

FLUE GAS DESULFURIZATION BY MECHANOCHEMICALLY ACTIVATED DOLOMITE

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ABSTRACT: Energy production by combustion of S-containing non-renewable fuels requires huge consumption of limestone for the necessary Flue Gas Desulfurization (FGD) treatment in order to meet stringent SO₂ emission limits. FGD (wet, dry or semi-dry) is an expensive, energy intensive, process due to its overall poor efficiency and to the need of using finely micronized CaCO₃. Wet FGD laboratory tests with dolomite slurry have shown that up to ~ 50% higher performance and faster SO₂ uptake occur if the mineral is micronized by high energy mill, yielding mechanochemical activation of the solid. Further benefits arise from the use of dolomite which consistently contains Mg carbonate.

KEYWORDS: flue gas desulfurization; mechanochemical activation; limestone or dolomite micronization; SO₂ emission.

1 INTRODUCTION

Sulfur dioxide, a major cause of acid rain, is one of the 6 main air pollutants¹ for which the *EU Clean Air Program* commands stricter emission limits by 2020 and 2025 for large [1] and medium-small [2] combustion plants respectively. Due to the scarcity and the cost of no-S fuels², coal and oil with high ($\leq 8\%$) or low ($\leq 4\%$) S-content are traditionally used in large power stations and the resulting flue gas, containing finite amount of SO₂, must undergo specific desulfurization treatment in order to cope with the existing SO₂ emission limits (125/350 $\mu\text{g}/\text{m}^3$ as hourly/daily concentration) [3].

Flue Gas Desulfurization (FGD) is a worldwide known process that adsorbs SO₂ through micronized calcite (CaCO₃)[4-5], of which Italy is a major producer (≈ 35 Mt/yr, 33% of total EU production)[6]. FGD is an expensive and energy-consuming process with capital and O&M costs ≤ 500 U.S.\$/t_{SO₂} in large power plants (400 MW) [7]. In addition to the operating conditions and the adsorbent nature, FGD performance depends largely on physiochemical characteristics of the micronized calcite [8-9].

The aim of this paper is to investigate sulfation properties of CaCO₃ micronized by high-energy mill according to the mechanochemical theory, compared with the same adsorbent micronized by conventional milling.

2 BASIC THEORY

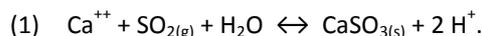
FGD processes differ mainly for the technique (*wet*, *dry* or *semi-wet*) and the adsorbents used (CaO, *lime*; CaCO₃, *limestone*; NaOH+Na₂CO₃, *dual-alkali*). Wet-FGD, where the flue gas is washed in a scrubber fed countercurrent by a

¹ Sulphur dioxide, nitrogen oxides, volatile organic compounds, ammonia, particulate matter and methane.

² The stoichiometric S content in solid fuels to meet SO₂ emission limits is 0.23%.

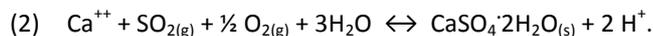
limestone slurry, is the most popular, in spite of the amount of wastewater to be treated before discharge and the large facilities (ponds) usually required to reclaim the slow-settling CaSO_3 .

Basic FGD chemistry calls for a 3-phasic reaction, represented in simplified form by



Gaseous SO_2 facing the slurry is captured by Ca^{++} ion to form poor-soluble (0.045 g/L at 20°C) slowly settling CaSO_3 .

It is often preferred to oxidize SO_2 to SO_3 in order to obtain CaSO_4 , more soluble than CaSO_3 (2 g/L at 20°C), but potentially marketable as *gypsum* ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Basic FGD chemistry then is written as a redox/precipitation process:



Wet-FGD must reach up to 98% efficiency, depending on S-content of the fuel used. To that aim, adsorbent physico-chemical characteristics (particle size, specific surface, CaCO_3 purity etc.) must be considered in addition to operating conditions (pH and concentration of slurry, gas/liquid flow ratio, adsorbent excess, type and concentration of the oxidant agent, scrubber geometry etc.). Limestone for wet-FGD application must typically exhibit $\leq 95\%$ CaCO_3 purity, $D_{0.90} \leq 50 \mu\text{m}$ (i.e., 90% of powder passing the 50 μm mesh size) and $\geq 1 \text{ m}^2/\text{g}$ specific surface.

The addition of Mg^{++} to the scrubber slurry can increase SO_2 removal efficiency to as high as 99%, due to the higher solubility (hence faster Mg^{++} reactivity with sulfite/sulfate ions) of Magnesium than Calcium carbonate [10]. Accordingly, the use of *dolomite* (mixed Ca and Mg carbonate) is often preferred in FGD plants of large power stations [11].

For FGD applications limestone must undergo micronization, a unit operation quite common in mineral industry, where plenty of equipment with different grinding tools (balls, hammers, rollers, blades etc.) exist and are effectively used [12-13]. Minerals micronization, however, is characterized by poor energy efficiency (5÷25%), exponentially decreasing with particle size, and by the increase of particle size with prolonged micronizing duration, due to *clustering* of the micro-particles [14].

Mechanochemistry (MC) is a known technique where solids are micronized by the action of the mechanical forces developed during collisions, capable of modifying the solid structure at nanoscale level, thus greatly enhancing its reactivity and allowing for unfavorable reactions to occur even at room conditions [15÷19]. Used successfully in several fields (e.g., preparation of catalysts, functional ceramics etc.), in the last decade MC has also been proposed with promising results for environment protection, e.g., treatment of hazardous waste [20-21], reuse of waste [22-23], decontamination of soils [24] and marine sediments [25].

Although based on different mechanisms (planetary, attrition, nutation etc.), H/E mills typically consist in a rapidly rotating ($\leq 1,000$ rpm) reactor containing a number of steel balls that collide thousands of times per second, compressing the reactants at extreme pressure and temperature ($\geq 1,000^\circ\text{C}$) for extremely short time-span ($\geq 10^{-13}$ s) [16]. Such myriad collisions produce the "*mechanochemical activation*" of the reactants through solid matrix deformation and transition from elastic to plastic morphology as well as sound-speed propagating fractures into the solid matrix that promote and, moreover, increase to the 3rd power the number of existing active sites, thus boosting exponentially the overall reactivity of the system [26].

3 MATERIALS AND METHODS

Two types of limestone from a major private quarry (Italcave SpA, near Taranto, S. Italy) were considered, made by pure calcite and by dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$ with $\approx 2/1$ Ca/Mg molar ratio) respectively. Tab.1 reports their characteristics (ASTM standards), Fig.1 their typical DTG and DTA profile (STA 409 thermo-analyzer, Netzsch, I).

Table 1. Typical characteristics of calcite and dolomite samples investigated

Parameter (%w/w)	Calcite	Dolomite (code IC_T00-12)
CaCO ₃	99.13	61.11
MgCO ₃	0.12	18.94
Al ₂ O ₃	0,05	5.93
Fe ₂ O ₃	0.02	5.85
SiO ₂	0.04	5.63
Sn	0.52	0.04
Pb	0.84	0.92
Mn	<0.01	<0.01
Cu	<0.01	1.58
Cd	<0.01	<0.01
LOI ⁽¹⁾	39.57	42.36
H ₂ O	3.09	2.11
pH	9.12	
Bulk density (kg/L)	2.671	
D _{0,9} (μm) ⁽²⁾	3,000	3,0000
Specific surface (m ² /g)	1,2	0,9
Color	Pale Yellow	Bright white

⁽¹⁾Loss On Ignition = weight loss after calcination; ⁽²⁾ mesh-size passed by 90% of product

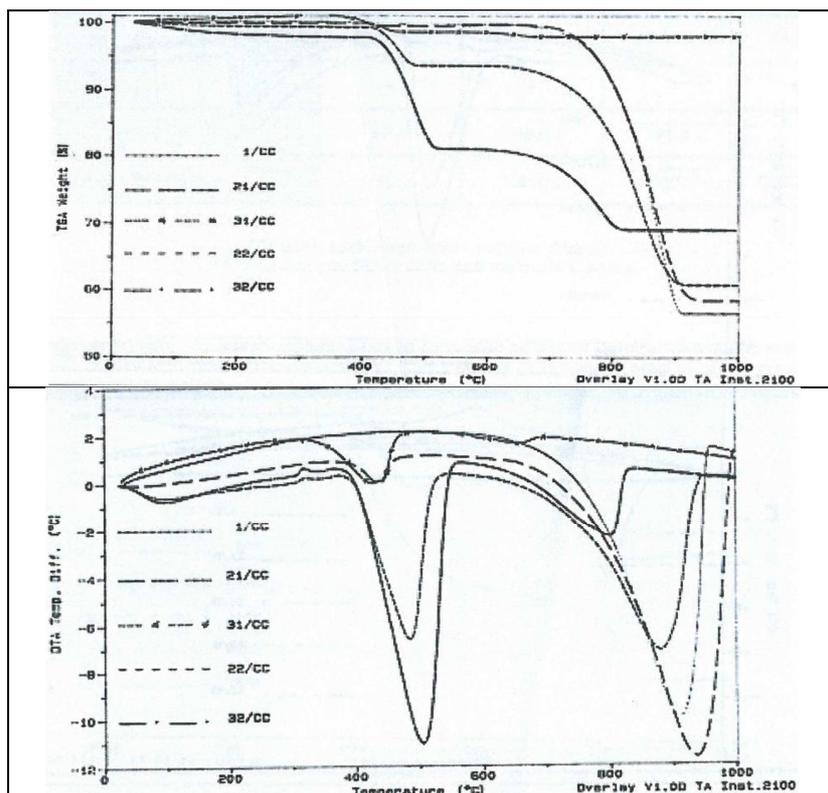


Fig.1. DTG (above) and DTA analysis (below) of the limestone investigated

In order to exploit Mg beneficial effect toward SO₂ absorption, only the dolomite product was used in FGD experiments. To that aim suitable samples of IC_T00-12 product were micronized to D_{0,9} ≤50 μm with a laboratory Hicom 15 nutation H/E mill (Hicom Technol., Pinkeba, Australia) (Fig.2 and Tab.2) under different operating conditions.

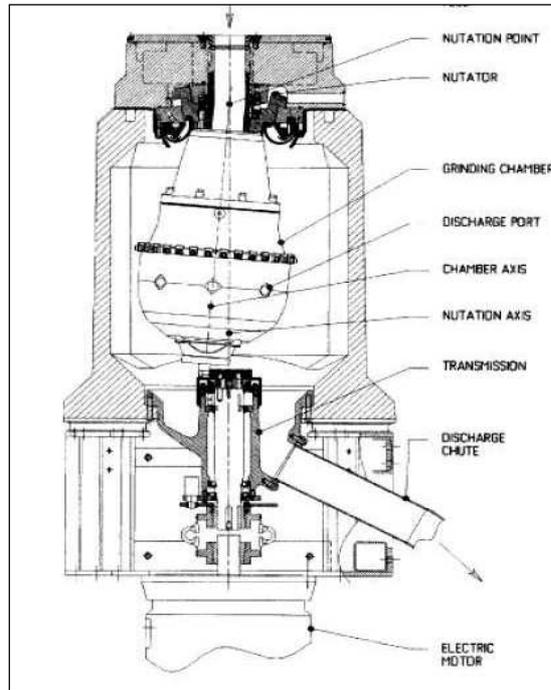


Fig.2. Scheme of Hicom 15 nutation H/E mill

Table 2. Technical characteristics and operating conditions of the Hicom 15 Nutation H/E mill

Jar net volume and material	5.3 L, Stainless Steel AISI 304
Milling balls diameter and material	Ø 10 mm, Stainless Steel AISI 420C

At given intervals, a sample of the milled material was analyzed for size granulometry (Laser Mastersize 2000, Malvern, UK) and for specific surface (Monosorb BET Analyzer, Quantachrome, FL).

To compare the sulfation capability of dolomite micronized by H/E and by a conventional roller mill (type PM 60 U3, Neuman & Esser, Germany), code DE, the FGD tests were carried out according to [9] with the lab set shown in Fig.3.

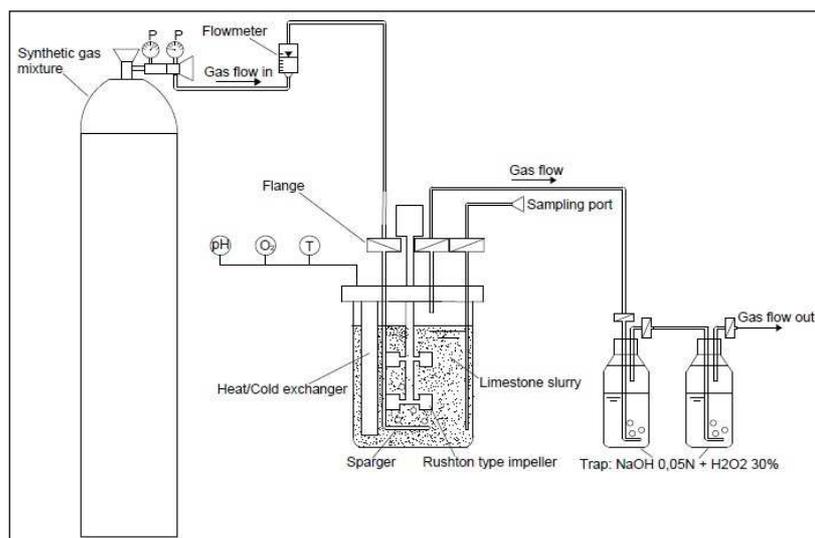


Fig.3. Flow-sheet of the FGD laboratory set

An Esedra Plus 3.5 glass reactor (Solaris Biotechnologies, Italy), containing 2L of distilled water thermostated at 25°C and stirred at 700 rpm, was added with enough micronized dolomite and concentrated HCl to achieve a 1% slurry concentration at pH 7.6. A synthetic gas mixture mimicking typical flue gas from a coal power plant (10% CO₂, 5% O₂, 0.5% SO₂ and a balance of N₂ by volume, expressly prepared by Sapio, Italy) was then fed into the reactor at a constant flow rate (100 ml/min) for 6 hours. Two traps in series on the outgoing gas stream, containing 125 ml of 0.05N NaOH and 30% H₂O₂, confirmed that during the test no SO_{2/3} escaped from the reactor (≈100% SO₂ absorption). During each test, 5 mL aliquots of the slurry were withdrawn every hour and the amount of SO_{2/3} absorbed was determined by standard iodometric titration.

4 RESULTS AND DISCUSSION

4.1 HIGH ENERGY MICRONIZATION TESTS

Tab.3 shows the characteristics of ground dolomite sample (code IC_T00-12) and after H/E micronization in various operating conditions, compared with the corresponding conventionally-micronized product (code DE). Fig.4 reports particle-size distribution in the various samples, from which the D_i values in Tab.3 were calculated.

Table 3. Characteristics of the investigated dolomite micronized by H/E or by conventional mill

Sample code	Milling technique	Milling time	rpm	b (kg)	c (kg)	b:c	D _{0,10} (μm)	D _{0,50} (μm)	D _{0,90} (μm)	S (m ² /g)
DE	Conventional	≥30'					2,9	12,2	84,2	0,88
IC_T00-12	H/E	/	/	/	/	/			>3.000	1,20
IC_V15-4	H/E	10'	930	9,41	0,79	12:1	1,5	5,3	25,2	13,10
IC_V25-3	H/E	20'	930	9,41	0,79	12:1	2,0	14,0	64,2	15,70
IC_RY-2	H/E	30'	930	9,41	0,79	12:1	1,9	11,2	65,7	13,50
IC_14-11	H/E	10'	770	4,89	2,45	2:1	1,5	5,4	31,9	
IC_3C-10	H/E	10'	770	8,30	1,38	6.1	1,6	7,6	42,9	
IC_78-9	H/E	10'	770	9,41	0,79	12:1	1,6	7,9	45,3	

b = total milling body weight; *c* = total dolomite weight; *D_i* = mesh-size passed by *i*-th % of product; *S* = specific surface

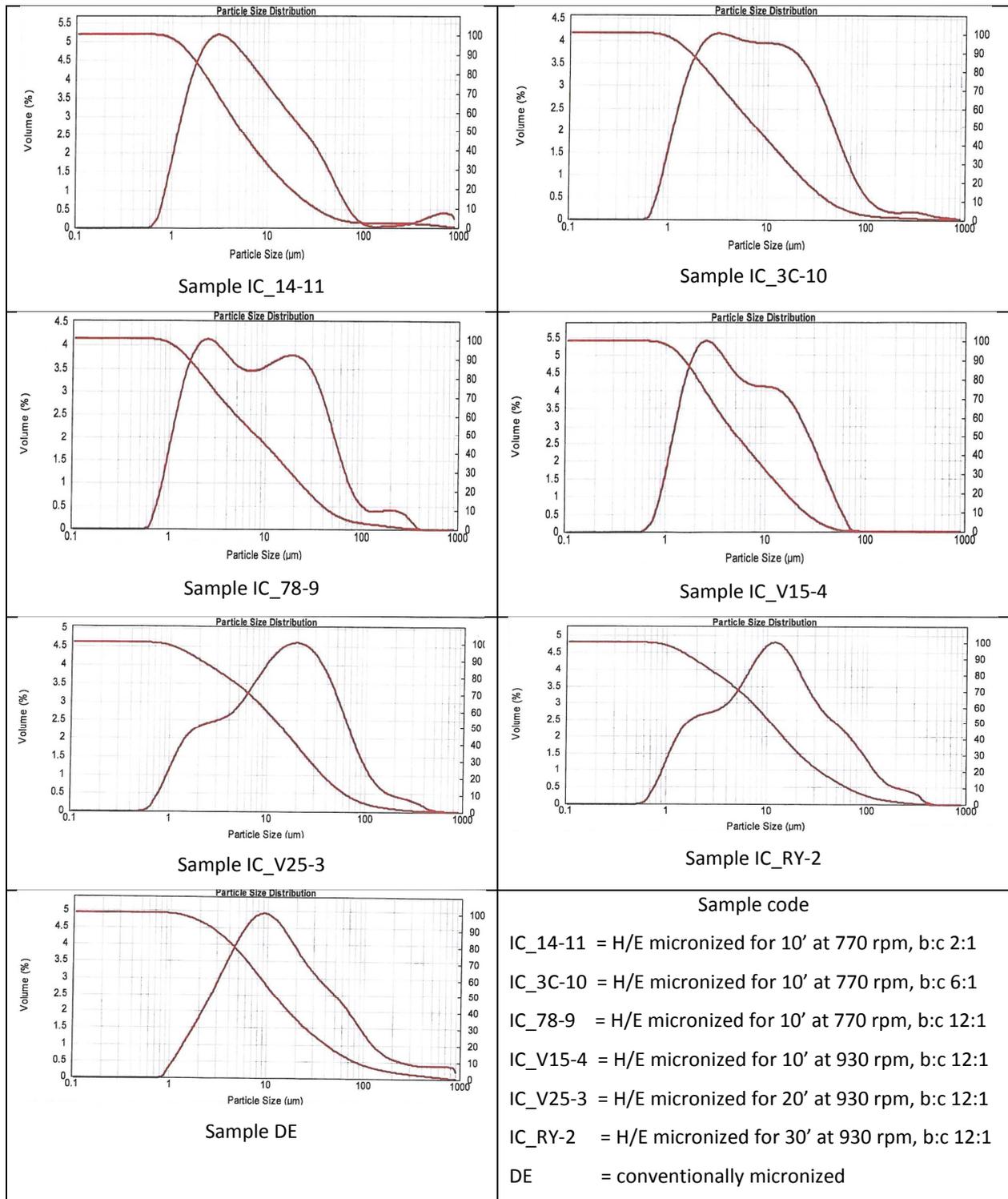


Fig.4. Particle-size distribution on samples of H/E or conventionally micronized dolomite samples

First of all, it must be noted that, as already seen with DE sample, containing higher Fe and Cu amount (Tab.1), micronization allowed almost complete color disappearance, yielding bright whiteness (i.e., higher market value) to all samples, due to a modified position of the chromophore in the new crystallographic morphology [22].

From the data in Tab.3 it clearly appears that in the experimental conditions investigated H/E micronization permits to reach the target solid size ($D_{0.90} \leq 50 \mu\text{m}$) faster ($\leq 10'$) than with conventional mills ($\geq 30'$), with a relatively low rotation speed (700 rpm) and high (2:1) reactor filling ratio (see sample IC_14-11 vs. DE), i.e., with lower overall energy consumption. This is

particularly important in the mineral industry due to the well-known poor efficiency of grinding operation, where a major energy quote of is lost with loud noise, thermal dissipation and friction resistances. The higher energetic efficiency of H/E micronization was anticipated by the well-known mechanical Bond theory, as recently updated [27], based on the Work Index (W_i), i.e., the energy required to comminute from ∞ to 100 μm the mean diameter of 1g of solid [kWh/t].

Fig.5 shows the general grinding-energy function, embodying the major theoretic models that relate energy consumption with material size [28].

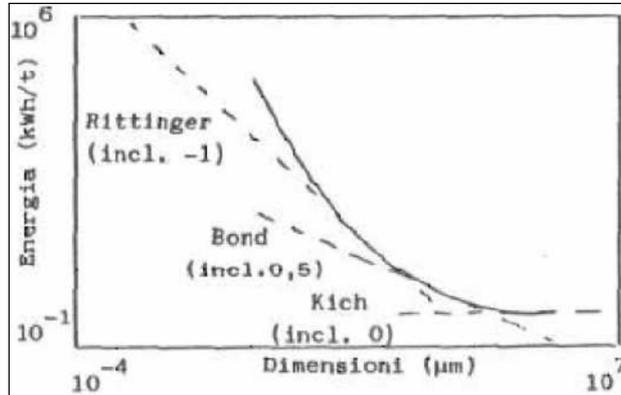


Fig.5. Major models relating grinding energy consumption with final solid size

Best curve-fitting in Fig.5 is provided by the following differential equation [29]:

$$(3) \quad (dW/d\phi) = - K/\phi^x$$

where

W = overall grinding energy consumption [kWh/t]

K = constant

ϕ = solid diameter (μm)

and the exponent $x = 2, 1$ or $1,5$ in the model of Rittinger, Kick-Kirpicev or Bond respectively.

In the ϕ range $1\div 100 \mu\text{m}$ interesting this study Bond theory prevails hence eq. (3) becomes:

$$(4) \quad W = 10^x W_i [(1/\sqrt{\phi}) - (1/\sqrt{\phi_0})].$$

By means of a laboratory H/E planetary ball mill, W_i was measured experimentally for a number of minerals, including dolomite ($W_i = 11.3\text{kWh/t}$) and calcite ($W_i = 12.7 \text{kWh/t}$) [28]. Using conservatively this latter value, $\phi_0 \approx 3.000 \mu\text{m}$ and $\phi_{0,9} = 45,3 \mu\text{m}$ for the unmilled and H/E micronized mineral (samples IC_T00-12 an IC_78-9 respectively in Tab.3), eq. (4) yields $W \approx 16,6 \text{ kWh/t}$, a figure largely lower than expected with conventional mills [7]. Though real figures with full scale mills may vary with plant characteristics and operating conditions, it may be anticipated that at least a $\approx 50\%$ overall energy saving would occur if dolomite micronization is carried out using H/E instead of conventional mills.

The experimental results in Tab.3 are plotted in Figs.6 and 7 to show the influence of milling time on specific surface and particle size of the mineral.

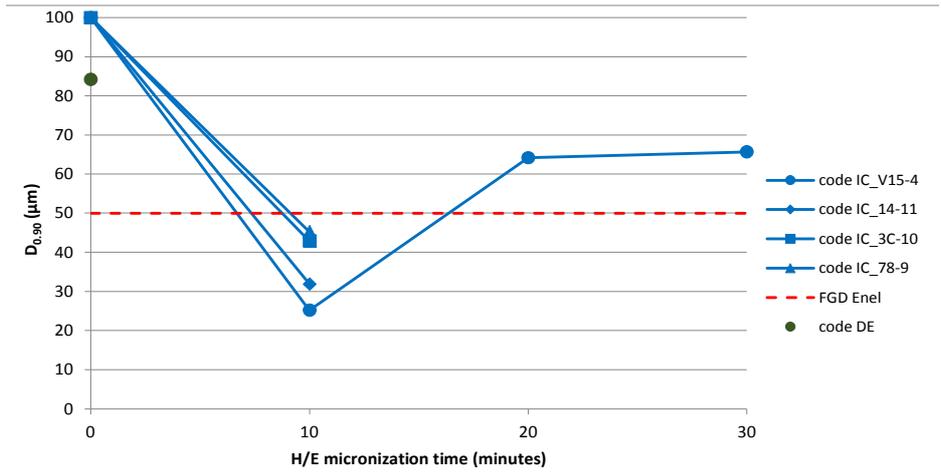


Fig.6. Influence of H/E milling duration on micronized mineral size

As expected, Fig.6 shows that milling beyond an optimal duration causes an increase of mean particle size, due to known phenomena of *clustering* among micro and nanoparticles already formed [30].

Quite interestingly, the plot in Fig.7 indicates that conventional micronization does not produce finite increase of dolomite specific surface, which in turn may increase up to $\approx 1500\%$ when an H/E mill is used. Being gas absorption and, in general, solids reactivity dependent on specific surface, this finding may have a paramount importance in practical limestone application like FGD.

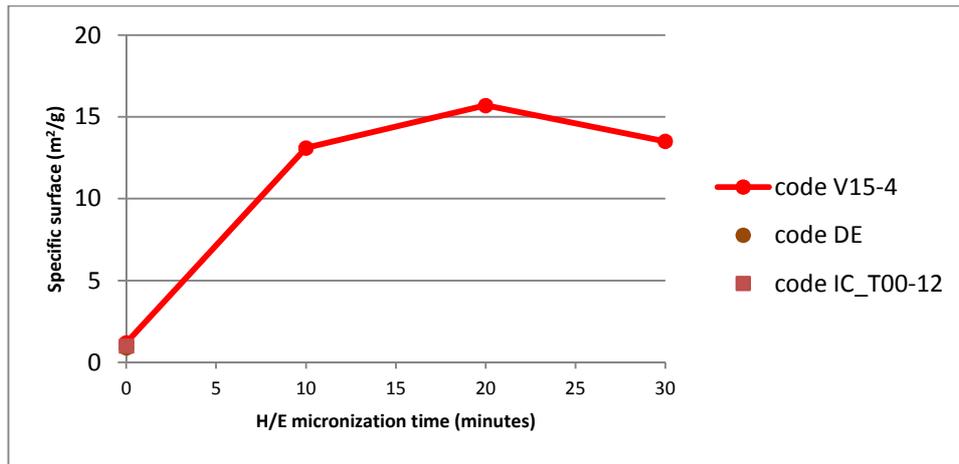


Fig.7. Influence of H/E milling duration (min) on the specific surface of the micronized solid

4.2 FLUE GAS DESORPTION TESTS

Fig.8 shows the results of FGD laboratory tests with conventionally and H/E micronized dolomite.

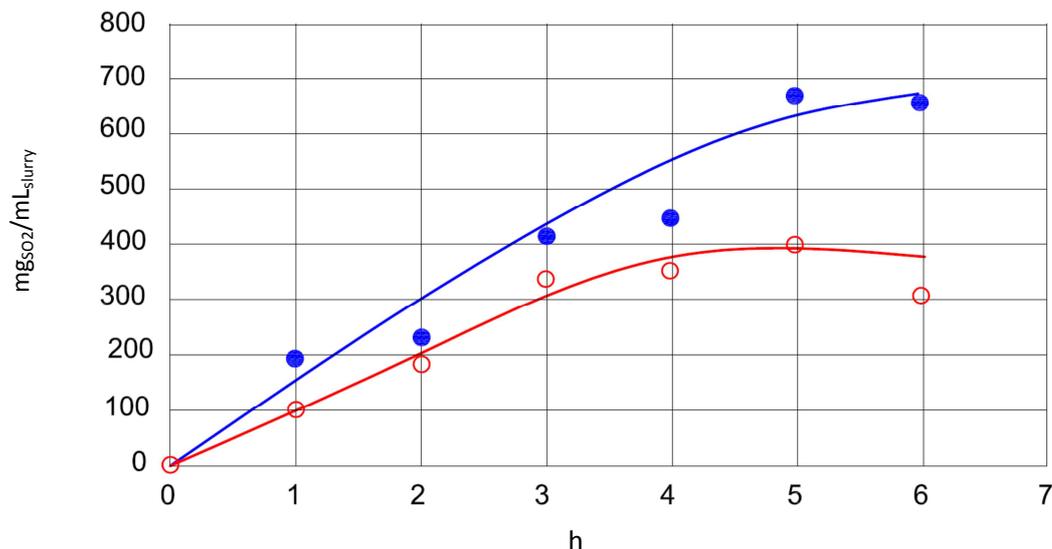


Fig.8. Results of laboratory FGD tests

(● H/E micronized sample, code IC_V15-04; ○ conventionally micronized sample, code DE)

As expected, experimental results indicate a much better FGD performance with H/E micronized than with conventionally micronized mineral in terms of both thermodynamics (equilibrium absorption capacity ≈ 650 vs. ≈ 400 $\text{mg}_{\text{SO}_2}/\text{mL}_{\text{slurry}}$) and kinetics (≈ 140 vs. ≈ 90 $\text{mg}_{\text{SO}_2}/\text{mL}_{\text{slurry}}\cdot\text{h}$). This finding stems from the higher specific surface and, moreover, from the much higher number of active sites obtained through H/E micronization, according to the mechanochemical theory [30].

Furthermore, the present results (≈ 400 $\text{mg}_{\text{SO}_2}/\text{mL}_{\text{slurry}}$) with conventionally micronized dolomite are much better than ≈ 60 $\text{mg}_{\text{SO}_2}/\text{mL}_{\text{slurry}}$ obtained in similar laboratory FGD tests with various Turkish limestones [8-9], thus confirming the positive influence of Mg on sulfation.

5 CONCLUSIONS

According to the well-established mechanochemistry theory, mineral micronization with High Energy instead of conventional mills increases the solids reactivity through higher specific surface and more activated sites. This has been confirmed in FGD laboratory tests, where H/E micronized dolomite showed $\approx 50\%$ higher and faster SO_2 uptake performance than the same product micronized with conventional mill. Further benefits were due to the appreciable presence of Mg ion in the mineral.

It may be concluded that the use of H/E micronized dolomite in FGD plants at coal-fueled power stations would allow consistent savings in terms of energy efficiency, process rate and material consumption.

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