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Acid emissions monitoring needs in ceramic tile industry: challenges derived from new policy trends

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Abstract. The emission of acid compounds during the manufacture of ceramic tiles is strongly related to the presence of precursors in the raw materials and/or fuels used, with some exceptions such as the production of thermal NO_X. The stages with the potential to produce significant emissions of these compounds have been identified as the suspension spray drying and tile firing stages. The monitoring of emission levels of acid pollutants in these stages has turned in a great importance issue from a regulatory and industrial aspect. The DREAM project (https://www.spire2030.eu/dream) will tackle the regulation of acidic emissions focusing in the firing stage. The initial stages of the project have made it possible to identify the design requirements for the monitoring system. This will allow the control of acid pollutants emissions and other key parameters such as pressure, flow, temperature and humidity. One of the tasks developed has been the review and compilation of current emissions monitoring systems detailing technical specifications such as: position (in situ or extractive), measurement principle and frequency. The future policy trends in air pollution are encouraging the continuous monitoring across the European industry. The present document assesses the advantages regarding environmental impact control, highlighting the main challenges for the ceramic tile industry.

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1 Background

Emission of acid compounds during the manufacture of ceramic tiles is strongly dependant to the presence of precursors in the raw materials and/or fuels used, with some exceptions such as the production of thermal NO_X. Therefore, these compounds can be generated in the stages where combustion processes take place and/or where the processed materials reach high temperatures. Consequently, the stages that could have significant emissions of these compounds are the suspension spray drying and, mainly, tile firing stages [1].

In the specific case of the ceramic kilns, the emission of acid compounds entails the necessity to treat and monitor the exhaust gases emitted to ensure the accomplishment of the Emission Limit Values (ELVs) applied.

As the ceramic industry is affected by the Industrial Emissions Directive (known as IED), the Best Available Techniques (BATs) and ELVs associated, are reviewed periodically [2]. Next review will start during 2018 and could imply a tightening of the current ELVs associated to BATs and/or including new pollutants or new requirements regarding industrial emissions monitoring.

This is in part the rationale for DREAM, a European project funded by the EC through the SPIRE-H2020 Program, which aims to design, develop and demonstrate a radically improved architecture for ceramic industrial furnaces which include reduced emissions obtained by substantially enhancing emissions abatement system, beyond pollutants and ELV applied nowadays.

1.1 European Regulatory Framework BREF

In the EU, the application of IED obliges companies of the Directive to obtain an Integrated Environmental Authorisation (IEA), which includes ELV for different atmospheric pollutants and per manufacturing stages as shown in annex 1. Public authorities set permit conditions and fix the ELV applicable for each installation with regards to the Best Available Techniques (BAT). The proceedings have been implemented by European Commission as a EU Decision, a document containing the parts of a BAT reference document, their description, information to assess their applicability, the emission levels associated with the best available techniques (ELV-BAT), associated monitoring, associated consumption levels and, where appropriate, relevant site remediation measures.

The BAT findings from the Ceramic manufacture process have not yet been published or categorised under a directive, so 2007 BREF should be used. In near future, it is expected a revised and updated version of ELV will be produced with regards to the existing IED directive.

Table 1 highlights the emission values defined for firing stage in ceramic tile manufacture in the EU as ELV-BAT, the values are considered as a maximum reference for fixing ELV in national IEA.

The IED dictates the required monitoring methods and requires sampling and analysis conducted on all polluting substances as per CEN-standards. Alternative standards apply if CEN standards are not available such as ISO, national or other international standards with an equal quality and scientific integrity.

Table 1. ELV-BAT in firing stage in the BREF for ceramic tile manufacture, in mg/Nm^3: concentration in standard conditions: 273 K and 101,3 kPa, as a daily average value.

Parameter	ELV-BAT [1)]
Fluoride stated as HF	1–5[2)]
Chloride stated as HCl	1–30[3)]
NO_X, stated as NO_2 for kiln gas temperatures < 1300ºC	< 250
NO_X, stated as NO_2 for kiln gas temperatures > 1300ºC	< 500
SO_X stated as SO_2. Sulphur content in raw material < 0.25%	< 500
SO_X stated as SO_2. Sulphur content in raw material > 0.25%	500–2000[4)]

[1)] The ranges depend on the content of the pollutant (precursor) in the raw materials, i.e. for firing processes of ceramic products with a low content of the pollutant (precursor) in the raw materials, lower levels within the range are BAT and for firing processes of ceramic products with a high content of the pollutant (precursor) in the raw materials, higher levels within the range are ELV BAT.
[2)] The higher BAT level can be lower depending on the characteristics of the raw material.
[3)] The higher BAT level can be lower depending on the characteristics of the raw material. Also, the higher ELV BAT should not prevent the re-use of waste water.
[4)] The higher BAT level only applies to raw material with an extremely high sulphur content.

1.2 Acid compound emissions in the ceramic industry

The main acidic compounds are released during the firing of ceramic tiles and are identified as: HF, HCl, SO_X and NO_X. Among them, fluorine compounds are present within exhaust streams and are characterised as ceramic industry pollutants. The concentration of fluorine based emission stems from the presence and level of fluorine ions in clays used as raw materials in ceramic tile manufacture.

Fluorine ions replace OH- groups in the crystalline mica structures, and other present clay minerals such as montmorillonite, illite, kaolinite, etc. [3, 4]. Fluorine compound emissions usually start with the dehydroxylation of these minerals at temperatures of the order of 500–700°C [5–7]. The major compounds that form are hydrofluoric acid, silicon tetrafluoride and, to a lesser extent, alkaline fluorides in particle form, the presence of these alkaline fluorides being practically negligible [8-10]. In the presence of water vapour, a typical situation in industrial combustion kilns, fluorine is mainly emitted as hydrofluoric acid [11].

The formation of chlorine based emissions mainly stem from the presence of chlorine ions in the water used during the manufacturing process. Many clays and mixtures contain trace levels of chlorine. The production of chlorine based emissions occur during the firing process at temperatures above 850ºC, from the decomposition of chlorine-containing mineral salts. In addition, the decomposition of organic compounds that contain chlorine leads to HCl emissions in the 450–550ºC range [12].

On the other hand, sulphur based 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 sulphites in the form of pyrite or calcium and magnesium sulphates such as gypsum, and sulphur in organic compounds. Fossil fuels can also generate sulphur emissions. Natural gas is the most widely used fuel, and contains practically no sulphur in its composition; however, if fuel oil, coal or coke is used, sulphur emissions can be higher [12].

Nitrogen compounds are emitted in the form of nitrogen oxides, and are related to the formation of thermal NO_X in high-temperature processes when a reaction takes place between

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nitrogen and oxygen in the combustion air. This reaction is encouraged in processes that unfold at high temperature (particularly at temperatures above 1400ºC).

However, NO_X formation can even be significant at process temperatures below 1200ºC, when the burners run at high flame temperatures [12]. The decomposition and combustion of nitrogen compounds present in the raw materials, admixtures, or fuels can also be a source of NO_X at lower temperatures.

1.3 Current acid pollutant emissions in ceramic tile manufacture

Previous studies conducted in the ceramic sector showed that main fluoride and chloride compounds mainly emitted as HF and HCl, respectively, are the most significant due to the presence of H_2O in industrial kiln. In many cases emissions exceeds the currently proposed ELV–BAT, Figure 1 [1]. Therefore, according to these results and considering ELVs from BREF, many companies need to introduce preventive and/or corrective measures to reduce HF emissions in the kilns. In contrast, in all cases studied, the SO_2 and NO_X emissions lie below the ELV–BAT in firing.

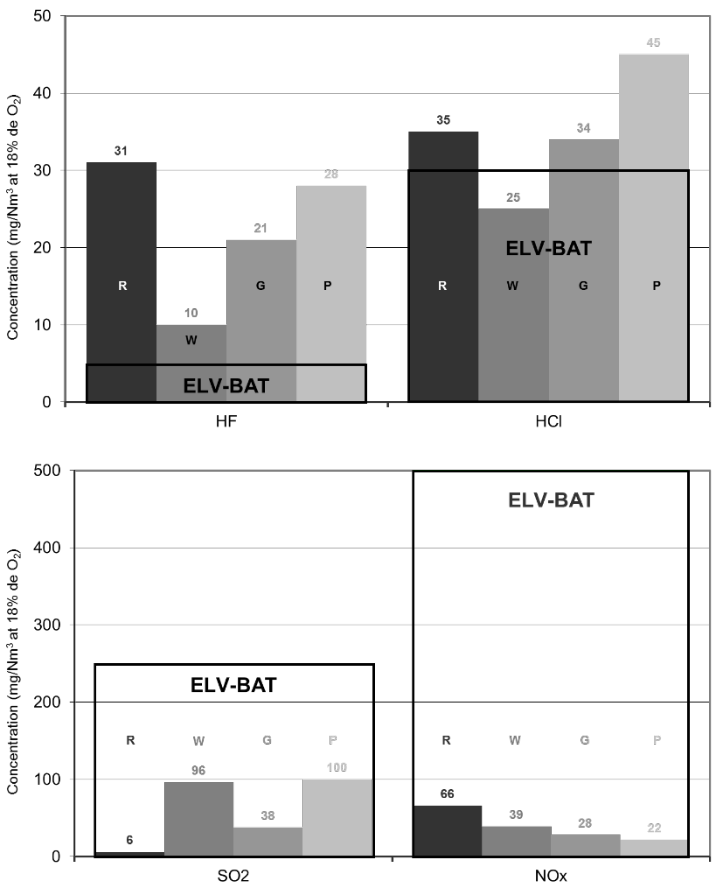

Fig. 1. Median acid pollutant concentrations for earthenware (red (R) and white (W)-firing body), glazed stoneware tile (G) and porcelain stoneware tile (P) in the firing stage.

Acid emissions vary considerably but not due to the variation in acid compound contents in the raw material, but also because of differences in the manufacturing technology used. During firing stage, factors such as: larger shapes, sizes and thickness, technological advancements, increasing personalization/customization trends, etc., are all major influencers in the variation of emissions. All these new product developments make it necessary to update the acid emission levels and documentation in ceramic tile firing.

2 Acid emissions measurement methods in channelled emissions from ceramic tile industry

Under this legislative framework and the current emissions regulations, monitoring is a key issue to consider regarding legislation accomplishment.

Stack emissions monitoring approaches can be classified into two types: periodic monitoring and continuous emissions monitoring systems (CEMS). One approach is not inherently superior to the other; both have their own strengths and weaknesses depending upon the application. In general, it is recognised that CEMS provide increased confidence for both regulatory purposes and process control [13].

2.1 Periodic measurements

Periodic measurements can be done through manual systems or automatic systems. The manual systems are single measurement methods in which a representative stack sample is extracted and analysed by logical sequences operations, next to the stack or at laboratory. By the other hand, automatic systems analyse pollutants through a measurement device that obtains gas stream concentration.

Even if the manual method looks to be quite simple, several factors can strongly influence the final results. The competencies and knowledge of the accredited laboratory operators performing the SRM measurements have to be carefully checked.

Moreover, the currently required periodic measurement, does not represent a realistic value of the environmental impact generated in the firing stage, due to the high temporal variability of the processed material, as it has been mentioned above.

The measurement methodology used to determine the acid gaseous pollutants emitted in the ceramic industry is described in various specific test standards, outlined in Table 2. As described below, these methodologies include manual and automatic measurement methods, ISO or EN standard. The EN standards produced in Table 2 are considered as Standard Reference Method (SRM) by CEN (the European Committee for Standardization).

Table 2. Standards on air pollutant measurements.

Pollutant	Reference standard	Period	SRM (CEN)
Chlorides stated as HCl	EN 1911	Manual	Yes
Fluorides stated as HF	ISO 15713	Manual	No
SO_2	EN 14791	Manual	Yes
NO_X stated as NO_2	EN 14792	Automatic	Yes

The European SRM for HCl measurement describes three alternative analytical techniques for determining gaseous chlorides content emitting to atmosphere from ducts and stacks. All compounds which are volatile at the temperature of filtration and produce chloride ions upon dissolution during sampling are measured by this method, which gives therefore the volatile inorganic chlorides content of the waste gas. This European Standard can be used as a SRM; provided the overall uncertainty of the method is less than 30% relative at the daily Emission Limit Value (ELV) for incineration and large combustion plants or at the ELV prescribed by the specific regulations for other plants.

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On the other hand, HF can be measured in a similar way to HCl as described in an ISO standard, because CEN has not published a specific manual method for HF. This method does not determine the overall uncertainty of the method but it is considered the same uncertainty as HCl (30%) due to similar reactive nature and measurement technique [13].

Both methods may not reflect the chemical nature of the compounds, typically these gaseous chlorides and fluorides are measured manually at the filtration system. The drawback to such a measuring method is the lack of identification of hydrogen chloride (HCl) or hydrogen fluoride (HF), and are passed through the filtration system.

For SO_2, SRM is a manual method, whereas that for NO_X the SRM is an automatic analyser using chemiluminescence absorption principle. Both methods, manual for SO_2 and automatic for NO_X, are specifics for SO_2, NO and NO_2, without complications with other species. In fact, it is possible the use of automatic devices for SO_2 when the equivalence with the SRM has been demonstrated. The uncertainty regarding to SO_2 and NO_X are less than 20% and 10%, respectively.

Compliance assessment monitoring for SO_2 and NO_X are not problematic due to their emissions level values in ceramic kiln, contrary to what happens with chlorides and fluorides. For this reason, the rest of the article focuses in the selection of the automated measurement system best value for money for HF and HCl.

2.2 Continuous emission measurement systems (CEMS)

The on-line measurement of a pollutant through a CEMS enables systematic monitoring of fluctuations within an exhaust stream. On-line measurements are increasingly becoming of great interest, since this allows the observation of fluctuations in the emission with across a specific time frame. The study of fluctuating emissions allows a direct relationship to be made about changes occurring in the manufacturing process, or the addition of emissions treatment. The addition of online systems provides information for appropriate decision-taking and correct eco-management, for instance by optimizing emission treatment systems.

There is no legal requirement to implement a CEMS in the ceramic industry but the installation of CEMS is in the best interest of the ceramic industry. For example, a better knowledge of HF emissions behaviour has been obtained using continuous monitoring device adapted to the characteristics of the ceramic industry [1, 5, 6, 10], showing that:

- HF emissions are continuous and constant in time, their value depending mainly on the mass flow and the type of product being processed. This always happen if the ceramic kiln is running in a steady state.
- Modifications in realistic industrial manufacturing conditions, such as in heat treatment and in the dry bulk density of the tiles produced, does not significantly reduce HF emissions.
- Tile glazing, performed to provide certain surface properties, effectively reduces HF emissions.

The measurement of HCl and HF by CEMS is technically difficult due to the amount of specialised systems. The systems have been created to identify specific chlorides but this does not include other inorganic chlorides or fluorides. As the manual method measures total inorganic salts of chloride and fluoride, they are measuring the pollutants specified in the BAT conclusions.

The measuring technology for the HF and HCl in CEMS are based on optical technology and mainly on infrared absorption method. The attenuation of infrared light passing through a sample cell is a measure of the concentration of gas of interest in the cell, according to the Lambert- Beer law. Not only HCl or HF but also most hetero-atomic molecules absorb infrared light, in particular, water and CO_2 have broad bands that can interfere with the measurement of HCl or HF. Different technical solutions have been developed to suppress cross-sensitivity, instability and drift in order to design automatic monitoring systems with acceptable properties. For instance: Gas Filter Correlation (GFC), Tunable Diode Laser (TDL), Fourier Transform Infrared Spectroscopy (FTIR) and newer developments like: Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS) and Differential Optical Absorption Spectroscopy (DOAS).

All CEMS have to be tested prior to their installation on site in order to prove that they are suitable for the intended monitoring purposes. The tests are performed by an accredited laboratory in accordance with the EN 15267, part 3 and part 4, and the tests results are summarized in a QAL1 certificate. Individual contributors to the total measuring uncertainty are identified and quantified.

The Certified Measuring Range (CMR) can be no higher than 2.5 times the daily ELV for large combustion plants (1.5 times the daily ELV for waste incinerators). The global uncertainty, expressed as a % of the CMR, must be less than 75% of the maximum uncertainty allowed by the IED. The remaining 25% is left for other uncertainty sources such as the variation of the uncertainties between two CEMS of the same type, the representativeness of the sampling point, the peripheral measurements like temperature, O_2, etc.

For HCl and HF, the maximum uncertainty allowed by the IED is 40% of the daily ELV. Consequently, the global uncertainty, calculated on the basis of the QAL1 certificate for HF and HCl CEMS is 30% of the ELV given in mg/Nm^3.

In conclusion, compared with limits value applied in EU, HF and HCl emissions need to be corrected by appropriate cleaning systems before such emissions are released into the air. According to the BREF ceramic manufacture industry, for firing ceramic tiles fluorides and chlorides have to be tested using periodic methods. The fact that on-line measurement has not been considered as a legal requirement in ceramic industry, it is recognised that continuous monitoring provide increased confidence for both regulatory purposes and process control, in general.

From the process control point of view, the use of CEMS is of great interest because supply information which could relate emissions at stacks with operating parameters of the kiln, raw materials or of cleaning system.

From the regulatory purposes point of view, the use of CEMS strengthens the control on the cleaning system used and offers better levels of confidence and transparency of the environmental behaviour to the public authority and the general society. It is necessary to consider aspects such as operation activities related to quality assurance schemes (via EN 14181), as it is technically challenging to generate certified reference material for checking monitoring system's integrity for acid compounds.

In general, the economic impact derived from the use of CEMS is highly relevant for the industry, considering the investment required, the maintenance and calibration costs. In the ceramic tile industry, a medium size facility may have between 2 to 4 kilns. So, this additional cost should be considered by public authorities and companies during regulations development adjusting control necessities to the real environmental impact.

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