

Evaluation of solid sorbents for acid flue gas emissions treatment.

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Abstract Removal of acid gases from exhaust emissions still represents a challenge for many industrial sectors, in particular for waste to energy facilities. In dry sorption processes, the efficiency of solid reagents is influenced by the specific surface area of the solid, the degree to which it is mixed with the gas, the concentration of the gas to be adsorbed, the temperature and humidity of the gas flow and the concentration of the reagent. Recently, new formulation of calcium- and sodium-based sorbents have been investigated. The objective of the present study is the characterization of the dry sorption capacity of HCl gaseous emissions of five different formulations of calcium-based sorbents based on the same operating conditions. To this end, an experimental installation was designed and applied. Scanning electronic microscopy (SEM) analyses were also carried out. The results showed a sorption capacity range of 8.1 – 10.8 mg Cl⁻·mg sorbent⁻¹ after 30 minutes. Samples C1 and C5 showed the highest sorption capacity. Samples C2 and C3 showed variable trends during the tests. Overall, for all the samples, the variance of sorption capacity increased with time. The possible reasons of such differences could be connected to the chemical composition, heterogeneous size distribution, and particle agglomeration effects.

Keywords: Flue gas treatment; HCl; calcium hydroxide, sodium bicarbonate; Chemisorption.

1. Introduction

Removal of acid gases (SO_x, HCl, HF) from exhaust emissions of industrial applications still represents a challenge for many sectors, in particular for waste to energy facilities. New and existing installations must comply with even tighter emission requirements as new regulations are implemented. Typically, these industrial facilities employ wet or dry scrubbing technologies for compliance.

In dry chemisorption processes, the solid reagent (typically Ca(OH)₂ or NaHCO₃) is injected countercurrent to the gas in a reaction chamber that allows for optimal contact modes and times between the phases. Efficiency is influenced by the specific surface area of the solid (m²·kg⁻¹ reagent), the degree to which it is mixed with the gas, the concentration of the gas to be adsorbed, the temperature

and humidity of the gas flow and the concentration of the reagent, usually expressed in terms of stoichiometric ratio. The achievable yields of dry processes are lower than those of wet systems and require the use of large excess reagent, resulting in the need for at least a partial recirculation of the separated solids. The main advantage of these systems is the absence of liquids and the problems of fouling and corrosion associated with them, although the problems regarding the disposal of the solid residues produced remain (Kumar and Jana, 2022).

The objective of the present study is the characterization of the dry chemisorption capacity of HCl gaseous emissions of five different formulations of calcium-based sorbents based on the same operating conditions. To this end, an experimental installation was designed and applied. Sorbents samples were also characterized by mean of scanning electronic microscopy (SEM).

2. Materials and methods

2.1 Experimental test

The tests were conducted using an experimental set up that simulates the operating conditions present in Duct Injection Sorbent (DSI) systems (Bodéan and Deniard, 2003). The unit included two input pipelines fed by gas cylinders. The first line served as an input of the acid gas. A mixture of HCl and nitrogen, specifically designed for this tests, was used. HCl concentration in the mixture was 558 ppm. The second line provided a pure nitrogen gas flow. Nitrogen was employed to wash the system for 3 minutes after each test. The input flow was regulated with a flowmeter to 0.5 l·min⁻¹. The flow velocity was 0.3·m s⁻¹. The HCl/N₂ gas was injected continuously in a sealed DuranTM glass bottle containing the solid sorbent to be tested. Five different types of calcium-based sorbents were tested (named C1 to C5). The principal component of the samples is hydrated lime (Ca(OH)₂). A mass of 3 g of sorbent was used for each test. The sorbent was uniformly distributed over the bottom of the bottle in order to create a layer of approximately 5 mm of thickness. For temperature conditioning, the bottle was placed in a DuranTM glass reactor with a thermal chamber connected to a heat exchanger. Tests were performed at 25°C. The

unreacted HCl exiting the bottle entered in a borosilicate glass absorber containing 100 ml ultrapure water. PTFE tubes were used for the gas lines, in order to avoid corrosion phenomena and undesired reactions. The process scheme of the experimental installation is reported in Figure 1.

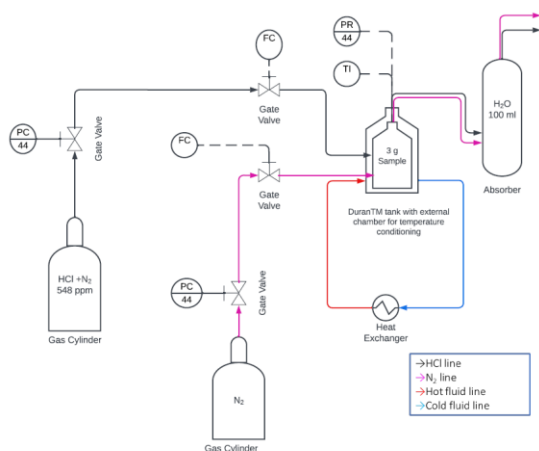


Figure 1. Process scheme of the experimental installation.

The chemisorption capacity of each sorbent was determined by measuring the concentration of chlorides absorbed in the water. Chloride concentration in the absorbing water was measured by mean of an ion chromatograph (Metrohm, ECO IC). The complete duration of each test was 30 minutes. In each test, samples of the absorbing water were taken after 5, 10, 20, and 30 minutes and the chloride concentration was measured. To determine the efficiency of the water absorber, a number of tests was carried out without sorbent. Sorbent samples were also analyzed by mean of scanning electronic microscopy (SEM), before chemisorption.

3. Results

3.1 SEM analyses

SEM pictures of the calcium hydroxide samples (Figure 2) showed a common main feature, i.e. the presence of both fine and coarse particles. Fine particles seem to constitute the main solid matrix, while granules with a seemingly crystalline structure possibly constitute a minor component. Fine dust particles have generally a radius of approximately 1 – 5 microns. From the images taken of sample 2, the presence of numerous granules covered with very fine particles can be observed. Sample 2 appears more heterogeneous than the other samples. Also, for sample 2, the difference in size between the granules and fine powder seems greater than in the other samples. Sample 3 and Sample 4 showed smaller particle sizes that tend to agglomerate, forming a so-called “cauliflower structure” that has been observed in previous studies (Nethe and Uwe, 2008). The difference in consistency of Sample 4 with respect to other samples could be perceived also during sample handling. In the analysis of Sample 5, tubular fibers were detected.

SEM elemental analyses (microanalyses) showed a common feature among all samples, i.e. that three main

elemental peaks could be identified, which are represented by the elements calcium (Ca), oxygen (O), and carbon (C). The peak relating to carbon (C) is probably due to the polycarbonate film used as a support. The ratio of the calcium and oxygen peaks confirms that the fine powder is composed of calcium hydroxide. In Sample 2 and Sample 5 magnesium (Mg) was also detected. This means that both calcium and magnesium hydroxide were present in these samples. Finally, a higher carbon content was found in Sample 5 with respect to the other samples. This could be due to two possible reasons: either a higher content of unreacted limestone (CaCO_3) or to the tubular fibers detected in this sample, possibly of organic nature.

3.1 Chemisorption tests

Sorption tests were carried out at 25°C. The chlorine mass absorbed by the samples, averaged at the different time steps, is reported in Table 1. The chlorine mass absorbed in time by each sample is reported in Figure 3.

Table 1. Average mass of chlorides absorbed by the solid samples.

Sample	Cl absorbed (mg)			
	5 min	10 min	20 min	30 min
C1	1.98	3.86	7.29	10.79
C2	1.95	3.61	6.38	8.11
C3	1.95	3.71	6.77	8.27
C4	1.89	3.58	5.37	8.47
C5	1.92	3.63	6.46	10.40

It is observed that sample C1 has on average the highest adsorption capacity, its trend is linear and it is characterised by a low variance. Similarly, sample C5 follows a linear trend and the points are affected by a low variance. Sample C4 is characterised by a lower adsorption capacity. This could be related to the finer grain size of this sample which, although it results in a greater specific surface, could favor the formation of agglomerates of particles which compromises the chemisorption capacity. Samples C2 and C3 also show lower adsorption than samples C1 and C5. In addition, a high variability of the performance was found for these samples, demonstrated by the high variance. Each of these two samples showed two different trends during the sorption tests. Some tests showed a higher adsorption capacity with a linear increase. Other tests showed limited adsorption capacity and a non-linear trend.

4. Discussion

The results of this study showed that small variations of the size distribution and composition of the hydrate lime samples could affect the average adsorption capacity of the solid matrix. Two samples (C2 and C3) showed variable trends during the tests. The origin of this behavior is not clear; the possible reasons could be connected to the heterogeneous size distribution and possible particle agglomeration effects. Also, small variations of room humidity in particular could have affected the results to a lesser extent, as a higher humidity may have increased the adsorption capacity of the hydrated lime. Overall, it was observed that, for all the samples, the variance of adsorption capacity increased with time. This is probably

also due to the fact that as time increases, the chemisorption phenomena occurring within the sample are more affected by the heterogeneities present in the sample. Additional experimental analyses are needed towards a more complete characterization of these materials. Also,

the adsorption capacity will be evaluated at higher temperatures (up to 140-160°C), which are closer to the real operating conditions of industrial installations.

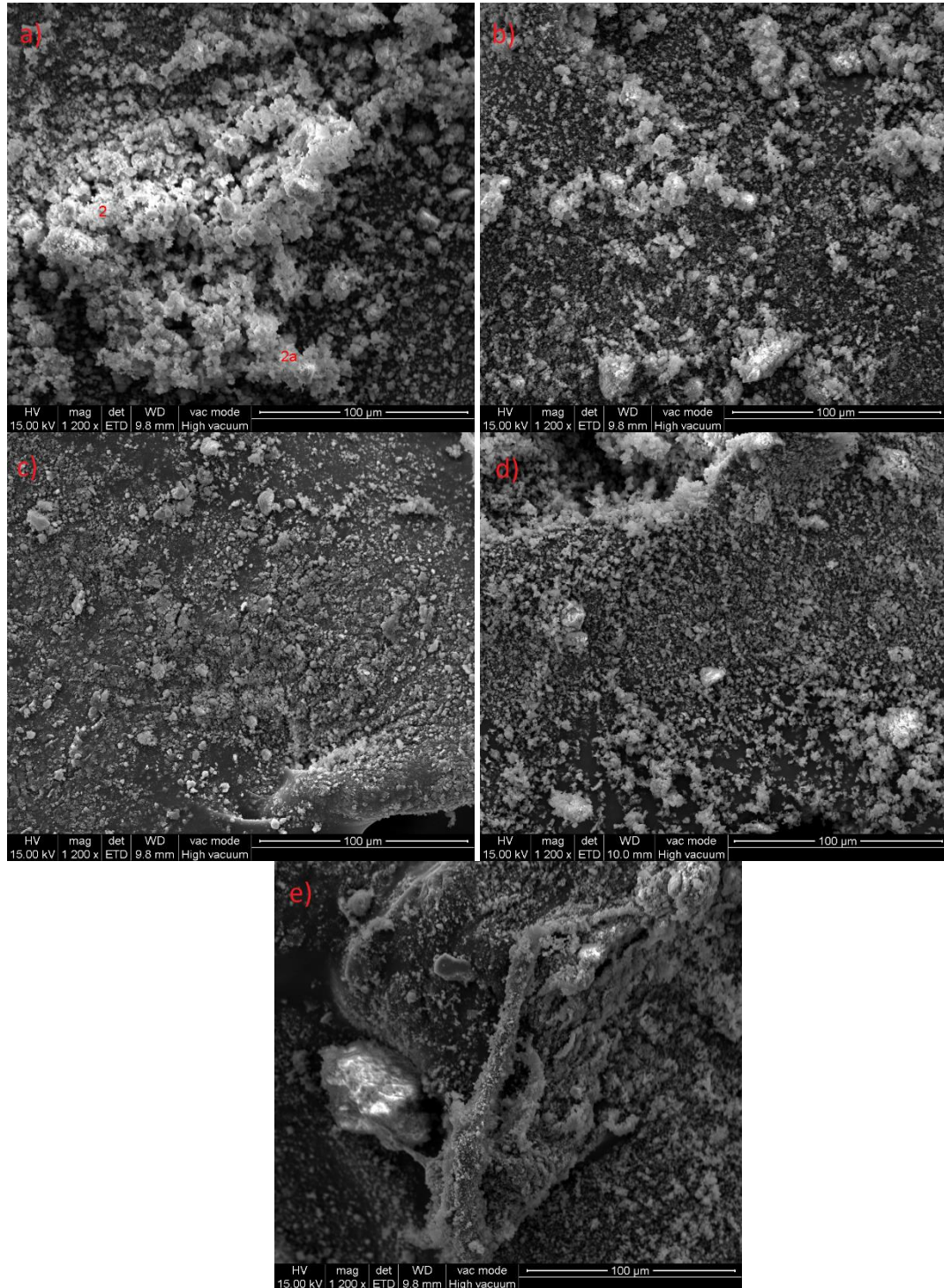


Figure 2. SEM pictures of Sample 1 (a), Sample 2 (b), Sample 3 (c), Sample 4 (d), and Sample 5 (e).

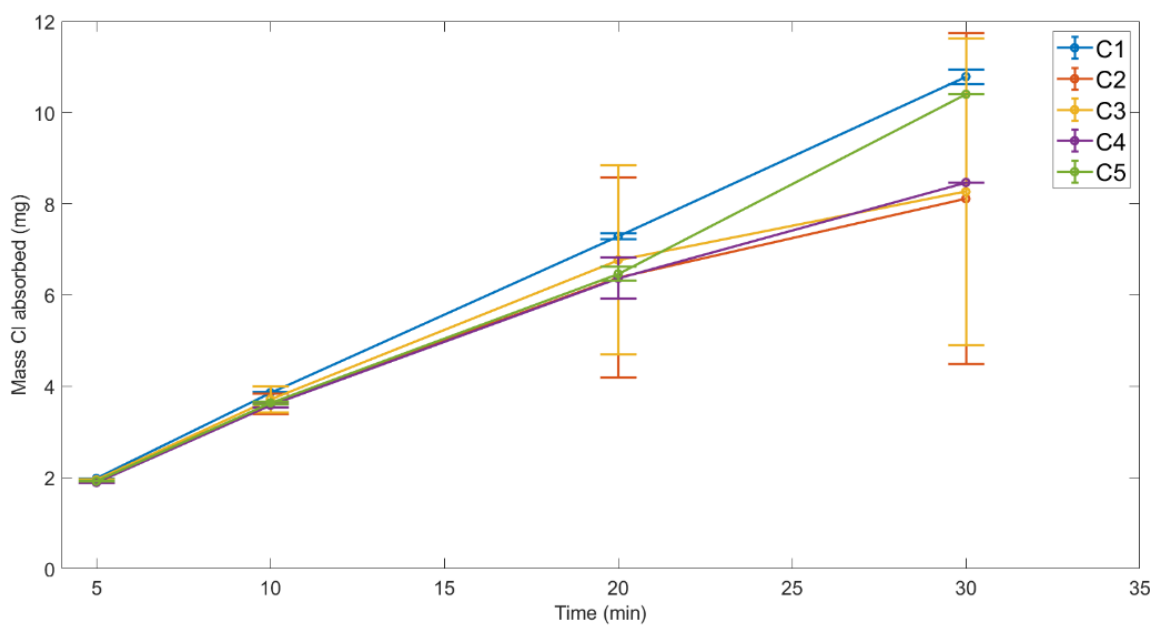


Figure 3. Trend in mean absorbed mass of chlorides over time.

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