High temperature abatement of acid gases from waste incineration. Part I: Experimental tests in full scale plants

Laura Biganzoli [a],*, Gaia Racanella [a], Lucia Rigamonti [a], Roberto Marras [b], Mario Grosso [a]

[a] *Politecnico di Milano, Department of Civil and Environmental Engineering, Piazza L. daVinci 32, 20133 Milano, Italy*
[b] *Unicalce S.p.A., R&D Department, Via Tonio da Belledo 30, 23900 Lecco, Italy*

1. Introduction

The use of calcium- or sodium-based sorbents to control the emissions of acid gases is widespread in the waste incineration sector. Usually these chemicals are dosed along the flue gas treatment line at a temperature between 140 °C and 180 °C, depending on the type of reactant and on the overall layout of the treatment section. Due to the increase of the selective waste collection and to the decrease of waste generation mostly caused by the economic crisis, but also to the implementation of some prevention measures aimed at reducing waste at the source (Nessi et al., 2013), in Northern Italy several waste-to-energy (WTE) plants have suffered a considerable decrease of available residual municipal waste. In order to feed a constant thermal load to the furnace, the operators were then forced to turn to the market of commercial wastes, with a consequent change of the overall composition of waste incinerated (ISPRA, 2013). Commercial wastes generally have a different composition compared to the municipal waste, being frequently more contaminated by elements such as chlorine (Cl), sulphur (S), and fluorine (F) (Cossu et al., 2012; Viganò et al., 2010;

Llewellyn, 2006). During the combustion process, these elements will turn into acid gases such as hydrochloric acid (HCl), sulphur dioxide (SO_2) and hydrofluoric acid (HF). By increasing the amount of commercial waste into the mixture, acid gases concentrations in the flue gas will likely increase, giving further operational problems in terms of fouling and corrosion of the heat exchange surfaces inside the boiler. Moreover, this will affect the downstream deacidification unit operating at low temperature, generally based on a single-stage absorption not very flexible in reacting to possible peaks of the pollutant input, which can in turn lead to the risk of exceeding the emission limits. In this regard, flue gas treatment alternatives characterized by the redundancy of acid gases removal steps, able to cope even with the most problematic wastes, are urgently needed to allow a smoother operation of the plants.

The addition of a first absorption stage at high temperature, consisting in the injection of a calcium- or magnesium-based sorbent directly in the combustion chamber, can answer to the flexibility and redundancy requirements. Through a minimally invasive intervention, which does not require significant changes to the system, it allows a preliminary partial removal of acid gases, reducing their residual concentration in the flue gas entering the low temperature stage of absorption, as well as their peaks. This allows on the one hand to level-up the system operations and on the other

* Corresponding author. Tel.: +39 02 23996415.
  E-mail address: laura.biganzoli@mail.polimi.it (L. Biganzoli).

to reduce the consumption of lime or sodium bicarbonate in the flue gas treatment line.

Until now, this technology has been applied mainly to coal-fired power plants (Blythe, 2004; Offen et al., 1987; Anthony and Granatstein, 2001; Fan et al., 1999), even if its possible application to the WTE sector, especially to fluidised bed combustors, is also reported in the literature (Niessen, 2002; EU commission, 2006). Verdone and De Filippis (2004) thermodynamically investigated the behaviour of calcium-based sorbent (Ca(OH)$_2$) in the removal of acid gases both at low and at high temperature, in order to show the theoretical limits achievable. A similar study was carried out by Matsukata et al. (1996) and investigates the chlorination and sulphation kinetic of calcined limestone at high temperature using thermogravimetry. Evaluations of the chemistry of calcium-based sorbents in presence of HCl and SO$_2$ at high temperature are also reported by Partanen et al. (2005a,b) and Xie et al. (1999). They observed that in presence of both HCl and SO$_2$, chlorination of CaO and CaCO$_3$ is considerably suppressed whereas sulphation is enhanced. Shemwell et al. (2001) evaluated the reduction of HCl emissions by in-furnace dry-injection of calcium-based sorbent in a laboratory furnace, finding that the reactions of the sorbent with HCl ceases at a certain extent without complete conversion of the sorbent. The HCl removal efficiency reaches 80% at a temper-ature of 1000 °C, with a calcium actual utilization of about 20%.

However, all these studies were based on the evaluation of the chemical equilibrium and did not report data from full scale plants during standard operation. In full scale plants, operating conditions such as the residence time of the sorbent in the furnace–boiler section or the quality of the contact between the sorbent and the gas, are very different compared to controlled laboratory conditions, thus leading to a low sorbent utilization and low acid gases removal efficiencies.

This study aims to fill such a gap by providing primary data gathered on full scale WTE plants where a first absorption stage at high temperature was introduced. The focus is on the effects on the practical operation and not on detailed thermodynamic and kinetic considerations of the absorption process, which can be more easily evaluated at the laboratory scale. The specific aim is to quantify the environmental and energy performances of an innovative dolomitic sorbent composition, named Depurcal®MG, recently developed and marketed by the Italian manufacturer of limestone and lime-based products Unicalce S.p.A.

The performances are measured on the abatement of HCl, HF and SO$_2$ as a result of the feeding of the dolomitic sorbent, by evaluating the acid gases removal efficiency in the boiler section and the consequent saving of sodium bicarbonate in the low temperature downstream deacidification unit. An energy evaluation was also carried out, to assess the influence of the dolomitic sorbent on the electric energy conversion efficiency of the plants.

2. Material and methods

2.1. Depurcal®MG

Depurcal®MG is a dolomitic sorbent comprising calcium hydroxide (Ca(OH)$_2$), magnesium hydroxide (Mg(OH)$_2$) and magnesium oxide (MgO); the inert fraction is generally less than 0.6% of the total mass of the sorbent, and it is mainly composed by SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ in traces. The sorbent consists in a micronized powder ready to use. Typically the particle size distribution is characterized by d_{10} = 0.5–2 μm, d_{50} = 8–12 μm and d_{90} = 60–90 μm, where d_{10}, d_{50} and d_{90} indexes describe respectively the diameter where 10%, 50% (median) and 90% of the distribution has a smaller particle size and the complement percent of the distribution has a larger particle size; the average particle diameter is generally ranging from 25 μm to 45 μm.

Depurcal®MG is characterized by a high magnesium/calcium mass ratio (Mg/Ca > 0.58) and improved physical characteristics (BET specific surface area >18 m^2/g and BJH pore volume >0.07 cm^3/g). Moreover, it can be fed in the hot section of the plant, at temperature above 800 °C; this condition promotes the thermal activation of the dolomitic sorbent with an immediate development of further specific surface area (BET > 30 m^2/g) and pore volume (BJH > 0.10 cm^3/g), with particular increase in the range of meso and macropores.

The effects of the thermal activation on the physical properties of Depurcal®MG were evaluated by means of a series of laboratory tests carried out using a fixed-bed reactor, maintained at a predefined temperature of about 1000 °C and under an inert nitrogen atmosphere. The sample of dolomitic sorbent tested was left in the reactor at the above temperature for 15 s (activation time), this duration being considered the maximum operating time of the sorbent under real application conditions. The activated sorbent was cooled in a laboratory drier and then subjected to a porosimetric examination by means of a gas sorption analyzer Quantachrome Instruments Nova 2000 Series using nitrogen physisorption and desorption isotherms at −196 °C in order to measure the specific surface area according to the multipoint BET method (Brunauer et al., 1938) and the pore volume according to the BJH method (Barrett et al., 1951).

The microstructure and the surface morphology of Depurcal®MG in its raw form and after thermal activation were studied through Scanning Electron Microscopy (SEM): SEM micrographs (Fig. 1) were acquired by means of a Tescan Vega-II XMU Scanning Electron Microscope coupled with an Oxford Inca Energy Dispersive X-ray (EDX) spectroscopy detection system.

2.2. Main characteristics of the WTE plants

Four plants located in Northern Italy have been selected for the experimental evaluations: Milano – *Silla* 2, Valmadrera, Piacenza and Como.

The key features of the four WTE plants considered for this study are shown in Table 1. For all of them, the amount of commercial waste treated has been increasing in recent years, and especially for Como and Valmadrera (Fig. 2).

2.3. Evaluation of the environmental performance of Depurcal®MG

The assessment of the new sorbent at high temperature was focused on its environmental performances. In particular, the expected benefits were measured on the concentration of HCl, HF and SO$_2$, by evaluating their abatement efficiency at the boiler outlet and the consequent saving of sodium bicarbonate used in the flue gas cleaning system at low temperature. Data were directly acquired from the plant operator via the Distributed Control System (DCS), including raw gas concentrations which were measured by dedicated FTIR (Fourier Transform Infrared spectroscopy) in-line analysers at the boiler outlet.

Where possible, a further analysis was performed to determine the behaviour of the dolomitic sorbent in response to peaks of acid gases concentration in the raw gas following a sudden increase of their precursor elements in the incinerated waste.

The following two scenarios were defined: the conventional acid gases removal, based on sodium bicarbonate (reference operation) and the new one (Depurcal®MG scenario), based on the injection of Depurcal®MG at high temperature, followed by sodium bicarbonate at low temperature at a lower feeding rate than during reference operation.

Moreover, two different approaches were used to analyse the effects of the dolomitic sorbent:
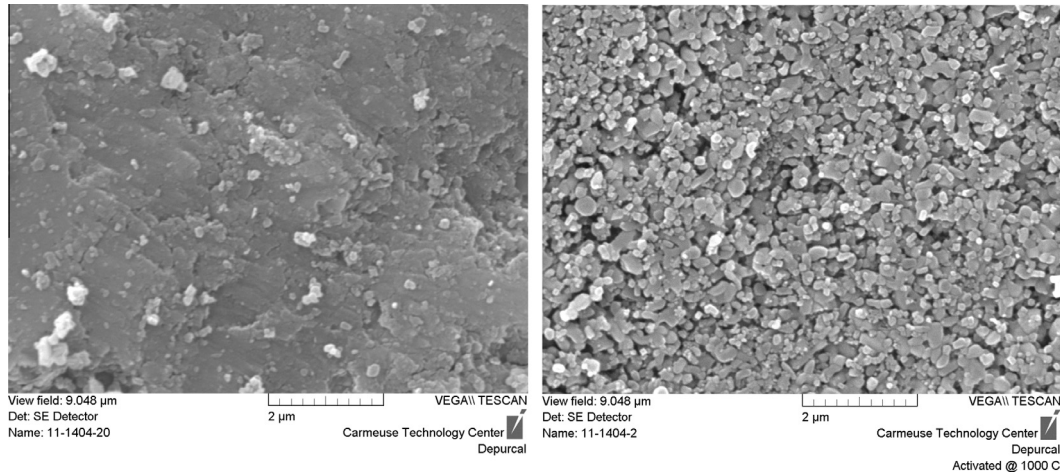
Fig. 1. SEM images of Depurcal®MG before (left) and after (right) thermal activation at 1000 °C.

Table 1
Main characteristics of the WTE plants considered in the study.

Plant	No. lines	Capacity	Type of waste	Gas treatment line	Energy recovery
Milano – *Silla* 2	3	24.17 t/h per line 555,000 t/year	MSW + Comm.	ESP + AC and sodium bicarbonate + FF + SCR (double filtration)	225 t/h steam @ 52 bar; 425 °C 59 MWe 112 MWth
Valmadrera	2	Line 1: 6 t/h Line 3: 9.5 t/h 87,000 t/year	MSW + Comm. + HW	AC and sodium bicarbonate + FF + SCR + WS	54.5 t/h steam @ 40 bar; 400 °C 10.5 MWe
Piacenza	2	7.5 t/h per line 120,000 t/year	MSW + Comm. + HW + SS	SNCR + SCR[a] + ESP + AC and sodium bicarbonate + FF (double filtration)	58.4 t/h steam @ 39 bar; 390 °C 11.63 MWe
Como	2	Line 1: 6.25 t/h Line 2: 5.2 t/h 90,000 t/year	MSW + Comm.	ESP + AC and sodium bicarbonate + FF + SCR (double filtration)	43.2 t/h steam @ 38 bar; 380 °C 6 MWe 39 MWth

MSW: Municipal Solid Waste; Comm.: commercial waste; HW: hospital waste; SS: sewage sludge; ESP: electrostatic precipitator; AC: activated carbon; FF: fabric filter; SCR: selective catalytic reduction; SNCR: selective non-catalytic reduction; WS: Wet Scrubber.

[a] Since February 2009 on Line 1 and March 2011 on Line 2 as a result of economizer 3rd tube bank removal.

(a) a comparative evaluation of different timeframes on the same line of the plant (i.e. same line-different period)

(b) a comparative evaluation of two different lines of the same plant during the same timeframe (i.e. different lines-same period).

In case (b) the effect of the possible variation of waste composition is minimized as the different lines (of the same plant) are loaded concurrently with the waste taken from the same bunker. On the contrary, in case (a) the possible variation of waste composition may have a certain influence on the results, but, on the other hand, the effect of possible differences in the behaviour of two lines of the same plant is excluded.

Table 2 summarises the approach used for the analyses carried out on the four investigated WTE plants.

The data processing was performed, first of all, by adjusting the available datasets from outliers. Then, acid gases concentrations evaluated at the boiler outlet in the two scenarios were statistically compared (*t*-test), using the IBM SPSS statistics software. Finally, the abatement efficiency of the acid gases was evaluated as:

$$\text{Acid gas removal efficiency} = (C_{\text{reference operation}} - C_{\text{Depurcal®MG scenario}})/ \\ C_{\text{reference operation}} * 100 \quad (1)$$

where C is the concentration of HCl, SO$_2$ or HF at the boiler outlet. The main assumption is that the concentration in the raw gas before the injection of the dolomitic sorbent in the Depurcal®MG scenario is the same as the one at the boiler outlet during reference operation. This is of course a simplification, due to the fact that the actual concentration of the acid gases in the furnace–boiler section is not available, since no measurement systems are present.

2.4. Evaluation of the energy performance of Depurcal®MG

For one out of the four WTE plants (Piacenza), it was also possible to analyse in more details some parameters related to energy production, and in particular the production of steam, the thermal efficiency, the electric power at the generator and the production of electric energy. Such parameters, together with the plant availability, were used to evaluate the possible influence of the dolomitic sorbent dosage on the overall energy production efficiency.

The plant availability is influenced by the periodic shutdowns for ordinary and extraordinary maintenance, always including the cleaning of the boiler surfaces. Since cleaner boiler surfaces require less frequent shutdowns, and obviously allow for a better heat exchange, this parameter can be assumed as a proxy indicator of the effect of Depurcal®MG on the energy production.

The thermal efficiency is the maximum amount of heat that is available for the steam production. It was evaluated as:

$$\eta_c \; [\%] = (1 - \text{total thermal losses/waste thermal load}) * 100 \quad (2)$$

This value was then normalized, by introducing some corrections for the waste lower heating value (LHV), the air temperature and the flue gas volume, as reported in the following equation:
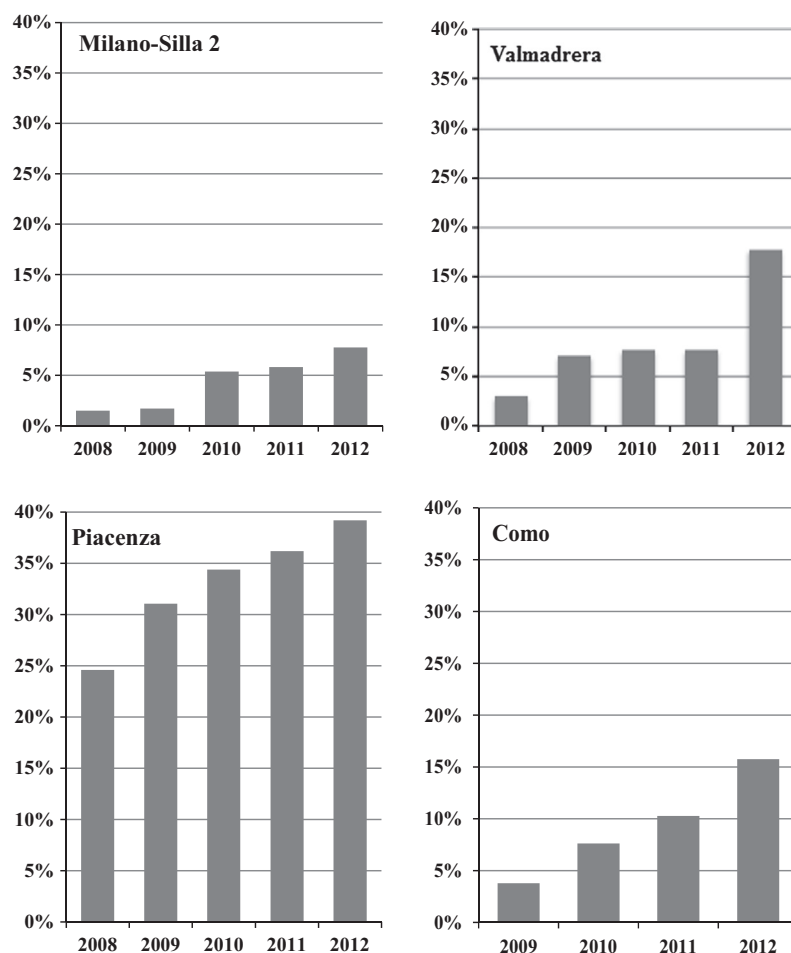
Fig. 2. Commercial waste incinerated as a percentage of the total treated waste in the Milano – *Silla* 2, Valmadrera, Piacenza and Como WTE plants.

Table 2
Approaches used for the analyses carried out in the four WTE plants.

Plant	Test #	Analysis approach	Reference operation	Depurcal®MG scenario	Depurcal®MG dosage rate
Milano – Silla 2	1	a	Line 1 1–25 June 2010	Line 1 26 June–28 July 2010	Increment fixed step 60; 80; 120 kg/h
	2	b	Line 3 26 June–28 July 2010	Line 1 26 June–28 July 2010	Increment fixed step 60; 80; 120 kg/h
	3	a	Line 3 12–14 October 2011	Line 3 1–11 October 2011 15–31 October 2011	Increment fixed step 70; 100; 150 kg/h
	4	b	Line 2 1–11 October 2011 15–31 October 2011	Line 3 1–11 October 2011 15–31 October 2011	Increment fixed step 70; 100; 150 kg/h
Valmadrera	1	a	Line 3 1 April 2010–31 August 2010	Line 3 1 September 2010–15 November 2010	Constant dosage 55 kg/h
	2	a	Line 3 1 April 2010–31 August 2010	Line 3 15 November 2010–31 January 2011	Automatic dosage based on a set point of 800–850 mg/m^3 HCl at the boiler outlet (with a minimum of 40 kg/h)
Piacenza	1	b	Line 1 February, March, 2010	Line 2 February, March, 2010	Constant dosage 33 kg/h
Como	1	a	Line 2 November–December 2011	Line 2 November–December 2012	Automatic dosage based on a set point of 600–850 mg/m^3 HCl at the boiler outlet (limited between 20 and 60 kg/h)
	2	b	Line 1 November 2012	Line 2 November 2012	Automatic dosage based on a set point of 600–850 mg/m^3 HCl at the boiler outlet (limited between 20 and 60 kg/h)

Note – Analysis approach a: same line/different period. Analysis approach b: different lines/same period.

$\eta_N \; [\%] = \; \eta_C + $ correction for LHV

$\qquad + $ correction for the air ambient temperature

$\qquad + $ correction for the flue gas volume $\qquad\qquad$ (3)

More details about the evaluation of the thermal efficiency can be found in the additional materials.

As for the environmental analysis, the aforementioned parameters calculated for the two scenarios (without and with Depurcal®MG) were analyzed statistically. The Reference operation refers to the year 2009, whereas the Depurcal®MG scenario refers to the year 2011 (Depurcal®MG dosage of about 33 kg/h).

3. Results and discussion

3.1. Evaluation of the environmental performances of Depurcal®MG

Results obtained in the four investigated WTE plants in terms of HCl, SO_2 and HF removal efficiency and sodium bicarbonate saving, as a consequence of Depurcal®MG dosage, are reported in Table 3.

The average concentration of HCl, SO_2 and HF measured during the tests in the raw gas and the corresponding average dosage of Depurcal®MG and sodium bicarbonate are reported in Chapter B of the additional materials.
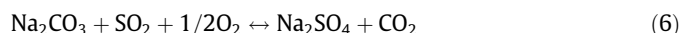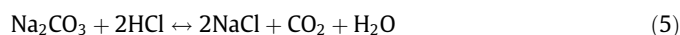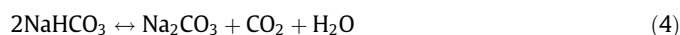
3.1.1. Milano – Silla 2
The experimental investigations carried out on the Milano –Silla 2 WTE plant were divided into four different evaluations, according to the aforementioned approaches. Overall, HCl and SO_2 removal efficiencies were in the range of 7–37% and 34–95%, respectively, for a Depurcal®MG feeding rate of about 3–6.5 kg per tonne of waste. In addition, a saving of sodium bicarbonate was observed, between 13% and 49% (Table 3).

In detail, the analyses carried out in 2010 (test 1 and test 2) show a similar HCl and SO_2 abatement efficiency for a Depurcal®MG dosage of 60 kg/h and 80 kg/h, with a significant improvement when the dosage increases to 120 kg/h.

Different results were found in the analyses carried out in 2011 (test 3 and test 4), where a clear difference appears between the results obtained with the two approaches of analysis. The removal efficiency of acid gases resulting from the comparison of the same line (Line 3) at different periods are lower than those resulting from the comparison between two different lines (Line 2 and Line 3) in the same period and seem not related to the sorbent dosage. In the first case, it is likely that the variation of the characteristics of the treated waste has influenced the results, contrary to what has emerged from the comparison between the two different lines during the same timeframe. In the latter case, the increase of the high temperature sorbent dosage resulted in an almost proportional increase of the average removal efficiency of HCl and SO_2.

For what concerns the sodium bicarbonate saving, on the contrary, no clear trend is observed following the increase of the Depurcal®MG dosage even for tests 3 and 4 (Table 3). However, the comparison between the actual amount of sodium bicarbonate injected in the line and the stoichiometric one (evaluated on the basis of Eqs. (4)–(6) and adopting a stoichiometric excess equal to 35%) suggests a general overdose of the reactant, as reported in the additional materials (Chapter C). The possible saving of sodium bicarbonate may thus be greater, between 50% and 60%.

$$2NaHCO_3 \leftrightarrow Na_2CO_3 + CO_2 + H_2O \qquad\qquad (4)$$

$$Na_2CO_3 + 2HCl \leftrightarrow 2NaCl + CO_2 + H_2O \qquad\qquad (5)$$

$$Na_2CO_3 + SO_2 + 1/2O_2 \leftrightarrow Na_2SO_4 + CO_2 \qquad\qquad (6)$$

As a final observation, a greater amount of fly ash, from an average of 32 kg/t_{waste} to an average of 35 kg/t_{waste}, was collected from the first dedusting device (electro-static precipitator) and from the boiler, compensated by a lower production of residual sodium salts, from 17 kg/t_{waste} to 14 kg/t_{waste}, from the second one (fabric filter). This is perfectly in line with the fact that residues from Depurcal®MG are removed in the upstream filter, while the lower dosage of sodium bicarbonate affects the amount of residues from the second one.

3.1.2. Valmadrera
In the Valmadrera WTE plant the two approaches of analysis gave similar results. For a Depurcal®MG feeding rate of about 8.5 kg per tonne of waste, the abatement efficiency ranges between

Table 3
Environmental performances of Depurcal®MG on the four investigated WTE plants.

Plant	Test #	Analysis approach	Depurcal®MG dosage		HCl removal efficiency (%)	SO₂ removal efficiency (%)	HF removal efficiency (%)	Sodium bicarbonate saving (%)
			kg/h	kg/t_WASTE				
Milano – Silla 2	1	a	60	2.6 ± 0.1	16	69	n.a.	24
			80	3.4 ± 0.1	18	67	n.a.	23
			120	5.4 ± 0.3	34	90	n.a.	43
	2	b	60	2.6 ± 0.1	16	90	n.a.	36
			80	3.4 ± 0.1	14	87	n.a.	28
			120	5.4 ± 0.3	28	95	n.a.	45
	3	a	70	2.8 ± 0.1	16	34	n.a.	19
			100	4.5 ± 0.4	7	51	n.a.	13
			150	6.4 ± 0.5	17	66	n.a.	21
	4	b	70	2.8 ± 0.1	19	48	n.a.	37
			100	4.5 ± 0.4	22	56	n.a.	45
			150	6.4 ± 0.5	37	79	n.a.	49
	Range		60–150	2.6–6.4	7–37	34–95	n.a.	13–49
Valmadrera	1	a	55	8.9 ± 4.0	26	83	80	38
	2	a	51.5 ± 8.0	8.0 ± 4.0	28	88	77	42
	Range		About 55	About 8.5	26–28	83–88	77–80	38–42
Piacenza	1	b	33	4.5 ± 0.4	33	66	n.a.	17
Como	1	a	29.7 ± 15.2	7.5 ± 6.1	35	59	39	21
	2	b	30.7 ± 15.1	7.7 ± 5.6	23	79	56	20
	Range		About 30	About 7.5	23–35	59–79	39–56	20–21
Average				5	23	71	63	31

Note – Analysis approach a: same line/different period. Analysis approach b: different lines/same period.

26% and 28% for HCl, 83–88% for SO$_2$ and 77–80% for HF, and the sodium bicarbonate saving ranges between 38% and 42% (Table 3).

The overall consumption of dry reactants is only marginally affected by Depurcal®MG dosage, and it increases from an average of 15 kg of sodium bicarbonate per tonne of waste in the reference operation to about 8.5 kg of Depurcal®MG plus 9 kg of sodium bicarbonate per tonne of waste (Table B.2 of the additional materials).

3.1.3. Piacenza

In the Piacenza plant, Depurcal®MG was fed at about 4.5 kg per tonne of waste. On average, the acid gases abatement efficiencies were 33% for HCl and 66% for SO$_2$, while sodium bicarbonate saving averaged 17% (Table 3). Sodium bicarbonate saving might be greater (46% on average) with a better management of the dosage, as shown in the additional materials (Table C.2 of the additional materials).

3.1.4. Como

The use of Depurcal®MG in the Como plant (average feeding rate of 7.5 kg per tonne of waste) resulted in an abatement efficiency in the range of 23–35% for HCl, 59–79% for SO$_2$ and 39–56% for HF (Table 3). Consequently, the dosage of sodium bicar-bonate decreased by about 20%. A further analysis of the effective-ness of the dolomitic sorbent in response to peaks of acid gases concentration in the raw gas was also performed. As reported in Fig. 3, during a peak the dosage of DepurcalMG was able to reduce the concentration of HCl, SO$_2$ and HF by about 30%, 85% and 59% respectively, allowing also for an average 35% saving of sodium bicarbonate. It must be pointed out that such analysis is based on the assumption that the concentration of acid gases in the raw gas before the Depurcal®MG injection point was the same in the two lines of the plant. This is not necessary the case when peaks of contaminants are considered, since they might be related to a single waste load fed to the furnace by the crane.

Another aspect investigated was the variation of the amount of residues, by comparing the production of fly ash (included boiler ash) and of residual sodium salts. Considering the analysis mode (a) (same line/different period), when dosing Depurcal®MG the fly ash production increased by 19% (from 15 kg/t$_{waste}$ to 17.5 kg/t$_{waste}$), while the exhausted salts decreased by 26% (from 11 kg/t$_{waste}$ to 8 kg/t$_{waste}$), due to the sodium bicarbonate saving in the flue gas treatment line. The overall production then decreased by 8%.

Overall, the results obtained in the four WTE plants show an actual abatement of acid gases (SO$_2$, HCl) and the consequent sav-ing of sodium bicarbonate in the flue gas treatment line. A good performance was also highlighted for HF in those plants where its monitoring was available.

3.2. Stoichiometric considerations on Depurcal®MG

The actual thermodynamic and kinetic of chlorination and sulphation reactions of Depurcal®MG were not investigated. Sev-eral works are reported in the literature which focus on the chem-istry of different calcium-based sorbents in the presence of HCl and/or SO$_2$ at high temperature (for example Verdone and De Filippis, 2004; Shemwell et al., 2001; Han et al., 2005). Simulta-neous removal of HCl and HF using Ca-based sorbents is reported in Schmal et al. (1989) and Qi et al. (2008). However they all refer to a laboratory scale; in addition the behaviour of these compounds can considerably change on the basis of their actual composition (Ca and Mg content, impurities) and of their physical characteristics (particle size distribution, specific surface area, total pore volume and pore volume distribution) (Ye et al., 1995; Fierro et al., 2004; Partanen et al., 2005a). A dedicated study on Depurcal®MG would thus be needed to assess its thermodynamic and kinetic behaviour, which is out of the scope of this paper.

Some considerations can be, however, drawn from the compar-ison between the actual dosage of Depurcal®MG in the furnace and the stoichiometric one. The latter is evaluated based on the reac-tions in Eqs. (7)–(9) under the assumption of the total abatement of acid gases in the raw gas, and assuming that after thermal acti-vation in the WTE plant furnace CaO and MgO represent 46% and 32% of the mass of the sorbent, respectively. More details about the calculations are reported in Chapter D of the additional materials.
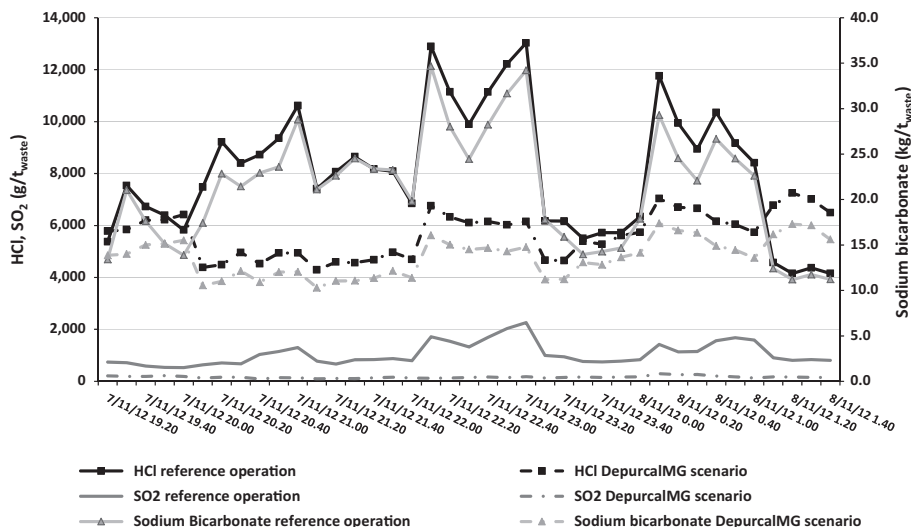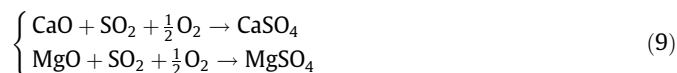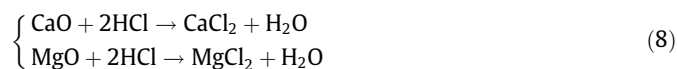
$$\begin{cases} CaO + 2HF \rightarrow CaF_2 + H_2O \\ MgO + 2HF \rightarrow MgF_2 + H_2O \end{cases} \tag{7}$$

$$\begin{cases} CaO + 2HCl \rightarrow CaCl_2 + H_2O \\ MgO + 2HCl \rightarrow MgCl_2 + H_2O \end{cases} \tag{8}$$

$$\begin{cases} CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \\ MgO + SO_2 + \frac{1}{2}O_2 \rightarrow MgSO_4 \end{cases} \tag{9}$$

Fig. 3. Effects of Depurcal®MG towards the peaks of acid pollutants.

Despite the actual dosage exceeds on average the stoichiometric value, as reported in Table 4, only a fraction of the sorbent actually reacts with the acid gases. Acid gases removal efficiencies (Table 3) are in fact significantly lower than 100% and the ratio between the amount of Depurcal®MG that actually reacts with the acid gases and the stoichiometric amount shows a Depurcal®MG utilization in the range of 11–42% (Table 4). These values are in agreement with those reported by Shemwell et al. (2001) for the calcium carbonate and demonstrate that an intrinsic limit is present in the sorbent utilisation. This fact can be related to the intrinsic behaviour of the dolomitic sorbents, in which it is the calcium fraction that mainly reacts, with the magnesium one only contributing to a minor extent. The amount of inert MgO in the particles may act as a structural agent, preventing the collapse of the pores due to sintering phenomena and favouring the diffu-sion of the pollutants inside the particles. This increases the CaO utilisation, since the access of acid gases towards unreacted CaO within the particles may be easier (Muzio and Offen, 1987; Uemiya et al., 2001; Partanen et al., 2005a).

3.3. Evaluation of the potential energy performances of Depurcal®MG

In all four WTE plants, following the use of Depurcal®MG the operators have reported a lower degree of fouling of the boiler and, when present, of the high-dust Selective Catalytic Reduction (SCR) system, that also resulted less affected by sulphur poisoning phenomena. During the periodical inspections of the most critical components of the boiler, the ash deposits appeared more breakable, of powdery nature and characterized by a lower tendency to agglomerate. This resulted in easier cleaning operations of the heat exchange surfaces during routinely maintenance, without the need to rely on explosive techniques as it is often the case.

Since cleaner boiler surfaces mean a better heat exchange and thus an improved production of steam, this suggests that Depurcal®MG might actually help to improve the energy performance of the plants.

In order to quantitatively assess the energy performance of the sorbent, the operating data of Piacenza WTE plant during the year 2009, when Depurcal®MG was not used yet, were compared with those of year 2011. For this analysis, both lines were considered since they feed one single steam turbine for electric energy production. The results of the analysis are reported in Table 5.

It has to be pointed out that the lower availability for Line 2 during Depurcal®MG dosage was actually due to a shutdown for a major technical intervention. This was the installation, inside the boiler, of a high dust SCR system for NOx abatement, replacing some heat exchangers in the economizer section. This has affected the normalized thermal efficiency, despite the increase of the steam production.

This was not the case for Line 1, whose configuration was not modified in the two years. Therefore, focusing only on Line 1, the main parameters that define the energy performances of the system have slightly increased (+8% for the average availability, +7%for the steam production and +1.3% for the normalized thermal efficiency), and this might be due to the use of Depurcal®MG. This suggests that the sorbent is effective in keeping the boiler inner surface cleaner, thus increasing the heat exchange efficiency, with a consequent increase in the production of superheated steam.

Table 4
Comparison between the actual dosage of Depurcal®MG and the stoichiometric one (average values).

Plant	Test #	Analysis approach	Depurcal®MG dosage kg/t$_{WASTE}$		Reacted Depurcal®MG kg/t$_{WASTE}$	Stoichiometric factor	Depurcal®MG utilization[a] (%)
			Actual dosage	Stoichiometric dosage			
Milano – *Silla* 2	1	a	2.6	3.3	0.6	0.8	19.0
			3.4	3.3	0.7	1.0	20.5
			5.4	3.3	1.2	1.6	36.9
	2	b	2.6	3.7	1.0	0.7	26.8
			3.4	3.5	0.4	1.0	23.4
			5.4	3.3	0.4	1.6	36.3
	3	a	2.8	2.0	0.4	1.4	17.6
			4.5	2.0	0.2	2.2	11.1
			6.4	2.0	0.4	3.2	21.1
	4	b	2.8	2.1	0.5	1.3	22.5
			4.5	2.2	0.6	1.8	25.5
			4.0	2.7	1.1	2.3	41.8
Valmadrera	1	a	8.9	6.1	1.7	1.5	28.1
	2	a	8.0	6.1	1.9	1.3	30.8
Piacenza	1	b	4.5	4.1	1.5	1.1	37.4
Como	1	a	7.5	5.4	2.0	1.4	36.8
	2	b	7.7	5.1	1.5	1.5	29.5
Range			2.6–8.9	2.0–6.1	0.2–1.9	0.7–3.2	11.1–41.8

Note – Analysis approach a: same line/different period. Analysis approach b: different lines/same period.
[c] Evaluated as: reacted Depurcal®MG/Stoichiometric dosage.

Table 5
Results of the energy analysis on the Piacenza plant.

Scenario	Line	Average availability (%)	Average superheated steam Q (t/h)	Thermal efficiency (%)	Normalized Thermal efficiency (%)	Average electric power at the generator (MW)	Electric energy production (MWh/year)	Specific electric energy (kWh/t$_{WASTE}$)
Baseline operation (year 2009)	1	85.2	25.1	82.8	83.0	9.9	83,157	702
	2	90.1	25.7	83.2	83.8			
Depurcal®MG scenario (Year 2011)	1	92.2	26.8	84.6	84.1	10.5	86,014	717
	2	89.6	26.3	85.4	83.5			

Considering the electricity production, the electric power of the steam turbine has increased by +6.4%, the specific electric energy production by 2.1% and the yearly energy production by 3.4%.

4. Conclusions

A new dolomitic sorbent to be fed at high temperature has gone through intensive long-lasting tests in four WTE plants during standard operation, in order to assess its performance in terms of acid gases abatement efficiency, sodium bicarbonate saving and solid residues production variation. Also its energy performances were evaluated, mostly in qualitative terms except for one plant, where some quantitative estimates were achieved. The following conclusions can be drawn:

- The dosage of Depural®MG in the high temperature section of a WTE plant allows to obtain good removal efficiencies of acid pollutants at the boiler outlet, a saving of sodium bicarbonate, and to dampen sudden peaks that might arise due to the characteristics of the treated waste. The results obtained in the four WTE plants show an abatement at the boiler outlet in the range of 7–37% for hydrochloric acid (HCl), 34–95% for sulphur dioxide (SO_2) and of 39–80% for hydrofluoric acid (HF). An average 30% decrease of the dosage of sodium bicarbonate in the flue gas treatment line was also measured.
- The energy evaluation carried out on one of the four plants shows an increase of the specific electric energy production (+2.1%) and of the thermal efficiency (+1.3%) as a consequence of Depural®MG dosage.
- The production of boiler and fly ash increased as a consequence of the sorbent feeding, but this was compensated by a decrease of the production of the residual sodium salts.
- The use of the new sorbent, which showed a perfect compatibility and an easy integration also into existing plant facilities, requires minor interventions on a WTE plant, limited to the storage, dosing feeder and pneumatic transport and injection systems.

The results obtained in this study, together with the simplicity of adoption of this technology, suggest that it may find wide application in the WTE sector. Furthermore, in a long term perspective, the design phase of thermal cycles for WTE plants might also benefit of such achievements. In fact the preventive abatement of acid gases, and especially of HCl, might pave the way for more ambitious steam parameters and the consequent increase of electric energy production efficiency.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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