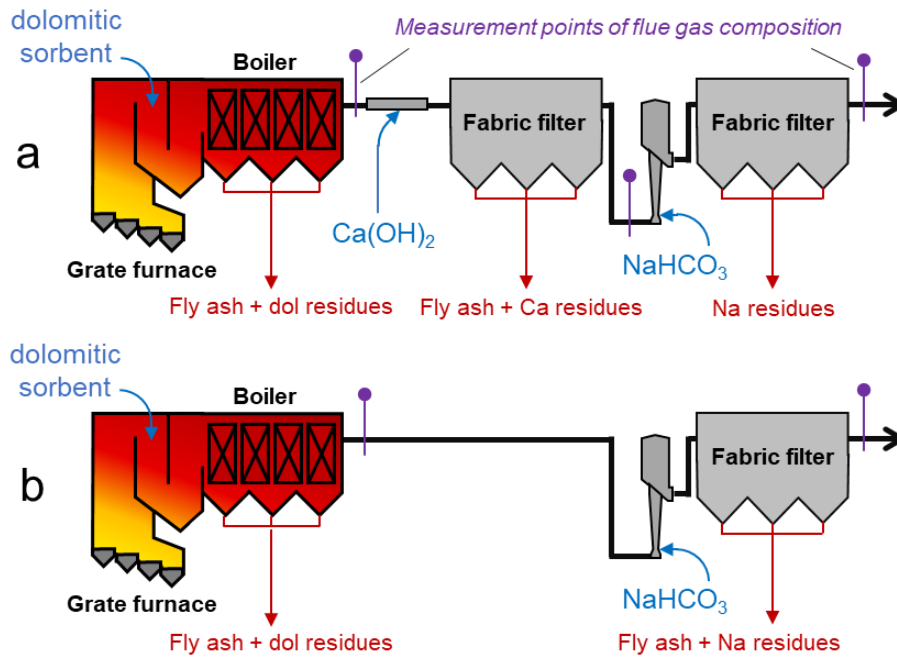
112 The acid gas treatment lines of the two selected facilities represent two of the most common
 113 configurations for WtE flue gas treatment [31] and are both listed among the best available
 114 techniques for waste incineration [10]. The reactions between the solid sorbents and the acid
 115 gases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

116

117 **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

118



119
120

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

126

127 2.3 Test configurations and protocols

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

137

138 2.3.1 Test runs in specific operating conditions

139 The relationship between DS feed rate and HCl/SO_2 removal was analysed quantitatively by
140 dedicated test runs. The test runs were carried out injecting the reactant at incremental steps
141 of constant feed rate for defined time intervals. The steps of feed rate tested were: 40, 60,
142 90, 100 and 200 kg/h for plant A, ranging from to 0.36 to $1.8 \text{ kg}/10^3 \text{ Nm}^3$; 40, 120 and 200
143 kg/h for plant B, ranging from 0.62 to $3.1 \text{ kg}/10^3 \text{ Nm}^3$. The injection of reactant was stopped
144 for 40 min between each feed rate step to allow monitoring the acid gas concentrations in
145 the untreated gas and to avoid any residual effect of the injected DS in the previous step of
146 feed rate on the following step. Table 2 provides the list of all the tests completed.

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

150 of HCl or SO₂ related to each step of DS feed rate was calculated from the difference in acid
 151 gas concentration before and after the start of DS injection:

152
$$\frac{C_{\text{acid gas, w/o DS}} - C_{\text{acid gas, w DS}}}{C_{\text{acid gas, w/o DS}} - C_{\text{acid gas, w DS}}}$$
 (1)

153 where $C_{\text{acid gas, w/o DS}}$ is the concentration measured in the minute before DS injection and C_{acid}
 154 $_{\text{gas, w DS}}$ is the pseudo-stationary concentration measured during DS injection after the
 155 transient of concentration decrease was concluded. Similarly, the conversion of acid gases
 156 related to each step of DS feed rate was also calculated when DS injection was stopped. In
 157 these cases, $C_{\text{acid gas, w DS}}$ was taken as the concentration measured in the minute before the
 158 interruption of DS injection, while $C_{\text{acid gas, w/o DS}}$ was the pseudo-stationary concentration
 159 measured after DS injection was interrupted and the concentration increase transient was
 160 concluded.

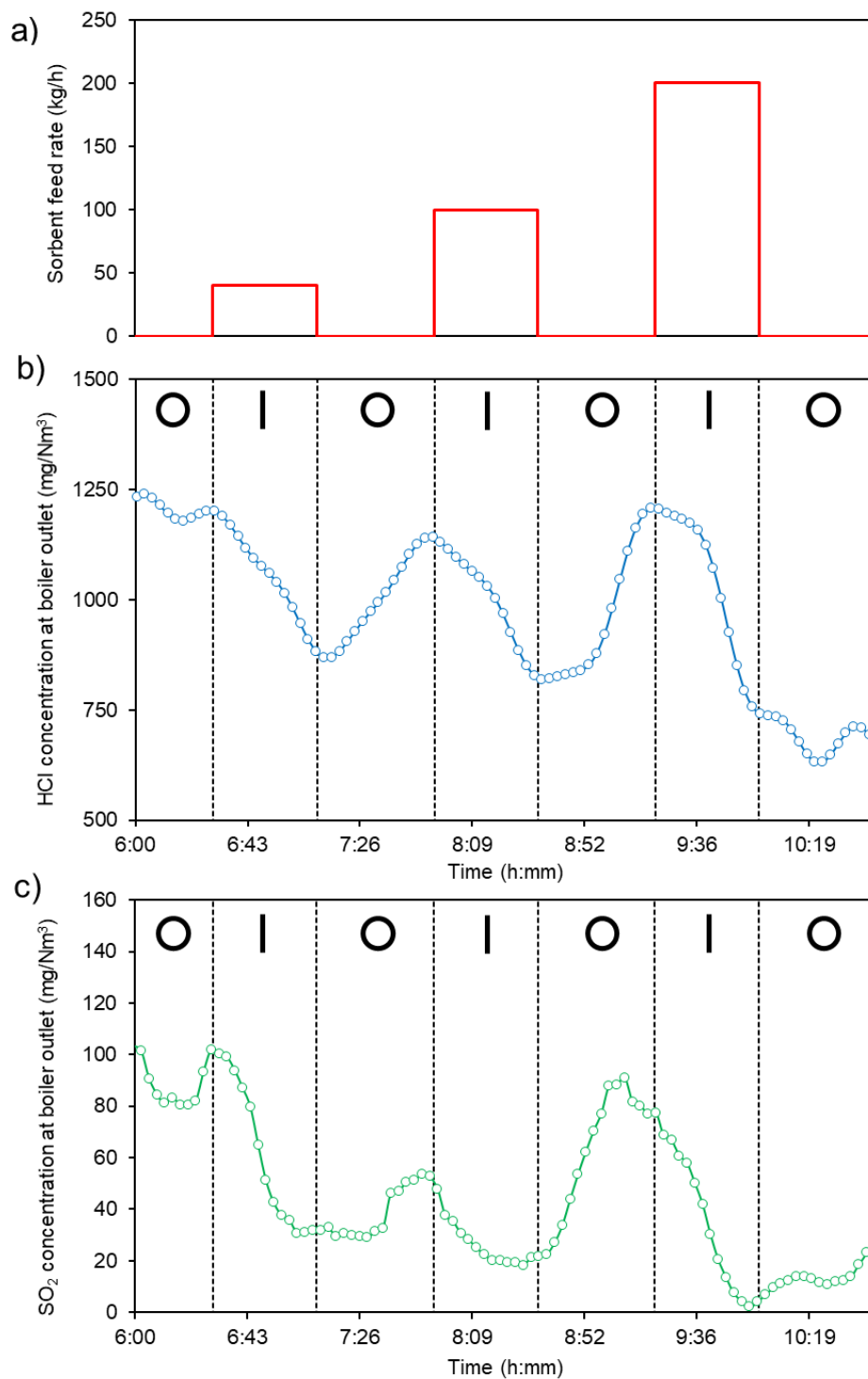
161 A screening protocol was established to accept the experimental data, given the uncertainty
 162 due to fluctuations in acid gas concentration formed in combustion flue gas. The exclusion of
 163 outliers (i.e. data for which an abrupt variation of HCl and SO₂ generated by waste
 164 combustion either covers or magnifies the effect of DS injection) was performed during
 165 model fitting by least trimmed squares regression [35], as described in section 3.1.

166
 167 **Table 2.** Test runs performed and steps of reactant feed rate.

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

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

170



171
 172 **Figure 2.** (a) Feed rate of dolomitic sorbent, and corresponding (b) HCl and (c) SO₂ outlet
 173 concentration during test 3A. The symbols I and O indicate respectively the time intervals
 174 with and without DS injection. Dots are 5-min moving average values of measured
 175 concentration.

176
 177
 178
 179
 180

181

182 *2.3.2 Test run in normal operating conditions*

183 In plant A, the injection of DS was also tested for 3 consecutive months during normal
184 operation of the facility. DS was fed to the flue gas treatment line at a constant feed rate of
185 60 kg/h (0.55 kg reactant/10³ Nm³ of flue gas, considering the average flow rate reported in
186 Table 1). The values of HCl and SO₂ concentration at the boiler outlet, continuously
187 monitored by the FTIR device during the test period, were collected and compared to the
188 same data measured in the previous 3 months of operation without DS injection. The
189 comparison was made considering for the two periods the distribution of the hourly averages
190 of concentration values. **The overall 3-month average concentration in the period \bar{C}_{period} and
191 the related standard deviation σ_{period} were calculated starting from the hourly average
192 concentrations, as follows:**

193 _____ (2)

194 _____ (3)

195

196 **The total cumulative mass flow of HCl and SO₂ at the boiler outlet over the 3 months was
197 also compared between the two periods.**

198 The main objective of this analysis was to assess the global effect of the dolomitic sorbent in
199 reducing the average concentration of acid gases exiting the combustion chamber. **This
200 comparison is based on** the underlying assumption that the average concentration of acid
201 pollutants in the raw flue gas upstream of DS injection during the 3 months of DS injection is
202 approximately the same as that measured at the boiler outlet in the previous 3 months
203 without DS injection. **This assumption is valid only if there is no significant seasonal effect in
204 waste composition that varies the raw HCl and SO₂ concentration between a 3-month period
205 and the following.** The validity of this assumption was checked by comparing the
206 concentration data at boiler outlet for the same two 3-month periods in the previous year
207 (referred to in the following as ‘control year’), when no DS testing was carried out. As
208 discussed in section 4.1, no appreciable variation of acid gas concentration at boiler outlet
209 was found between the two 3-month periods of the control year.

210

211

212 **3. Models**

213

214 **3.1 Modelling of the performance of dolomitic sorbent**

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

218 _____ (4)

219 The development of the porous structure promotes the reactivity of the sorbent towards acid
220 gases. The possible reactions with HCl and SO₂ are the following:

221 _____ (5)

222 (6)

223 (7)

224 (8)

225 However, it is generally assumed that MgO is chemically inert to acid gases at the
226 temperatures of interest (800-1000 °C), on the basis of experimental findings at laboratory
227 [21] and pilot scale [15]. A wide literature on the high-temperature CO₂ sorption by dolomitic
228 compounds provides similar evidence [23,36]. In addition, a thermodynamic analysis of
229 reactions 5-8, shown in section S1 of the Supplementary Material, confirms that, at
230 temperatures higher than 900°C, only the reactions between acid gases and the Ca-based
231 phase of the sorbent present a negative Gibbs free energy of reaction. Therefore, in the
232 activated dolomitic sorbent after reaction 4, it is considered that CaO is the reactive
233 compound towards acid gases, while MgO acts almost exclusively as structural agent,
234 preventing the collapse of the porous structure developed in reaction 4, as suggested by
235 Biganzoli et al. [30].

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

241 _____ (9)

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

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

251 _____ (10)

252 Linear regression was then used to fit the model to the test run data and the least trimmed
253 squares procedure [35] for outlier exclusion was applied until a satisfactorily high value of R^2
254 was obtained for the fitted model ($R^2 > 0.99$ for HCl, $R^2 > 0.95$ for SO₂).

255 In order to apply the model to the dolomitic sorbent, it was assumed that its sorption capacity
256 towards acid gases is entirely ascribed to the Ca-based fraction (*i.e.* Ca(OH)₂ that
257 decomposes to CaO upon furnace injection), while the Mg-based compounds (MgO,
258 Mg(OH)₂) have only the role to avoid the high-temperature sintering of the material and do
259 not participate to the gas-solid reactions, **as discussed above**. Therefore, the SR was
260 defined on the basis of the Ca content in the sorbent. According to the typical composition of
261 the sorbent reported in section 2.1, the weight fraction of Ca(OH)₂ in the DS is 0.58. A
262 weight fraction of 0.42 is obtained when considering the amount of CaO formed from
263 hydroxide dehydration at high temperature after DS injection in the furnace. It was thus

300 different repartitions of abatement between the stages were explored in the simulations,
 301 because each sorbent has a different relative reactivity towards HCl and SO₂. Nonetheless,
 302 given the significantly lower amount of SO₂ compared to HCl in the raw flue gases
 303 considered in Table 3, the concentration of SO₂ at stack resulted similar and lower than 1
 304 mg/Nm³ in all the simulations.

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

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

312 (13)

313 where C_{reactants} and C_{residues} are the costs respectively associated to the purchase of reactant
 314 and the management of process residues for each treatment stage. The values adopted for
 315 the unit costs are listed in Table 4. These numbers are average values for the Italian
 316 context. For a detailed overview on the cost data of dry acid gas treatment operations the
 317 reader is referred to Dal Pozzo et al. [37]. Here, it is worth recalling that the management
 318 of process residues is associated to two different fates and costs. Streams of residues
 319 that are mixed with fly ash coming from the combustion chamber and potentially
 320 carrying hazardous materials in traces (heavy metals, organochlorinated compounds)
 321 are to be sent to dedicated landfill sites [38,39]. Hence, recalling the schemes in Figure
 322 1, this is the case for the residues of dolomitic sorbent, calcium hydroxide, and
 323 sodium bicarbonate, if no upstream dedusting equipment is installed (see Fig. 1b).
 324 Conversely, the process residues generated by the reaction between sodium bicarbonate
 325 and acid pollutants can be sent to dedicated recycling facilities [40] if a fabric filter is
 326 installed upstream of NaHCO₃ injection to collect separately the fly ash (see Fig. 1a).

327

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

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

329

330

331 4. Results and discussion

332

333 4.1 Test run in normal operating conditions: effect of DS injection on the 334 concentration of HCl and SO₂ leaving the furnace

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

337 furnace/boiler. The outcome of the test run on plant A in normal operating conditions was
338 evaluated comparing the hourly data of HCl and SO₂ concentrations in the gas at the boiler
339 outlet (first sampling point in Figure 1a) for the two 3-month periods with and without DS
340 injection, as described in the sampling protocol of section 2.3.2.

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

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

349 More specifically, the cumulated mass flow curves in Fig. 3a trace how the hourly data of
350 HCl concentration measured at the boiler outlet contributed to the total mass flow in the two
351 3-month periods. The concentration of HCl measured at the sampling point fluctuates over
352 time as a natural consequence of the variable Cl content of the waste burnt in the furnace: in
353 this plant, Fig. 3a shows that during the 3-month period without DS injection the HCl
354 concentration varied mostly from 400 to 1500 mg/Nm³ with peaks up to 3000 mg/Nm³. In the
355 3 months of DS injection this range of variation moved towards lower values (the cumulated
356 mass flow curve with DS injection is shifted leftward compared to that for the period without
357 DS injection). This is further clarified by the distributions of the hourly averages of HCl
358 concentration at the boiler outlet for the two reference periods shown in Fig. 3b. The hourly
359 values of HCl concentration recorded at the boiler outlet during the two 3-month periods
360 were subdivided in the 5 classes of the figure. For each class, the frequency of occurrence
361 of concentration values within that class range is reported as percent of the total hourly
362 concentration data in the 3-month period. The furnace injection of DS clearly resulted in a
363 shift of the distribution of HCl concentration towards lower values. With DS injection, the
364 frequency of concentrations higher than 800 mg/Nm³ is more than halved, while the
365 occurrence of concentrations in the interval 400-600 mg/Nm³ is approximately tripled.

366 The overall 3-month average of the hourly HCl concentration data at the boiler outlet with DS
367 injection resulted of 702 mg/Nm³, compared to a value of 897 mg/Nm³ for the 3-month
368 period without DS injection. This corresponds to an average 22% reduction of the HCl load
369 leaving the combustion chamber thanks to the DS effect. Furthermore, also the standard
370 deviation of the hourly HCl concentration data exhibited a noticeable decrease: a value of
371 287 mg/Nm³ was obtained during DS injection, with respect to a value of 323 mg/Nm³ in the
372 period without DS injection. A reduction of the standard deviation means that the hourly HCl
373 concentration values at the sampling point were less dispersed during DS injection and,
374 thus, less peaks at high HCl concentration were present compared to the period without DS
375 injection.

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

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

387 The results observed with reference to SO₂ are similar to those obtained for HCl. Fig.
388 3c shows that the cumulative mass flow of SO₂ in the 3 months of DS injection was
389 equal to 5.3t, a 37% reduction compared to the 8.4 t calculated for the 3-month period
390 without DS injection.

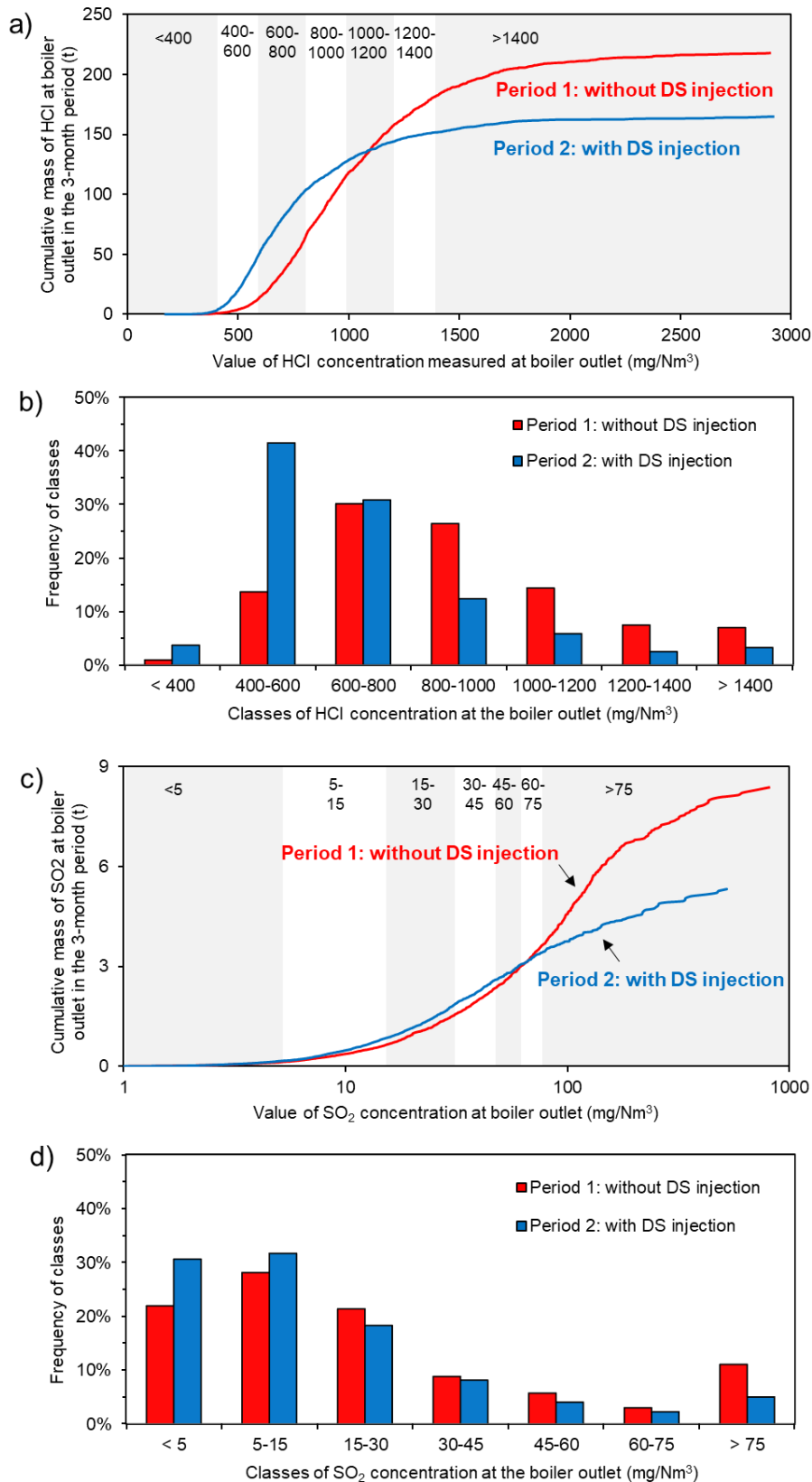
391 It is evident that during DS injection, as observed for HCl, lower SO₂ concentrations at
392 the sampling point appeared more frequently than in the reference period without DS
393 injection. As shown in Fig. 3d, more than 60% of the hourly SO₂ concentration data
394 measured in the period with DS injection show values lower 15 mg/Nm³, while the
395 occurrences in all the frequency classes higher than 15 mg/Nm³ diminish systematically
396 compared to the period without DS injection.

397 The overall 3-month average of the hourly SO₂ concentration data at the boiler outlet in the
398 3-month period with DS injection resulted of 22.7 mg/Nm³, compared to a value of 31.4
399 mg/Nm³ without DS injection (a 28% reduction). Again, also the standard deviation of the
400 hourly SO₂ concentration data was noticeably lower during DS injection: 40.6 mg/Nm³ vs.
401 52.6 mg/Nm³.

402 For the control year (see section S2 in the Supplementary Material), no significant difference
403 in the global 3-month average concentration was recorded: the average SO₂ concentration
404 at the boiler outlet was 32.1 mg/Nm³ in the first period and 31.0 mg/Nm³ in the
405 second period. The total mass flow of SO₂ measured in the 3 months varied less than 2%
406 between the two periods. Again, it is confirmed that in normal operation the overall
407 conditions at the boiler outlet remains generally constant between contiguous 3-month
408 periods, thus the observed reduction of HCl and SO₂ mass flow for the 3 months of
409 DS testing can be reasonably ascribed to the effect of DS injection.

410

411



412
 413
 414
 415
 416
 417

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 SO₂ at the boiler outlet in the two periods; d) distribution of the hourly averages of SO₂ concentration at the boiler outlet in the two periods.

418 **4.2 Test runs in specific operating conditions: effect of DS feed rate**

419 As introduced in section 2.3.1, the test runs at specific operating conditions were carried
420 out varying the feed rate of the DS injected in the furnace. The objective of this specific
421 set of test runs was to collect data with a finer time resolution than the macroscopic
422 analysis of section 4.1 and to provide a quantitative evaluation of the relation between
423 feed rate of reactant and removal efficiency of the acid pollutants. The test runs allowed
424 collecting data on the difference in HCl and SO₂ concentration measured at the sampling
425 point before and after DS injection at different feed rates, hence obtaining a dataset
426 of HCl and SO₂ conversion at different SR of dolomitic sorbent injection. Tables S2 and
427 S3 in section S3 of the Supplementary Material report the complete datasets obtained,
428 which were used to calibrate the phenomenological model developed for acid gas
429 conversion. The detailed results of all the test runs are also provided in section S3 of the
430 Supplementary Material.

431

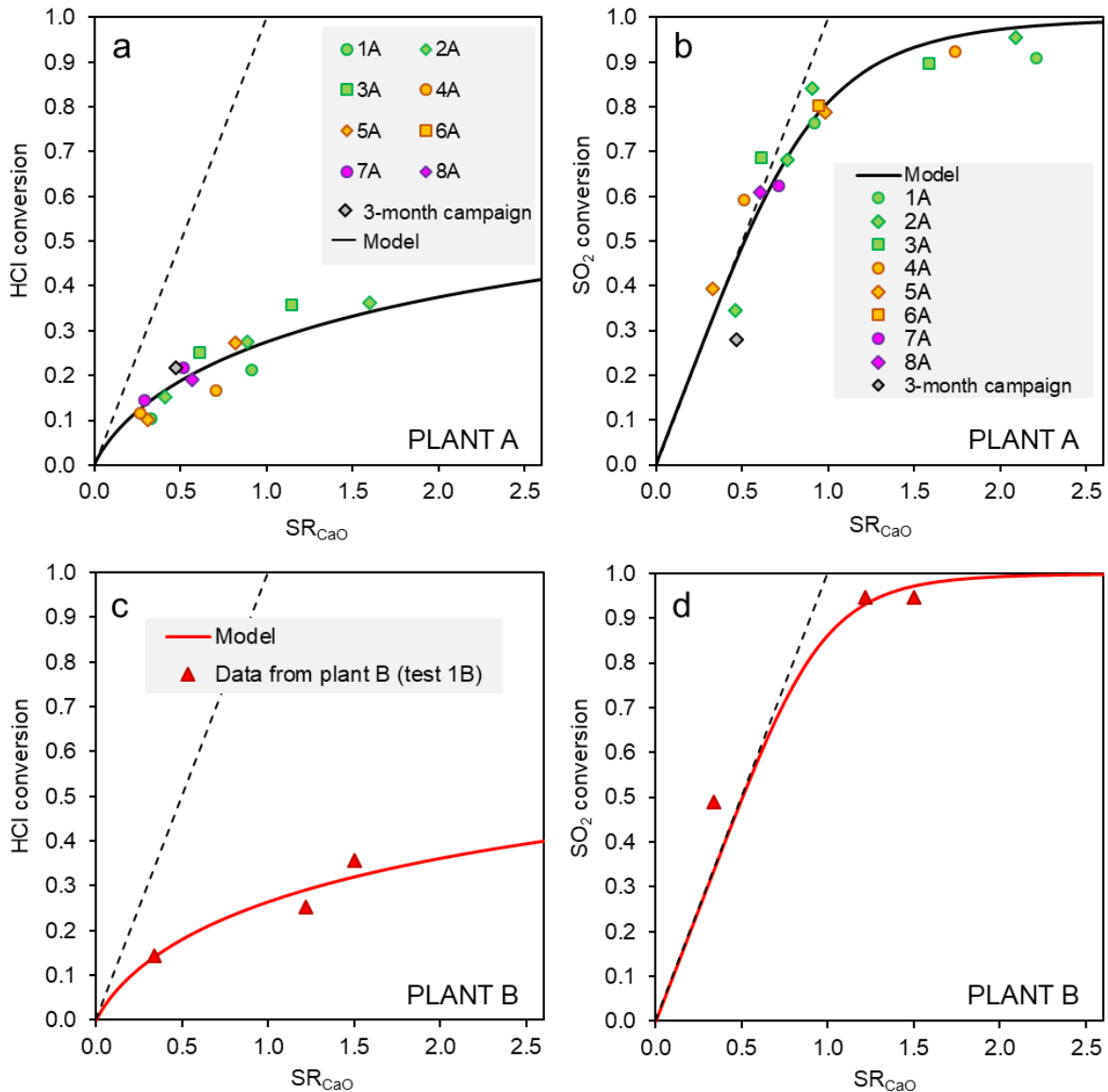
432 **4.3 Model results**

433 The datasets related to plant A and plant B obtained from the test runs were used
434 to calibrate the phenomenological model presented in section 3.1 and to determine the
435 values of parameter n for the two acid pollutants. As mentioned in section 3.1, the least
436 trimmed squares method was adopted for concurrent outlier exclusion and model
437 fitting. The following values of n were obtained for plant A: 1.38 for HCl and 5.26
438 for SO₂. The corresponding values of n obtained for plant B are: 1.36 for HCl and 7.29 for
439 SO₂.

440 The fitting of calibration data points for plant A is shown in Fig. 4a and 4b, for HCl and
441 SO₂ sorption respectively. Only the sample points after outlier removal are reported,
442 while the complete dataset is presented in section S3 of the Supplementary Material. An
443 additional data point representing the average performance of the dolomitic sorbent during
444 the 3-month campaign analysed in section 4.1 is also reported in the figure, showing
445 a quite good alignment with the data from the test run campaign. Fig. 4c and 4d reports
446 the fitting of data points for plant B.

447 In relative terms, the dolomitic sorbent shows a markedly higher sorption capacity
448 towards SO₂ than towards HCl. Hence, the DS behaves differently than the reactants
449 injected at low temperatures (calcium hydroxide and sodium bicarbonate), which exhibit a
450 higher reactivity towards HCl (see data in section S4 of the Supplementary Material).

451 In absolute terms, the reactivity of the DS via furnace injection towards SO₂ is
452 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.

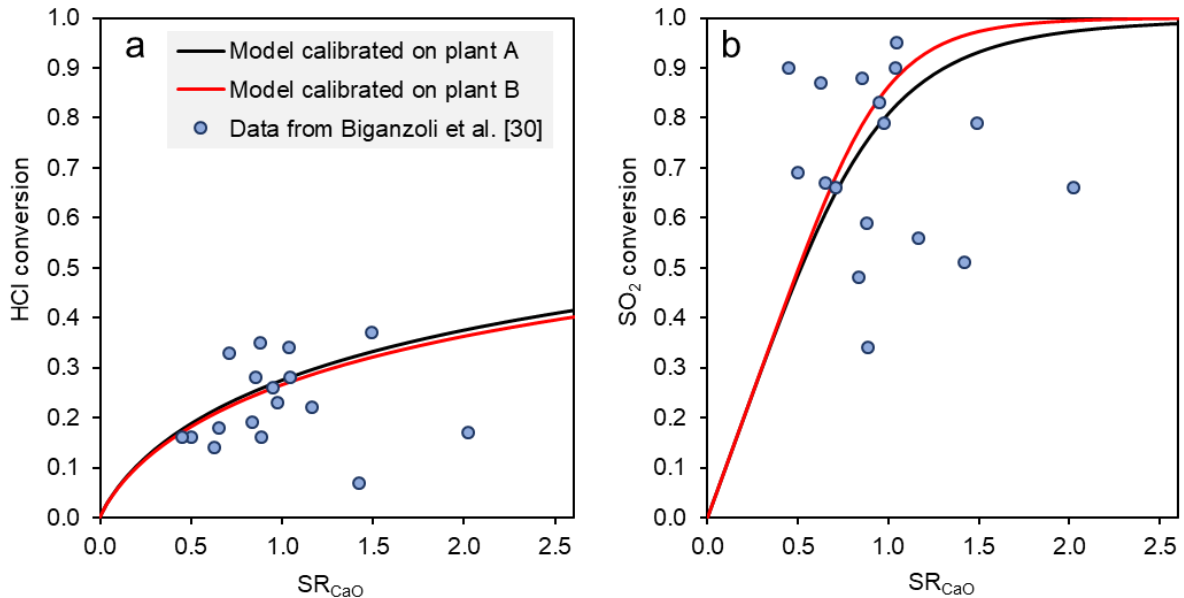


453
 454 **Figure 4.** Phenomenological model results (continuous line) compared to calibration data for
 455 plant A: a) HCl removal, b) SO₂ removal; and plant B: c) HCl removal, d) SO₂ removal.
 456 The dotted line corresponds to stoichiometric efficiency.

457
 458 The model results for plant A and plant B were compared to each other in Fig. 5. The
 459 tests on plant B had the main intent to confirm the general trends identified on plant A.
 460 Indeed, the model curve obtained fitting the data points available for plant B appears quite
 461 similar to the model curve obtained for plant A. Clearly enough, the semi-empirical nature
 462 of the model implies that its calibration parameter, n , is site-specific, thus valid only for the
 463 description of the performance of the plant where the model was calibrated via test runs.
 464 However, the results in Fig. 5 confirm that the model has the potential to fit (after a
 465 specific tuning) experimental results across different WtE facilities, with different
 466 capacity, layout and average acid gas loads.

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

470 by calculating the SR of DS injection from the information on reactant feed rate and acid gas
471 concentrations given by the authors, under the assumptions of section 3.1.
472 At least for HCl, there is a fairly good agreement between the model results and the
473 experimental data set by Biganzoli et al. [30], even if no specific tuning of the model was
474 made. This further supports the comparability of HCl removal efficiency data by DS furnace
475 injection across different WtE facilities.
476 With respect to SO₂, the data by Biganzoli et al. [30] exhibit a much wider scatter than those
477 presented in Fig. 4b, arguably owing to the uncertainty associated to the lower and more
478 variable loads of this pollutant formed in waste combustion across different WtE plants. In
479 that regard, a merit of the test runs of the present study is to offer a robust and ample set of
480 homogeneous data on SO₂ removal by DS injection obtained in a single WtE plant (Fig. 4b).
481 In general, the analysis of the results in Fig. 5 support the robustness of the experimental
482 and modelling approach adopted in the present study.
483 In addition, the data of Fig. 4 are of clear interest for WtE operators, because only full-scale
484 testing can assess the performance of sorbent in presence of specific process conditions
485 (e.g. fluid-dynamics of the process in the furnace/boiler environment, interference between
486 gas species, morphological evolution of sorbent particles injected in the furnace) that are not
487 easily reproducible at laboratory scale. For instance, laboratory data available for the
488 dolomitic sorbent [29], collected in a fixed bed reactor at 900 °C, showed a conversion of
489 SO₂ in the range 78-82% (tests in SO₂/N₂ atmosphere, SO₂ inlet concentration of 1070
490 mg/Nm³, SR_{CaO} = 2) and a conversion of HCl in the range 67-72% (tests in HCl/N₂
491 atmosphere, HCl inlet concentration of 1430 mg/Nm³, SR_{CaO} = 2). The present full-scale
492 results demonstrated that the conversion of HCl that should be expected in a real furnace is
493 lower than the laboratory results (here, a SR_{CaO} = 2 corresponds to a HCl conversion slightly
494 lower than 40%; see Fig. 4). Conversely, the conversion of SO₂ registered at full-scale is
495 higher than that observed at laboratory scale (here, a SR_{CaO} = 2 corresponds to a SO₂
496 conversion higher than 90%; see Fig. 4), presumably owing to the significantly lower
497 concentration of SO₂ typically measured at plant (< 200 mg/Nm³) compared to the value
498 adopted in laboratory, and a possible synergic effect on SO₂ sorption given by the presence
499 of HCl or its product of reaction CaCl₂ [41,42]. It is thus clear that the quantification of
500 removal efficiencies at full scale is necessary to obtain reliable data for the economic
501 assessment.
502



503
504
505
506
507
508

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.

509
510
511
512
513
514
515
516

4.4 Optimisation of multi-stage acid gas removal processes

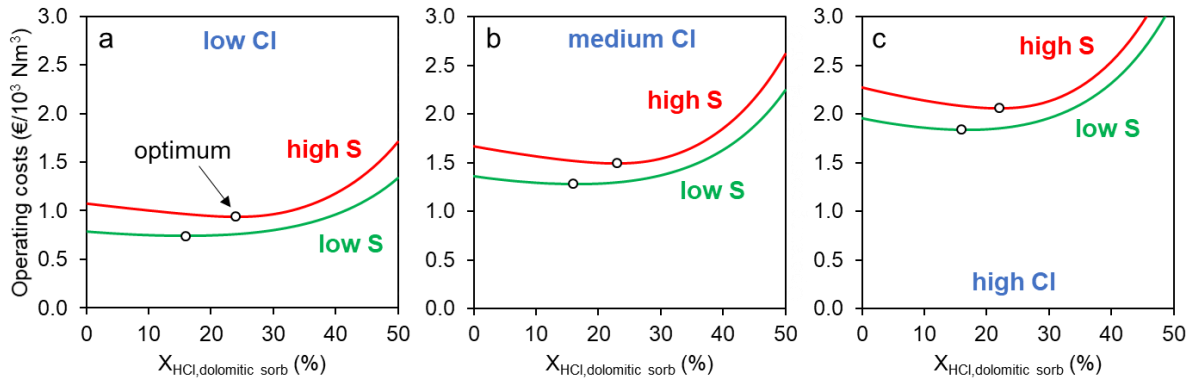
The developed phenomenological model allows addressing the minimisation of the operating costs of multi-stage acid gas removal processes. In the following, the cost-effectiveness of introducing a FSI of dolomitic sorbent was preliminarily assessed for both plants A and B, given the process constraints 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].

517

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

518
519
520
521
522
523
524
525
526
527
528
529

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 $X_{HCl, dolomitic\ sorb} = 0\%$.



530
 531 **Figure 6.** Operating costs of the dolomitic sorbent + NaHCO₃ two-stage system as a
 532 function of HCl conversion in the DS stage for the six cases of flue gas composition in Table
 533 3: a) low content of Cl; b) medium content of Cl; c) high content of Cl. Open circles: minimum
 534 cost.

535
 536 The curves for the six scenarios considered for flue gas composition exhibit a common
 537 behaviour. There is a region where variation of costs is limited ($X_{\text{HCl,dolomitic sorb}} < 30\%$), while
 538 costs start increasing steeply at higher $X_{\text{HCl,dolomitic sorb}}$ values. As shown by the open circles,
 539 an optimum is always present and it corresponds to a $X_{\text{HCl,dolomitic sorb}}$ value of 16 and 23%,
 540 respectively for the low S and high S scenarios. The cost savings of the optimal operating
 541 point of the DS + NaHCO₃ configuration with respect to the single stage NaHCO₃ injection
 542 are of about 6% for the low S cases. For the high S cases, instead, the savings range from
 543 10% to 13%. The cost-effectiveness of the DS injection at higher SO₂ concentration and
 544 higher S/Cl ratio in the inlet flue gas stems from the higher relative reactivity of the dolomitic
 545 sorbent towards SO₂ compared to sodium bicarbonate.

546 Figure 7 details the contribution of the different entries to the overall operating cost for the
 547 scenarios of medium Cl and low or high S in the flue gas. The single stage NaHCO₃ system
 548 and the DS + NaHCO₃ configuration at the optimal operating point are compared. The
 549 addition of DS reduces the total cost related to reactant procurement, as the expense for DS
 550 and NaHCO₃ in the two-stage system is 11 and 20% lower than the expense for NaHCO₃
 551 alone in the single stage configuration, respectively for the low and high S cases.
 552 Conversely, when DS injection is present, the cost associated to the management of
 553 process residues increases of 5 and 10% for the low and high S cases. This is due to the
 554 combined effect of a higher unit cost for the management route of DS residues (see Table 4)
 555 and the weight gain associated with acid gas capture: considering the sorption of HCl, a
 556 mole of dolomitic sorbent, upon dehydration and chloridation (Eqs. 1 and 2), exhibits a
 557 22% mass increase, while a mole of sodium bicarbonate, after thermal activation and
 558 chloridation, undergoes a 69.5% net weight loss. On the whole, the net effect of DS
 559 injection at the optimal feed rate is the slight reduction of operating costs shown in Fig. 6,
 560 resulting from lower costs for reactants and higher costs for residues handling.

561

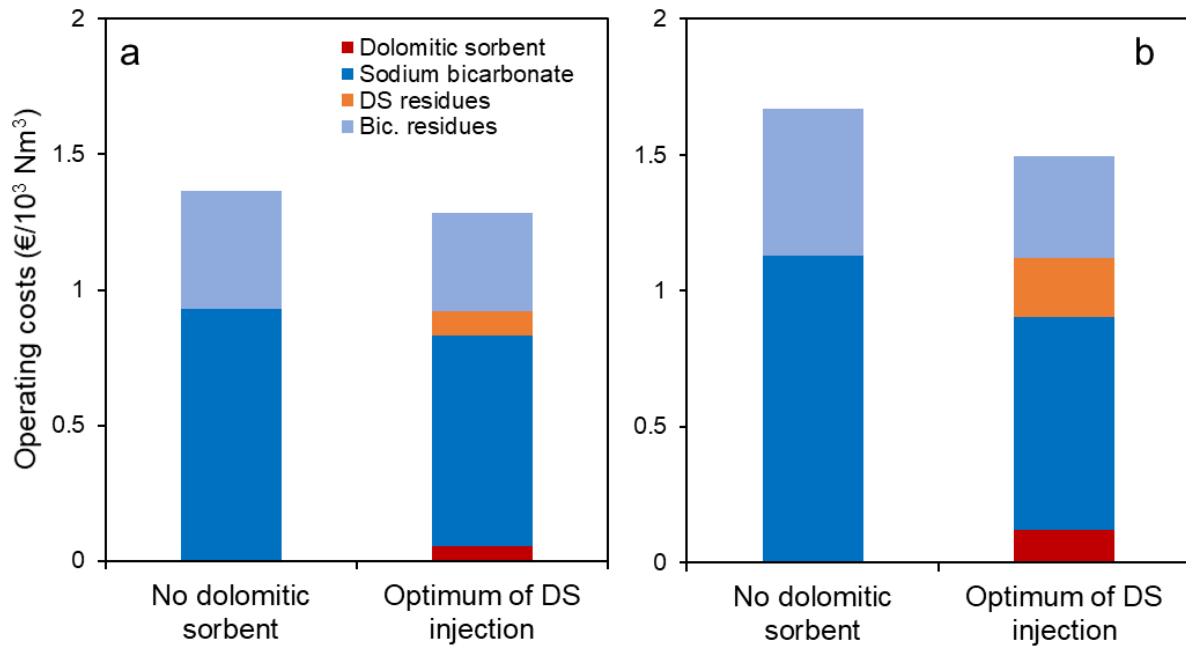


Figure 7. Contribution of the different cost entries to the overall operating costs of acid gas removal for the single stage bicarbonate system (no furnace injection) and for the two-stage system with DS injection at the optimal operating point (optimum). Medium Cl and: a) low S, b) high S compositions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

4.4.2 Three-stage optimisation: dolomitic sorbent + $\text{Ca}(\text{OH})_2$ + 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 $\text{Ca}(\text{OH})_2$ 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% $X_{\text{HCl,dolomitic sorb}}$ for the low S cases and to 16-20% $X_{\text{HCl,dolomitic sorb}}$ 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 $\text{Ca}(\text{OH})_2/\text{NaHCO}_3$ system, which corresponds to values in the range 47-50% $X_{\text{HCl,Ca}(\text{OH})_2}$ when $X_{\text{HCl,dolomitic sorb}}$ is set to zero. Actually, a properly operated $\text{Ca}(\text{OH})_2/\text{NaHCO}_3$ 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 $\text{Ca}(\text{OH})_2/\text{NaHCO}_3$ 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

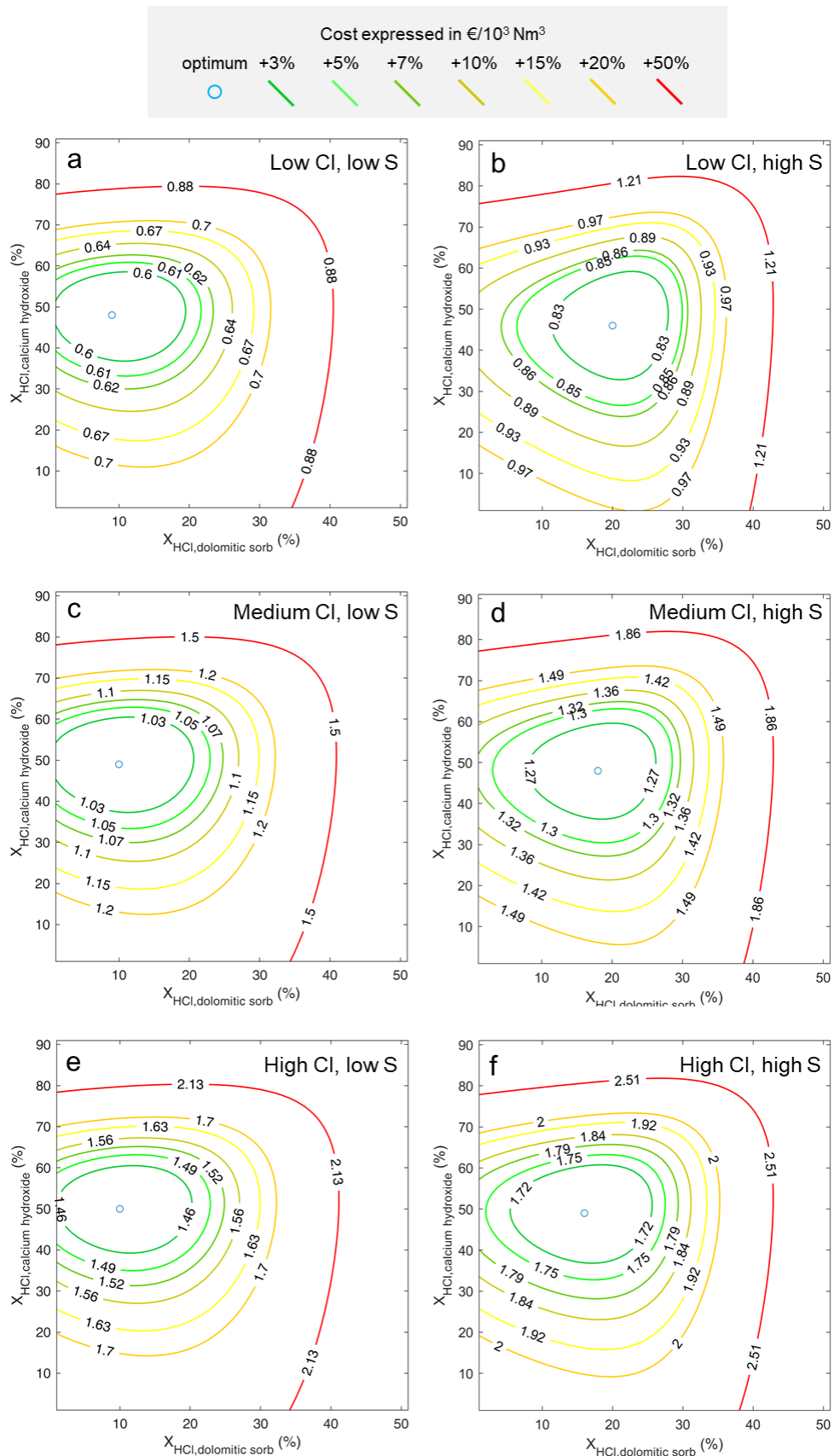
593 costs within +10% of the optimum, without DS injection, is comprised between $X_{\text{HCl,Ca(OH)}_2}$
 594 ranging from 35 to 55%, while for a DS injection corresponding to $X_{\text{HCl,dolomitic sorb}} = 20\%$, it is
 595 possible to remain within +10% of the minimum operating costs even for $X_{\text{HCl,Ca(OH)}_2}$ ranging
 596 from 20 to 65%. Therefore, the addition of a dolomitic sorbent stage flattens the cost
 597 variation related to the repartition of acid gas removal between the treatment stages,
 598 possibly limiting the deviation from optimal operation.

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

605
 606 **Table 5.** Specific feed rate of dolomitic sorbent ($\text{kg}/10^3 \text{ Nm}^3$ of flue gas) corresponding to the
 607 optimal $X_{\text{HCl,dolomitic sorb}}$ 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 ($\text{kg}/10^3 \text{ Nm}^3$)	Optimal DS feed rate ($\text{kg}/10^3 \text{ Nm}^3$)
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

608
 609
 610
 611



612
613
614
615
616

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

617 *4.4.3 Effect of unit cost variability*

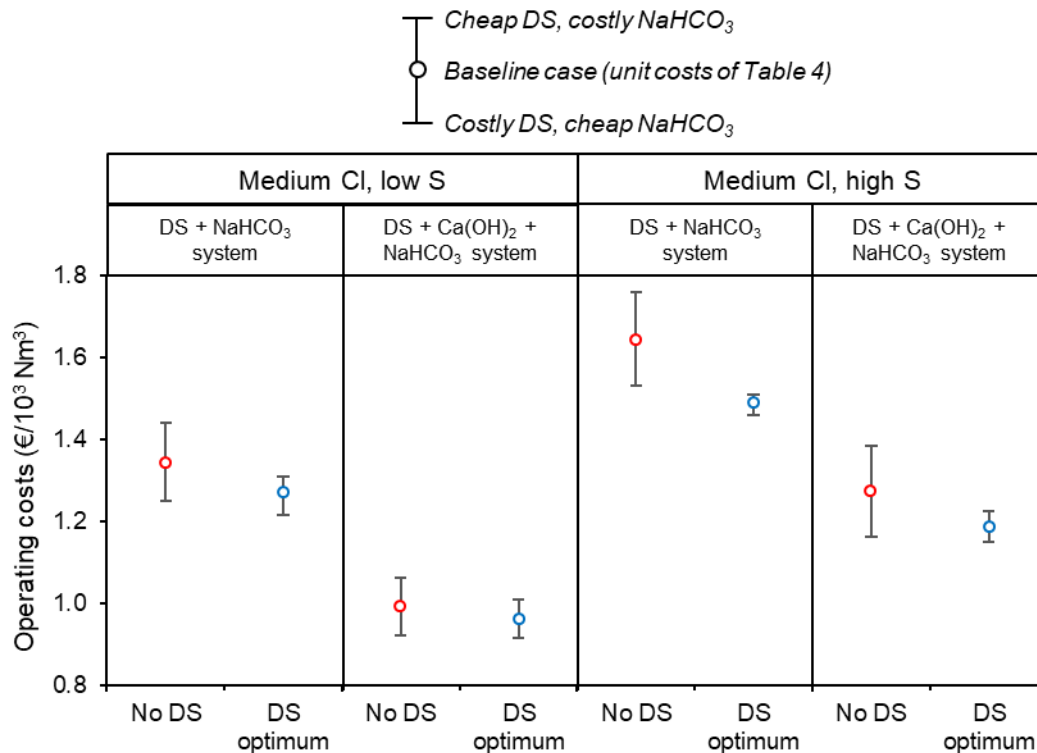
618 The economic analysis in sections 4.4.1 and 4.4.2 is clearly influenced by the adopted
619 unit cost values for the considered cost entries. To assess the effect of different unit costs
620 than those listed in Table 4 on the economic optimisation, two scenarios were explored:

- 621 • an unfavourable scenario for the DS, named '*costly DS, cheap NaHCO₃*', in which
622 the costs for the procurement of DS and the disposal of process residues are 20%
623 higher than the values in Table 4, while the costs for the procurement of sodium
624 bicarbonate and the costs for the recycling of Na-based process residues are 20%
625 lower than the values in Table 4;
- 626 • a favourable scenario for the DS, named '*cheap DS, costly NaHCO₃*', in which – vice
627 versa – the costs for the procurement of DS and the disposal of process residues are
628 20% lower than the values in Table 4, while the costs for the procurement of sodium
629 bicarbonate and the costs for the recycling of Na-based process residues are 20%
630 higher than the values in Table 4.

631 The ±20% range assumed is a conservative interval of variation, considering the
632 relatively low differences in unit costs reported by several technical and scientific
633 sources (see the overview of cost data by Dal Pozzo et al. [37]).
634 The overall operating costs estimated for the systems without DS injection and for
635 the systems with DS injection at the optimal operating point were compared for the different
636 cost scenarios, as shown in Fig. 9. The comparison was carried out for both the two-
637 stage and the three-stage system, with reference to medium Cl and high or low S flue gas
638 composition cases.

639 The first evidence is that the '*costly DS, cheap NaHCO₃*' scenario always generates
640 lower overall operating costs, while the upper end of the operating costs range corresponds
641 to the the '*cheap DS, costly NaHCO₃*' scenario. This finding is obvious for the cases with
642 no DS injection. For the cases with optimal DS injection, it results from the much higher
643 NaHCO₃ feed with respect to the DS feed rate in the optimal repartition of feed rate
644 between stages, that results in a higher fraction of the total costs (as shown in Fig. 7).
645 In the '*costly DS, cheap NaHCO₃*' scenario, the slight cost savings ensured by DS
646 injection, discussed in sections 4.4.1 e 4.4.2, are further reduced, and the operating
647 costs of the systems with and without DS injection are almost equivalent. The exception
648 is the case of the DS + NaHCO₃ system in presence of a flue gas composition with high
649 S, for which the injection of DS still results in a 7% cost reduction.
650 Vice versa, in the '*cheap DS, costly NaHCO₃*' scenario the gap between the operating
651 costs with and without DS injection is enlarged. The addition of DS results in savings,
652 ranging from 9 to 16% for the NaHCO₃ system and from 5 to 12% for the Ca(OH)₂/NaHCO₃
653 system (lower and upper end of the range are for the flue gas compositions with
654 low and high S, respectively).
655 Overall, these results clarify that, even in presence of uncertainty in the unit costs,
656 the introduction of a DS injection stage reduces the variation of the total operating
657 costs, as evident from the reduction of the cost brackets in Fig. 9. In the cost
658 scenario that is unfavourable for DS, the overall costs of the system with or without DS
659 injection are the same, while in the cost scenario that is favourable for DS, its injection
660 generates appreciable savings. Therefore, from the viewpoint of WtE operators, adding a
661 furnace injection of DS can increase the robustness of the entire acid gas treatment line.

662



663
 664 **Figure 9.** Operating costs of acid gas removal in the different cost scenarios indicated in the
 665 legend. Comparison between no DS injection and DS injection at the optimum, for the DS +
 666 NaHCO₃ two-stage system and for the DS + Ca(OH)₂ + NaHCO₃ three-stage system
 667 with DS injection at the optimal operating point (optimum). Medium Cl and: a) low S, b)
 668 high S compositions were considered for flue gas.
 669

670 5. Conclusions

671
 672 A quantitative analysis of the HCl and SO₂ removal performance of a dolomitic
 673 sorbent injected in the combustion chamber of WtE plants was carried out. Data
 674 obtained via dedicated test runs at full plant scale and their interpretation by
 675 means of a phenomenological model allowed deriving a non-linear relationship
 676 between the stoichiometric ratio of sorbent feed rate and the resulting conversion of acid
 677 pollutants. At the typical concentrations of HCl and SO₂ expected in WtE flue gas, a SR of
 678 sorbent equal to 1 was found to achieve a mean 27% HCl conversion and 83% SO₂
 679 conversion, while a SR of 2 resulted in conversions of HCl and SO₂ respectively equal to
 680 37% and 98%.

681 Since the introduction of a furnace injection of DS can be considered as an
 682 additional deacidification stage to the existing acid gas treatment line of a WtE facility, the
 683 developed model was used to identify the optimal feed rate of DS, *i.e.* the feed rate that
 684 minimises the overall operating costs of the line, for a WtE plant already equipped with a
 685 single or a two-stage acid gas treatment system. An optimum is generally present because
 686 the DS injected at high temperature, as opposed to calcium hydroxide or sodium
 687 bicarbonate injected at low temperature, has a higher relative reactivity towards
 688 SO₂ than HCl, hence it is complementary to the low-temperature sorbents, and it is
 689 cheaper than sodium bicarbonate, hence it is suitable as a pre-treatment step to limit the
 consumption of the more expensive reactant.

690 In particular, for WtE plants operating with furnace DS injection plus a single
691 downstream acid gas removal stage, the optimal operating point consists in demanding a
692 conversion of HCl in the range 16-23% from DS injection. Such an optimised feed rate of
693 DS can achieve a reduction of operating costs, which was estimated as high as 13% when
694 the concentration of SO₂ in the raw flue gas is relevant.

695 For WtE plants operating with furnace DS injection plus a downstream two-stage acid
696 gas treatment system, the optimal feed rate of DS corresponds to a conversion of HCl
697 in the range 9-20%, depending on the SO₂ concentration in the flue gas. The savings that
698 may be obtained thanks to the use of DS were estimated to be limited (less than 10%
699 reduction of operating costs even for flue gas with high SO₂ concentration). However, the
700 DS injection can still be a valid addition in order to stabilise the operation of the multi-
701 stage acid gas removal process, smoothing the variability of acid gas load coming from
702 the combustion chamber.

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

707

708 **Acknowledgments**

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

711

712 **References**

- 713 [1] P. Lu, Q. Huang, A.C. Bourtsalas, N.J. Themelis, Y. Chi, J. Yan, Review on fate of
714 chlorine during thermal processing of solid wastes, *J. Environ. Sci.* 78 (2019) 13-28.
- 715 [2] M. Bal, T.T. Reddy, B.C. Maikap, Removal of HCl gas from off gases using self-
716 priming venturi scrubber, *J. Haz. Mat.* 364 (2019) 406-418.
- 717 [3] A. Dal Pozzo, R. Moricone, A. Tugnoli, V. Cozzani, Experimental Investigation of the
718 Reactivity of Sodium Bicarbonate toward Hydrogen Chloride and Sulfur Dioxide at
719 Low Temperatures, *Ind. Eng. Chem. Res.* 58 (2019) 6316-6324.
- 720 [4] K.-D. Kim, S.-M. Jeon, N. Hasolli, K.-S. Lee, J.-R. Lee, J.-W. Han, H.-T. Kim, Y.-O.
721 Park, HCl removal characteristics of calcium hydroxide at the dry-type sorbent
722 reaction accelerator using municipal waste incinerator flue gas at a real site, *Korean
723 J. Chem. Eng.* 34 (2017) 747-756.
- 724 [5] C. Li, Z. Jia, X. Ye, S. Yin, Simulation on deacidification performance of waste
725 incinerator flue gas by rotating spray drying, *Energy* 152 (2018) 652-665.
- 726 [6] J. Vehlow, Air pollution control systems in WtE units: An overview, *Waste Manage.*
727 37 (2015) 58-74.
- 728 [7] A.L. Brooks, S. Wang, J.R. Jambeck, The Chinese import ban and its impact on
729 global plastic waste trade, *Sci. Adv.* 4 (2018) eaat0131.
- 730 [8] W. Wang, N.J. Themelis, K. Sun, A.C. Bourtsalas, Q. Huang, Y. Zhang, Z. Wu,
731 Current influence of China's ban on plastic waste imports, *Waste Disposal Sust.*
732 *Energy* 1 (2019) 67-78.
- 733 [9] J. Van Caneghem, K. Van Acker, J. De Greef, G. Wauters, C. Vandecasteele,
734 Waste-to-energy is compatible and complementary with recycling in the circular
735 economy, *Clean Technol. Environ. Policy* 21 (2019) 925-939.

- 736 [10] European IPPC Bureau, Best Available Techniques (BAT) Reference Document for
737 Waste Incineration. Technical draft, 2018. Available at:
738 eippcb.jrc.ec.europa.eu/reference/BREF/WI/WI_BREF_FD_Black_Watermark.pdf
739 (last accessed: 18/11/2019).
- 740 [11] S. Belosevic, I. Tomanovic, N. Crnomarkovic, A. Milicevic, D. Tucakovic, Numerical
741 study of pulverized coal-fired utility boiler over a wide range of operating conditions
742 for in-furnace SO₂/NO_x reduction, *Appl. Thermal Eng.* 94 (2016) 657-669.
- 743 [12] L. Shi, G. Liu, B.S. Higgins, L. Benson, Computational modeling of furnace sorbent
744 injection for SO₂ removal from coal-fired utility boilers, *Fuel Proc. Technol.* 92 (2011)
745 372-378.
- 746 [13] B.G. Miller, Formation and Control of Sulfur Oxides, in: *Clean Coal Engineering*
747 *Technology*. 2nd ed. Oxford: Butterworth-Heinemann, 2017, pp 467-506.
- 748 [14] M.J. Miller, Retrofit SO₂ and NO_x control technologies for coal-fired power plants.
749 *Environ. Prog.* 5 (1986) 171-177.
- 750 [15] L.J. Muzio, G.R. Often, Assessment of Dry Sorbent Emission Control Technologies
751 Part I. Fundamental Processes, *JAPCA* 37 (1987) 642-654.
- 752 [16] J. Cheng, J. Zhou, J. Liu, Z. Zhou, Z. Huang, X. Cao, X. Zhao, K. Cen, Sulfur
753 removal at high temperature during coal combustion in furnaces: a review, *Prog.*
754 *Energy Combust. Sci.* 29 (2003) 381-405.
- 755 [17] W.Z. Khan, B.M. Gibes, SO_x emissions from a fluidized-bed combustor with and
756 without limestone addition, *Energy* 21 (1996) 105-113.
- 757 [18] J. Zhou, J. Cheng, X. Cao, J. Liu, X. Zhao, Z. Huang, K. Cen, Experimental research
758 on two-stage desulfurization technology in traveling grate boilers, *Energy* 26 (2001)
759 759-774.
- 760 [19] S. Petrini, H. Eklund, I. Bjerle, HCl-Absorption durch Kalkstein (in German),
761 *Aufbereitungstechnik* 6 (1979) 309–311.
- 762 [20] G. Mura, A. Lallai, Reaction kinetics of gas hydrogen chloride and limestone, *Chem.*
763 *Eng. Sci.* 49 (1994) 4491-4500.
- 764 [21] J. Partanen, P. Backman, R. Backman, M. Hupa, Absorption of HCl by limestone in
765 hot flue gases. Part I: the effects of temperature, gas atmosphere and absorbent
766 quality, *Fuel* 84 (2005) 1664-1673.
- 767 [22] R.H. Borgwardt, Sintering of nascent calcium oxide, *Chem. Eng. Sci.* 44 (1989) 53-
768 60.
- 769 [23] A.M. Kierzkowska, R. Pacciani, C.R. Müller, CaO-Based CO₂ Sorbents: From
770 Fundamentals to the Development of New, Highly Effective Materials,
771 *ChemSusChem* 6 (2013) 1130-1148.
- 772 [24] B. Shemwell, Y.A. Levendis, G.A. Simons, Laboratory study on the high-temperature
773 capture of HCl gas by dry-injection of calcium-based sorbents, *Chemosphere* 42
774 (2001) 785-796.
- 775 [25] A.A. Patsias, W. Nimmo, B.M. Gibbs, P.T. Williams, Calcium-based sorbents for
776 simultaneous NO_x /SO_x reduction in a down-fired furnace, *Fuel* 84 (2005) 1864-
777 1873.
- 778 [26] B. Courtemanche, Y.A. Levendis, Control of the HCl Emissions from the Combustion
779 of PVC by In-Furnace Injection of Calcium-Magnesium-Based Sorbents, *Environ.*
780 *Eng. Sci.* 15 (1998) 123-135.
- 781 [27] Y.A. Levendis, W. Zhu, D.L. Wise, G.A. Simons, Effectiveness of calcium magnesium
782 acetate as an SO_x sorbent in coal combustion, *AIChE J.* 35 (1993) 30-36.

- 783 [28] J.M. Valverde, P.E. Sanchez-Jimenez, L.A. Perez-Maqueda, Ca-looping for
784 postcombustion CO₂ capture: A comparative analysis on the performances of
785 dolomite and limestone, *Appl. Energy* 138 (2015) 202-215.
- 786 [29] R. Moreschi, R. Marras, International patent n° WO/2014/080373, 2014. Available at:
787 <https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2014080373&tab=PCTBIBLIO>
788 (accessed 03/09/2019).
- 789 [30] L. Biganzoli, G. Racanella, L. Rigamonti, R. Marras, M. Grosso, High temperature
790 abatement of acid gases from waste incineration. Part I: Experimental tests in full
791 scale plants, *Waste Manage.* 36 (2015) 98-105.
- 792 [31] A. Dal Pozzo, D. Guglielmi, G. Antonioni, A. Tugnoli, Environmental and economic
793 performance assessment of alternative acid gas removal technologies for waste-to-
794 energy plants, *Sustainable Prod. Consumption* 16 (2018) 202-215.
- 795 [32] CEN, EN 14181:2014—Stationary source emissions—quality assurance of
796 automated measuring systems, Brussels (2014).
- 797 [33] T.O.M. Smith, R.A. Robinson, M.D. Coleman, Modelling European quality assurance
798 procedures for analysers monitoring emissions under the EU's Industrial Emissions
799 Directive, *Accreditation and Quality Assurance* 24 (2019) 443-449.
- 800 [34] European Parliament, Directive 2010/75/EU on industrial emissions (integrated
801 pollution prevention and control), *Off J Eur Union L* 334 (2010) 17–119.
- 802 [35] P.J. Rousseeuw, Least Median of Squares Regression, *J. Am. Stat. Assoc.* 79
803 (1984) 871–880.
- 804 [36] R. Filitz, A.M. Kierzkowska, C.R. Müller, Highly Efficient CO₂ Sorbents: Development
805 of Synthetic, Calcium-Rich Dolomites, *Environ. Sci. Technol.* 46 (2012) 559-565.
- 806 [37] A. Dal Pozzo, G. Antonioni, D. Guglielmi, C. Stramigioli, V. Cozzani, Comparison of
807 alternative flue gas dry treatment technologies in waste-to-energy processes, *Waste*
808 *Manage.* 51 (2016) 81-90.
- 809 [38] A. Dal Pozzo, A. Armutlulu, M. Rekhina, C.R. Müller, V. Cozzani, CO₂ Uptake
810 Potential of Ca-Based Air Pollution Control Residues over Repeated Carbonation–
811 Calcination Cycles, *Energy Fuels* 32 (2018) 5386-5395.
- 812 [39] M. Margallo, M.B.M. Taddei, A. Hernandez-Pellon, R. Aldaco, A. Irabien,
813 Environmental sustainability assessment of the management of municipal solid waste
814 incineration residues: a review of the current situation, *Clean Technol. Environ.*
815 *Policy* 17 (2015) 1333-1353.
- 816 [40] L. Ninane, J.F. Adam, C. Humblot, Method for Producing an Aqueous Industrial
817 Sodium Chloride Solution, U.S. Patent 5478447, 1995.
- 818 [41] T. Chin, R. Yan, D. T. Liang, J.H. Tay, Hydrated Lime Reaction with HCl under
819 Simulated Flue Gas Conditions, *Ind. Eng. Chem. Res.* 44 (2005) 3742-3748.
- 820 [42] R. Han, F. Sun, J. Gao, S. Wei, Y. Su, Y. Qin, Trace Na₂CO₃ Addition to Limestone
821 Inducing High-Capacity SO₂ Capture, *Environ. Sci. Technol.* 51 (2017) 12692-12698.
- 822 [43] P. Quicker, M. Rotheut, Y. Noel, M. Schulten, U. Athmann, Treating WTE Plant Flue
823 Gases with Sodium Bicarbonate, *Power* 158 (2014) 59-63.
- 824
825
826
827

Supplementary Material

[Click here to download Supplementary Material: SupplementaryMaterial_Depurcal_JHM.docx](#)

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 SO₂ 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

STATEMENT OF NOVELTY

Techno-economic performance HCl and SO₂ 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/SO₂ conversion.