

Spray-dry desulfurization of flue gas from heavy oil combustion

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An experimental investigation on SO₂ removal in a pilot scale spray-dryer from the flue gas generated by combustion of low-sulfur heavy oil is reported. The facility is equipped with an oil burner producing 60Nm³/h of flue gas with SO₂ concentration up to 1200mg/Nm³, depending on the oil sulfur content. A lime-water slurry was sprayed through an ultrasonic two fluid atomizer in the spray-dry chamber and the spent sorbent was collected downstream in a pulse-jet baghouse together with fly ash. Flue gas was sampled in different points in order to measure the desulfurization efficiency after both the spray-dry chamber and the baghouse. Parametric tests were performed to study the effect of the following variables: gas inlet temperature, difference between gas outlet temperature and adiabatic saturation temperature, lime to sulfur ratio, and average size of lime particles in the slurry. The average droplet size in the spray was also characterized, because of its influence on the total desulfurization efficiency.

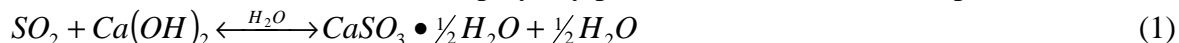
Results indicated that spray-drying is an effective technology for the desulfurization of low-sulfur fuel oil flue gas, provided operating conditions are chosen carefully. In particular the lowest gas inlet and outlet temperatures compatible with baghouse operation should be selected as well as a sufficiently high lime to sulfur ratio. The attainment of a small lime particle size in the slurry is critical for obtaining a high desulfurization efficiency.

1. Introduction

Flue gas desulfurization by spray-dry absorption in conjunction with baghouse particulate collection represents a viable alternative to wet scrubbing in boilers burning low to medium sulfur coal or fuel oil [1-5]. The advantages of spray-drying over other possible technologies include: the production of a dry waste byproduct not requesting sludge handling equipment; no scaling and corrosion problems enabling the use of cheaper materials; smaller space needed and possibility of easily retrofitting existing plants; no requirement of flue gas reheating; flexibility in operation with regard to varying boiler load; low energy consumption; reduced installation and operating costs.

In the spray-drying process the flue gas is contacted with a fine spray of alkaline suspension, usually lime, in a reaction chamber where a droplet residence time of 10-15s is provided. The sprayed droplets simultaneously evaporate and react with SO₂ in the flue gas and eventually a solid product is precipitated. The dried product leaves the spray-dry chamber holding only few percents of free moisture and is separated in a downstream collection device, usually a baghouse.

The SO₂ absorbed in the sprayed droplets reacts in the alkaline aqueous phase with the dissolved sorbent. For a lime based spray-dry process the overall sulfur capture reaction is:



where the resulting calcium sulfite precipitates as a consequence of the low solubility in water. Part of the sulfite (usually a small fraction) is oxidized in the aqueous phase and precipitates as calcium sulfate.

The overall desulfurization efficiency in a spray-dryer is the result of the competition of two processes: SO₂ absorption in the slurry droplets and water evaporation from the droplets [6-9]. Both processes are highly enhanced near the atomizer where high slip velocities result in increased mass and heat transfer between the flue gas and the droplets. Much lower transfer rates are achieved further on in the spray-dry chamber and in the baghouse, especially after the precipitated solids begin to form a coherent shell around the drying droplets. In general higher overall removal efficiencies are obtained by slowing down the evaporation rate (for example by approaching the adiabatic saturation temperature at the dryer outlet) and by enhancing the SO₂ mass transfer rate (for example by increasing the lime to sulfur feed ratio and by decreasing the average size of lime particles dispersed in the slurry). The atomization characteristics, i.e. the droplets size distribution and velocity, have a more complex influence on the process because affect in the same way both SO₂ absorption and drying rates.

Typical spray-dryers performance hardly exceeds 70% SO₂ removal efficiency at lime to sulfur ratios of 1-2 [4,7,9], as opposed to figures higher than 90% for wet scrubbing. Utilization of larger lime to sulfur ratios slightly enhances the desulfurization efficiency but leads to uneconomical operation. For this reason the spray-dry technology has resulted cost-effective only for plants burning low to medium sulfur content fuels, where lower removal efficiencies are needed in order to comply with local SO₂ emission limits. Better performances have been achieved by spray-dryers with waste solids recirculation, at the expense of augmented installation costs and equipment wear [1,3-5].

Most of the pilot and full scale spray-dry experimental activity reported in the literature to date has been concerned with coal fired boilers, as these are the majority of the utility boilers in operation in the USA [1-3,5,10,11]. On the contrary a large fraction of energy production in Italy relies on heavy oil combustion. The aim of this work is to investigate in a pilot plant the possibility to effectively remove SO₂ from flue gas generated in low-sulfur oil fired boilers by means of spray-dry technology. To this end a lime-water slurry was sprayed in a pilot scale spray-dry chamber and the spent sorbent was collected downstream in a pulse-jet baghouse. Parametric tests were performed to study the effect of the main operating variables, i.e. the gas inlet temperature (130-160°C), the difference between gas outlet temperature and adiabatic saturation temperature (10-20°C), the lime to sulfur ratio (1-2), and the surface mean diameter of lime particles in the slurry (2.45-3.35µm).

2. Experimental

2.1 Pilot plant description

A layout of the pilot spray-dryer is reported in Figure 1. The plant is fully automated and controlled by a PC. It can be conceptually divided in the following sections: a) flue gas generation section; b) lime slurry preparation section; c) spray-dry section; d) baghouse section; e) gas analysis section.

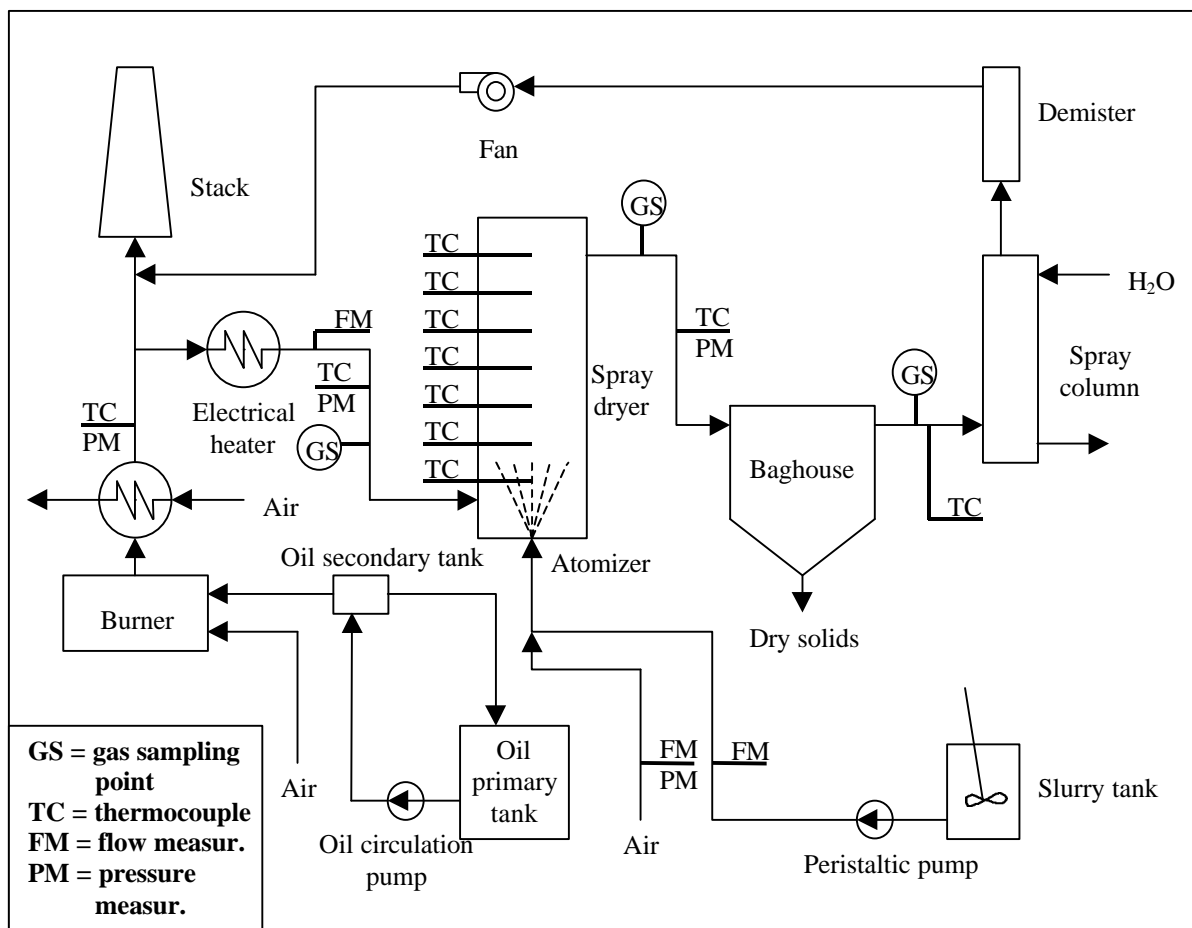


Figure 1 Layout of the pilot spray-dryer.

Flue gas is generated in a commercial heavy oil burner (Riello PRESS 30N) operable with one or two nozzles and feeding total oil rates between 2.5 and 30kg/h, corresponding to thermal powers of about 30 to 340kW. In the present work a steady oil feed rate of about 3.5kg/h was used, generating a flue gas flow rate of 60Nm³/h. Low-sulfur heavy oil was burned, whose properties are reported in Table 1. The typical flue gas composition is reported in Table 2. Generated flue gas is rapidly cooled in an air heat exchanger and then directed alternatively to the stack or to the spray-dry section.

Table 1 Fuel oil properties.

Composition (wt %):	
Carbon	86.2 – 86.7
Hydrogen	11.8 – 12.3
Sulfur	0.5 – 1.0
Oxygen	0.3
Nitrogen	0.2
Ash	< 0.05
Kinematic viscosity (mm ² /s at 50°C):	< 300
Relative density (at 15°C):	0.95
Low heating value (kJ/kg):	41000

Table 2 Typical flue gas composition.

N ₂	(% vol)	75 – 76
CO ₂	(% vol)	9 – 12
H ₂ O	(% vol)	8 – 10
O ₂	(% vol)	4 – 8
SO ₂	(ppm)	150 – 400
CO	(ppm)	400 – 1000
NO _x	(ppm)	100 – 200
SO ₃	(ppm)	< 20

In most of the experiments the lime slurry was prepared directly from commercial slaked lime (40% by weight calcium hydroxide) by mixing with the desired proportion of water in a stirred tank. Lime particle size distribution in the slurry was analyzed by means of a particle size analyzer (Malvern Mastersizer 2000). The surface (Sauter) mean diameter of the lime particles was $2.45\mu\text{m}$. In few experiments two different reagent grade dry lime samples were used to prepare the slurry. The corresponding surface mean diameter of the lime particles in the slurry were $2.76\mu\text{m}$ and $3.35\mu\text{m}$. The prepared slurry was fed continuously through a peristaltic pump to the atomizer.

Before entering the spray-dryer, flue gas passes through an electrical heater for inlet temperature control. The spray-dryer is a stainless steel (AISI 316L) cylindrical empty column, 2.6m high with a volume of 0.27m^3 , providing a gas residence time of approximately 12s at the present operating conditions. Flue gas enters tangentially at the column bottom section in order to have a swirling motion in the droplet-gas contact zone where good mixing must be achieved. The gas inlet duct section is $60\times 115\text{mm}$ with axis at 300mm above the column base. The lime slurry is atomized 1.0m above the column base by means of an ultrasonic two fluid atomizer (Dumag GS40). Typical generated droplets Sauter mean diameter and initial velocity are about $20\text{--}40\mu\text{m}$ and $60\text{--}70\text{m/s}$, respectively.

Flue gas exits from the top section of the column and is directed to a pulse-jet fabric filter (Dalamatc DU 102) made of TeryleneTM for particulate removal. The filter is divided into 10 bags and has a total filtration area of 10m^2 . The cleaning cycle time of the baghouse is about 2min. After the baghouse, flue gas passes through a water spray column and a demister for final purification before discharge to the atmosphere through the stack.

Flue gas is sampled in three different points of the plant in order to measure the desulfurization efficiency after both the spray-dry chamber and the baghouse. Sampled gas is filtered and sent to the gas analysis rack through heated lines. Gas is rapidly cooled to 4°C for water separation and the dry gas is analyzed (Maihak Multor 610) for O_2 (electrochemical cell), CO_2 , CO , SO_2 , NO_x (non-dispersive infra red analysis).

The whole plant is fully insulated with 0.06m thick mineral fiber wool and aluminum external lagging. The plant is equipped with a number of temperature, pressure and flow measurement devices as shown in Figure 1.

2.2 *Experimental procedure*

Each experimental desulfurization test had a typical duration of 10 hours. During plant start up (~3 hours) the spray-dryer and the baghouse were first heated to 80°C by means of an air flow passed through the electrical heater, in order to avoid water condensation when feeding the combustion flue gas. Then the burner was started up burning gasoil and sending the flue gas directly to the stack. Subsequently the fuel feed was slowly switched to heavy oil and the flue gas was directed to the spray-dryer. The electrical heater setpoint was adjusted in order to achieve the desired inlet flue gas temperature in the spray-dryer. After steady state conditions were reached (1-2 hours) the lime slurry was fed to the atomizer. The slurry composition and flow rate were adjusted in order to achieve the desired lime to sulfur molar ratio and approach to adiabatic saturation temperature at the spray-dryer outlet. New steady state conditions were reached in 30-60min. At this point gas concentrations were measured alternately in the three sampling points in order to calculate the SO_2 removal efficiency after the spray-dryer and the baghouse. At the end of the measurements the slurry feed was switched to water while a new slurry was prepared in the tank. This procedure allowed to keep almost stationary temperature conditions in the plant and at the same time to clean the slurry ducts to avoid subsequent contamination of the new slurry.

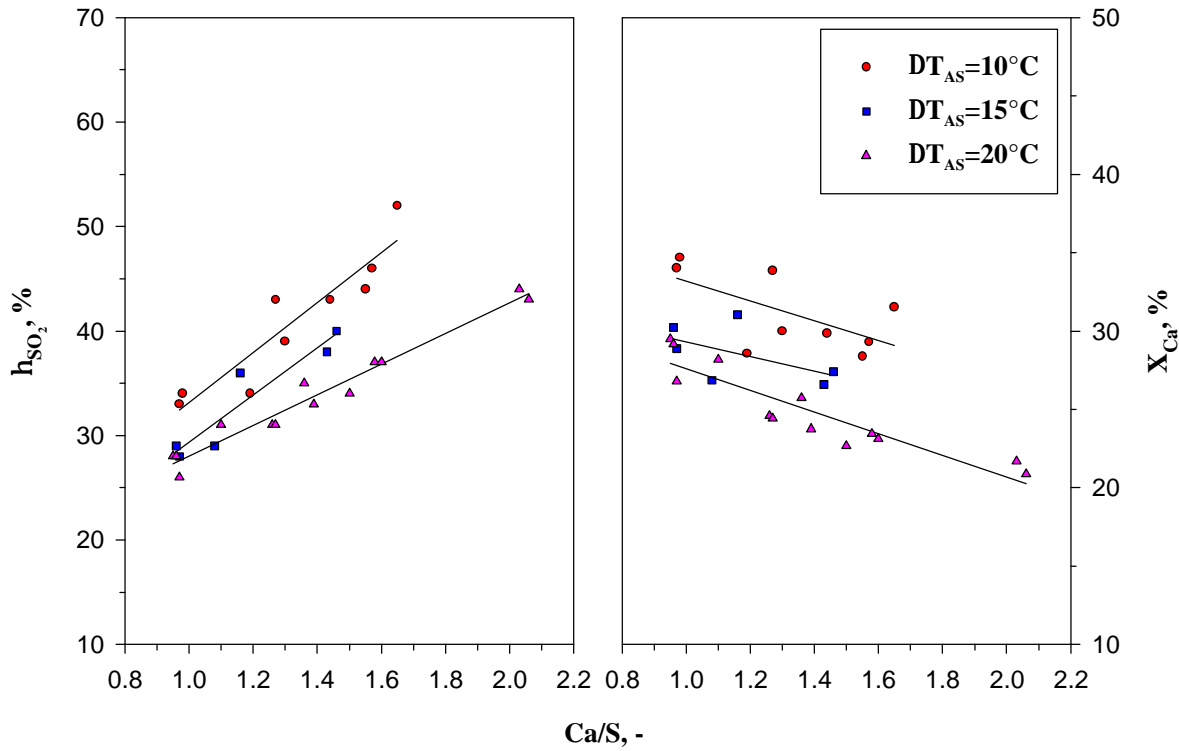


Figure 2 Spray-dryer SO₂ removal efficiency (left) and calcium utilization (right) as a function of Ca/S for different approach to adiabatic saturation temperature values. T=130°C.

After the new slurry was prepared, the atomizer feed was switched again from water to slurry. When new steady operating conditions were reached, gas concentration measurements were carried out as described before. Typically three different operating conditions were investigated in one test run. During the test run it was usually varied the lime to sulfur ratio (Ca/S) from one operating condition to the other, while keeping constant the inlet gas temperature (T) and the approach to adiabatic saturation temperature (ΔT_{AS}), in order not to vary the steady temperature conditions in the plant.

3. Results and discussion

The performance of the pilot spray-dryer/baghouse system has been analyzed in terms of SO₂ removal efficiency (h_{SO_2}) and calcium conversion degree (or calcium utilization) (X_{Ca}) after both the spray-dry section and the baghouse. Figures 2 through 5 report experimental results of SO₂ removal efficiency and calcium utilization as a function of Ca/S for different approach to adiabatic saturation temperature values. Figures refer to the 2.45 μm lime slurry at two different flue gas inlet temperatures (Figures 3 and 5 to T=130°C and Figures 4 and 6 to T=160°C).

Figures 2 and 3 show the spray-dryer column performance: the SO₂ removal efficiency increases with the calcium to sulfur molar ratio and decreases as the approach to adiabatic saturation temperature decreases. These results are in line with typical spray-dryer performance trends reported in the literature [4,5,9]. Capture of sulfur dioxide increases with Ca/S as a consequence of the increase of the slurry concentration that reduces the liquid mass transfer resistance in the droplets [7,9]. A decrease of ΔT_{AS} leads to a slower evaporation rate, thus providing extended droplet lifetime for sulfur dioxide absorption.

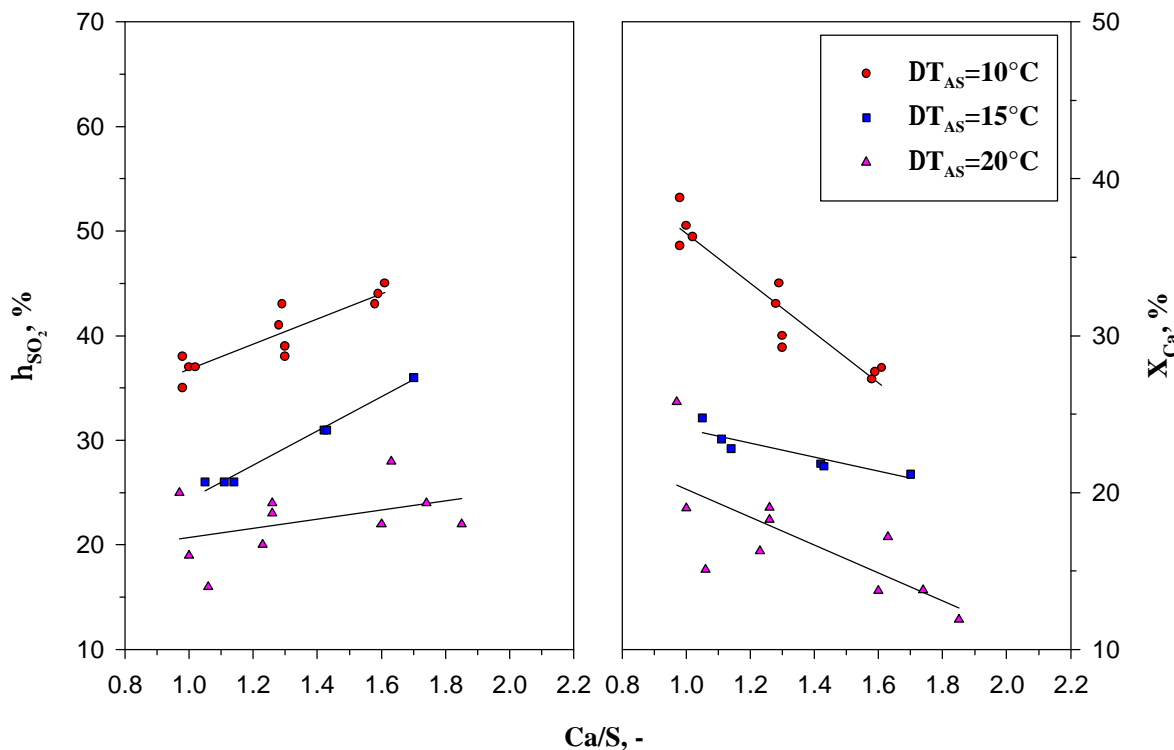


Figure 3 Spray-dryer SO₂ removal efficiency (left) and calcium utilization (right) as a function of Ca/S for different approach to adiabatic saturation temperature values. T=160°C.

As regards calcium utilization, figures show that a larger utilization is achieved at a lower Ca/S ratio and ΔT_{AS} . The decrease of calcium utilization with the stoichiometric ratio is due to the fact that the sulfur capture efficiency increases less than linearly with Ca/S [7,9]. The effect of the other variable is straightforward.

Figures 4 and 5 report the global plant performance, that is the total SO₂ removal efficiency and calcium conversion degree after the spray-dryer plus baghouse. Experimental data show that an additional 5-10% sulfur dioxide removal is achieved in the baghouse, corresponding to a 5-10% additional calcium utilization. This result is in line with similar data reported in the literature [5,12] and indicates that the sorbent particles still hold some moisture at the spray-dryer outlet section and continue to react with sulfur dioxide in the flue gas on the baghouse fabric, even if at a lower rate.

On the whole experimental results show that sulfur dioxide removal efficiencies as large as 60-70% can be achieved with a spray-dryer/baghouse system on low-sulfur heavy oil flue gas with lime to sulfur ratios of the order of 1.5-2. To this end it is of particular importance to lower as much as possible the approach to adiabatic saturation temperature. The lowest operating value for this variable is determined by safety considerations: it has to be avoided accidental water condensation on the baghouse fabrics that may lead to formation of mud and consequently to fabric plugging. This would result in the necessity of plant shut down for baghouse regeneration.

Additional options to enhance the performance of the spray-dryer have been reported [4,6- 9,13]. These rely on an accurate control of the atomization characteristics (drop size) and of the average size of lime particles dispersed in the slurry. Increasing the drop size leads to a decrease of the rate of external mass transfer while the droplet lifetime increases; these two factors tend to compensate each other. It has been reported, however, that drop sizes lower than about 10-20 μ m lead to a lower calcium utilization [7,13].

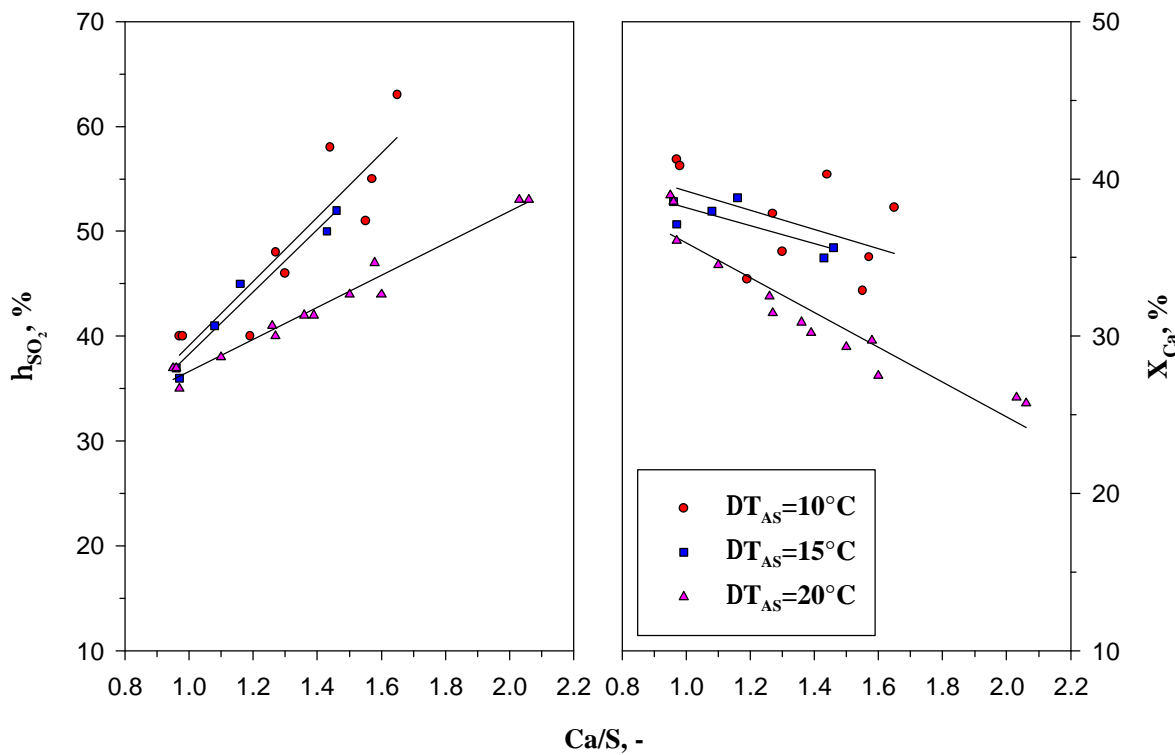


Figure 4 Total SO₂ removal efficiency (left) and calcium utilization (right) as a function of Ca/S for different approach to adiabatic saturation temperature values. T=130°C.

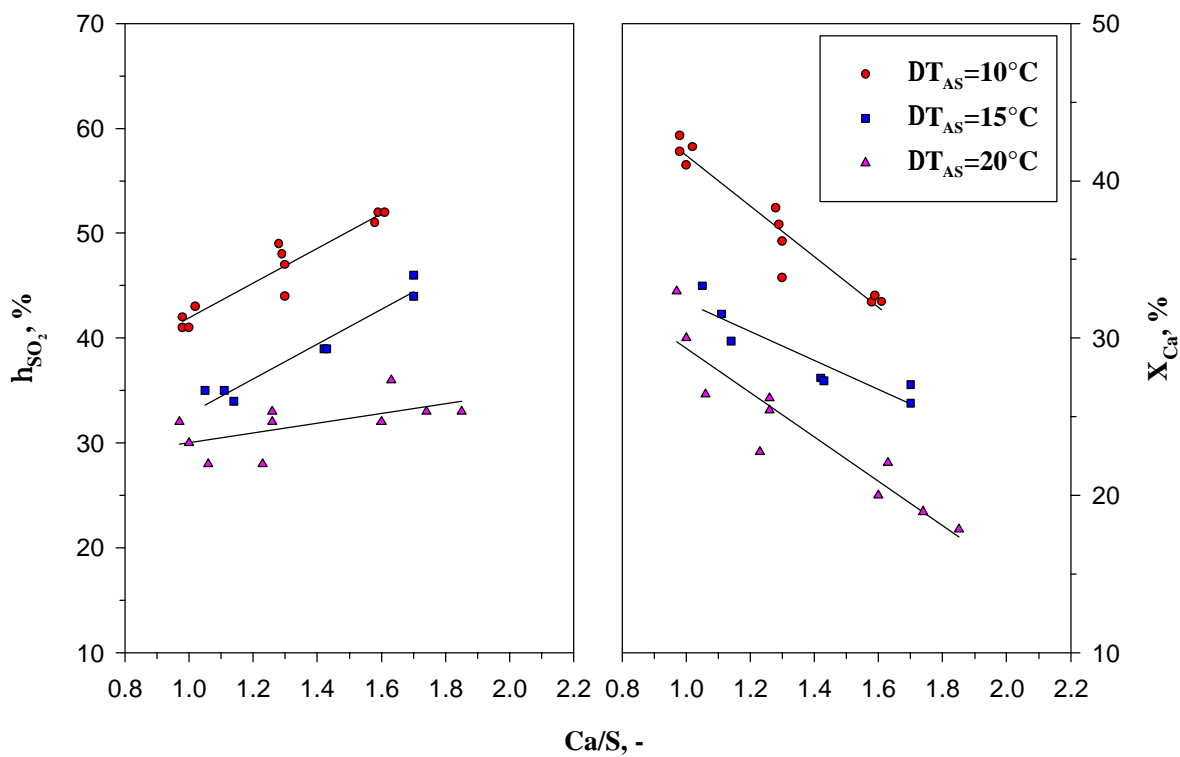


Figure 5 Total SO₂ removal efficiency (left) and calcium utilization (right) as a function of Ca/S for different approach to adiabatic saturation temperature values. T=160°C.

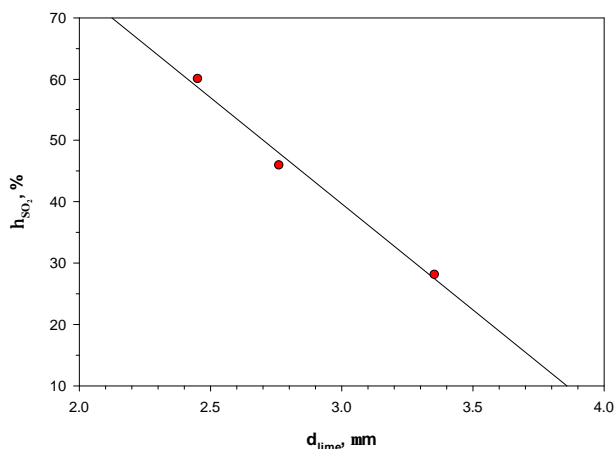


Figure 6 Spray-dryer SO_2 removal efficiency as a function of the surface mean diameter of the lime particles in the slurry. $T=130^\circ\text{C}$; $\Delta T_{\text{AS}}=10^\circ\text{C}$.

The size of lime particles dispersed in the slurry depends on the lime slaking process and on the properties of the parent quicklime [2,6]. Reduction of the lime particles size leads to an enhancement of the solids surface area and consequently of the dissolution rate in the drops. It has been shown that this variable exerts a significant influence on the spray-dryer performance [4,8,9]. A few experiments were carried out using slurries with lime particles of different size. Figure 6 reports the spray-dryer performance as a function of the lime particle mean size in the slurry under similar operating conditions. It is confirmed that a smaller lime particle

size in the slurry corresponds to a much better desulfurization performance.

As regards the sulfur dioxide concentration in the flue gas the present work has been carried out with concentrations between 150 and 400ppm ($400\text{-}1200\text{mg/Nm}^3$). It has been reported [3,5,7,8] that as the SO_2 concentration increases the spray-dryer performance worsens, because higher slurry concentrations are needed leading to a reduced drops lifetime. As a consequence it is anticipated that the spray-dry/baghouse system is less attractive for desulfurization of high-sulfur heavy oil flue gas.

4. Acknowledgements

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