ACID EMISSION CLEANING SYSTEM WITH SODIUM BICARBONATE FOR TILE KILNS

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1. ABSTRACT

Flue gases from ceramic tile kilns usually contain highly varying proportions of hydrofluoric acid (HF), hydrochloric acid (HCl) and sulphur dioxide (SO_2).

The traditional gas cleaning method has involved injecting powdered slaked lime (calcium hydroxide– $Ca(OH)_2$) in the gas stream, subsequently eliminating the dust in a bag filter and recovering the reaction salts. This method is highly selective with HF but provides low yields with HCl and no yield at all with SO_2, even on proportioning extremely high stoichiometric ratios.

The proposed system uses powdered sodium bicarbonate ($NaHCO_3$) as a reagent, which was shown to provide very good removal yields for the three pollutant compounds, in practice by using stoichiometric ratios close to unity.

In turn, the proposed cleaning facility presents new solutions such as: use of the flue system itself as a reactor, employing for final dust cleaning an electrostatic precipitator that runs at high temperatures with very little charge loss, and using an on-line HF analyser to minimise waste salt production.

The system allows reusing waste flue gas heat, since remaining acid pollutant concentrations are so small that no risks are involved for production facilities.

2. INTRODUCTION

The pollutants typically encountered in hot gas emissions in the ceramic industry are usually composed of fluorine, chlorine and sulphur in a gas phase.

Fluorine comes especially from the clays, and appears in the clay crystal structure as a result of an ionic substitution phenomenon owing to size similarity between F and OH ions. The fluorine emission is produced by the break-up of the clay mineral structure in the firing process at temperatures above 500-600°C.

The chlorine compounds can come from many sources: from chlorides in the water used as a raw material, from additives employed in glaze preparation and application processes, etc.

Sulphur compounds can arise as a result of employing fuels containing sulphur as an impurity (on using natural gas or propane, this contribution is insignificant), or from impurities in the raw materials, mainly pyrites (iron sulphide) or gypsum (calcium sulphate), and from sulphur in the water (dissolved sulphates).

2.1. AIR EMISSION LEGISLATION

2.1.1. LEGISLATION IN THE EUROPEAN UNION

Table 1 presents a summary of the emission limits in certain European countries, in which important differences and peculiarities can be observed.:

- In some countries like Belgium and France, particulate emission (dust) limits vary in terms of the flow rate emitted particulate matter, so that the concentration limit is brought down on raising particulate mass flow. The upper and lower concentration limits in these two countries coincide, and for emission sources with a flow rate exceeding around 7000 Nm^3/h, the applicable limit is 50 mg/Nm^3.

- In Italy, in the Emilia Romagna Region, a specific legislation has been drawn up for tile manufacturing and ceramic frit producing companies. This legislation sets the strictest emission limits to be found in Europe regarding air pollution for this industrial branch.

- The SO_x emission limit in Germany varies according to the sulphur content in raw materials.

- Table 1 clearly shows how Spanish legislation lags behind that of the major EU States.

As Table I indicates, particulate emission limits are usually expressed in concentrations, although there is a tendency, already applied in some countries, to use emission or mass flow factors (emitted quantity per unit product), and to express the concentrations at a given oxygen content in the flue gases, to avoid the dilution effect that arises on expressing the emission in concentrations.

On the other hand, it is to be noted that emission limits are not invariable and that the trend in the European Union is the progressive implementation with newly appearing technologies of ever-stricter requirements, and harmonisation amongst EU Member States. This approach has recently led to the publication of Directive 96/61/CE on Integrated Pollution Prevention and Control (IPPC), which underscores the importance of the BAT (Best Available Techniques) concept. In this sense, discussions on the applicable BAT for each industrial branch are going to play a key role in defining emission limits.

COUNTRY	PARTICULATES (DUST)	SO$_X$ (SO$_2$)	NO$_X$ (NO$_2$)	(HCl)	(HF)	CO
GERMANY	50	500 (1) 1500	500	30	5	-
BELGIUM (Flanders)	50 (F>0.5 kg/h) 150 (F<0.5 kg/h)	500	500	30	5	100
SPAIN	150	4300	615	460	80	625
FRANCE	50 (F>1 kg/h) 150 (F<1 kg/h)	500	500	50	5	-
GREECE	100	350	-	-	80	-
HOLLAND	10	200	200	30	5	-
ITALY (Emilia Romagna)	30 milling and spray drying 10 pressing and glazing 5 firing tile 30 fusing frits	-	-	-	5	-
PORTUGAL	150	1500	-	-	50	-
UNITED KINGDOM	50	1500	-	30	5	200

F: emission factor or mass flow rate (kg/h) (1) Clay sulphur content <0.12%

Table 1. *Overview of air emission limits in EU States (values in mg/Nm^3) Source: Societé Française de Céramique 1994.*

2.1.2. SPANISH LEGISLATION

Annex IV of Decree 833/75 establishes air pollutant emission levels for potentially air-polluting industries. The ceramic branch is specifically mentioned in Section 10, but the only pollution referred to in this case involves dust emissions.

The emission limits set in Decree 833/75 are detailed in Tables 2 and 3. The limit currently applied in practice in Spain appears in these tables as the predicted value for 1980.

	Emission levels (mg/Nm^3)		
	Existing facilities	New facilities	Prediction for 1980
Dust emission	500	250	150

Table 2. *Section 10 of Annex IV of D833/75. Ceramics*

Pollutants	Measurement units	Emission levels
Particulates	mg/Nm^3	150
SO$_2$	mg/Nm^3	4300
CO	p.p.m.	500
NO$_x$ (measured as NO$_2$)	p.p.m.	300
F total	mg/Nm^3	80
Cl	mg/Nm^3	230
HCl	mg/Nm^3	460
SH$_2$	mg/Nm^3	10

Table 3. *Section 27 of Annex IV of D833/75. Ceramics.*

2.1.3. CET ENVIRONMENTAL REQUIREMENTS

The European Ceramic Tile Manufacturers' Federation (CET), to which the Spanish Ceramic Tile Manufacturers' Association - Asociación Española de Fabricantes de Aulejos, Pavimentos y Baldosas Cerámicas (ASCER) – belongs, has drawn up and approved environmental requirements to be met by European ceramic tile manufacturers by the year 2000. These requirements are subsequently to be periodically reviewed.

The environmental requirements include limits on: air pollutant emissions, water consumption, pollutant discharge in wastewater, energy consumption and minimum levels of waste recovery in the ceramic process.

The most important of these requirements from an air pollution point of view are as follows:

- Air emission limits, see Table 4.
- An energy consumption limit, which sets a primary energy specific consumption of less than 12 GJ/t of product, where total primary energy (thermal and electric) is calculated relative to finished product mass on a yearly basis.

Process stage	Particulates (mg/Nm^3)	Fluorine as HF (mg/Nm^3)
Milling, forming, etc.	100	-
Spray drying	75	-
Glazing	20	-
Firing (values expressed at 18% of O_2)	25	10

Table 4. *CET environmental requirements in air emissions*

It can be observed in Table 4 that one of the requirements is limiting fluorine emissions in the flue gases produced on firing ceramic tiles.

3. THE NEUTREC® CHEMICAL PROCESS: COMPARISON WITH OTHER DRY GAS-CLEANING SYSTEMS

A description follows of the chemical neutralisation process of the acid constituents in the gases exiting the kilns by means of dry systems. First, the theoretical stoichiometric ratios are presented. Subsequently, on the basis of experimental data, the excess reagents are derived and hence neutralisation salts production, needed in practice to achieve targeted cleaning levels.

In order to have a reference point with which to compare these data, all the ratios were evaluated for a dry system using sodium bicarbonate and for a traditional system using slaked lime (calcium hydroxide).

To determine the arising reactions, the acid pollutants contained in the gas streams were assumed to be HF, SO_2 and HCl.

The NEUTREC chemical process is patented as detailed in the references.

3.1. REACTION STOICHIOMETRY

3.1.1. SODIUM BICARBONATE (NEUTREC®)

Using sodium bicarbonate ($NaHCO_3$) as a reagent, the pollutant capturing reactions are:

a) $HF + NaHCO_3 \rightarrow NaF + CO_2 + H_2O$

b) $SO_2 + 2NaHCO_3 + {}^1/_2\, O_2 \rightarrow Na_2SO4 + 2CO_2 + H_2O$

c) $HCl + NaHCO_3 \rightarrow NaCl + CO_2 + H_2O$

Taking into account the above reactions yields the following stoichiometric reagent consumption ratios:

$$a)\ 1g\ HF \times \frac{1mol\ HF}{20g\ HF} \times \frac{1mol\ NaHCO3}{1mol\ HF} \times \frac{84g\ NaHCO3}{1mol\ NaHCO3} = 4{,}20\ g\ NaHCO_3$$

$$b)\ 1g\ SO_2 \times \frac{1mol\ SO2}{64{,}1g\ SO2} \times \frac{2mol\ NaHCO3}{1mol\ SO2} \times \frac{84g\ NaHCO3}{1mol\ NaHCO3} = 2{,}62\ g\ NaHCO_3$$

$$c)\ 1g\ HCl \times \frac{1mol\ HCl}{36{,}5g\ HCl} \times \frac{1mol\ NaHCO3}{1mol\ HCl} \times \frac{84g\ NaHCO3}{1mol\ NaHCO3} = 2{,}30\ g\ NaHCO_3$$

The industrial purity of the sodium bicarbonate used exceeded 99%, so that for proportioning purposes it can be considered 100%.

The salt production stoichiometric ratios are:

$$a)\ 1gHF \times \frac{1mol\ HF}{20g\ HF} \times \frac{1mol\ NaF}{1mol\ HF} \times \frac{42g\ NaF}{1mol\ NaF} = 2{,}10\ g\ NaF$$

$$b)\ 1gSO_2 \times \frac{1mol\ SO2}{64{,}1g\ SO2} \times \frac{1mol\ Na2SO4}{1mol\ SO2} \times \frac{142{,}1g\ Na2SO4}{1mol\ Na2SO4} = 2{,}22\ g\ Na_2SO_4$$

$$c)\ 1gHCl \times \frac{1mol\ HCl}{36{,}5g\ HCl} \times \frac{1mol\ NaCl}{1mol\ HCl} \times \frac{58{,}5g\ NaCl}{1mol\ NaCl} = 1{,}60\ g\ NaCl$$

The non-reacted reagent is found as follows:

d) $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

$$1g\ NaHCO_3 \times \frac{1mol\ NaHCO3}{84g\ NaHCO3} \times \frac{1mol\ Na2CO3}{1mol\ NaHCO3} \times \frac{106g\ Na2CO3}{1mol\ Na2CO3} = 0{,}63\ g\ Na_2CO_3$$

3.1.2. TRADITIONAL CALCIUM HYDROXIDE SYSTEM

Using powdered calcium hydroxide ($Ca(OH)_2$) as a reagent, the pollutant capturing reactions are:

a) $HF + {}^1/_2\,Ca(OH)_2 \rightarrow {}^1/_2\,CaF_2 + H_2O$

b) $SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O$

This reaction is not real, since at working temperature calcium sulphite is found in a hemihydrate form, so that the reaction (water forming part of $CaSO_3 \cdot {}^1/_2\,H_2O$ *is lost beyond 250°C):*

$SO_2 + Ca(OH)_2 \rightarrow CaSO_3 \cdot {}^1/_2\,H_2O + {}^1/_2\,H_2O$

c) $HCl + {}^1/_2\,Ca(OH)_2 \rightarrow {}^1/_2\,CaCl_2 + H_2O$

Thus, between 30 and 200°C, calcium chloride appears in a dehydrated form and therefore the actual arising reaction is:

$HCl + {}^1/_2\,Ca(OH)_2 + H_2O \rightarrow {}^1/_2\,CaCl_2 \cdot 2H_2O$

Taking into account the foregoing reactions, the following reagent consumption stoichiometric ratios are found:

a) $$1g\ HF \times \frac{1mol\ HF}{20g\ HF} \times \frac{1/2mol\ Ca(OH)2}{1mol\ HF} \times \frac{74g\ Ca(OH)2}{1mol\ Ca(OH)2} = 1{,}850\ g\ Ca(OH)_2$$

b) $$1g\ SO_2 \times \frac{1mol\ SO2}{64g\ SO2} \times \frac{1mol\ Ca(OH)2}{1mol\ SO2} \times \frac{74g\ Ca(OH)2}{1mol\ Ca(OH)2} = 1{,}156\ g\ Ca(OH)_2$$

c) $$1g\ HCl \times \frac{1mol\ HCl}{36{,}5g\ HCl} \times \frac{1/2mol\ Ca(OH)2}{1mol\ HCl} \times \frac{74g\ Ca(OH)2}{1mol\ Ca(OH)2} = 1{,}014g\ Ca(OH)_2$$

Moreover, a series of secondary reactions can also arise in the lime reactor. To be noted are especially the following:

- ◆ $CaSO_3 \cdot {}^1/_2\,H2O + {}^1/_2\,O_2 \rightarrow CaSO_4 \cdot {}^1/_2\,H_2O$
- ◆ $CaSO_3 \cdot {}^1/_2\,H2O + {}^1/_2\,O_2 + {}^3/_2\,H_2O \rightarrow CaSO_4 \cdot 2H_2O$
- ◆ $CaO + SO_2 \leftrightarrow CaSO_3$
- ◆ $SO_3 + Ca(OH)_2 + H_2O \rightarrow CaSO_4 \cdot 2H_2O$

These reactions are very difficult to assess and their quantitative and qualitative significance is much less than the ones detailed above, so that they were not considered.

The commercial purity of calcium hydroxide is usually about 90%, which requires raising reagent consumption accordingly.

Salt production stoichiometric ratios are:

$$\text{a) } 1g\ \text{HF} \times \frac{1mol\ \text{HF}}{20g\ \text{HF}} \times \frac{1/2mol\ \text{CaF}_2}{1mol\ \text{HF}} \times \frac{78g\ \text{CaF}_2}{1mol\ \text{CaF}_2} = 1,950\ g\ \text{CaF}_2$$

$$\text{b) } 1g\ \text{SO}_2 \times \frac{1mol\ \text{SO}_2}{64g\ \text{SO}_2} \times \frac{1mol\ \text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}}{1mol\ \text{SO}_2} \times \frac{129g\ \text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}}{1mol\ \text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}} = 2,016g\ \text{CaSO}_3\ 1/2\ \text{H}_2\text{O}$$

$$\text{c) } 1g\ \text{HCl} \times \frac{1mol\ \text{HCl}}{36,5g\ \text{HCl}} \times \frac{1/2mol\ \text{CaCl}_2 \cdot 2\text{H}_2\text{O}}{1mol\ \text{HCl}} \times \frac{147g\ \text{CaCl}_2 \cdot 2\text{H}_2\text{O}}{1mol\ \text{CaCl}_2 \cdot 2\text{H}_2\text{O}} = 2,014g\ \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$$

The excess reagent does not react and is collected on the filter together with the neutralisation salts.

3.1.3. OVERVIEW OF THE STOICHIOMETRIC CALCULATIONS

To facilitate the calculations, all the reagent consumption and salt production data computed in Sections 3.1.1 and 3.1.2 have been summarised in Tables 5 and 6.

	Stoichiometric consumption			Stoichiometric ratio	Real consumption		
Reagent	HF	SO_2	HCl		HF	SO_2	HCl
$NaHCO_3$	4.2	2.62	2.3	1.2	5.04	3.14	2.76
$Ca(OH)_2$	1.85	1.16	1.01	8.3	15.36	9.59	8.42

Table 5. Reagent consumption (g reagent /g pollutant)

Reagent	HF	SO_2	HCl	Excess reagent
$NaHCO_3$	2.10	2.22	1.60	0.63
$Ca(OH)_2$	1.95	2.02	2.01	1

Table 6. Salt production (g salts /g pollutants)

3.2. EFFICIENCY TESTS

Having determined the stoichiometry of each major arising neutralisation reaction, it was necessary to determine each reaction's yield in order to estimate each system's exploitation ratio. Various reports are available on facilities with running dry gas cleaning systems using calcium hydroxide, which could serve as a reference to estimate the reagent excesses relative to the stoichiometric values needed for efficient reaction. The study conducted by the Environmental Authority (Presidio Multizonale di Prevenzione (PMP)) of Reggio Emilia, Italy, seemed particularly useful in this sense.

On installing a dry gas cleaning system with sodium bicarbonate at the RSU incinerator in Reggio Emilia, the Environmental Authority (PMP) undertook a study in 1993 to establish the suitability of this system for cleaning flue gases in the ceramic industry, comparing this system with existing lime-using systems.

The trial was run at a stoneware factory of Ceramiche Ariostea, in Castellarano (MO). The cleaning system consisted of a bag filter, before which the reagent was injected, with an extraction fan and stack. After cleaning, the gases were released into the atmosphere with no energy reclaim. The same facility was used for the trials with both reagents.

During three weeks of tests gas temperature, flow rate, oxygen percentage, HF, HCl and SO_2 were measured or analysed for at kiln and stack exits. Samples were also taken of the residual salts collected on the bag filter to analyse reagent excesses.

The conclusions of the study have been set out in Table 7.

	Sodium bicarbonate system	Lime system
HF removal	- Very high reaction yield. - Results clearly met legalisation requirements.	- Low reaction yield. - Legalisation requirements can be met but only by severely penalising reaction yield.
HCl removal	- Very high reaction yield. - Results clearly met legalisation requirements	- Scarce reaction yield
SO_2 removal	- Very high reaction yield. - Results clearly met legalisation requirements	-Virtually zero efficiency.

Table 7. *Conclusions of the study performed by Presidio Multizonale di Prevenzione .*

These tests, corroborated by the available literature on the subject, confirmed the difficulty of comparing reagent consumption and neutralised salt production, given the highly different behaviour of both reagents regarding the various pollutants. In order to determine reaction yields it was thus necessary to set working conditions and neutralisation targets.

In the solution being studied, the aim was to meet legislation requirements by a sufficient degree of gas cleaning without a cooling stage, to allow energy recovery. Under these conditions, assuming a legal limit of 5 mg/Nm^{3}and a required HF removal rate of 97.5%, sodium bicarbonate will exhibit a joint action on the three pollutants with an excellent yield. Removal will be attained of around 99% for HCl and SO_2, with an overall stoichiometric excess of 1.2.

Using lime, given its HF selectivity, to obtain a 97.5% HF removal, even with an overall stoichiometric excess of 8.3, HCl removal will only be 35%, with a very weak effect on SO_2, namely of below 10% removal. Raising stoichiometric excesses to over 10, removal rates can be achieved of around 98% for HF and 65% for HCl, however without acting upon SO_2,. Both the required excesses and scarce effect on sulphur oxides make using these excesses an unfeasible method, as to achieve complete cleaning a second neutralisation stage would be needed, for example using a caustic soda scrubber.

Tables 8 and 9 detail the comparative exploitation ratios of the two systems, without taking into account the costs that would be involved in a second neutralisation stage, as mentioned above, according to the results found in the industrial trials.

Parameters	Units Dry gas. 11%O_2	Input	Output	$NaHCO_3$	
				Consumption (kg/h)	Salt production (kg/h)
Flow rate	Nm^3/h	15000	15500		
HF	mg/Nm^3	65	1.6	4.8	2.0
SO_2	mg/Nm^3	125	1.3	5.8	4.1
Cl	mg/Nm^3	45	0.5	1.8	1.1
Reagent excess					1.3
TOTAL				12.5	8.5

Table 8. Results obtained at Ceramiche Ariostea with $NaHCO_3$.

Parameter	Units Dry gas. 11%O_2	Input	Output.	$Ca(OH)_2$	
				Consumption (kg/h)	Salt production (kg/h)
Flow rate	Nm^3/h	15000	15500		
HF	mg/Nm^3	65	2.0	14.5	1.8
SO_2	mg/Nm^3	125	112.5	1.3	0.3
HCl	mg/Nm^3	45	14.4	3.8	0.9
Excess reagent					17.2
TOTAL				19.6	20.2

***Table 9.** Results obtained at Ceramiche Ariostea with $Ca\ (OH)_2$.*

4. INDUSTRIAL IMPLEMENTATION OF THE NEUTREC® PROCESS

In traditional facilities, the bag filters used to remove waste salt dust can only be utilised at temperatures below 180°C, which means previously cooling the gases or bleeding in cold air. Both solutions seriously limit the possible benefits to be gained from waste heat recovery from clean flue gases.

Furthermore, bag filters produce a high charge loss in the facility, producing greater energy consumption. This charge loss is not constant. It increases as the bags collect dust and drastically drops when they are cleaned. These variations can lead to regulation problems in the facility and in the under-pressure of the kiln from which gases are being drawn.

However, the advantage of these filters lies in easily being able to retain over 99.8% of the dust, a figure that is hard to achieve with traditional electrostatic filters, which as set out below require using high yield electrostatic precipitators.

During several months continuous measurements were taken of the emissions from a scale cleaning facility that was specially built for this purpose. The test revealed that the pollutant emissions were highly variable across time, and basically depended on:

- Amount of fired material in the kiln per unit time, in terms of fired tile size and thickness.
- Environment conditions such as humidity and temperature, as these condition inner kiln atmosphere and affect release mechanisms.

- Moisture content of the fired material.

The foregoing explains the interest in an on-line determination of pollutant concentrations present in the flue gases in order to proportion the most suitable reagent quantities. This allows minimising reagent quantities and waste production at each instant.

It was until recently quite difficult to determine HF concentrations continuously as this lay outside the range of the available technology in gas spectrometry since the absorption band in the hydrofluoric acid spectrum is very narrow, and lies close to the H_2O and CO_2. spectra.

However, the new infrared analysis technology with a fine-tuned laser allows building instant response analysers with sufficient selectivity to enable analysing HF with an accuracy of 0.001 ppm.

Such an analyser was used at the trial facility, performing modifications of the original extractive probe design to adapt it to the peculiarities of the installation in a ceramic facility. In the actual installation, a similar analyser was used with a specifically designed extractive probe for the application, which considerably reduced maintenance and checking, while improving its reliability.

In the proposed system, with a view to working at high temperatures and reducing charge loss in the facility, it was decided to use an electrostatic precipitator (F) for dust removal. Waste heat from clean gases could thus be recovered.

To raise precipitator efficiency, needle-shaped metal inserts were installed across the entire surface of the positive plates so that the whole plate would act as a discharge crown and thus increase inter-plate electrostatic field intensity. This gave higher throughput rates for the precipitator modules and a higher yield.

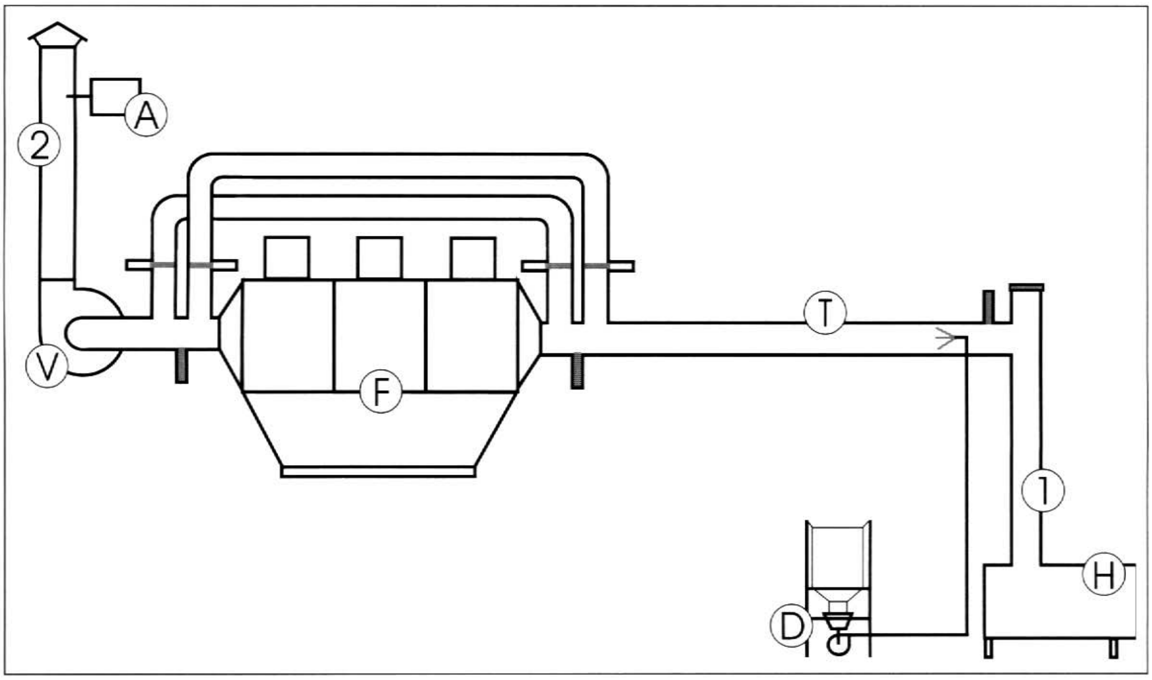

Figure 1. Schematic of the industrial facility.

Another important problem with conventional electrostatic precipitators arises when the last field is to be cleaned, since there is then no field behind to collect the dust that is drawn along by the gas stream. This has been solved in the present facility by installing two auxiliary pipes connecting precipitator entrance and exit, so that on using the six valves fitted for this purpose, the gas circulation direction can be inverted when the last field needs cleaning.

Figure 1 presents a schematic of the facility with its constituent parts.

The entire gas flow is drawn by a fan (V) controlled by a frequency modulator that receives a set value from the control room in order to keep a steady under-pressure in the kiln (H).

The proportioning system (D) injects the necessary amount of sodium bicarbonate into the tube (T) by pneumatic transport to neutralise the pollutants present. The quantity of reagent to be added is determined from the data obtained via on-line analysis by the gas analyser (A).

In facilities with bag filters, the contact time of reagent powder with the gases can be small, since reaction ends in the bags themselves, when the gases cross the reactive coating layer.

When an electrostatic precipitator is used for dust removal, the reaction needs to be ended when the gases reach the filter, as the gases do not cross any reactive layer as in the bag filters. Therefore, to ensure that no sodium bicarbonate settles, the tubing must be designed so as to allow sufficiently high velocity. At the same time however, adequate contact time of the reagent with the flue gases must be ensured.

The first requirement imposes a minimum velocity, which, based on an established flow, sets a maximum tube diameter. Knowing the gas rate and required minimum contact time then allows calculating minimum tube length.

As a minimum distance is needed between bicarbonate injection and the electrostatic precipitator, it becomes possible to choose a precipitator location at a point where waste heat could be reused. In our case, a position close to the presses was chosen as waste heat could be subsequently reused in the dryers.

5. EMISSION ANALYSIS.

5.1. EXPERIMENTAL TECHNIQUES

5.1.1. DETERMINATION OF FLUORINE AND CHLORINE COMPOUNDS

Fluorine and chlorine compounds in tile kiln emissions, as previously mentioned, are basically to be found as gas compounds.

To capture these elements a test method was designed at the Instituto de Tecnología Cerámica, based on several procedures proposed in U.S. Environmental Protection Agency (EPA) regulations (specifically in methods EPA 13B, EPA 26 and EPA 26A) as well as in European Draft Standard 1911.

In the adopted procedure, sampling takes place simultaneously in the same test for both the elements to be determined. The main characteristics of the test are as follows:

- Sampling need not take place under isokinetic conditions as both elements are found in a gas phase.
- Suction flow rate should be low, around 5 l/min.
- To avoid gas reactions with the metal part of the probe and the glass, these were covered internally by a tube of inert material that undergoes no chemical reactions with the elements to be studied, and releases no compounds of these elements.
- The capturing solution used as a reagent was NaOH.

The analysis methods used on the capturing solution were:

- Fluorine: selective electrode according to ASTM D1179.
- Chlorine: argentometric method according to UNE 77-041.

5.1.2. DETERMINATION OF CO, CO_2, SO_2 AND SO_X

CO, CO_2, SO_2 and SO_3 were determined by electrochemical sensors. In these sensors the gas samples are run through a cell in which on crossing a diffusion barrier, the gases to be analysed reach a cathode that produces a specific chemical oxidation-reduction reaction for each compound, giving rise to a voltage proportional to pollutant concentration.

SO_x was found as the sum of SO_2 and SO_3, expressed as SO_2.

On the other hand, the CO_2 was calculated as a function of the oxygen content in the flue gases and the composition of the fuel used.

5.2. EXPERIMENTAL ASSEMBLY FOR EMISSION ASSEMBLY

In order to evaluate the facility, the values needed to be simultaneously determined of the pollutant concentrations at kiln exit and after the dust removal filter. These points have been indicated in the schematic of the system (Fig. 1) as (1) and (2) respectively.

5.3. RESULTS AND DISCUSSION

As the system put in place was capable of self-regulating reagent consumption in terms of targeted and real exiting HF concentrations, two tests were run setting two different concentration values.

In these tests, simultaneous analysis was carried out at system input and output. The resulting data have been detailed in Tables 10, 11 and 12.

	Test 1 (C_L = 3 mg/Nm^3)			Test 2 (C_L = 5 mg/Nm^3)		
	Input (mg/Nm^3)	**Output (mg/Nm^3)**	**ç (%)**	**Input (mg/Nm^3)**	**Output (mg/Nm^3)**	**ç (%)**
HF	57	3	94.7	46	4	91.3
HCl	127	1	99.2	76	<2	>97.4
SO_2	204	<3	>98.5	266	<3	>98.8

Table 10. *Pollutant concentration values at % of real O_2l*

	Test 1 (C_L = 3 mg/Nm^3)			Test 2 (C_L = 5 mg/Nm^3)		
	Input (mg/Nm^3)	**Output (mg/Nm^3)**	**ç (%)**	**Input (mg/Nm^3)**	**Output (mg/Nm^3)**	**ç (%)**
HF	33	2	93.9	28	3	89.3
HCl	74	1	98.6	45	<2	>96
SO_2	120	<3	>97.5	157	<3	>98

Table 11. *Pollutant concentration values at 18% de O_2.*

	Kg $NaHCO_3$/h	**Stoichiometric ratio**
Test 1 (C_L = 3 mg/Nm^3)	15	1.2
Test 2 (C_L = 5 mg/Nm^3)	13.2	1.01

Table 12. *Resulting stoichiometric ratios*

The data shown in the tables clearly indicate that to keep the HF emission under 5mg/Nm^3 (89% HF removal), the stoichiometric ratio was close to unity.

However, if the cleaning objective is also to reuse waste heat, it is interesting to lower the acid compound concentration much further. It can be observed that on decreasing the HF concentration below 3mg/Nm^3, the stoichiometric ratio rose slightly to 1.2.

6. CONCLUSIONS

A gas emission cleaning system for tile kilns was designed and implemented based on the use of an electrostatic precipitator and the addition of sodium bicarbonate as a reagent. The system was also fitted with an on-line HF analyser that allows setting a HF emission value in the exiting clean gas stream, thus optimising reagent consumption.

The results obtained in the initial industrial trials indicate good performance in the cleaning yields for the studied pollutants hydrofluoric acid, hydrochloric acid and sulphur oxides, as detailed in Tables 10, 11 and 12. Using this kiln emission cleaning system allows meeting emission limits in all the countries of the European Union, besides meeting the CET environmental requirements set for the ceramic tile industry.

The system also enables acid pollutant concentrations to be cut back to non-harmful values for the plant facilities themselves, with very low stoichiometric ratios, on implementing waste heat reuse.

The cleaning yields obtained with this system were compared to values found in the literature involving bag filters and calcium hydroxide additions. It was observed that similar results were produced, although the proposed system, besides cleaning sulphur and chlorine compound emissions, used much lower stoichiometric ratios.

The use of sodium bicarbonate in the proposed system allows recovering the energy value of the clean gases on using these as drying air, and makes it possible to reuse the arising cleaning waste in the same manufacturing process.

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