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Enhancing the recovery of gypsum in limestone-based wet flue gas desulfurization with high energy ball milling process: A feasibility study

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ABSTRACT

The most common system for flue gas desulfurization (FGD) is the wet scrubbing process in which, the contact between the flue gases to be treated and an alkaline sorbent such limestone is realized with the correspondent production of gypsum. In this way, the production of gypsum represent a perfect example of how is possible to obtain a new product for the market starting from the need of environmental protection (the sulphur dioxide (SO₂) removal). Today, limestone is ground in long drum mill reaching a size in the range 5–10 mm. With the intent of increasing the specific surface of limestone and consequently gypsum production, the raw limestone was treated in a high-energy mill. The performance of such micronized limestone in terms of gypsum production and SO₂ removal were then evaluated by means of bench scale desulfurization tests. Subsequently, a feasibility study with the goal to verify possible advantages simulating the application of micronized limestone on a full-scale Waste-to-Energy (WtE) plant was realized. Results showed how the micronization process occurred securely, with a greater production of gypsum and better performance in terms of SO₂ removal. Additionally, the micronization solutions tested in the present study showed the suitability also from economic and environmental point of view. Since there are many power plants and WtE plants worldwide and, in many cases, they adopt a wet FGD, this study may be attractive for plant operators. Since there are many power plants or WtE plants worldwide and, in many cases, they adopt a wet desulfurization, this study may be attractive for plant operators. The greater production of gypsum through the use of micronized limestone may help reduce the consumption of raw materials, which increased in recent years due to growing demand of the building industry.

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1. Introduction

Flue gas desulfurization (FGD) involves the removal of sulphur dioxide
 (SO₂) contained in gases produced by the combustion of fossil fuels
 such as coal, oil, municipal solid waste and many industrial processes.
 SO₂ emissions are a primary contributor to acid rain and have been

regulated by every industrialized nation in the world (Córdoba, 2015; Dou et al., 2009). 30

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The most common types of FGD system are based on the contact between the flue gases and an alkaline sorbent such as lime or limestone (Wang et al., 2005). Furthermore, the major types of large-scale power plant FGD systems include (i) spray towers, (ii) spray dryers and

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(iii) dry sorbent injection systems (Song et al., 2012). These FGD systems
 can achieve about 50–70% removal of SO₂ by means of the injection of
 dry sorbent just downstream of the air preheated. The resultant solids
 are then recovered in the electrostatic precipitators along with the fly
 ash.
 In power plants burning pulverized coal, wet FGD that contacts the

In power plants burning pulverized coal, wet FGD that contacts the flue gases with lime or limestone slurries (wet scrubbers) can achieve 95% SO₂ removal without the addition of additives and plus than 99% removal by adding additives (Wang et al., 2005). Today, wet FGD represent the most commonly adopted system worldwide and it is well established and commercially proven technology (Córdoba, 2015).

Among the reasons for the success of the wet FGD system, there is 46 the possibility of recovering a new product to be allocated on the market 47 namely gypsum (He and Lee, 2014). In fact, the synthetic gypsum suit-48 49 able for several applications such as wallboard manufacturing is the by-product of the SO₂ scrubbing process for scrubbers using lime or 50 51 limestone as a sorbent material. In this way, the production of gypsum represent a perfect example of how is possible to obtain a new product 52 for the market starting from the need of environmental protection (the 53 SO₂ removal). 54

With reference to the two mentioned sorbents, the most problematic is undoubtedly the limestone since it is more difficult to dissolve in water with consequent higher operating cost (He and Lee, 2014). In contrast, the price of limestone is considerably lower than the price of lime and this condition ensure that limestone is the most widely used sorbent material in wet FGD systems worldwide.

In this regard, the U.S. Environmental Protection Agency (EPA) doc-61 umented as early as the 80's a first report related to the production 62 63 of gypsum by means of wet FGD system highlighting the advantages 64 from an environmental and economic point of view (O'Brien et al., 1984). Recently, Suárez et al. (2016) demonstrated the environmental 65 and economic benefits associated with the use of such a type of "recy-66 cled gypsum" instead of using new natural resources from extraction 67 processes. 68

The state-of-the-art about the FGD systems includes several stud-69 70 ies briefly described. Tesárek et al. (2007) studied the basic mechanical, 71 hydric and thermal properties of the gypsum obtained from a wet FGD system in order to reuse the gypsum in the construction and 72 73 building sector. Glomba (2010) investigated the role of the parameters influencing the pH value of suspension absorbent used in FGD 74 system. He and Lee (2014) studied the incentive mechanism linked 75 to the production of gypsum from FGD in the US Iannacone et al. 76 (2009) investigated the characteristic of FGD particulates in equaliza-77 tion basins by powder X-ray diffraction, scanning electron microscopy 78 with energy dispersive spectroscopy and more. Li et al. (2015) analyzed 79 the potential utilization of FGD gypsum and fly ash for manufactur-80 ing fire-resistant panels while Song et al. (2014) studied the factors 81 82 affecting the precipitation of pure calcium carbonate during the direct aqueous carbonation of flue gas desulfurization gypsum. De Blasio et al. 83 84 (2012) investigated the dissolution of carbonate rocks such as limestone by utilizing hydrochloric acid modelling, subsequently, the mass 85 86 transport phenomena involved in batch stirred tank reactors. Recently, Córdoba (2015) reviewed the FGD technologies currently used to abate 87 sulphur emissions from coal-fired power plants also highlighting the 88 major physic-chemical processes occurring during wet limestone FGD. 89 90 Wang et al. (2005) reviewed the ways to optimize the FGD processes including forced oxidation modifications (FOM) as well as addition of 91 chemical additives as adipic acid or magnesium oxide. Furthermore, 92 Wang et al. (2005) highlighted the systems commonly adopted for the 93 grinding of limestone such as long drum or tube mill and the Hardings 94 95 ball mill. Generally, these ball mills consist of a rotating drum loaded with steel balls that crush the limestone by the action of the tum-96 bling balls as the cylindrical chamber rotates, until obtaining a size 97 less than 3 mm. From the above, it is evident that limited informa-98 tion in terms of improvement of limestone characteristics by means 99 of suitable aging treatments of limestone (also for the improvement of 100 gypsum production) is reported. 101 102

2000). At the critical values of these stresses, the crystal is generally destroyed and if not processing results in the deformation of the solid. During mechano-chemical activation, particles undergo a large number of direct impacts (because of milling mass) and the surface properties of the material modify in time; these impacts create micro defects and electrostatic charges on the particles increasing their surface energy and chemical reactivity (Suryanarayana, 2001). Different types of high-energy (H-E) milling equipment are used to produce mechanically alloyed powders. They differ in their capacity, efficiency of milling and additional arrangements for cooling, heating, etc. as reported in Suryanarayana (2001). By means of the numerous collisions that occur between molecules of the material inside the mill, processes that create chemicals reactions leading to a high particle size reduction of the inlet material object of micronization are activated. Furthermore, the no-hydrostatic efforts applied, due to the high mechanical energy provided and to the high friction between the components of the same material, are very high (Boldyrev and Tkacova, 2000).

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Such mechanic-chemical processes could be applied also in the case of limestone with the intent to reduce the particle size and obtain a product with a greater specific surface area respect to the raw limestone.

Thus, in this context, the aim of the study was to investigate the technical feasibility of mechanic-chemical treatment of the raw limestone with the intent to obtain a micronized limestone able to increase the production of gypsum in a wet FGD system. In detail, the subobjectives were as follows:

- Determination of the grading curve of different micronized limestone by varying the rotation speed of the H-E mill (750 and 950 rpm) adopted in our investigation and that implements a mechanicchemical treatment;
- Testing of the "limestone–water solutions" previously identified by means of a bench-scale reactor capable of simulating a wet FGD system, and;
- Assess the feasibility of using such micronized limestone in a wet FGD system of a real Waste-to-Energy (WtE) plant using a Multi-Criteria Approach (MCA) that take into account economic, environmental and cost factors.

At the best of our knowledge, really limited information related to the application of mechanic-chemical as aging treatment for raw limestone in a wet FGD system are available.

Below, a brief description of the theoretical knowledge of FGD process chemistry and gypsum production is given.

1.1. FGD process chemistry and gypsum production

The most common limestone FGD process is shown in Fig. 1. The flue gas, from which fly ash has been removed in a particulate collection device such as an electrostatic precipitator or a fabric filter, is brought into contact with the limestone slurry in the absorber, where SO_2 is removed.

The chemical reaction of limestone with SO_2 from the flue gas produces waste solids which must be removed continuously from the slurry loop. These waste solids are concentrated in a thickener and then dewatered in a vacuum filter to produce salable gypsum. The principal chemical reactions for the limestone FGD process are presented below Q6 according to (i) SO_2 absorption and (ii) limestone dissolution (Córdoba, 2015; De Blasio et al., 2008).

1.1.1. Sulfur dioxide absorption

The chemical reactions for SO₂ absorption in a scrubber/absorber are Q7 ¹⁶¹ as follows: ¹⁶²

SO_2 (g) $\rightarrow SO_2$ (aq)	(1)	163

- $SO_2 (aq) + H_2O \rightarrow H_2SO_3 (aq)$ (2) 164
- $H_2SO_3 (aq) \rightarrow HSO_3^- (aq) + H^+ (aq)$

Mainly used in other industrial sectors, mechano-chemical processes consist in producing shear stresses in particles of the processed solid by compression, tension and fracture (Boldyrev and Tkacova,

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Fig. 1 - Limestone FGD process flow diagram.

(4)

(5)

(6)

 $_{166}$ HSO_3^- (aq) \rightarrow SO_3^{2-} (aq) + H^+ (aq)

¹⁶⁷ SO_3^{2-} (aq) + 0.5 O_2 (aq) $\rightarrow SO_4^{2-}$ (aq)

 $_{168}$ $\mbox{ HSO}_3{}^-$ (aq) + 0.5O_2 (aq) \rightarrow $\mbox{ SO}_4{}^{2-}$ (aq) + $\mbox{ H}^+$ (aq)

169where g is the gas phase, aq is the aqueous phase, HSO_3^{-} is the bisulfite170ion, SO_3^{2-} is the sulfite ion, SO_4^{2-} is the sulfate ion, O_2 is oxygen, H^+ is171the hydrogen ion, and SO_2 is sulfur dioxide.

172 1.1.2. Limestone dissolution and limestone FGD chemical reactions

The chemical reactions for limestone dissolution in a scrubber/absorber are as follows (Córdoba, 2015; Wang et al., 2005):

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$$CaCO_3(s) \rightarrow CaCO_3 (aq)$$
 (7)

176 $CaCO_3 (aq) \rightarrow Ca^{2+} (aq) + CO_3^{2-} (aq)$ (8)

177 $\text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq})$ (9)

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$$SO_3^{2-}(aq) + H^+(aq) \rightarrow HSO_3^-(aq)$$
 (10)

¹⁷⁹
$$Ca^{2+}(aq) + SO_3^{2-}(aq) + 1/2H_2O \rightarrow CaSO_3 \cdot 1/2H_2O$$
 (s) (11)

¹⁸⁰
$$Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$$
 (s) (12)

Furthermore, the use of limestone in a FGD process system resultsalso yields carbon dioxide:

$$SO_2 + CaCO_3 + H_2O \rightarrow CaSO_3 + H_2O + CO_2$$
(13)

where SO₂ is sulfur dioxide, CaCO₃ is calcium carbonate (limestone),
and CO₂ is carbon dioxide. The final product from the limestone
FGD chemical reactions is calcium sulfite (CaSO₄) from the scrubber/absorber.

1.1.3. Main process parameters

The main process parameters in a limestone FGD system are the (i) stoichiometric ratio (SR), (ii) the liquid/gas ratio, (iii) the slurry pH, (iv) the relative saturation and (v) other important overall FGD system parameters such as reagent type, water loop, solids dewatering, absorber parameters, reheat, reagent preparation, and fan location (Córdoba, 2015; De Blasio et al., 2008).

The SR is defined as the ratio of the actual amount of SO_2 reagent, calcium carbonate (CaCO₃) in limestone fed to the absorber, to the theoretical amount required to neutralize the SO_2 and other acidic species absorbed from the flue gas. Theoretically, 1 mol of CaCO₃ is required per mole of SO_2 removed (SR=1.0). In practice, however, it is usually necessary to feed more than the stoichiometric amount of reagent in order to attain the degree of SO_2 removal required.

The ratio of slurry flow in the absorber to the quenched flue gas flow, usually expressed in units of gal/1000 ft³ is termed the liquid-to-gas (L/G) ratio. Normal L/G values are 60–100 gal/1000 ft³ for limestone systems (Wang et al., 2005). A high L/G ratio is an effective way to achieve high SO₂ removal. This also tends to reduce the potential for scaling, because the spent slurry from the absorber is more dilute with respect to absorbed SO₂. Increasing the L/G ratio can also increase system capital and operating costs, because of greater capacity requirements of the reaction tank and associated hold tanks, dewatering equipment, greater pumping requirements, slurry preparation and storage requirements, and reagent and utility necessities.

Commercial experience has shown that fresh slurry pH as it enters the absorber should be in the range 5.5–6.0 for limestone systems (Wang et al., 2005). As the SO₂ is absorbed from the flue gas, the slurry becomes more acidic and the pH drops. The pH of the spent slurry as it leaves the absorber is in the range 4.0–5.0 for limestone systems.

In limestone FGD processes, the term "relative saturation" (RS) pertains to the degree of saturation (or approach to the solubility limit) of calcium sulfite and sulfate in the slurry. RS is important as an indicator of scaling potential, especially of hard scale, which can present severe maintenance problems. Relative saturation is defined as the ratio of the product of calcium and sulfate ion activities (measured in terms of concentrations) to the solubility product constant. The solution is subsaturated when RS in less than 1.0, saturated when RS equals 1.0, and supersaturated when RS is greater than 1.0. Generally, limestone

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Fig. 2 – Experimentation plan: (a) flow diagram of our investigation; (b) view of the Hicom 15 high—energy mill for limestone micronization.

processes will operate in a scale-free mode when the RS of calcium sulfate is maintained below a level of 1.4 and the RS of calcium sulfite is maintained below a level of approx 6.0. Operation below these levels provides a margin of safety to ensure scale-free operation (Wang et al., 2005).

2. Materials and methods

232 2.1. Experimentation plan

233 The plan of the experimentation, schematized in Fig. 2a, included the following main phases: (1) preliminary lime-234 stone grinding; (2) setting of high-energy (H-E) micronisation 235 parameters; (3) mechano-chemical treatment of limestone 236 previously sieved by means of an H/E Hicom 15 mill; (4) 237 desulfurization tests; (5) assessment of calcium sulphates 238 concentrations both in solution and in the precipitate; (6) 239 estimation of the SO_2 removal efficiency; (7) assessment the 240 technical feasibility using the MCA. 241

The device used for the grinding and micronization of the previously crushed limestone was the Hicom 15 H/E mill (see Fig. 2b). This device is a vertical-axis cylindrical mill whose grinding bodies are made up of numerous steel balls. During the rotation of the cylindrical container, the steel balls collide with the raw material allowing the grinding of the same.

Additionally, the Hicom 15 mill realizes a dry grinding that is based on the use of high pressures, with grinding systems able to withstand high stresses. This technique is the most frequently adopted for obtaining fine particles, especially of flat morphology.

253 2.2. Raw limestone size reduction by micronization

10 kg of limestone, variables in the range 5–12 mm, were preliminarily crushed and screened to reach a size of 3 mm (see
Fig. 2a). The operation took place in compliance with the standard safety regulations.

Subsequently, the H/E mill process parameters were set on 258 the basis of preliminary experiences (Cagnetta et al., 2009; 259 Intini et al., 2009). Differently from Cagnetta et al. (2009) 260 and Intini et al. (2009), that operate with the Polverisette 261 6 (Fritsch, Germany) small-scale laboratory monoplanetary 262 mill at 400-450 rpm, greater velocities have been adopted, as 263 explained below. This is due to the greater robustness of the 264 Hicon 15 H/E mill in handling the high temperatures, limit-265 ing factor in such processes. The H/E mill process parameters 266 267 are the following: (i) grinding time (t); (ii) rotation speed (in rpm, revolutions per minute); (iii) mass of the grinding bodies (m_B); (iv) mass of raw material to be treated (m_C); (v) relationship between m_B and m_C (m_B/m_C). The values used during the micronisation tests are shown in Table 1.

As may be observed, two different rotation speeds (750 and 950 rpm) of the mill were adopted. Instead, the grinding time was set at 10 min for each sample.

In compliance with the safety standards, the mass of the limestone was introduced in the mill by means of a funnel. Then, the steel balls, forming part of the milling mass, were introduced. After the feeding phase, the inlet of the mill was closed and sealed, and then the system was electrically connected.

After setting the milling parameters, which values are reported in Table 1, the micronization activity was performed for each sample of limestone. During the experiment, pH and temperature were controlled paying attention to the rapid increase of the latter.

At the conclusion of the two grinding operation (at 750 and 950 rpm), the contents of the each jar were sieved in order to clean the grinding media. In this way, the value of the mass output the mill was as much as possible the same as the mass input. The obtained limestone, weighed and stored in containers of 11, appeared pulverized to the eye and touch, completely homogeneous and with different particle size of the two samples, variable in the range of 50–70 μ m. The final product was ready to be used.

2.3. Desulfurization tests

A bench scale reactor connected to a controller was used (see Fig. 3) with the intent to simulate a wet FGD process that takes place in a typical industrial absorber. The experimental apparatus was constituted by (i) a power cylinder containing the flue gas, (ii) the Esedra reactor for testing the absorption of SO₂ from the gas to the liquid phase, (iii) the control system and (iv) the flasks to trap any non-absorbed SO₂ in the liquid phase, as visible in Fig. 3. The desulfurization tests were conducted in the Esedra reactor (see Fig. 3c) specially adapted to the case. Thus, the experimental setup is much simpler than that used in other research such as De Blasio et al. (2012, 2008).

The gas used in input to the reactor was composed as follows: 84.4% nitrogen, 9.9% carbonic dioxide, 4.8% oxygen and 0.9% sulfur dioxide.

The Esedra reactor was set with a contact time in the reactor of 10 min in accordance to the Integrated Pollution Prevention and Control document (European Commission, 2006).

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Table 1 – Process parameters values adopted in mechanic-chemical treatment tests.				
Parameter	Unit	Treatment test		
		Sample 2 (750 rpm)	Sample 3 (950 rpm)	
Grinding time	min	10	10	
Rotation speed	rpm	750	950	
Mass of grinding bodies (m _B)	kg	9.41	9.41	
Mass of raw material to be treated (m_C)	kg	0.79	0.70	
Ratio m _B /m _C	-	12/1	12/1	



Fig. 3 – Bench scale system for the desulfurization tests: (a) main components; (b) sampling into the reactor; (c) view of the Esedra reactor. The solution into the reactor consisted of calcium carbonate, hydrogen chloride and water.

Each test was conducted in 4 h with the intent to measure the calcium sulphate concentration over time. For each test, 8 samples were collected considering both the precipitate in the reactor (4 samples, one at each hour) both the liquid solution (also in this case, 4 samples, one at each hour).

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The liquid solution and the precipitate were characterized in terms of calcium sulphates concentration by means of the ion chromatography and gravimetric analysis, respectively.

Three desulfurization tests were carried out. The first test referred to the use of standard limestone normally used in a wet FGD system. The other two tests used micronized samples at different rotation speeds as previously mentioned (750 and 950 rpm).

For all tests, a solution of limestone and hydrochloric acid 326 (HCl) was prepared according to the following composition: 327 0.1 M of limestone and 16 ml of hydrochloric acid (HCl) at 37%. 328 The hydrochloric acid was used because limestone is not sol-329 uble in water. Therefore, by using a strong acid such as HCl, 330 it was possible to obtain a solution as homogeneous as pos-331 sible ensuring fast dissolution of the limestone (De Blasio 332 et al., 2012). Furthermore, the adoption of HCl was also due 333

to technological motivations as described herein. First of all, HCl represent a typical constituent of the flue gas produced in a power plant or a WtE plant. The typical range of HCl, before its removal in the flue gas line, was for WtE plant of 450–1000 mg/m³ although dependent on the fuel burned. Therefore, the commercial HCl (at 37%) was diluted until the concentration of HCl in the liquid was equal to the theoretical one present in the gaseous flow (450–1000 mg/m³). More details on the methodology adopted for the dissolution of limestone are reported in Lund and Fogler (1975).

Once prepared, 1l of solution was transferred into the reactor (characterized by a volume of 3l), as shown in Fig. 3a.

After sealing the reactor by means of two steel wheels based on 6 bolts, a plastic membrane and parafilm were added. In this way, a closed system was set avoiding penetration of the air into the reactor. Then, two flasks were connected in series to the reactor as schematized in Fig. 3. These flasks were first filled with a solution of 125 ml of NaOH (0.05 M) and 250 μ g/l of H₂O₂ and subsequently sealed with rubber stoppers. Such a flask system had the purpose to catch those amounts of sulfur

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Table 2 – Main process parameters in the simulated limestone FGD system.					
Parameter	Unit		Treatment test		
		Sample 1	Sample 2 (750 rpm)	Sample 3 (950 rpm)	
Stoichiometric ratio ^a	-	1.1–1.4	1.1–1.4	1.1–1.4	
Liquid/Gas ratio ^b	gal/1000 ft ³	60-100	60–100	60–100	
Slurry pH ^c	-	5.5–9.5	5.5–9.5	5.5–9.5	
Relative Saturation ^d	-	<6	<6	<6	

^a The stoichiometric ratio (SR) is defined as the ratio of the actual amount of SO₂ reagent and the calcium carbonate (CaCO₃) in the limestone fed to the absorber.

^b The ratio of slurry flow in the absorber to the quenched flue gas flow, usually expressed in units of gal/1000 ft³ is termed the liquid-to-gas (L/G) ratio.

 $^{\rm c}~$ pH of the slurry in the Esedra reactor.

^d In limestone FGD process, the term "relative saturation" (RS) pertains to the degree of saturation (or approach to the solubility limit) of calcium sulfate in the slurry.

dioxide which, in a first moment, escaped to the absorption of 354 the limestone particles inside the reactor. 355

Still, the controller and the flow meter of the system 356 357 allowed setting the following process parameters for all 358 the desulfurization tests: (i) temperature = $25 \degree C$; (ii) agitator 359 rotation speed = 600 rpm; (iii) gas mixture flow = 1000 ml/min. Other process parameters such as stoichiometric ratio, liq-360 uid/gas ratio, slurry pH and relative saturation are reported 361 in Table 2. 362

2.4. Multi-criteria assessment 363

The feasibility study aims to verify the potential application of 364 the mechanical-chemical treatment considering a real plant. 365 Since different aspects have to be considered as economic or 366 environmental, the multi-criteria approach (MCA) was con-367 sidered. This approach is commonly adopted in "problems of 368 selection of the best solution" given a finite set of alternatives 369 to be compared to each other, as documented from the large 370 literature available (De Gisi et al., 2014; Langhans et al., 2014; 371 De Feo et al., 2013). 372

Specifically, the feasibility study has foreseen the follow-373 ing phases: (i) definition of the scenarios to be compared; (ii) 374 definition of the evaluation criteria; (iii) determination of the 375 weight vector; (iv) resolution of the alternatives matrix iden-376 tifying, in addition, the best suitable scenario. 377

In order to facilitate the discussion of results, the feasi-378 bility study was applied to a full scale WtE plant which burns 379 solid recovered fuel (SRF) in a boiling bed combustor. The main 380 characteristics of the WtE plant as well as the flow diagram are 381 given in Table 3 and Fig. 4, respectively. 382

With reference to the first point, three scenarios were con-383 sidered as listed below: 384

- Scenario 1. It involves the use of limestone after coarse 385 milling: 386
- Scenario 2. It involves the use of micronized limestone hav-387 ing used the H-E mill with 750 rpm; 388
- Scenario 3. As in the case of the scenario 2, however using 389 the H-E mill with 950 rpm. 390

With reference to the second point, three evaluation crite-391 ria were defined: 392

393 • I₁ = Gypsum production: the criterion quantifies the annual production of gypsum (ton/year); 394

Table 3 – Characteristic data of the WtE plant used in the feasibility study (from De Gisi et al., 2016).

Parameter	Unit	Values
SRF feeding ^a	ton/month	7400.8
SRF heating value	MJ/kg	20.2
Sulfur content	%	0.6
Flue gas flow-rate	Nm³/h	89,745.0
Hours of operation per year ^b	h	7000
Flue gas production	Nm³/year	6.28×10^8
SO ₂ produced	ton/year	23.4
SO ₂ emitted	ton/year	1.872
SO ₂ removed	ton/year	21.528
Limestone used	ton/year	1386.8
Gross electricity production	MWh/year	73,091
^a SRF = solid recovered fuel		

^b Estimated as 80% of annual hours.

- I₂ = SO₂ removal efficiency: the criterion quantifies the SO₂ percentage removal that is obtained as a result of the desulfurization process (%);
- I₃ = Milling operation cost: the criterion quantifies the cost of grinding, expressed in terms of electricity consumption for the grinding operations (MWh/year).

The three criteria were applied to the case study of the WtE plant of Fig. 4.

The weights vector of the evaluation criteria (third point), indicated by $W = (w_1, w_2, w_3)$ with w = scalar number, were determined by means of the Paired Comparison technique (PCT) as defined by Mondy and Noe (2008).

With reference to the fourth point, the initial alternatives matrix, as will be shown in Section 3.3, was normalized by means of the application of the max/min method (Langhans et al., 2014). Denoted by x_{ii} the performance of the alternative i-th (i.e. scenario 1) with respect to the j-th evaluation criterion (i.e., criterion I₁), the normalized value was calculated with the following relations:

$$\bar{\mathbf{x}}_{ij} = \mathbf{x}_{ij} / \text{Max}(\mathbf{x}j) \tag{14}$$

$$\bar{\mathbf{x}}_{ij} = \operatorname{Min}\left(\mathbf{x}_{j}\right) / \mathbf{x}_{ij}$$
 (15) 415

The selection of the relation depends on the nature of the 416 criterion, if it was to maximize (14) or minimize (15) in respect 417 to the general goal (to select the best scenario). In the specific 418 case, the I1 and I2 criteria were to be maximized while, the 419 criterion I3 to minimize.

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Fig. 4 - Flow diagram of the WtE plant considered in the feasibility study.

Finally, the last step focused on the resolution of alter-421 natives matrix starting from the normalized alternatives 422 matrix. Specifically, the construction of the composite indi-423 cator involved the adoption of the linear aggregation method, 424 commonly used in literature (Sabia et al., 2016; Langhans et al., 425 2014). The preference index indicated with PI and defined as 426 the parameter that aggregates the information of the three 427 evaluation criteria (or indicators), was the result of the follow-428 ing relation: 429

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$$PI_i = \sum_{j=1}^{m} \bar{x}_{ij} = \sum_{j=1}^{m} x_{ij} \cdot w_j$$
 (16)

The method described above allowed to evaluate the single
scenario in respect of the three criteria described above and,
further, to identify the best suitable scenario.

Finally, the inventory of additional data (i.e., electricity con-434 sumption) used during the feasibility assessment was herein 435 described. In terms of gypsum production, a production of 436 3-4t of gypsum per ton of SO2 removed was assumed (Le 437 Cloirec, 2012). In terms of SO₂ removal, the removal efficiency 438 $[SO_2\% = (SO_{2,IN} - SO_{2,OUT})/SO_{2,IN}]$ was evaluated indirectly by 439 means of a material balance referred to the sulfur content and 440 considering the Esedra reactor as control volume (see Fig. 5). 441

With reference to the milling costs, the electricity con-442 sumption was considered the most significant item according 443 to Baláž (2008). In fact, raw material preparation is an 444 electricity-intensive production step requiring generally about 445 25-35 kWh/t (of raw material). Modern ball mill may use 446 between 32 and 37 kWh/t. However, Worrell and Galitsky (2008) 447 highlighted how the modern state-of-the-art concepts such 448 as Horomill[®] (Edec, 2008) allowed obtaining an electric energy 449 saving of 20-50%. 450

Still, the values related to the use of a coarse grinding were451clearly higher than that experimented by Zeng and Forssberg452(1991), that have estimated a cost in the range of 8–10 kWh/t.453Therefore, based on the cited literature, the following costs454were adopted:455

- Cost for grinding (coarse) = 25 kWh/t;
- Cost for grinding with H-E mill at 750 rpm = 35 kWh/t × 0.8 (20% saving by adopting modern machinery) = 28 kWh/t;
- Cost for grinding with H-E mill at 950rpm=28kWh/t× (1+0.08) (8% increase due to higher speed)=30kWh/t.

3. Results and discussion

3.1. Limestone micronization

Fig. 6 shows the results related to the particle size analysis with reference to the sample 1 (labeled "tq", not-micronized), the sample 2 (labeled "750 rpm" and micronized with 750 rpm rotation speed) and the sample 3 (labeled "950 rpm" and micronized with 950 rpm rotation speed).

In particular, Fig. 6a shows how the grading curve tends to assume a more vertical position starting from the sample 1 to the sample 3 highlighting, therefore, the presence of materials with more homogeneous size. Similar results were obtained by Samanli et al. (2008) in a study in which the comparison of grinding performance of an H-E mill in terms of particle size was performed by varying the main process parameters such as the rotation speed or time of the milling.

Furthermore, Fig. 6b shows how the H-E mill micronization increases the fine fraction of the limestone. Considering the case of the sample 3, it is possible to observe a greater volume of material with a size less than $1 \mu m$ as well as a corresponding reduction in volume of the coarser fraction. Overall, 456

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Fig. 6 – The milling results with reference to the samples 1 (tq), 2 (750 rpm) and 3 (950 rpm): (a) grading curves particle size (in μm)—passing percentage; (b) particle size distribution (in %).

a shift of the curve of the sample 3 towards the fine fraction(see Fig. 6b) was observed.

(a)

Still, the obtained results show how the micronization 482 effect is most effective in correspondence with a greater 483 rotation speed (950 rpm). In this regard, a common problem 484 relating to the grinding process using H-E mills is represented 485 by the control of temperature (Boldyrev and Tkacova, 2000). 486 The high pressures internal to the system as well as the high 487 frictional forces between the material and the ground bod-488 ies could quickly increase the temperature in the mill. As a 489 consequence, with temperature close to 80°C, the grinding 490 process runs the risk of stopping, making it discontinuous. 491 So, for grinding of up to 10 min, it is good to wait until the 492 temperature of the mill is approximately 50 °C before starting 493 the new milling. 494

Taking into account these considerations, operating with a contact time of 10 min, any plant shutdown was observed in our experiments.

498 3.2. Desulfurization tests

Fig. 7 shows the results of the desulfurization tests. In detail,
Fig. 7a and b shows the calcium sulphate concentrations in
the case of sample 1 (tq) for precipitate and liquid solution,
respectively. Instead, Fig. 7c-f shows the calcium sulphate

concentrations in the cases of the sample 2 (750 rpm) and sample 3 (950 rpm), respectively.

(b)

It is possible to observe how the calcium sulphate concentration in the precipitate is almost always greater in the case of micronized limestone compared to the non-micronized one. Furthermore, the calcium sulphate concentration was greater with reference to pH values in the range 5.5–6.0 which corresponds to the optimum range for limestone-based wet FGD. In this regard, Wang et al. (2005) and Córdoba (2015) highlight how operation of limestone FGD systems at low pH levels, approaching 4.5, improves reagent utilization. However, low pH values also reduce SO₂ removal efficiency and also increase the danger of hard scale formation because of increased oxidation at lower pH levels. Instead, operation of limestone FGD systems at high pH level, above 6.0, tends to improve removal efficiency as well as to increase the danger of soft scale formation.

Generally, the micronized samples work better than the sample 1 (tq) in terms of gypsum production and SO_2 removal, as illustrated afterwards. Most probably, this is due to the greater absorbent surface area of the micronized samples (2 and 3). As above is in line with Lee et al. (2005) that high-light the important role of the absorbent surface area to obtain absorbent with high desulfurization activity.

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The physical observation of the tests made it possible to 527 add additional items for discussion as herein reported. With 528 reference to the case of sample 2 (750 rpm), the initial pH 529 value was 9.05 and the solution in the reactor appears cloudy. 530 However, after few minutes, the solution assumed a light 531 homogeneous colour. During the test, the limestone was dis-532 solved in an optimal way and the pH value, after the first 533 sampling (after 1 h), fell to 8.00. Considering the sample 3 534 (950 rpm), the initial pH value was around 8.00. During the 535 tests, in addition to a decrease in pH, the solution appeared 536 colourless and sometimes crystalline. This meant that lime-537 stone was dissolved optimally. At the end of the test, the pH 538 value was approximately 4.5. Instead, with reference to the 539 sample 1 (tq), limestone was not dissolved already in the first 540

hour. In fact, the aqueous solution appeared cloudy and a deposit of material on the bottom of the reactor was clearly visible. Due to these conditions, the whole test was compromised. The high particle size of the limestone, milled with a standard mill, produced an accumulation of limestone on the bottom of the reactor. Therefore, after these problems, a second mixing was put in place for the sample 1 in accordance to the methodology reported in Lund and Fogler (1975). Consequently, the results of Fig. 7a, b refer to this second trial.

Still, the results of Fig. 7 show another interesting aspect. During the carrying out of the test, a decrease in the concentration of calcium sulfate in the aqueous solution was observed (see Fig. 7a, c, e). As above were more accentuated in cases of micronized samples compared to the sample 1. This decrease 541

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Fig. 8 – Results of the desulfurization tests: (a) calcium sulphate as total (in solution + in precipitate) vs. time; (b) SO₂ removal efficiency vs. time.

Table 4 – Preliminary assessment of the gypsum production with reference to a full scale WtE plant used for the comparison.^a

Scenario	Assessment of gypsum production [ton/year]	Specific production of gypsum		Percentage variation respect to the scenario 1 [%] ^b
		[kg/m ³ of flue gas]	[ton/MWh]	
Using sample 1 (t.q.) Using sample 2 (750 rpm) Using sample 3 (950 rpm)	75.3 87.4 89.4	$\begin{array}{c} 1.20 \times 10^{-4} \\ 1.39 \times 10^{-4} \\ 1.42 \times 10^{-4} \end{array}$	$\begin{array}{c} 1.031 \times 10^{-3} \\ 1.196 \times 10^{-3} \\ 1.223 \times 10^{-3} \end{array}$	- 16.0 18.6

^a Data related to the WtE plant considered for simulating the calculation: (i) feeding (as quantity) = 7400.8 t/month; (ii) type of fuel = SRF; (iii) heating value = 20.2 MJ/kg; (iv) flue gas flow-rate = 89,745.0 Nm³/h; (v) hours of operation per year = 7000 h; (vi) flue gas production on yearly basis = 89,745.0 (Nm³/h) × 7000 (h/year) = 6.28 × 10⁸ Nm³/year; (vii) SO₂ removed from flues gas = 21.528 t SO₂/year.

^b The percentage increase shall be evaluated with the following relation: $[(x_2-x_1)/x_1] \times 100$, where x_2 is the values of the gypsum production (in ton/year) with reference to the scenario 2 or 3 and x_1 the values of the gypsum production (in ton/year) considering the starting scenario (scenario 1).

was due to the non removal of precipitate from the bottom
 of the reactor by generating, in addition, a consequent loss of
 performance of the wet FGD system investigated.

Although the concentration of calcium sulphate as total (intended as the sum of calcium sulphate concentration in the precipitate and in the aqueous solution) increased over time (see Fig. 8a), the performance of the wet FGD system decreased as visible in Fig. 8b. Furthermore, the SO₂ removal efficiency had values even lower than those set by the BREF for Large Combustion Plants (BREF-LCP, 2016).

These results were in line with the technical literature: the 565 FGD technology needs a removal system of the precipitate dur-566 ing the course of desulfurization as schematically shown in 567 Fig. 1. Additionally, if we consider the "scale effect" due to the 568 fact that our investigation was at bench scale, the "accumula-569 tion of precipitate in the reactor" was responsible for the low 570 yields of the wet FGD system implemented, compared to the 571 expected results (BREF-LCP, 2016). 572

However, tests carried out after 1 h were not affected by the
accumulation of the precipitate. Therefore, the data obtained
at 1h, considering the three investigated samples (sample
1–3), were used in the feasibility study since considered representative of the yields of the wet FGD system implemented.

578 3.3. Feasibility analysis

The specific production of gypsum was estimated taking into account that generally 3–4 t of gypsum per ton of SO₂ removed in the system are produced (Le Cloirec, 2012). With reference to the WtE plant under investigation, the SO₂ created during the combustion process and that emitted to the chimney were 23.40 and $1.87 \text{ t } \text{SO}_2$ /year, respectively (De Gisi et al., 2016). The SO₂ removed in the cleaning system was (23.4–1.87) ton/year = 21.53 t/year. Therefore, the production of gypsum with reference to the scenario 1 was in the range 64.6–86.1 t/year, with an average value of 75.3 t/year (see Table 4).

As reported in the previous paragraph, an increase in the calcium sulfate production was generated with the micronization of limestone. Considering the results after 1 h of investigation, this percentage was found approximately of +16.0 and +18.6% for the scenario 2 (750 rpm) and 3 (950 rpm), respectively. Therefore, the production of gypsum was estimated of 87.4 and 89.4 t/year for the scenario 2 and 3, respectively.

Additionally, Table 4 shows the specific production of gypsum equal to 1.20×10^{-4} , 1.39×10^{-4} and 1.42×10^{-4} kg/m³ of flue gas for scenarios 1, 2 and 3, respectively. The so obtained values of gypsum specific production were in line with Tognotti (2007) that, with reference to the ENEL power plant of La Spezia (Italy), fed with coal and characterized by an hourly capacity of 2,370,000 Nm³/h of flue gas, a yearly mass flow of removed SO₂ of 29,364.3 t SO₂ removed/year and a yearly gypsum production of 70,000 t/year, showed a specific production of 4.22×10^{-3} kg/m³ of flue gas. However, the production of gypsum may depend on various factors such as the 581

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Table 5 – Alternative matrix for scenarios comparison with reference to the investigated WtE plant. ^a				
Scenario	Criteria			
	Gypsum production [ton/year]	SO ₂ removal efficiency [%]	Electricity consumption for grinding [MWh/year] ^b	
Using sample 1 (t.q.)	75.3	84.2	34.67	
Using sample 2 (750 rpm)	87.4	97.7	73.50	
Using sample 3 (950 rpm)	89.4	99.9	76.27	

^a Data related to the WtE plant considered for simulating the calculation: (i) feeding (as quantity)=7400.8 t/month; (ii) type of fuel=SRF; (iii) heating value=20.2 MJ/kg; (iv) flue gas flow-rate= $89,745.0 \text{ Nm}^3$ /h; (v) hours of operation per year=7000 h; (vi) flue gas production yearly= $89,745.0 \text{ (Nm}^3/h) \times 7000$ (h/year)= $6.28 \times 10^8 \text{ Nm}^3$ /year; (vii) SO₂ removed from flues gas= 21.528 t SO_2 /year.

^b The unit operation for the grinding of gypsum are the following: scenario 1 (coarse milling); scenario 2 (coarse milling+micronization at 750 rpm); scenario 3 (coarse milling+micronization at 950 rpm).

Table 6 - Normalized alternative matrix for scenarios comparison with reference to the investigated WtE plant. ^{a,b}

Scenario	Criteria		
	Gypsum production [ton/year]	SO ₂ removal efficiency [%]	Electricity consumption for grinding [MWh/year] ^b
Using sample 1 (t.q.)	0.842	0.843	1.000
Using sample 2 (750 rpm)	0.978	0.978	0.472
Using sample 3 (950 rpm)	1.000	1.000	0.455

^a Data related to the WtE plant considered for simulating the calculation: (i) feeding (as quantity)=7400.8 t/month; (ii) type of fuel=SRF; (iii) heating value=20.2 MJ/kg; (iv) flue gas flow-rate=89,745.0 Nm³/h; (v) hours of operation per year=7000 h; (vi) flue gas production yearly=89,745.0 (Nm³/h) × 7000 (h/year)=6.28 × 10⁸ Nm³/year; (vii) SO₂ removed from flues gas=21.528 t SO₂/year.

^b The result of the normalization consists of values in the range 0–1 (De Feo et al., 2013).

type of fuel used in the combustion, its sulfur content as wellas the absorbent solution adopted.

In terms of environmental protection, the wet FGD process simulated at bench scale showed different performance as mentioned in Section 3.2. Considering the results after 1 h of investigation, the SO₂ removal efficiency was equal to 84.2, 97.7 and 99.9% with reference to the sample 1 (tq), sample 2 (750 rpm) and sample 3 (950 rpm), respectively.

The increased absorption capacity was due to the greater 617 specific surface area of the micronized product in accordance 618 with Córdoba (2015). In this regard, Bazzoni (2014), using 6108 a commercial product with a higher specific surface area 620 (Sorbacal[®]SP) in a full scale experimentation (at the WtE plant 621 of Parona, Lombardy (Northern Italy), with a treatment capac-622 ity of 580,000 t/year of SRF), achieved better performance, in 623 terms of SO_2 removal, compared to the limestone reagent 624 commonly used in the company. 625

In terms of costs, the grinding of limestone undoubtedly 626 represents an additional item. In fact, the micronization must 627 be considered as an aging treatment, additional to the basic 628 treatment which relates to the grinding of the raw limestone. 629 Using the unit values reported in Section 2.3, the energy cost of 630 grinding processes amounted to 34.7, 73.5 and 76.3 MWh/year 631 for scenarios 1, 2 and 3, respectively. The higher cost of the sce-632 nario 2 respect to the scenario 1 was due to the micronization 633 understood as additional aging treatment. Instead, the higher 634 cost of the scenario 3, also compared to the case of the scenario 635 2, was the result of the adoption of a higher rotation speed 636 (950 rpm) with a consequent generation of higher energy con-637 sumption, as highlighted in Zeng and Forssberg (1991). In 638 this regard, recently, Fišteš et al. (2013) has estimated, albeit 639 with reference to chocolate grinding, the effect of processing 640 parameters such as steel balls mass or agitator shaft speed, 641 on energy consumption of ball mill. In the present study, the 642 increase in energy consumption of the scenario 3 compared to 643 that of the scenario 2 was estimated to 8% in accordance to the 644

technical standards for this type of mill available in literature (Cement Plant Environmental Handbook, 2015).

The estimated electricity consumption was widely covered from the electricity produced in plants of this type. In fact, with reference to the WtE under investigation, the total annual energy consumption was of 13,895 MWh/year (De Gisi et al., 2016). Consequently, the adoption of an additional treatment such as the micronization only leads to an increase of 0.5% of the energy consumptions.

From the foregoing points, the three evaluation criteria defined in Section 2.4 required different weights. In the present study, we hypothesized the following order of priority (indicated as an environmentalist): I_2 (environmental protection) > I_1 (production of gypsum) > I_3 (cost of additional treatment).

In order to synthesize in a single parameter the outcome of the comparison, Table 5 (indicated as alternatives matrix) summarizes the results of the feasibility study with reference to scenarios 1, 2 and 3.

The application of the max/min method to the alternatives of the normalized matrix (see Table 6) and of the SAW/PCT method for the determination of weights (in compliance with the criteria priority previously established), allowed the resolution of the normalized alternative matrix by means of the MCA, which results are showed in Fig. 9.

It is observed how, with reference to the environmentalist and gypsum production oriented cases, solutions with micronization are to be preferred when compared to the scenario 1. Instead, only in the balanced case, where the criteria weights have the same weight, the scenario 1 was found the best solution. However, the balanced case, in accordance to the technical motivations of above, was purely theoretical.

Finally, it is important to observe how, the obtained results need of insights such as the kinetics of the desulfurization process as well as other considerations of technological nature. This because, the limestone/gypsum desulfurization

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Fig. 9 – Scenarios comparison by means of the use of preference index (PI) as aggregation parameter and varying the weight vector of the evaluation criteria as follows: gypsum production oriented $(I_1 > I_2 > I_3)$; balanced $(I_1 = I_2 = I_3)$; environmentalist $(I_2 > I_1 > I_3)$, where, $I_1 =$ gypsum production; $I_2 = SO_2$ efficiency; $I_3 =$ costs of limestone grinding.

processes operate in an aggressive environment with potential problems of corrosion, abrasion and erosion that need
to be taken into account (Bodènan and Deniard, 2003; Van
Caneghem et al., 2012).

4. Conclusions

Based on the obtained results, the following conclusions can be drawn:

• The micronization process based on Hicom 15 H-E mill, con-687 ducted considering a raw limestone with 3 mm particle size 688 and a contact time of 10 min, occurred securely without 689 generating machine downtime due to high temperatures. 690 Furthermore, the ground material, considering both 750 and 691 950 rpm as rotational speeds, was more homogeneous and 692 with a greater percentage of the fine fraction compared to 693 that of the un-treated limestone; 694

- Considering the desulfurization tests for gypsum produc-695 tion, the adoption of limestone pre-treated with H-E mill is 696 to be considered preferable to the raw limestone milled with 697 a standard device. In fact, the micronized limestone is dis-698 solved in water better than the un-treated limestone. The 699 amount of calcium sulphate in the precipitate and aqueous 700 solution (the gypsum) was greater in the cases of micronized 701 limestone due to a higher value of the absorbent specific 702 surface area of the micronized media compared to that of 703 the raw limestone. Furthermore, in terms of environmen-704 tal protection, the results after 1 h of investigation showed 705 a SO₂ removal efficiency of 84.2, 97.7 and 99.9% with refer-706 ence to the sample 1 (tq), sample 2 (750 rpm) and sample 3 707 (950 rpm), respectively; 708
- Using the results obtained at laboratory scale, the feasi-709 bility study highlighted an increase in terms of gypsum 710 production compared to that of the scenario 1 (using the 711 raw limestone). The specific production of gypsum was 712 1.20×10^{-4} , 1.39×10^{-4} and 1.42×10^{-4} kg/m³ of flue gas, for 713 scenarios 1, 2 (using limestone gridding at 750 rpm rotation 714 speed) and 3 (using limestone gridding at 950 rpm rotation 715 speed), respectively; 716
- In terms of costs, the grinding of limestone undoubtedly represents an additional item. The energy cost of grinding processes amounted to 34.7, 73.5 and 76.3 MWh/year for scenarios 1, 2 and 3, respectively. Moreover, the estimated

electricity consumption was widely covered from the electricity produced in a WtE plant. The case study addressed highlighted how the adoption of an additional treatment such as the micronization only leads to an increase of 0.5% of the total energy consumptions;

• The application of the MCA approach has led to a multicriteria assessment which highlighted, with reference to environmentalist and gypsum production oriented scenarios, how solutions with micronization are to be preferred when compared to the scenario 1 (tq).

The obtained results need of further insights such as the kinetics of the desulfurization process. In order to better evaluate the production of gypsum over the time, an experimental reactor should be equipped with a device for the removal of the precipitate from the reactor bottom.

Furthermore, since the limestone/gypsum desulfurization processes operate in an aggressive environment with problems of corrosion, abrasion and erosion, additional investigations, in this direction, will have to be considered. Finally, studies that take into account the economic and environmental dimension of the problem, have to be conducted in order to scale-up on industrial level.

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