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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 (SO_2) 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 SO_2 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 SO_2 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 (SO_2) contained in gases produced by the combustion of fossil fuels such as coal, oil, municipal solid waste and many industrial processes. SO_2 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).

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 SO_2 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 flue gases with lime or limestone slurries (wet scrubbers) can achieve 95% SO_2 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 the possibility of recovering a new product to be allocated on the market namely gypsum (He and Lee, 2014). In fact, the synthetic gypsum suitable for several applications such as wallboard manufacturing is the by-product of the SO_2 scrubbing process for scrubbers using lime or 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 for the market starting from the need of environmental protection (the SO_2 removal).

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) documented as early as the 80's a first report related to the production of gypsum by means of wet FGD system highlighting the advantages from an environmental and economic point of view (O'Brien et al., 1984). Recently, Suárez et al. (2016) demonstrated the environmental and economic benefits associated with the use of such a type of "recycled gypsum" instead of using new natural resources from extraction processes.

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

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, 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).

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 sub-objectives 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 mechanic-chemical 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 SO_2 absorption in a scrubber/absorber are Q7 as follows:

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

$$SO_2\ (aq) + H_2O \rightarrow H_2SO_3\ (aq) \quad (2)$$

$$H_2SO_3\ (aq) \rightarrow HSO_3^-\ (aq) + H^+\ (aq) \quad (3)$$

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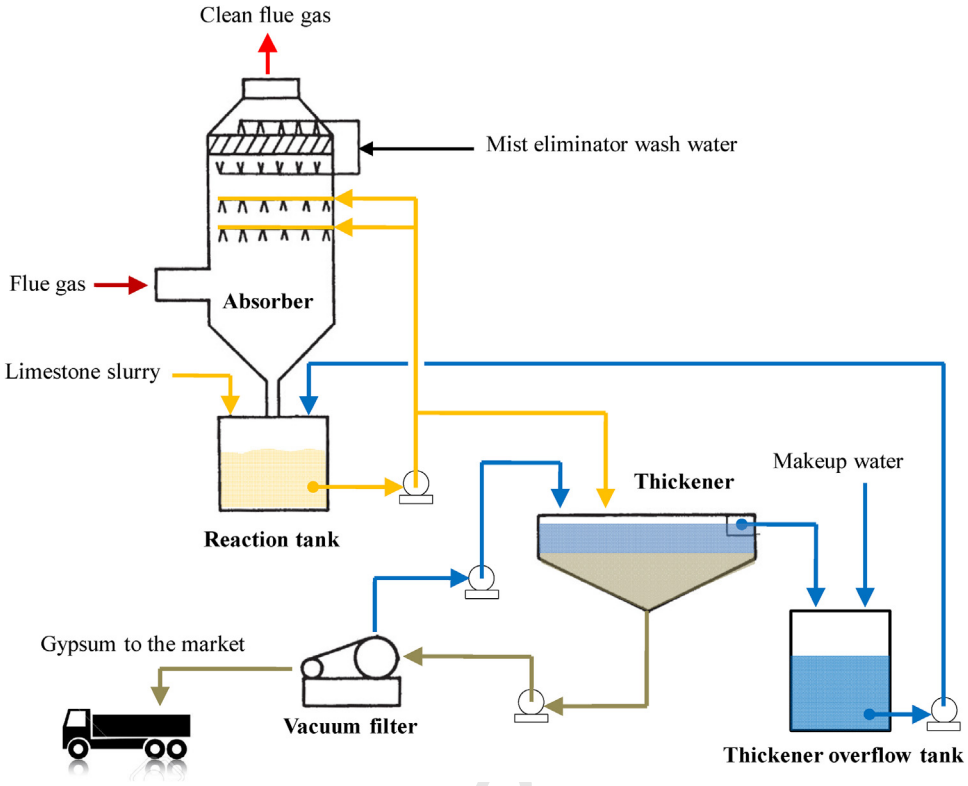


Fig. 1 – Limestone FGD process flow diagram.

$$HSO_3^- (aq) \rightarrow SO_3^{2-} (aq) + H^+ (aq) \quad (4)$$

$$SO_3^{2-} (aq) + 0.5\,O_2 (aq) \rightarrow SO_4^{2-} (aq) \quad (5)$$

$$HSO_3^- (aq) + 0.5O_2 (aq) \rightarrow SO_4^{2-} (aq) + H^+ (aq) \quad (6)$$

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

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):

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

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

$$CO_3^{2-} (aq) + H^+ (aq) \rightarrow HCO_3^- (aq) \quad (9)$$

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

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

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

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

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

where SO_2 is sulfur dioxide, $CaCO_3$ is calcium carbonate (limestone), and CO_2 is carbon dioxide. The final product from the limestone FGD chemical reactions is calcium sulfite ($CaSO_4$) 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 ($CaCO_3$) 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 $CaCO_3$ 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 ft^3 is termed the liquid-to-gas (L/G) ratio. Normal L/G values are 60–100 gal/1000 ft^3 for limestone systems (Wang et al., 2005). A high L/G ratio is an effective way to achieve high SO_2 removal. This also tends to reduce the potential for scaling, because the spent slurry from the absorber is more dilute with respect to absorbed SO_2. 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 SO_2 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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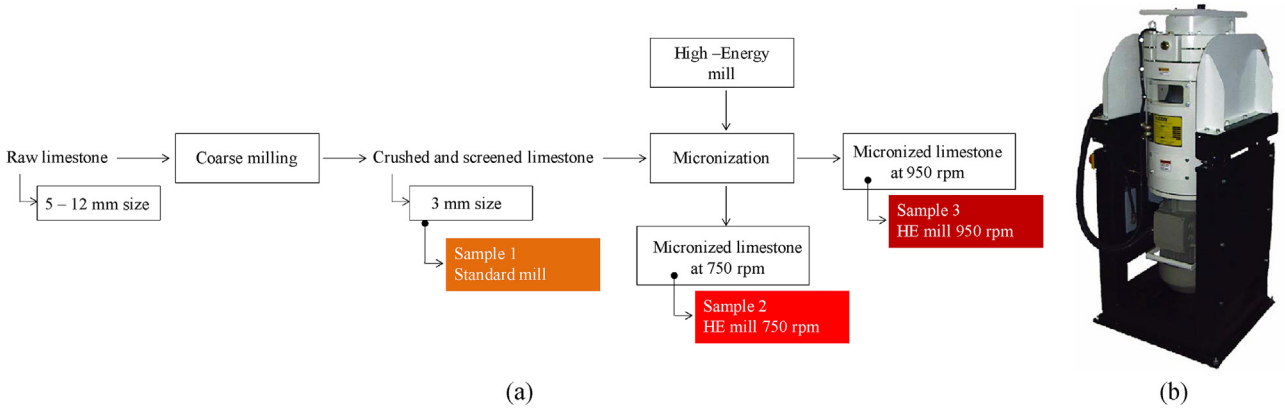


Fig. 2 – Experimentation plan: (a) flow diagram of our investigation; (b) view of the Hicom 15 high—energy mill for limestone micronization.

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

2.1. *Experimentation plan*

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

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.

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 the basis of preliminary experiences (Cagnetta et al., 2009; Intini et al., 2009). Differently from Cagnetta et al. (2009) and Intini et al. (2009), that operate with the Polverisette 6 (Fritsch, Germany) small-scale laboratory monoplanetary mill at 400–450 rpm, greater velocities have been adopted, as explained below. This is due to the greater robustness of the Hicon 15 H/E mill in handling the high temperatures, limiting factor in such processes. The H/E mill process parameters 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 1 l, 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 μm. 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 SO_2 from the gas to the liquid phase, (iii) the control system and (iv) the flasks to trap any non-absorbed SO_2 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

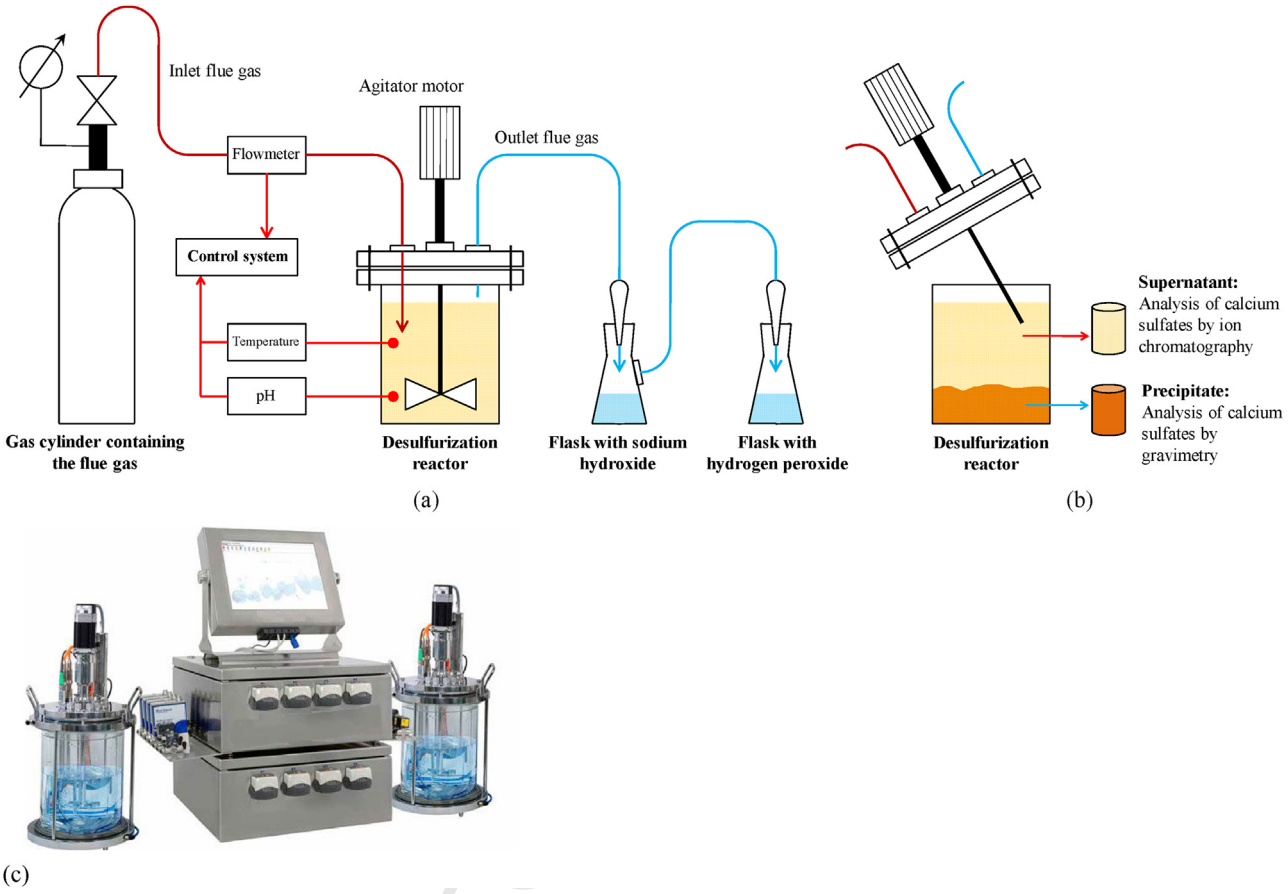


Fig. 3 – Bench scale system for the desulfurization tests: (a) main components; (b) sampling into the reactor; (c) view of the Esedra reactor. The solution into the reactor consisted of calcium carbonate, hydrogen chloride and water.

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).

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 (HCl) was prepared according to the following composition: 0.1 M of limestone and 16 ml of hydrochloric acid (HCl) at 37%. The hydrochloric acid was used because limestone is not soluble in water. Therefore, by using a strong acid such as HCl, it was possible to obtain a solution as homogeneous as possible ensuring fast dissolution of the limestone (De Blasio et al., 2012). Furthermore, the adoption of HCl was also due 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/m^3 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/m^3). More details on the methodology adopted for the dissolution of limestone are reported in Lund and Fogler (1975).

Once prepared, 1 l of solution was transferred into the reactor (characterized by a volume of 3 l), 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 μg/l of H_2O_2 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 SO_2 reagent and the calcium carbonate ($CaCO_3$) 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 ft^3 is termed the liquid-to-gas (L/G) ratio.
[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 the limestone particles inside the reactor.

Still, the controller and the flow meter of the system allowed setting the following process parameters for all the desulfurization tests: (i) temperature = 25 °C; (ii) agitator rotation speed = 600 rpm; (iii) gas mixture flow = 1000 ml/min. Other process parameters such as stoichiometric ratio, liquid/gas ratio, slurry pH and relative saturation are reported in Table 2.

2.4. *Multi-criteria assessment*

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

Specifically, the feasibility study has foreseen the following phases: (i) definition of the scenarios to be compared; (ii) definition of the evaluation criteria; (iii) determination of the weight vector; (iv) resolution of the alternatives matrix identifying, in addition, the best suitable scenario.

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

With reference to the first point, three scenarios were considered as listed below:

- Scenario 1. It involves the use of limestone after coarse milling;
- Scenario 2. It involves the use of micronized limestone having used the H-E mill with 750 rpm;
- Scenario 3. As in the case of the scenario 2, however using the H-E mill with 950 rpm.

With reference to the second point, three evaluation criteria were defined:

- I_1 = Gypsum production: the criterion quantifies the annual production of gypsum (ton/year);

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	Nm^3/h	89,745.0
Hours of operation per year[b]	h	7000
Flue gas production	Nm^3/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.

- I_2 = SO_2 removal efficiency: the criterion quantifies the SO_2 percentage removal that is obtained as a result of the desulfurization process (%);
- I_3 = 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_{ij} the performance of the alternative i-th (i.e. scenario 1) with respect to the j-th evaluation criterion (i.e., criterion I_1), the normalized value was calculated with the following relations:

$$\bar{x}_{ij} = x_{ij}/\mathrm{Max}(xj) \quad (14)$$

$$\bar{x}_{ij} = \mathrm{Min}\left(x_j\right)/x_{ij} \quad (15)$$

The selection of the relation depends on the nature of the criterion, if it was to maximize (14) or minimize (15) in respect to the general goal (to select the best scenario). In the specific case, the I_1 and I_2 criteria were to be maximized while, the criterion I_3 to minimize.

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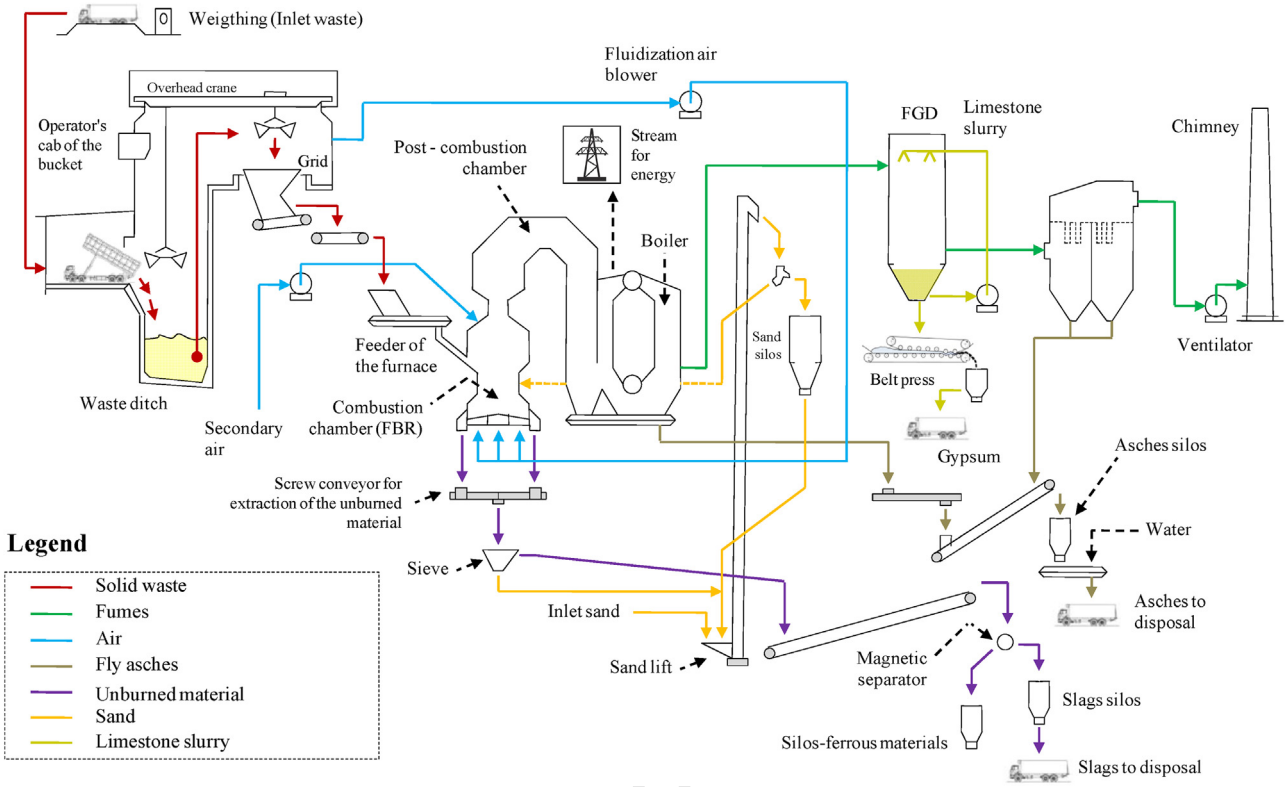


Fig. 4 – Flow diagram of the WtE plant considered in the feasibility study.

Finally, the last step focused on the resolution of alternatives matrix starting from the normalized alternatives matrix. Specifically, the construction of the composite indicator involved the adoption of the linear aggregation method, commonly used in literature (Sabia et al., 2016; Langhans et al., 2014). The preference index indicated with PI and defined as the parameter that aggregates the information of the three evaluation criteria (or indicators), was the result of the following relation:

$$PI_i = \sum_{j=1}^{m} \tilde{x}_{ij} = \sum_{j=1}^{m} x_{ij}.w_j \qquad (16)$$

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 consumption) used during the feasibility assessment was herein described. In terms of gypsum production, a production of 3–4 t of gypsum per ton of SO_2 removed was assumed (Le Cloirec, 2012). In terms of SO_2 removal, the removal efficiency [$SO_2\% = (SO_{2,IN} - SO_{2,OUT})/SO_{2,IN}$] was evaluated indirectly by means of a material balance referred to the sulfur content and considering the Esedra reactor as control volume (see Fig. 5).

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

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

- 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 950 rpm = 28 kWh/t × (1 + 0.08) (8% increase due to higher speed) = 30 kWh/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 μm as well as a corresponding reduction in volume of the coarser fraction. Overall,

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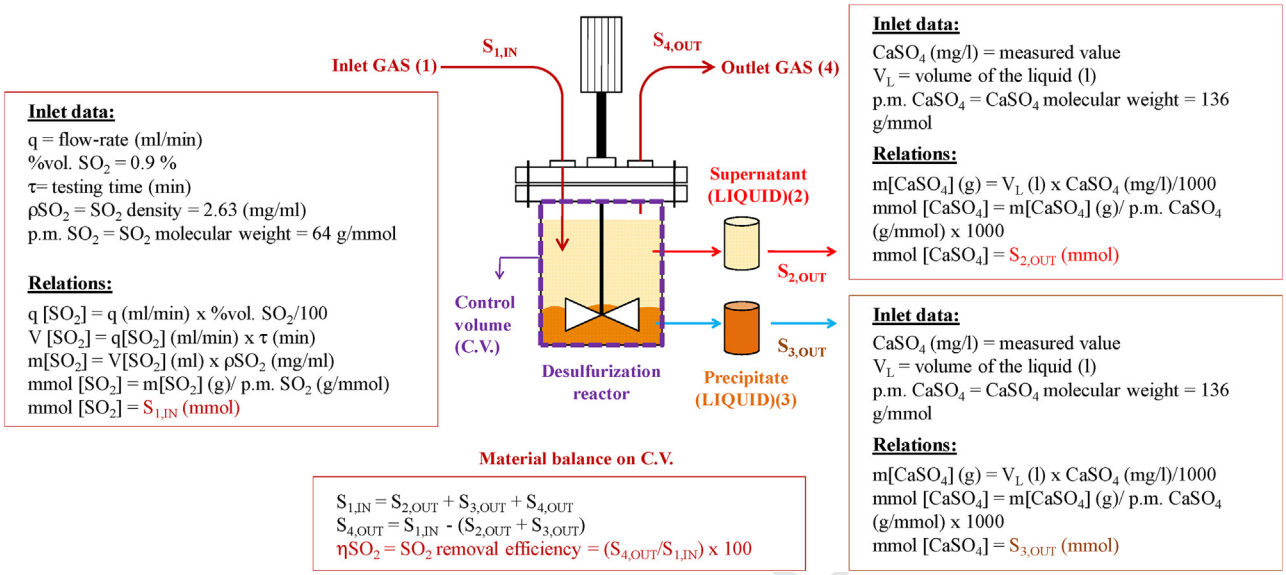


Fig. 5 – Material balance scheme for the assessment of SO_2 removal efficiency.

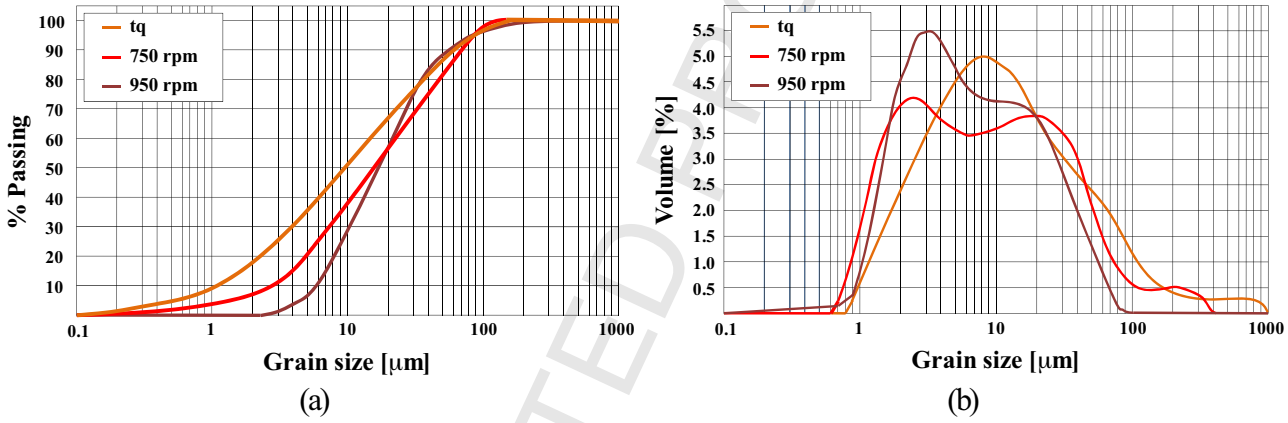


Fig. 6 – The milling results with reference to the samples 1 (tq), 2 (750 rpm) and 3 (950 rpm): (a) grading curves particle size (in μm)—passing percentage; (b) particle size distribution (in %).

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

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

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

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.

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 SO_2 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 highlight the important role of the absorbent surface area to obtain absorbent with high desulfurization activity.

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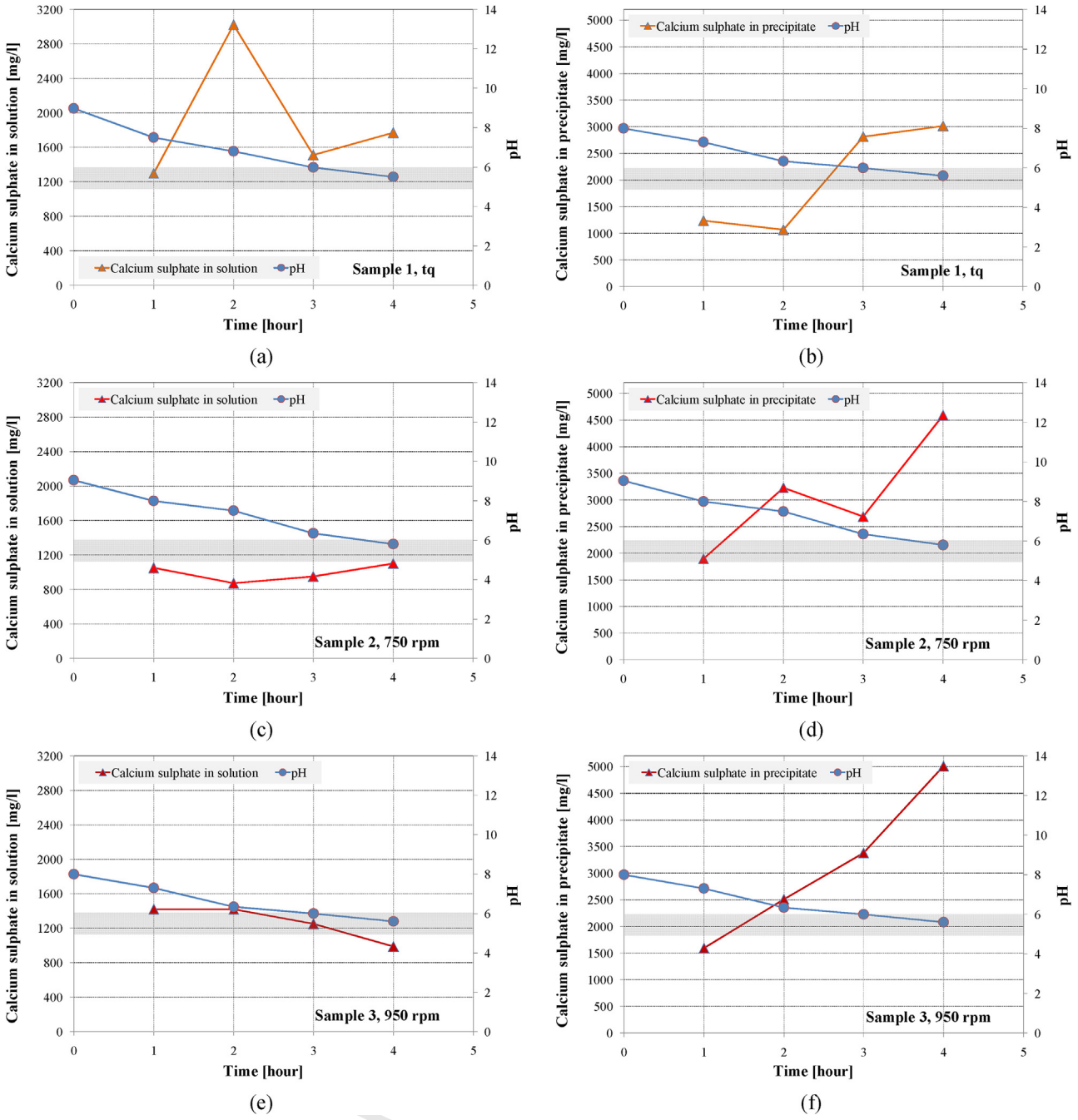


Fig. 7 – Results of the desulfurization tests: (a) profiles of calcium sulphate in solution and pH for the sample 1; (b) profiles of calcium sulphate in precipitate and pH for the sample 1; (c) profiles of calcium sulphate in solution and pH for the sample 2 (750 rpm); (d) profiles of calcium sulphate in precipitate and pH for the sample 2 (750 rpm); (e) profiles of calcium sulphate in solution and pH for the sample 3 (950 rpm); (f) profiles of calcium sulphate in precipitate and pH for the sample 3 (950 rpm).

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

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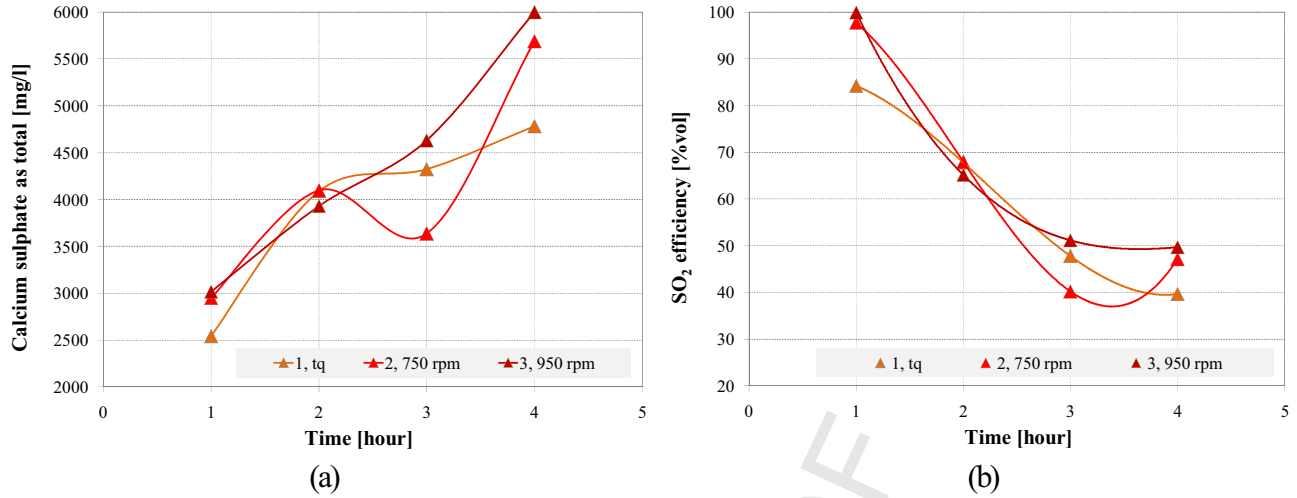


Fig. 8 – Results of the desulfurization tests: (a) calcium sulphate as total (in solution + in precipitate) vs. time; (b) SO_2 removal efficiency vs. time.

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.)	75.3	1.20×10^{-4}	1.031×10^{-3}	–
Using sample 2 (750 rpm)	87.4	1.39×10^{-4}	1.196×10^{-3}	16.0
Using sample 3 (950 rpm)	89.4	1.42×10^{-4}	1.223×10^{-3}	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 Nm^3/h; (v) hours of operation per year = 7000 h; (vi) flue gas production on yearly basis = 89,745.0 (Nm^3/h) × 7000 (h/year) = 6.28×10^8 Nm^3/year; (vii) SO_2 removed from flues gas = 21.528 t SO_2/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 SO_2 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 FGD technology needs a removal system of the precipitate during the course of desulfurization as schematically shown in Fig. 1. Additionally, if we consider the "scale effect" due to the fact that our investigation was at bench scale, the "accumulation of precipitate in the reactor" was responsible for the low yields of the wet FGD system implemented, compared to the expected results (BREF-LCP, 2016).

However, tests carried out after 1 h were not affected by the accumulation of the precipitate. Therefore, the data obtained at 1 h, 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.

3.3. *Feasibility analysis*

The specific production of gypsum was estimated taking into account that generally 3–4 t of gypsum per ton of SO_2 removed in the system are produced (Le Cloirec, 2012). With reference to the WtE plant under investigation, the SO_2 created during the combustion process and that emitted to the chimney were 23.40 and 1.87 t SO_2/year, respectively (De Gisi et al., 2016). The SO_2 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/m^3 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 Nm^3/h of flue gas, a yearly mass flow of removed SO_2 of 29,364.3 t SO_2 removed/year and a yearly gypsum production of 70,000 t/year, showed a specific production of 4.22×10^{-3} kg/m^3 of flue gas. However, the production of gypsum may depend on various factors such as the

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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 Nm^3/h; (v) hours of operation per year = 7000 h; (vi) flue gas production yearly = 89,745.0 (Nm^3/h) × 7000 (h/year) = 6.28×10^8 Nm^3/year; (vii) SO_2 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 Nm^3/h; (v) hours of operation per year = 7000 h; (vi) flue gas production yearly = 89,745.0 (Nm^3/h) × 7000 (h/year) = 6.28×10^8 Nm^3/year; (vii) SO_2 removed from flues gas = 21.528 t SO_2/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 well as 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 SO_2 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 specific surface area of the micronized product in accordance with Córdoba (2015). In this regard, Bazzoni (2014), using a commercial product with a higher specific surface area (Sorbacal® SP) in a full scale experimentation (at the WtE plant of Parona, Lombardy (Northern Italy), with a treatment capacity of 580,000 t/year of SRF), achieved better performance, in terms of SO_2 removal, compared to the limestone reagent commonly used in the company.

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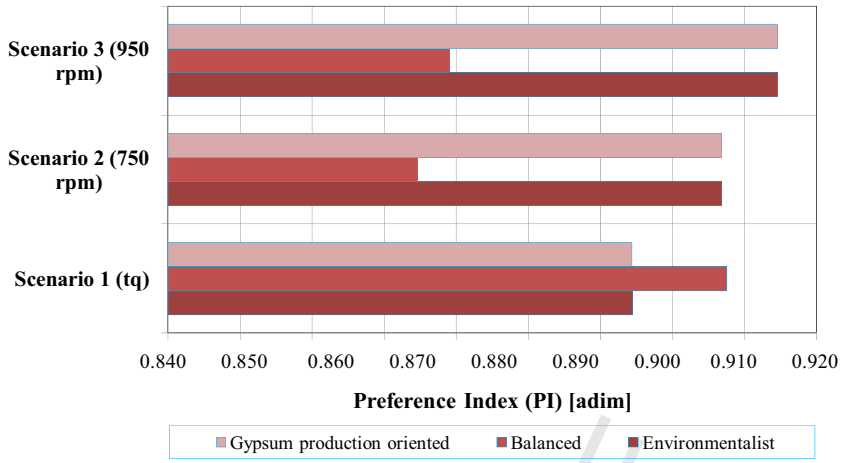


Fig. 9 – Scenarios comparison by means of the use of preference index (PI) as aggregation parameter and varying the weight vector of the evaluation criteria as follows: gypsum production oriented ($I_1 > I_2 > I_3$); balanced ($I_1 = I_2 = I_3$); environmentalist ($I_2 > I_1 > I_3$), where, I_1 = gypsum 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, conducted considering a raw limestone with 3 mm particle size and a contact time of 10 min, occurred securely without generating machine downtime due to high temperatures. Furthermore, the ground material, considering both 750 and 950 rpm as rotational speeds, was more homogeneous and with a greater percentage of the fine fraction compared to that of the un-treated limestone;
- Considering the desulfurization tests for gypsum production, the adoption of limestone pre-treated with H-E mill is to be considered preferable to the raw limestone milled with a standard device. In fact, the micronized limestone is dissolved in water better than the un-treated limestone. The amount of calcium sulphate in the precipitate and aqueous solution (the gypsum) was greater in the cases of micronized limestone due to a higher value of the absorbent specific surface area of the micronized media compared to that of the raw limestone. Furthermore, in terms of environmental protection, the results after 1 h of investigation showed a SO_2 removal efficiency of 84.2, 97.7 and 99.9% with reference to the sample 1 (tq), sample 2 (750 rpm) and sample 3 (950 rpm), respectively;
- Using the results obtained at laboratory scale, the feasibility study highlighted an increase in terms of gypsum production compared to that of the scenario 1 (using the raw limestone). The specific production of gypsum was 1.20×10^{-4}, 1.39×10^{-4} and 1.42×10^{-4} kg/m^3 of flue gas, for scenarios 1, 2 (using limestone gridding at 750 rpm rotation speed) and 3 (using limestone gridding at 950 rpm rotation speed), respectively;
- 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 multi-criteria 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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