PROJECT: DREAM – ACID EMISSIONS CLEANING IN CERAMIC TILE KILNS

I. Celades(1), S. Gomar(1), F. Romero(1), I. Agut(1) E. Monfort(1), L. Guaita(2), G. Frignani(3), N. Raule(4)

(1) Instituto de Tecnología Cerámica (ITC). Asociación de Investigación de las Industrias Cerámicas (AICE)
Universitat Jaume I. Castellón. España.

(2) Keraben Grupo S.A. Castellón. Spain.

(3) Sacmi Forni S.p.A. Salvaterra di Casalgrande. Italy.

(4) Centro di Ricerca e Innovazione Tecnologica S.R.L. (CRIT). Vignola. Italy.

ABSTRACT

This study sets out some of the results obtained in the study on air emissions conducted in the period 2016–2019 at the KERABEN Group production facilities. The work was performed in the frame of the DREAM project, funded by the European Commission under the H2020 programme.

The study involved revision of different aspects relating to management, control, and treatment of the emissions generated during the ceramic tile firing stage. Monitoring was performed with a FTIR (Fourier transform infrared) continuous optical measurement instrument. The experimental part was carried out in a pilot plant designed to study the arising emissions and to evaluate cleaning efficiencies in different technology scenarios under different operating conditions. The pilot plant was connected to the gas exhaust stack of a kiln at the KERABEN Group facilities.

The design and versatility of the pilot plant enabled very interesting results to be obtained, both for corporate decision-making processes, such as defining operating conditions in the cleaning system, and for use in discussion or revision processes of future regulations.

The work reports the most noteworthy results obtained in the campaigns conducted using a bag filter with reagent injection (BFR) system, in which the efficiencies in different work scenarios were quantified. The results show, among other things, that $Ca(OH)_2$ proved to be very effective in reducing HF, but not in reducing HCl or SO_2. In contrast, $NaHCO_3$ proved more effective in removing HCl and SO_2. To remove the three acid pollutants simultaneously, it would be necessary to work with a mixture of different reagents.

1. INTRODUCTION

The most noteworthy environmental aspect of the ceramic tile firing stage is the generation of air emissions. The most important pollutants in these emissions are particles and the gas pollutants of an acid nature (HF, HCl, and SO_x). The emissions of these pollutants in the firing stage stem mainly from the raw materials used in the manufacturing process and from the combustion process itself [4], [5], and [10].

The incorporation in recent years of a series of innovations such as digital printing at process level, and the manufacture of large formats at product level, has affected the resulting emissions profile in ceramic tile firing. An example of this situation is the possible consideration of the presence of odours as an emerging environmental aspect to be taken into account in future revisions of the regulations, such odours being related to the use of digital inks in the decoration process [7], [12], [13], and [16].

In this context, and with the upcoming revision process of the BREF on ceramic manufacturing [1] and [11] in 2020, which will foreseeably involve more stringent environmental regulations, the above reasons have led to this study, in the frame of the DREAM project, funded by the Horizon 2020 Programme in the period 2016–2019.

In this sense, the work conducted in the DREAM project addressed different technical aspects relating to management and treatment of industrial emissions of an acid nature [6].

In regard to management, the most innovative feature was the application of methods for continuous measurement of environmental parameters, owing to their increasing interest in an industry 4.0 setting, in which data collection and processing are an intrinsic part of the general management system and, hence, of the environmental management system [2], [3], [6], [9], and [15]. The results of the monitoring operations provide key information when it comes to establishing new emission limit values and cleaning needs, and demonstrating compliance with applicable limits, etc. [10].

On the other hand, the new environmental requirements will entail the need for optimised treatment systems, which are able, simultaneously, to achieve high efficiencies for several pollutants. To this end, a portable pilot plant was designed and assembled to study different cleaning equipment configurations and different reagents, in order to evaluate cleaning efficiencies in different technology scenarios, under different operating conditions.

Removal of gas compounds is based on acid–alkali chemical reactions, in which the acid gas compounds react with an alkali reagent to form a salt. In a bag filter with reagent injection (BFR) system, of the type studied here, the reactions between the reagent and the gas pollutants develop in the gaseous medium, as a result of the solid alkali reagent addition to the duct in the form of micronised powder, leading to uniform deposition on the bag filter. The reaction between the reagent and the gas pollutant, which develops fundamentally in the reagent layer itself, deposited on the bag filter, yields a solid salt as reaction product on the bag filter [8].

The choice of reagents is critical for technical and economic reasons. The most widely used reagents in dry systems like the BFR system examined in this study are calcium hydroxide and sodium bicarbonate. The chemical neutralisation reactions of these reagents with gas pollutants are detailed in Table 1.

Name	Chemical formula	Neutralisation reactions
Calcium hydroxide or slaked lime	$Ca(OH)_2$	$Ca(OH)_2$ (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	$NaHCO_3$	$2NaHCO_3$ (s) —> Na_2CO_3 (s)+ H_2O + CO_2 (g) (T=120-175ºC) Neutrec Process. Neutralization reactions: 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 1. *Neutralisation reactions with the reagents used.*

2. OBJECTIVES

The objectives of the present study were as follows:

- Designing and assembling a pilot plant to study acid pollutant cleaning.
- Evaluating and quantifying the efficiency of the bag filter with reagent injection (BFR) system, using different reagents and operating conditions.

3. METHODOLOGY

3.1. GAS MONITORING SYSTEM

The automatic monitoring system used in this study monitored the acid pollutants of interest: HF, HCl, and SO_2 simultaneously in real time. The apparatus involved was a portable FTIR (Fourier transform infrared) spectrophotometer and the sample extraction system was designed to assure sample representativeness, thus avoiding analyte loss owing to undesired concentrations and/or reactions.

The FTIR spectrophotometer uses a measurement principle in which a polychromatic light covers the infrared region that passes through the sample cell. Each compound in the sample absorbs the radiation at a certain wavelength, allowing it to be identified. The instrument can measure a wide variety of compounds, except for symmetrical molecules that exhibit no dipole charge on vibrating (O_2 and Cl_2), including compounds of an organic or inorganic nature.

The test method used in FTIR-based devices is grounded on engineering specifications CEN/TS 17337:2019 and on Technical Guidance Note M22 of the UK Environment Agency.

3.2. EXPERIMENTAL CAMPAIGNS

Table 2 details the experimental campaigns defined to achieve the study targets. The table indicates the cleaning system studied and the reagent used.

During the experimental part of the work, more than 70 different ceramic tile models crossed kiln no. 1. Total campaign time was about 3000 hours of continuous measurement.

Test	**Reagents used (kg/h)**			**Test**	**Reagents used (kg/h)**		
	$Ca(OH)_2$	**$NaHCO_3$**	**Recycled $Ca(OH)_2$**		**$Ca(OH)_2$**	**$NaHCO_3$**	**Recycled $Ca(OH)_2$**
1	0.10	--	--	**13**	--	0.50	--
2	0.15	--	--	**14**	0.5	0.2	--
3	0.20	--	--	**15**	0.5	0.7	--
4	0.30	--	--	**16**	0.5	0.5	--
5	0.50	--	--	**17**	0.5	0.4	--
6	--	0.30	--	**18**	0.3	0.4	--
7	--	0.50	--	**19**	0.2	0.4	--
8	--	0.55	--	**20**	0.2	0.3	--
9	--	0.60	--	**21**	0.1	0.3	--
10	--	0.65	--	**22**	0.15	--	0.15
11	--	0.70	--	**23**	0.21	--	0.09
12	--	0.80	--	**24**	0.08	--	0.23

Table 2. *Battery of tests conducted in the pilot plant bag filter.*

3.3. WORK PROTOCOL

Developing a work protocol that defined how to proceed before each experimental campaign was crucial to assuring the representativeness and comparability of the results.

A key aspect in the campaigns was maintaining an appropriate temperature throughout the circuit to avoid acid condensations that could bias the results. The temperature in every campaign was therefore kept above 180 °C throughout the circuit travelled by the gases.

On the other hand, as one of the treatment systems included injection of solid reagents into the duct, the microdispensers needed to be calibrated in each campaign to obtain a relationship between the frequency inverter and injected reagent mass flow rate.

To quantify efficiency in each campaign, first, the gases in the pilot plant input stream were monitored for about 12 hours, to establish a representative value. This operation was repeated whenever a new campaign began or whenever a product changeover took place in the kiln. These initial measurements allowed the optimum amount of reagent required in the case of the bag filter, and the necessary amount of reagent charged in the fixed-bed reactor, to be determined.

Once input concentration had been determined, the measurement system was installed in the output stream, to enable gas treatment efficiency to be continuously calculated. Efficiency was calculated from equation (1):

$$Rj(\%) = \frac{Cej - Csj}{Cej} \cdot 100 \qquad (1)$$

where:

R: pollutant *j* cleaning efficiency (%)

C_{ej}: pollutant *j* concentration before the cleaning system (mg/Nm^3)

C_{sj}: pollutant *j* concentration after the cleaning system (mg/Nm^3)

In every experimental campaign, to relate input concentration to the proportioned amount of reagent, the normalised stoichiometric ratio, hereafter, NSR, detailed in equation (2), was used [17]. To do so, the stoichiometry of the neutralisation reactions detailed in Table 1 was taken into account.

$$NSR = \frac{mj}{mS} \qquad (2)$$

where:

NSR: normalised stoichiometric ratio

mj: injected reagent mass flow rate (kg/h)

mS: minimum or stoichiometric reagent mass flow rate (kg/h)

4. RESULTS AND INTERPRETATION

4.1. DESIGN AND ASSEMBLY OF THE PILOT PLANT

The configuration of the proposed gas-cleaning pilot plant focused on treatment of emissions of an acid nature, i.e. HF, HCl, and SO_2. In designing the pilot plant, the contents of sectoral BREFs in regard to air emissions resembling those of the ceramic tile sector were taken into account.

The designed pilot plant included two modules: one for monitoring and the other for cleaning. The monitoring module enabled access to the input and output streams, all the pilot plant monitoring and control systems also being installed. As regards the cleaning modulus, it was made up of a bag filter with reagent injection (BFR) and two fixed-bed reactors (FBRs). The pilot plant was constructed according to the design shown in Figure 1.

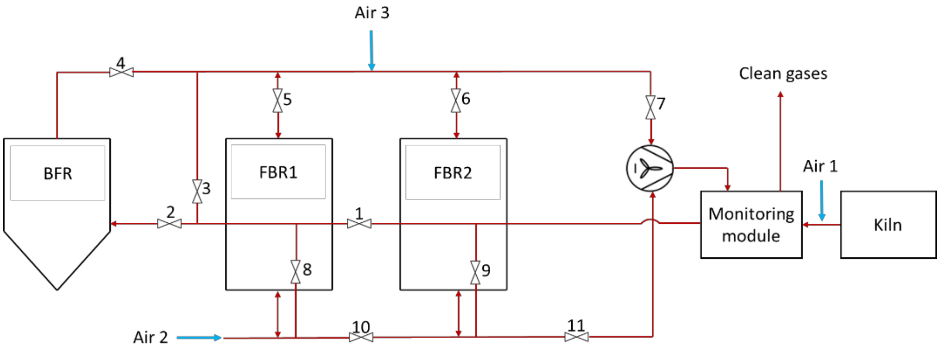

Figure 1. *Pilot plant scheme: gas cleaning systems module.*

The pilot plant, connected during the study to KERABEN Group kiln no. 1, was able to deal with a volume flow rate of 5000 Nm^3/h. Figure 2 shows a detail of the design scheme and a photo of pilot plant installation at the Keraben facility. Pilot plant design was very versatile and allowed the two abatement systems to run either individually or simultaneously.

This study only reports the results obtained in the study of the BFR.

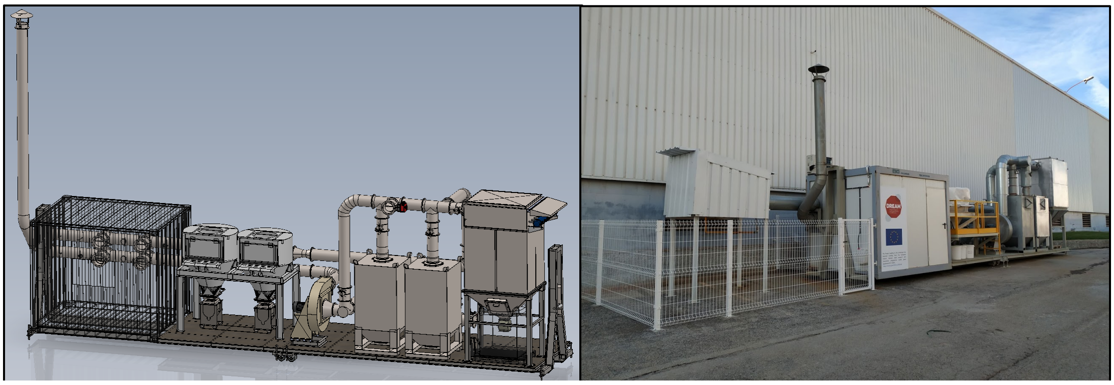

Figure 2. *Detail of pilot plant design and its installation at the KERABEN Group facility (at Nules, Castellón province).*

4.2. EXPERIMENTAL CAMPAIGNS

The minimum efficiencies were defined, in each campaign, that the cleaning technology needed to attain to assure compliance with the emission limits established in the integrated environmental authorisations awarded to tile companies in the Valencia Region and the emission limit values associated with the best available technologies (BATs) established in the current ceramic products BREF (2007) [11]. The reagents used were calcium hydroxide, sodium bicarbonate, and mixtures of both reagents in different amounts.

4.2.1. CALCIUM HYDROXIDE – $CA(OH)_2$

The removal efficiency versus the normalised stoichiometric ratio (NSR) for HF, HCl, and SO_2, respectively, is plotted in Figure 3. Each point in the figure represents the same proportioned quantity of reagent in kilograms per hour, though it corresponds to a different NSR, depending on the pollutant cleaned.

For this reagent, under these operating conditions, 100% efficiency was reached for HF in the NSRs above 4.5. In addition, the figure shows how efficiency increased at the same time as NSR.

In the case of HCl, the cleaning efficiency was lower than that obtained for HF, values being reached close to 40% for an NSR of 5.8. The variation in reduction developed more linearly than in the previous case, under the studied boundary conditions.

SO_2 cleaning efficiency was lower than that obtained for HCl and HF at the same proportioned quantity. A reduction was only observed at the point with the largest proportioned quantity. Note that this point represented a lower NSR when compared to that of HF and HCl. It was therefore likely that, when the NSR of this pollutant increased, efficiency also rose. The efficiency required for SO_2 is not indicated in Figure 3 as the concentrations before the cleaning system were already below the emission limit value set in the BREF and in the integrated environmental authorisations (IEA).

Observation of the removal efficiency of the three pollutants (Figure 3) enables it to be concluded that injected reagent affinity under the set pilot plant operating conditions was HF > HCl > SO_2.

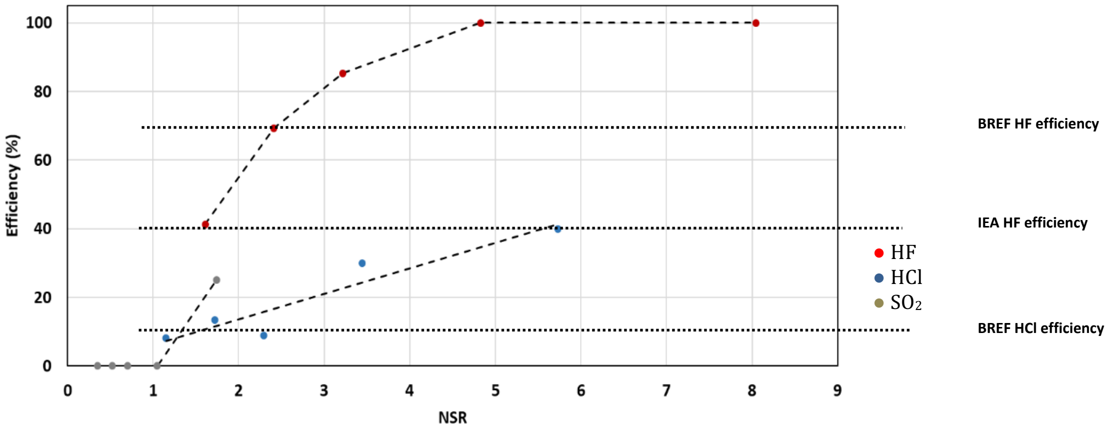

Figure 3. *Cleaning efficiency for HF, HCl, and SO2 with calcium hydroxide injection.*

4.2.1.1. RESIDUE OBTAINED WITH CA(OH)$_2$ INJECTION

To verify whether the spent reagent had fully reacted or not, its Ca(OH)$_2$ content was analysed in the laboratory. Analysis showed that 34% of the reagent had not reacted. It was therefore decided to study how the reduction efficiencies were affected by reinjecting the spent reagent after mixing it in different percentages with fresh reagent.

The efficiency obtained in each experiment is plotted in Figure 4. The figure shows that efficiency decreased as reagent spent percentage increased. However, the efficiency obtained for a composition with 100% used reagent was sufficient for the efficiency requirements established for HF (see Figure 3). In this sense, it may be noted that injecting a mixture of spent and fresh reagent could significantly reduce the costs of gas treatment, in particular, those stemming from consumption of fresh reagent and from management of resulting reagent waste.

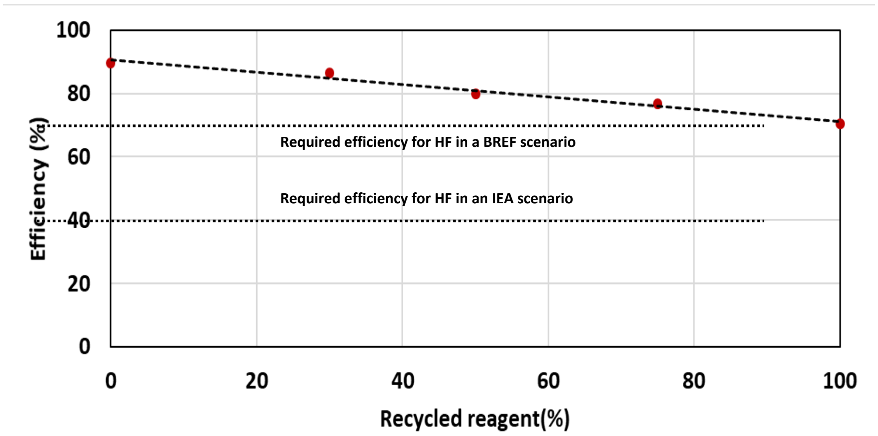

Figure 4. *HF cleaning efficiency with mixtures of used and fresh reagent.*

4.2.2. SODIUM BICARBONATE – NAHCO$_3$

The different trials performed with sodium bicarbonate allowed the efficiency for each studied pollutant to be plotted. These efficiencies are observed in Figure 5. In the efficiencies study, the recommendations for use of the sodium bicarbonate supplier were taken into account [15].

Cleaning efficiency varied with the NSR, depending on the pollutant involved. In the case of HF, efficiency reached 75% at high NSRs. However, the proportioned quantity needed in the mass flow rate was much larger than in the case of calcium hydroxide.

For HCl, the NSR required to obtain high efficiencies was above 2.5. Comparison of the efficiency obtained for calcium hydroxide shows that sodium bicarbonate was more efficient for HCl at a lower NSR. With regard to SO$_2$, efficiency was very high at NSR close to 1. This reagent exhibited greater efficiency in removing SO$_2$ than calcium hydroxide. The affinity of the reagent injected under pilot plant operating conditions was SO$_2$> HCl > HF.

Just as in Figure 3, the efficiency required for SO_2 is not indicated, as the concentration values before the cleaning system were already below the emission limit value in the BREF and in the integrated environmental authorisations (IEA)

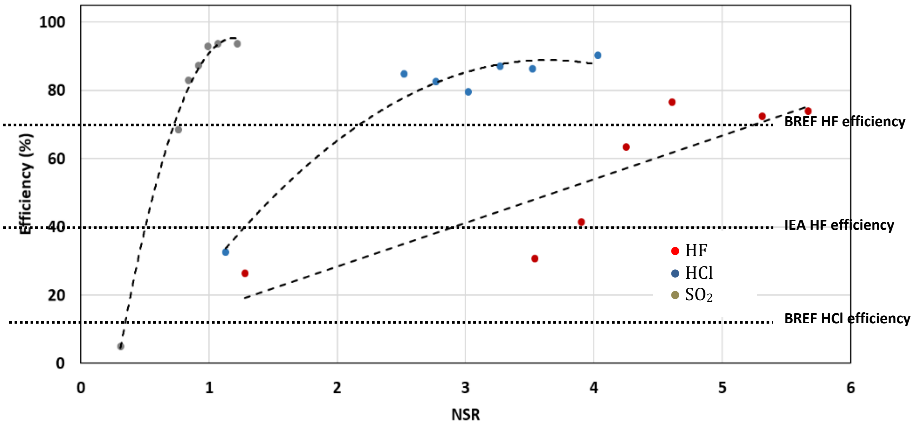

Figure 5. *Cleaning efficiency for HF, HCl, and SO_2 with sodium bicarbonate injection*

4.2.3. MIXTURES OF CA(OH)$_2$ AND NAHCO$_3$

In view of the results obtained individually in the case of the two reagents, it was deemed of interest to study the resulting cleaning efficiencies on injecting mixtures of both reagents. By way of example, though the cleaning efficiency for all three test pollutants was studied, Figure 6 shows the results obtained for SO_2.

Figure 6 depicts the efficiency obtained in reducing SO_2, for each studied mixture of reagents. The horizontal axis shows the NSR for calcium hydroxide (R1), while the vertical axis shows the NSR for sodium bicarbonate (R2). Efficiency is represented directly in percentage units (%) in the circle of each experimental campaign.

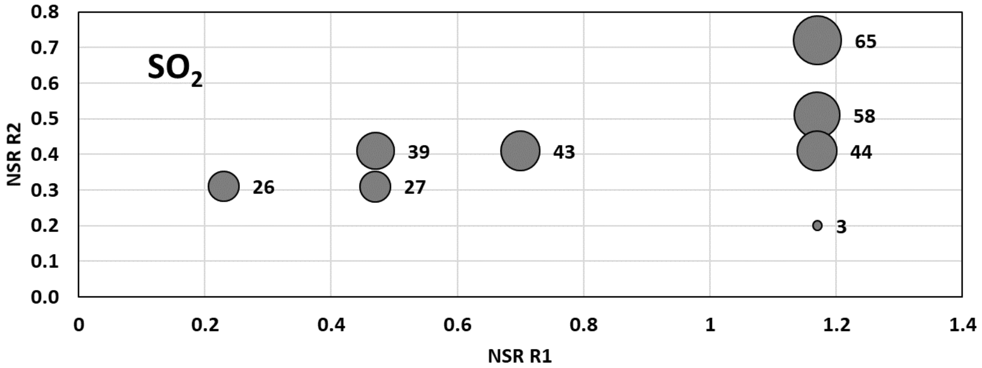

Figure 6. *BFR efficiency (%) for SO_2 removal with injection of different mixtures of $Ca(OH)_2$ and $NaHCO_3$*

In the case of SO_2, the resulting efficiencies indicate that this pollutant exhibited greater affinity for sodium bicarbonate than for $Ca(OH)_2$. This was confirmed by the results obtained individually with each reagent. The results for HF and HCl also confirmed the results obtained in the previous campaigns. In short, it was interesting that mixing both reagents enabled the three pollutants to be simultaneously cleaned, with favourable efficiencies.

5. CONCLUSIONS

A series of conclusions on each of the aspects considered in the study are set out below.

- The versatile design of the pilot plant used allowed different configurations to be studied and pilot plant operating conditions to be varied in a relatively simple way. The portable pilot plant designed in this project is deemed of great usefulness in designing the optimum configuration for the acid gas cleaning system in different scenarios, thus enabling the cleaning system to be optimised from an environmental and economic viewpoint.
- In relation to the studied reagents, the use of $Ca(OH)_2$ was observed to reduce HF with high efficiencies, but it exhibited much lower efficiency in reducing HCl and SO_2. However, the use of $NaHCO_3$ exhibited greater selectivity in reducing HCl and SO_2 than in reducing HF. Consequently, when it was sought simultaneously to clean the three pollutants, mixtures of reagents needed to be used. The methodology proposed in this work allows optimisation of the most appropriate mixture for each case, depending on the composition of gases to be treated and the required limit values.
- The results obtained on reusing the spent reagents suggest that this approach could be of great use in reducing reagent consumption and waste generation. The proposed methodology could be very useful in determining the optimum number of cycles.

6. ACKNOWLEDGEMENTS

This project has received funding from the European Union’s Horizon 2020 research innovation and programme under grant agreement no. 723641.

7. REFERENCES

[1] Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast), (n.d.).

[2] DTI, Emission Monitoring Technologies for Combustion and Gasification Plants - Cleaner Fossils Fuel Programme, (2004).

[3] E. Agency, Technical Guidance Note M2, Monitoring of stack emissions to air, n.d. www.mcerts.net.

[4] E. Monfort, I. Celades, S. Gomar, J. Rueda, J. Martinez, Characterisation of acid pollutant emissions in ceramic tile manufacture, Boletín de la Sociedad Española de Cerámica y Vidrio, 50 (2011) 179–184.

[5] E. Monfort, J. García-Ten, I. Celades, M.F.F. Gazulla, S. Gomar, Evolution of fluorine emissions during the fast firing of ceramic tile, Appl. Clay Sci. 38 (2008) 250–258. doi:10.1016/j.clay.2007.03.001.

[6] E. Monfort, J. García-Ten, I. Celades, S. Gomar, Monitoring and possible reduction of HF in stack flue gases from ceramic tiles, J. Fluor. Chem. 131 (2010) 6–12. doi:10.1016/j.jfluchem.2009.09.008.

[7] G. Ferrari, P. Zannini. (2017). VOCs monitoring of new materials for ceramic tiles decoration: GC–MS analysis of emissions from common vehicles and inkjet inks during firing in laboratory. *Boletín de La Sociedad Española de Cerámica y Vidrio*, *56*(5), 226–236. https://doi.org/10.1016/J.BSECV.2017.04.004

[8] G. Mallol, E. Monfort, G. Busani, F.J. Lezaun. Depuración de los gases de combustión en la Industria Cerámica. 2001.

[9] I. Celades, S. Gomar, F. Romero, A. Chauhan, B. Delpech, Hussam Jouhara. Acid emissions monitoring needs in ceramic tile industry: challenges derived from new policy trends. E3S Web of Conferences 22, 00026 (2017). Doi: 10.1051/e3sconf/20172200026. ASEE17.

[10] J. García-Ten, E. Monfort, P. Gomez, S. Gomar, Influence of calcite content on fluorine compound emissions during ceramic tile firing, J. Ceram. Process. Res. 7 (2006) 75–82.

[11] IPTS, "Reference Document on Best Available Techniques in the Ceramic Manufacturing Industry," *Ceram. Manuf. Ind*. August, pp. 210–211, 2007.

[12] M. Dondi, M. Blosi, D. Gardini, D., & Zanelli, C. (2012). Ceramic pigments for digital decoration inks: An overview. *CFI Ceramic Forum International*, Vol. 89.

[13] S. Gomar, E. Monfort, A. Escrig, J. Martínez, F. Rueda (2012). Emisión de compuestos orgánicos volátiles en la fabricación de baldosas cerámicas. In: *Qualicer: XII Foro Global del Recubrimiento Cerámico.*

[14] Solvair solutions. Technical specifications for SOLVAir® process (2015).

[15] Study on AMS and SRM performances and their impact on the feasibility of lowering ELVs for air emissions in the context of the BREFs and BATs revision and of BATAELs elaboration according to the IED, (2016). https://www.fead.be/images/PDF/extranet-studies/Ineris_Report/2016.07.22_INERIS_study_on_monitoring_EN.pdf (accessed March 8, 2017).

[16] VV.AA. (2018). Especial Industria cerámica. *Ecoscienza. Volumen (2) 32-61. ISSN 2039-0432.*

[17] Y. Kong and J. Balland. Effective removal of HCl and SO_2 with dry injection of sodium bicarbonate or trona" pp. 2–6, 2016.