DEVELOPMENT OF ADSORBENTS FOR FIXED-BED TREATMENT OF ACID GAS POLLUTANTS

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ABSTRACT

In this study, new adsorbents have been developed that are able to clean acid gas emissions from high-temperature firing processes. The development consists of **an alternative adsorbent configuration** (eco-design), which provides a greater **adsorption capacity** per unit mass and a lower **charge loss** than that obtained by currently available commercial reagents. The new adsorbents exhibit changes in their composition and form that enhance internal pollutant diffusion and encourage flue gas passage through the bed.

Tests were conducted on a laboratory scale, as well as on a pilot scale in an industrial facility using a prototype that was able to work with a gas stream from a ceramic tile firing kiln. In each of these tests, the acid pollutants present in the studied gas stream were continuously monitored (before and after going through the adsorbent), and the adsorption capacity of each studied material was then determined.

1. INTRODUCTION

One of the major environmental impacts related to ceramics manufacture is gas emissions into the atmosphere. Such emissions can contain particulate matter and pollutants of an acid nature in the gaseous phase in the form of fluorine, chlorine, sulphur, and nitrogen compounds.

Acid compound emissions arise in production stages in which combustion processes take place and, therefore, high temperatures are reached. The acid compounds (HF, HCl, and SO_x) released in the ceramic tile firing stage stem from the use of raw materials and fuels that contain precursors for acid compound formation [1-9].

Fluorine compound emissions during ceramic tile firing are one of the most important emissions in this process stage, making these pollutants the most characteristic pollutants of the ceramic industry beside particulate matter. Their emissions originate basically from the presence of the fluorine ion in the structure of the clay minerals used as raw materials in tile body manufacture.

Chlorine compound emissions are mainly due to the presence of the ion chlorine in the water used in preparing the raw materials for the tile body. In addition, certain clays and admixtures contain trace levels of chlorine.

Sulphur compound emissions stem from the sulphur content in the raw materials and the type of fuel used. The clays used in ceramic tile manufacture can contain sulphides in pyrite form or calcium and magnesium sulphates such as gypsum and organic sulphates.

With regard to the type of fuel, it is the fossils **fuels** that can generate sulphur emissions. In the case of the ceramic industry, the principal fuel used is natural gas, which is practically sulphur-free, though when fuel oil, coal, or petroleum coke is used, sulphur emissions can be higher.

In the EU, the application of Directive 2010/75/EU on industrial emissions requires the companies included in Annex I of the Directive to obtain an Integrated Environmental Authorisation (IEA), which includes emission limit values (ELVs) for different air pollutants. When it comes to fixing the applicable ELVs for each installation, the authorities take into consideration the existing BREFs (BAT Reference Documents) for the industries involved. These are EU reference documents and they set out the best available techniques for each sector and propose sector-related emission values (ELV-BAT). The emission values defined for ceramic tile manufacture in the EU are detailed in Table 1.

Parameter	Units *	HF	HCl	SO_2	NOx (as NO_2)
Concentration	mg/m_o^3 at 18% O_2 and dry gas	5	30	500	250

*mg/m_0^3: concentration under normal temperature (273 K) and pressure (101.3 kPa) conditions.

Table 1. Emission values for the firing stage in ceramic tile manufacture according to the BREF on Ceramics.

In the BREF on ceramics manufacture [10], different types of BATs are identified for **acid gas emissions**. The BATs are broken down as follows:

a) Primary measures/techniques: one or more of the following techniques are applicable for combustion gases from kiln firing processes: i) Minimisation of the use of pollutant precursors in the raw materials; ii) Optimisation of the firing curve

b) Secondary measures/techniques in combination with primary measures/techniques: The application of one or more of the primary techniques and one or more of the following secondary techniques can reduce the emission of these types of compounds: i) Adsorbents with fixed-bed systems; ii) Gas cleaning with a dry filter (preferentially a baghouse), with reagent addition

2. FIXED-BED ADSORPTION TREATMENT SYSTEMS

The fixed-bed adsorption systems of cascade filters are considered secondary BATs [10]. These systems put the gas stream to be treated in contact with an adsorbent bed that reacts with the pollutants at issue contained in the stream.

2.1. Description of the equipment

The fixed bed or adsorbent may have different configurations, but the most widely used in the ceramic industry have **three differentiated parts** [10]. The top part is the **reagent storage bin**. The reagent is transported through the inner system by gravity and, as it is used, it is discharged through the bottom of the hopper at regular intervals by means of an endless screw.

The core of the treatment system is the **contact area** located between the bin and the discharge zone. In this area, the reagent encounters the gases to be cleaned, creating a **cross flow** between the solids stream and the gaseous stream.

The cross flow is achieved by the installation of different rows of concave baffle panels that reduce the rate of reagent fall and produce optimum gas stream dispersion inside the bed, thus increasing the reaction time and contact area, assuring efficient circulation and distribution of the gas stream.

2.2. Description of the usual adsorbents

The reagents commonly used in fixed-bed systems are solids in granulate form, unlike other dry treatment systems that use solids in the form of micronised powders.

Granule morphology is usually spherical, with an average diameter between 4 and 6 mm. One of the main characteristics required for good treatment efficiency is reagent **specific surface area**. The specific surface area of an adsorbent is the accessible area for the adsorbate molecules, in this case acid gases, in order to be able to react. This area may be located on the adsorbent surface or inside the surface pores. If the size of these pores is larger than that of the adsorbate molecules, this surface can be used to fix the pollutant molecules. However, using granules has certain advantages, for example, such as the high mechanical strength that this form entails, which allows simple and appropriate storage, handling, and transport of the material.

On a chemical level, this type of system is based on chemisorption, a phenomenon resulting from the chemical interaction between a solid and the substance adsorbed on its surface. The force of the chemical bond can vary considerably and it may even occur that an identifiable chemical compound as such does not form. Chemisorption is used to transform gaseous pollutants of interest into solid products. This is done through a chemical reaction involving acid–alkali neutralisation using different compounds.

The most widely used reagents in fixed-bed systems are calcium and sodium compounds, in particular, calcium carbonate, $CaCO_3$, calcium hydroxide or slaked lime, $Ca(OH)_2$, sodium bicarbonate, $NaHCO_3$, and sodium carbonate, Na_2CO_3 [9]. Mixtures of the foregoing reagents and commercial reagents based on these are also used together with admixtures that enhance some of their characteristics. The origin and neutralisation reactions of these reagents are detailed in Table 2.

Name and formula	Origin	Neutralisation reactions
Calcium carbonate. $CaCO_3$	Very abundant product in nature	$CaCO_3$ (s)+ 2HF (g) —> **CaF_2(s)** + CO_2 + H_2O (g) $CaCO_3$ (s) + 2HCl (g) —> **$CaCl_2$ (s)** + CO_2 + H_2O (g) $CaCO_3$ (s) + SO_2 (g) + ½ O_2(g) —> **$CaSO_4$ (s)** + CO_2 (g)
Calcium hydroxide or slaked lime. $Ca(OH)_2$	Industrial product obtained by calcining $CaCO_3$	$Ca(OH)_2$ (s)+ 2HF (g) —> **CaF_2(s)** + $2H_2O$ (g) $Ca(OH)_2$ (s) + 2HCl (g) —> **$CaCl_2$ (s)** + H_2O (g) $Ca(OH)_2$ (s) + SO_2 (g) + ½ O_2(g) —> **$CaSO_4$ (s)** + H_2O (g)
Sodium bicarbonate. $NaHCO_3$	Industrial product resulting from an intermediate Solvay process reaction.	$2NaHCO_3$ (s) —> Na_2CO_3 (s)+ H_2O + CO_2 (g) T= 120–175ºC; activated Na_2CO_3 with high specific surface area: 4–5 m^2/g
Sodium carbonate. Na_2CO_3	Industrial product obtained by the Solvay process	Na_2CO_3(s) + 2HF (g) —> 2NaF(s) + H_2O + CO_2 (g) Na_2CO_3(s) + 2HCl (g) —> 2NaCl (s) + H_2O + CO_2 (g) Na_2CO_3 (s)+ SO_2 (g) + ½ O_2 —> Na_2SO_4 (s) + CO_2 (g)

Table 2. Reagents customarily used in neutralisation reactions for acid compound treatment [10-12].

2.2.1. Newly developed adsorbents

In this study new adsorbent materials that display excellent physical, chemical and fluid-dynamic properties have been developed. Adsorbent chemical composition was selected on the basis of a series of preliminary tests, in which adsorbents of different nature, such as calcium compounds, activated charcoal, algae, etc., were studied

In these tests it was observed that the highest efficiencies for the removal of the compounds of interest were reached with materials based on calcium compounds, so that these were used in subsequent development. Various adsorbents of this last type were developed and studied, the most interesting results being obtained with the adsorbent referenced **SS-2**. Therefore, this paper presents the results obtained with this adsorbent, though all the tests described were conducted for the entire **SS series**.

From the viewpoint of their physical configurations, the new materials presented in this paper were prepared in the form of hollow cylinders by extruding pastes that contained the group of adsorbent compounds or their precursors, calcium carbonate and different natural silicates, to give them the desired shape. The formed green material was subjected to different thermal drying and calcination treatments in order to decompose the precursors into the active elements and to generate and stabilise the porous structure of the system, as well as to optimise not just the entire exposed surface but also the rate of gas diffusion inside the solid.

A comparison of the volume and pore size distribution characteristics obtained by mercury intrusion porosimetry of a conventional commercial adsorbent and those of the newly developed material is presented in Figure 1. The figure shows that the new material (SS-2) had a far higher pore volume than the commercial adsorbents (SB), mainly owing to a special development of the macro-porosity, which allowed it to notably decrease the diffusional constraints of these gases inside the adsorbent particles.

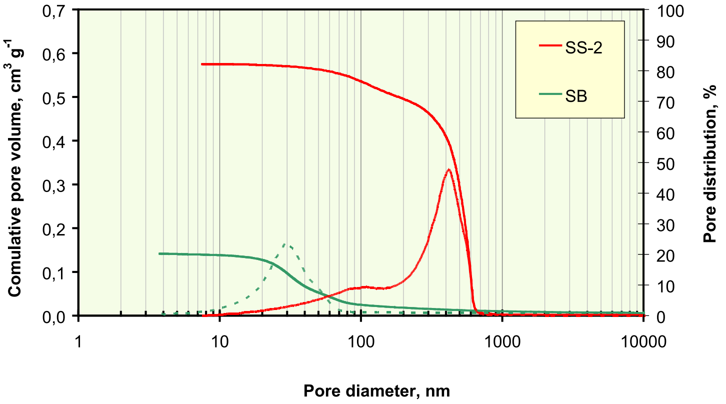


Figure 1. Cumulative pore volume and distribution of adsorbents SS-2 and SB.

3. EXPERIMENTAL METHODOLOGY

Tests were conducted to determine the adsorbent efficiencies on a laboratory, pilot plant, and industrial scale. The reference material chosen for the comparisons was a commercial reagent (referenced SB), widely used in cleaning acid emissions from high-temperature processes.

In the laboratory tests, synthetic gases were used, focusing on SO_2 which, of the gases of interest and in accordance with the literature reviewed, is the most difficult gas to remove owing to its low intrinsic reactivity with calcium and its larger molecular size. In the industrial-scale tests, the tests were carried out with real gases and the adsorbent performance with relation to all the pollutants at issue in the gas was studied, paying particular attention to HF.

3.1. Laboratory-scale tests

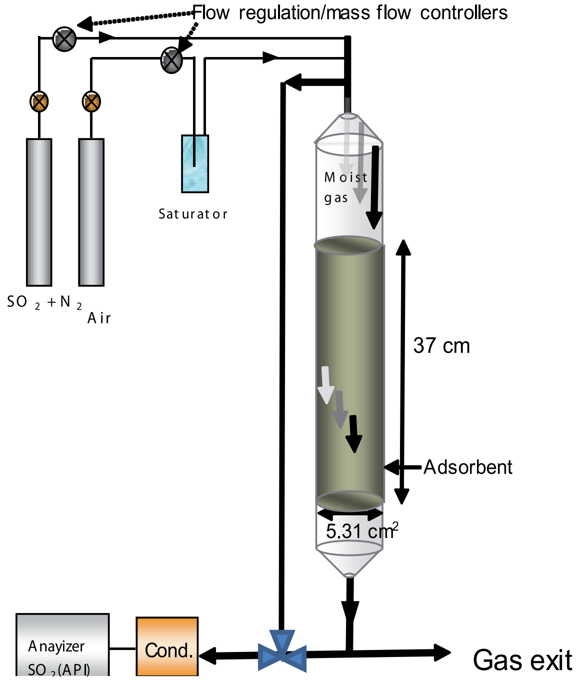
3.1.1. Determination of the value of $DAC_{(10)}$–RT

The dynamic adsorption capacity (DAC) of SO_2 was determined, until the output concentration was 10% of the input concentration, with a view to determining the real operational capability of the system under dynamic conditions (low contact times).

For this purpose, a sample of each studied adsorbent was introduced into a cylindrical reactor and a gas flow with a constant, known concentration of SO_2 was continuously passed through the adsorbent. The SO_2 concentration was continuously monitored at the reactor entry and exit with an API model 100AH fluorescence instrument. The test was conducted at room temperature. By way of example, the results obtained with one of the studied adsorbents, namely SS-2, are shown in Figure 2.

The graph shows a plot of the reactor input and output concentrations at every moment and the DAC (10%) and DAC(Total) values obtained with the selected reagent. Thus, setting an output concentration of 10% as input condition (i.e. 90% collection efficiency), the DAC (10%) value was 0.38 g SO_2/g versus a value of 0.58 g SO_2/g, as total adsorption capacity.

Under the same operating conditions, the commercial reference adsorbent exhibited a DAC(10%)=0.013 g SO_2/g adsorbent, which reflected the clear advantage of the new adsorbent compared with the commercial adsorbents being used to date in the case of SO_2.



Total Flow	5700	ml/min
$[SO_2]_0$	700	ppm
Air	balance	
GHSV	2014	h^{-1}
Contact time	1.8	s
Linear Velocity	0.18	m/s
Weight (dry adsorbent)	57	g
Bed length	37	cm

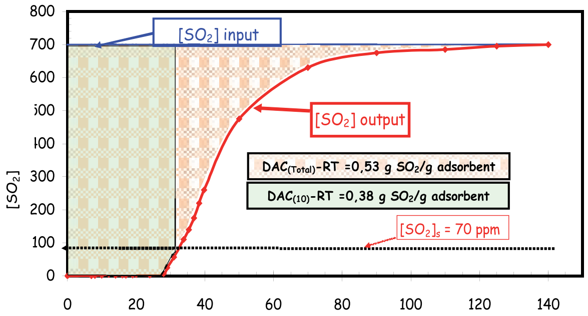


Figure 2. Schematic illustration of the experimental assembly used for the determination of the SO2 dynamic adsorption capacity (DAC) and results with adsorbent SS-2 at room temperature.

3.2. Industrial-scale tests

The following parameters were studied on an industrial scale:

a) **Cleaning efficiency** of different acid pollutants determined by emission measurement before and after the adsorbent bed, using continuous measurement systems based on tuneable diode laser (TDL) technology and electrochemical cells, depending on the pollutant measured.

b) **Adsorption capacity** of different acid pollutants, determined by chemical analysis of solid adsorbents before and after treatment. X-ray fluorescence spectrometry and ion-selective electrode potentiometry techniques were used for this purpose, depending on the element analysed.

In order to perform the tests on this scale, a prototype was developed that is able to work in industrial conditions, using only a small part of the emission gases of a conventional ceramic tile firing kiln. The use of a low-flow pilot plant exhibited the following advantages: accessibility to the material to be studied, use of a smaller reagent volume, homogeneity of the reagent bed cross-section, and thorough control of the test conditions (temperatures, humidity, charge losses, gas flow rates, etc.).

Working directly with industrial emissions allowed comparable results to those found in industrial practice to be obtained. The characteristics defining an industrial emission, compared with those of an emission simulated in a laboratory are gas stream temperature, humidity, and chemical composition since, in the type of emissions at issue, there is direct contact between the product being processed and the gas stream, which generates a complex mixture that is impossible to reproduce on a laboratory scale. A scheme and a photograph of the developed industrial prototype are shown in Figure 3.

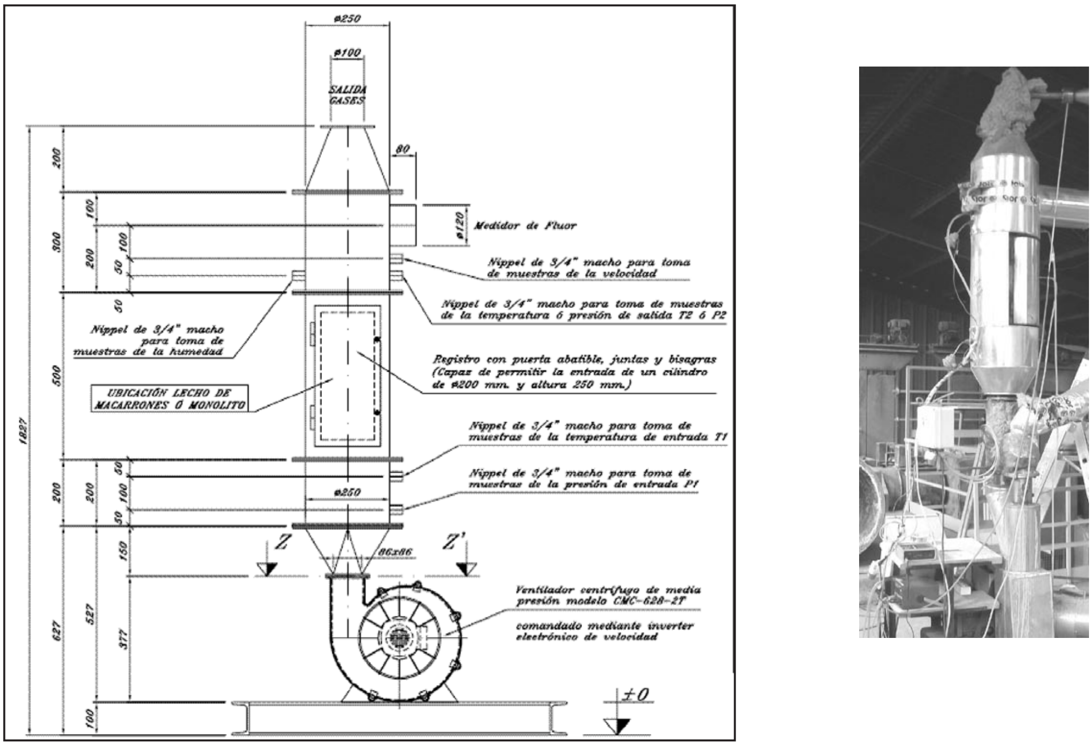


Figure 3. Details of the developed pilot plant for performing the industrial-scale tests.

4. RESULTS IN THE INDUSTRIAL PLANT

4.1. Performance of the selected adsorbent

4.1.1. Study of the HF removal efficiency

Tests were conducted on each of the developed adsorbents in the industrial prototype, determining the cleaning efficiency (reactor's HF input and output concentrations) and the charge loss (static pressure at the reactor inlet and outlet). By way of example, the results obtained for adsorbent SS-2 and the SB reference adsorbent are detailed in Table 3,

Reagent	HF removal efficiency (%)	Charge loss (Pa)
Reference adsorbent SB	37	3913
Adsorbent SS-2	48	3575

Table 3. Results obtained with the tested materials in the pilot plant.

The results show that adsorbent SS-2 exhibited an 11% higher efficiency than the reference adsorbent and that it also displayed smaller charge losses (about 9%).

4.1.2. Study of the adsorption capacity

To determine the adsorption capacity of the different pollutants, the adsorbents used in the previous test series were subjected to chemical analysis of the solid before (blank) and after the saturation test.

The results obtained for adsorbent SS-2 and reference adsorbent SB are given in Table 4. In addition to fluorine, the chlorine and sulphur content were also analysed.

Sampling	Reagent	Sulphur (% by weight)	Chlorine (% by weight)	Fluorine (% by weight)
Initial (blank)	SS-2	0.01	<0.01	0.15
	SB	0.02	<0.01	0.03
Average saturation values	SS-2	0.65	0.50	25.0
	SB	0.76	0.93	13.0

Table 4. Fluorine, chlorine, and sulphur concentrations in the supplied (blank) solid samples and after the adsorption test.

It may be observed that both adsorbent reagents (SB and SS-2) displayed a high selectivity in retaining fluorine compounds compared with that in chlorine and sulphur compound retention, which exhibited a retention below 1%. In the tests conducted, the fluorine adsorption capacity was notably greater in the adsorbent developed in this study (SS-2) than in the reference material (SB).

4.1.3. Obtainment of the DAC(10) values

In these tests, analysis of the variation of the input and output HF concentrations as a function of time yielded the curve shown in the Figure 4. Analysis of these results allowed a DAC value of 0.3 g HF/g adsorbent to be obtained for SS-2.

Considering the values of the chemical analysis in Table 4, a value of 25% fluorine was obtained for the SS-2 used. Therefore, the quantity of HF retained per gram of fresh adsorbent was 0.33 g HF/g adsorbent, a value very close to that determined from the breakthrough curve.

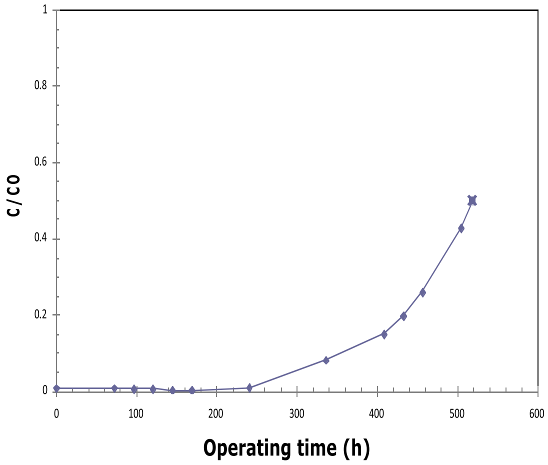


Figure 4. HF adsorption breakthrough curve for adsorbent SS-2.

4.2. Obtainment of the system design equations

4.2.1. HF adsorption kinetics

In order to obtain a kinetic model of the process, a reaction with a first order kinetics was assumed, a mass balance was applied to the reactor (assuming that it behaved as a plug-flow reactor), and using the HF removal data obtained in the industrial plant at high space velocities (low contact times) [13], the following equation was obtained:

$$k / GHSV = -\ln(1 - X_{HF}) \qquad [1]$$

where:

k: kinetic constant. The value was experimentally determined at various temperatures and the data were fitted to an Arrhenius-type equation, yielding k= (h^{-1})

GHSV: space velocity (gas flow rate/volume occupied by the bed) (h^{-1}). This is the number of equivalent volumes to that of the reactor fed per unit time.

X_{HF}: degree of HF conversion or removal

This equation allows the adsorbent bed volume needed in order to reach the desired 'immediate cleaning level' for a given gas flow rate to be determined: that is, the maximum flow rate that can be used in reactor design without being limited by the reaction rate. The dependence of the HF adsorption rate as a function of reactor size at a flow rate of 16000 m_o^3/h is depicted in Figure 5. The figure shows that the temperature does not significantly influence the HF adsorption rate, suggesting that the system is probably limited by mass transfer [14], which highlights the importance of the macroporosity of the new adsorbent for efficient HF collection.

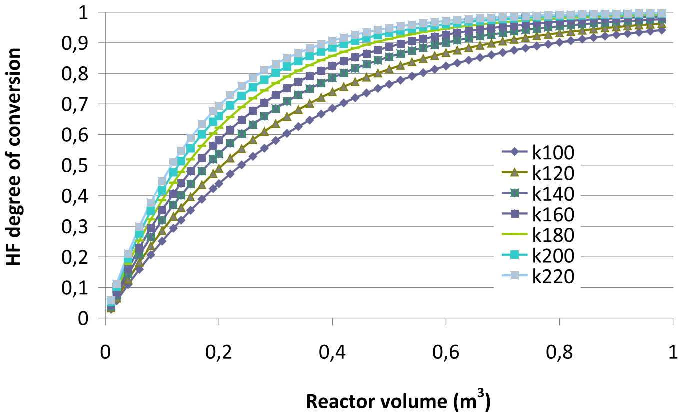


Figure 5. HF adsorption rate as a function of reactor size and operating temperature, for a gas flow rate of 16000 mo3/h.

In accordance with these results, when the operation is run at about 180–220°C (usual temperature range in the case of gases from ceramic tile firing kilns), in order to reach appropriate reaction rate conditions (>90% HF removal), and at a gas flow rate of 16000 m_o^3/h, a minimum reactor (bed) volume is required of about 0.5 m^3, which corresponds to a maximum GHSV value of 32000 h^{-1}.

4.2.2. Adsorbent charge losses

In addition, the charge loss produced by the adsorbent bed on a laboratory scale was analysed, and the results were verified and compared with the data obtained in the industrial plant. The pressure loss data obtained for different adsorbent samples (hollow cylinders with different dimensions) exhibited small differences, so that all values were fitted to the following empirical equation [15] (including the data obtained in the industrial test):

$$\Delta p / L = 91 \cdot v_L^2 + 38 v_L^2 \qquad [2]$$

where:

Δp: charge loss (mmwc)

L: adsorbent bed height (m)

v_L: gas average linear velocity through the bed (m/s)

5. CONCLUSIONS

The conclusions drawn from the study have been grouped as follows:

- **Work methodology**

The methodology developed in this study for the characterisation of adsorbent materials and in the study of their performance in treating gaseous pollutants of an acid nature, on both a pilot and an industrial scale, was shown to be appropriate. This facilitates the possibility of performing similar studies for other industrial applications and for another types of adsorbent materials developed for the removal of air pollutants.

One of the advantages of this methodology is, for example, the obtainment of design equations for a fixed-bed adsorption system, since these allow different configurations to be simulated so that the best one can be chosen for each industrial scenario considered (pollutant concentrations, flow rates, space needs, etc.), in addition to allowing various configurations of the same industrial application to be studied.

- **Performance of the developed adsorbents**

In the case of the adsorbents, the developed morphology (hollow cylinders) and their chemical composition (principally calcium compounds with additives) have enhanced the chemical and physical properties (adsorption capacity, specific surface area, mechanical strength, and charge loss) of the adsorbents. Thus, in the first preliminary results, they performed better in the treatment of the studied acid gases than the commercial reagents being used at present.

Furthermore, the developed adsorbents exhibited a high selectivity in retaining fluorine compounds, compared with chlorine and sulphur compound retention.

- **Reactor design**

The design equations and the type of adsorbent developed allow fixed-bed adsorption units to be designed, with an economical and simple (no moving parts) gas treatment system, with smaller space requirements than existing conventional treatment systems.

ACKNOWLEDGEMENTS

This study has been financed by the Ministry of Science and Innovation through the Centre for Industrial Technology Development (CDTI) by means of the Inter-business Cooperation programme.

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