

ACID GAS EMISSIONS FROM STRUCTURAL CLAY PRODUCTS CONTAINING SECONDARY RESOURCES: FOUNDRY SAND DUST AND WAE LZ SLAG

M. Coronado^{1,2}, A. Andrés^{1*}, C.R. Cheeseman²

¹ Department of Chemistry and Process and Resource Engineering.

University of Cantabria. Avda. Los Castros s/n., 39005 Santander, Spain

² Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom

ABSTRACT

The estimation of the main changes that occur on heating foundry sand dust (FSD), Waelz slag (WS) and the three clays (C₁, C₂, C₃) used to manufacture three ceramic products, wall bricks (850 °C), roof tiles (950 °C) and face bricks (1050 °C), have been studied at laboratory scale combining different analytical techniques as assessing tool. This involved using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) to characterise changes in the crystalline phases present and evolved gas analysis (EGA) to identify the temperatures at which emissions occur. The combination of these techniques, traditionally used to characterise materials, has been used as an indirect measurement to assess the acid gas emissions during ceramic processes. Acid gas emissions were estimated using mass balance data obtained on compacted samples of the materials by comparing the chemical results for the samples before and after the thermal treatment at 10 °C/min to the sintering temperature of the ceramic products. The percentage reduction in the content of the pollutants during firing was assessed in a representative number of ternary mixes (of clay, FSD and WS) selected using mixture design of experiments, fired simulating the industrial firing cycles used to obtain the products, and correlated to the acid gas emissions. A clear relationship was found between HF and SO₂ emissions and the CaO content in the as-received materials. Higher temperatures and lower firing rates gave higher emissions. High WS content was found to decrease the emissions of SO₂ and HF below certain temperatures due to the formation of CaF₂ and CaSO₄ while the emissions of HCl were controlled by the firing temperature. The mineral phases containing Cl decompose below the firing temperatures (850-1050 °C) promoting its emission.

Keywords: Acid emissions; Recycling; Structural ceramics; Foundry sand dust; Waelz slag.

1. INTRODUCTION

Chemical and mineralogical transformations that occur during the firing of ceramics are associated with the release of pollutants to the atmosphere due to decomposition of minerals present in the raw materials. Increasingly restrictive environmental regulations have forced the ceramics industry to examine their environmental impact and several authors have reported the emissions produced during manufacturing various types of ceramics. Previous research has investigated the effect on emissions of raw material composition (García-Ten et al., 2006) and firing conditions (Toledo et al., 2004; Monfort et al., 2008). Emissions from the ceramics industry have been reduced using gas cleaning systems (Monfort et al., 2010a), coatings (García-ten et al., 2011) and the addition of other compounds to ceramics such as calcite (Monfort et al., 2010b).

A wide range of alternative industrial by-products have recently been investigated for possible reuse in ceramics (Coronado et al., 2014b; Vieira et al., 2009; Safiuddin et al., 2010; Junkes et al., 2011). The use of industrial by-products as raw materials may affect gaseous emissions during firing and previous research has investigated these effects at industrial (Hammer et al., 2002; Anderson et al., 2002; García Ubaque et al., 2010; Quijorna et al., 2011, 2012) and at laboratory scale (Basegio et al., 2002; Dondi et al., 2002; Souza et al., 2008). However, only limited research has been reported on the effects of composition, mineral transformations and firing parameters on emissions during manufacturing of ceramics containing industrial by-products.

The emissions from traditional ceramics and new resource efficient ceramics using alternative raw materials have been determined at an industrial scale by determining the concentration of pollutants in off-gases (Hammer et al., 2002) and by using absorption systems to capture these gases (Basegio et al., 2002; Monfort et al., 2011). Laboratory scale studies usually assess emissions using either Evolved Gas Analysis (EGA) (Toledo et al., 2004; García- Ten et al., 2008) or using a mass balance approach (Dondi et al., 2002; González et al., 2002, 2006; Quijorna et al., 2011, 2012). The advantage of EGA is that measurements are continuous and they can readily be related to thermal analysis data. EGA determines not only the evolved gases but also the range of temperature over which emissions occur. In addition, this method allows the main mineral phases responsible for emissions to be identified (Gómez et al., 2007). The mass balance approach determines emissions by analysing and comparing the composition of materials before and after firing (Galán et al., 2002, González et al., 2006).

The work reported in this paper is part of a larger research programme that aims to develop alternative ceramic products containing foundry wastes, and particularly foundry sand and Waelz slag. Previous research has demonstrated the potential to produce commercial ceramic products using clay and foundry waste (Quijorna et al., 2011). The technological properties (flexural strength, water absorption, porosity, density, firing shrinkage, weight loss during firing) and the environmental behaviour (leaching tests) of these products have been previously assessed and modelled (Coronado et al., 2014a; 2015) using the methodology of mixture design of experiments (M-DoE) (software Statistica 7.0).

Previous work has also estimated the emissions of CO₂, NO_x, SO₂, HCl and HF using the mass balance approach from two extruded samples containing clays, FSD and WS fired at an industrial scale using natural gas as fuel (Quijorna et al., 2012). Significant reductions were found in CO₂ and NO_x emissions while high negative values of the SO₂ (between 500 and 7000 g/Ton) and small values of the HF emissions (40 g/Ton) were reported. The high negative values of the S emissions were attributed to the absorption of S from an external source, probably the kiln fuel (natural gas) as it has been also suggested by other authors (Dondi, et al., 1995, González et al., 2006), while the small negative values in the case of HF and HCl, might be due to errors of the measuring method (González et al., 2006).

In this work, the critical acidic gases (HCl, HF and SO₂), have been deeper studied to provide improved understanding of their release mechanisms. This study has assessed the emissions from three ceramic processes using three clays (C₁, C₂, C₃) fired at three different temperatures (850, 950, 1050 °C). In this study, in order to avoid potential external sources of pollutants such as the effect of the fuel on the emissions an electric furnace was used. The behaviour of both the wastes and clays, as well as ternary mixtures during the three firing processes have been characterized and estimated using different laboratory techniques traditionally used for materials characterization: (i) XRD at different temperatures (to try to observe the main mineral changes that can be related to the acid gas emissions (ii) EGA to establish the emissions temperature ranges for each element, (iii) mass balance to estimate emissions during firing the raw materials at their corresponding temperatures and finally, (iv) the selection of 10 different mixtures compositions clay-FSD-WS for each clay (v) calculation of the reduction of the initial content of the Cl, F, and S using three replicates of each mixture and their correlation with the emissions of acid gases (HCl, HF and SO₂). The effect of raw material composition and firing parameters on emissions were evaluated using a combination of techniques. This study has focused on: (i) identifying the main mineral phases containing Cl, F and S at different temperatures and the transformations of these mineral phases

occurring during firing that can be responsible for the emission of acid compounds (HCl, HF and SO₂), using differential scanning calorimetry (DSC) and X-ray diffraction (XRD), (ii) establishing the temperature at which emissions occur for each material using thermal coupled techniques (TG-MS-FTIR) and assessing the influence of firing rate on these emissions, (iii) quantifying the emissions using a mass balance approach, and (iv) investigating the effects of partial replacement of clay by FSD and WS in ternary mixtures on these emissions.

2. MATERIALS AND METHODS

2.1 Materials

The raw materials selected in this work are three illitic clays (C₁, C₂, C₃), traditionally used by the Spanish ceramics industry to produce wall bricks, (C₁), roof tiles (C₂) and face bricks (C₃), and two foundry by-products, foundry sand dust (FSD) and Waelz slag (WS). The FSD was supplied by Nissan Motor Ibérica S.A. and was obtained from the ventilation bag-house system at the automotive foundry facility located in Corrales de Buelna (Cantabria, Spain). The WS (Ferrosita[®]) was obtained from the electric arc furnace dust recycling plant of Befesa Zinc Aser (Abengoa Group), located in Erandio (Basque Country, Spain).

The chemical composition of the clays, FSD and WS were determined in Activation Laboratories in Ancaster, Canada. Concentration of Major Components (Al₂O₃, CaO, Fe₂O₃, K₂O, MgO, MnO, Na₂O), were analysed using FUS-ICP. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace and poured into a solution of 5% nitric acid and mixed continuously until completely dissolved. The samples were then run for major oxides on a combination simultaneous/ sequential Thermo Jarrell-Ash ENVIRO II ICP (Actlabs, 2015a). Instrumental neutron activation analysis (INAA) was used to determine the content of Cl. Sample was irradiated at a thermal neutron flux of 7 x 10¹² n cm⁻² s⁻¹ and after appropriate decay time, to allow aluminium and other very short lived isotopes to decay, the samples were counted sequentially (Actlabs, 2015a). Ion selective electrode (ISE) was used in the case of F. Samples were fused with a combination of lithium metaborate and lithium tetraborate in an induction furnace to release the fluoride ions from the sample matrix. The fuseate was dissolved in dilute nitric acid, prior to analysis, the ionic strength adjusted with an ammonium citrate buffer. The fluoride ion electrode was immersed in this solution to measure the fluoride-ion activity directly. An automated fluoride analyser

from Mandel Scientific was used for the analysis (Actalbs, 2015b). The total content of S was analysed by combustion and infrared detection (IR). Sample was introduced in a crucible in the induction furnace and an accelerator material was added to the sample. The inductive elements of the sample and the accelerator was inductively coupled with a high frequency field generated by the furnace. The pure oxygen environment and the heat generated by this coupling cause the sample to combust. During combustion, sulphur-bearing elements are reduced, releasing sulphur, which binds with oxygen to form SO₂. Sulphur was measured as sulphur dioxide in the infrared cell. An Eltra CS-800 was used for analysis (Actalbs, 2015c).

Table 1 shows the chemical composition of the clays, FSD and WS, the limits of quantification (LOQ) the standard deviation (SD) of three replicates and the uncertainty of the measurements. The oxide composition of the FSD is similar to the clays which contain similar proportions of SiO₂ (> 50 %) and Al₂O₃ (> 12 %). WS consists mainly of Fe₂O₃ (56 %) and CaO (16 %) which act as fluxes and may have a strong effect during sintering by favouring the development of a liquid phase that will reduce the firing temperature (Coronado et al., 2014a; Segadães, 2006). The main differences in the composition of the clays are the higher total S and CaO contents of clay C₁ (0.54 and 10 % respectively) compared to clays C₂ (0.03 and 0.62 % respectively) and C₃ (0.065 and 0.52 % respectively).

LOI is associated with clay minerals, hydroxides, organic matter and volatile components and is an important parameter in ceramic processing with implications for the development of porosity, firing shrinkage and the release of contaminants to the atmosphere. The LOI of FSD is much greater (25.6%) than the clays (5.8-14.5%). The negative LOI for WS of ~2% indicates weight gain during firing due to oxidation of Fe which is mainly present as FeO (Quijorna et al., 2012).

Clays C₁ and C₂ show similar contents of F (350 ppm and 400 ppm, respectively) while clay C₃ shows the lowest content in F (100 ppm). These values are low in comparison with the values found by other authors, Galán et al. (2002) (361-1253 ppm), González et al. (2006) (362-1299 ppm) and Dondi et al. (1995) (500-1200 ppm). The three clays (C₁, C₂, C₃) show similar contents of Cl (350 ppm, 250 ppm and 250 ppm, respectively) which fall within the ranges reported by Dondi et al. (1995) (100-6200 ppm) and González et al. (2006) (20-3490 ppm) but high compared to the results reported by Galán et al. (2002) (20-70 ppm). Differences found between the contents of Cl and F in the clays used in this study and those used by other authors are mainly attributed to differences in their mineralogy. According to González et al. (2006), fluorine in ceramic industries derives from decomposition of phyllosilicates (micas, smectites) fluorapatite and fluorite while chlorine derives from micas, halite, organic matter and

chlorapatite. The low contents in fluorine of the clays used in this study are attributed to their low content in these minerals in the clays (C₁, C₂, C₃)”.

Differences have also been found in the S content of the clays (C₁, C₂, C₃) that shows S contents of 5400 ppm, 300 ppm and 650 ppm, respectively. However, these values fall within the ranges reported by Dondi et al. (1995) (100-6200 ppm) and González et al. (2006) (100-11400 ppm).

The content of Cl, F and S in the foundry wastes, WS and FSD, are high compared to the clays. WS has the highest content of Cl (4550 ppm), F (5150 ppm) and total S (14600 ppm), exceeding by far the range of values, previously described, that other authors have reported (Dondi et al. 1995; González et al., 2006). Despite the high content of F, Cl and S in the as-received FSD these values are within the range reported by other workers (Dondi et al. 1995; González et al., 2006) previously described.

2.2 Methods

Representative process sampling for reliable data analysis of the materials was performed in this work (UNE-EN 14899). Mass balance approach was used to determine the composition of three replicates of each material sample and the standard deviation and the uncertainty of the measures were calculated.

Initial experiments were conducted on as-received clays (C₁, C₂, C₃), FSD and WS, to study the mineralogical behaviour and emissions during the firing process. The thermal behaviour was studied using differential scanning calorimetry analysis (DSC, Netzsch STA 449C Jupiter). The changes in the mineral phases during the thermal treatment up to the firing temperatures (850, 950 and 1050 °C) traditionally used to obtain wall bricks, roof tiles and facing bricks were determined by X-ray diffraction (XRD, D8 Advance Automatic Diffractometer) in Bragg-Brentano geometry. Cu K α ₁ radiation ($\lambda=1.5406$ Å) was employed with 0.03° 2 θ steps and constant 8 s acquisition time in the 10-70° 2 θ range. Emitted gases analysis (EGA) was used during the firing of the as-received materials using coupled thermal techniques (TGA-MS-FTIR). The combination of thermo-gravimetric analysis (TGA) with a quadrupole mass spectrometer (QMS 403Aëolos®) and FTIR (Bruker) allows the analysis of the major ions evolved and the corresponding emission temperatures during heating according to their mass-to-charge ratio ($m/z = 18, 20, 36$ and 64 , for water, F, Cl, and SO₂ respectively).

The EGA of HCl, HF and SO₂ used powder samples heated to 1200 °C in air (50 ml/min), using He as a protecting gas (25 ml/min) with a dwell time at peak temperature of 1 hour. In order to study the effect of a key parameter, the firing rate, on the acid gas emissions, two firing rates were selected to perform the EGA. A slow firing rate (2 °C/min), which is the lowest heating rate possible using the present experimental configuration to approach the firing rates used in brick manufacture and a fast firing rate (10°C/min), which is the most common firing rate used in the literature to perform EGA of clays (Parsosn et al., 1997). FTIR spectroscopy can only be used to conduct short-term fluorinated emission measurements from thermal processes because the infrared detector to measure fluorine requires liquid nitrogen cooling and this limits the operating time to 4 hours on a single charge (nitrogen). Therefore, the EGA of HCl and SO₂ used two firing rates: slow firing (2 °C/min) and fast firing (10 °C/min) while the EGA of HF was obtained only using fast firing (10 °C/min). The combination of these techniques allows the critical emission temperatures for each compound to be determined and correlated to the mineral phases responsible for the emissions.

Test specimens of the materials were formed by uniaxial powder pressing at 10 MPa (Mignon SS/EA Nanetti laboratory press) and fired in a laboratory electric furnace. The clays were fired simulating industrial firing cycles as described in previous work (Coronado et al., 2014a) using the firing temperature to obtain wall bricks (850 °C) in the case of clay C₁, roof tiles (950 °C) in the case of clay C₂ and facing bricks (1050 °C) for clay C₃. The by-products, FSD and WS, were fired simulating the three industrial firing cycles. The potential emission (Ψ) of acid pollutants (HCl, HF and SO₂) during the firing of clays and by-products were assessed using eq. 1 (Quijorna et al, 2012, González et al., 2006; Dondi et al., 2002).

$$\psi_i = 10000 * \frac{M_{wi}}{A_{mj}} * \left[\frac{100}{100-LOI} * C_r^j - C_f^j \right] \quad [1]$$

where i = polluting compounds (HCl, HF and SO₂); j = constituting elements (F, Cl and S) of the polluting compounds; Ψ_i = emission (in mg of compound i per kg of ceramic produced); LOI (%) = loss on ignition at the sintering temperatures (850, 950 and 1050 °C) of each clay (C₁, C₂, C₃) used at the companies to obtain the corresponding ceramic products (wall bricks, roof tiles, facing bricks); M_{wi} = molecular weight of the polluting compounds; A_{mj} = atomic mass of the element; C_r^j = concentration of element (j) in the raw material, and C_f^j = concentration of element (j) in fired product.

This equation assumes that elemental Cl, F and S are released into the atmosphere during the firing process in the form of HCl, HF and SO₂. F was measured by fusion and ion specific electrode (FUS-ISE), Cl by neutron activation (INAA) and total sulphur content by

combustion and infrared detection (IR). The limit of quantification (LOQ) for these techniques is 0.01 %.

Finally, in order to assess the environmental impact (in terms of gas emissions) derived from the partial substitution of traditional clays by foundry waste in the ceramic industry, ceramic specimens were prepared containing mixtures of the different clays, FSD and WS. In order to produce acceptable ceramic products the weight fraction of clay in the mix must be equal to, or greater than 0.6, with the remainder consisting of WS and/or FSD (Quijorna et al. 2012). Taking into account this restriction as shown in Table 2, for each process and its corresponding clay, ten mixes of the three raw materials (clay, WS, FSD) were selected using the methodology of mixture design of experiments (software Statistica 7.0) as described in Coronado, et al. (2014a). M-DoE is a statistical technique that enables the prediction of products behaviour with a minimum number of trials and is capable of evidencing various types of joint effects among variables. The basic assumption of this technique is that, when the process conditions are kept constant, the properties of the products (response variables) are simply determined by the proportion of the components in the mixture (input variables). These ten mixtures correspond to the minimum number of mixtures necessary to model and predict the technological properties (water absorption, flexural strength, open porosity, linear firing shrinkage, weight loss and apparent density) in terms of raw materials contents: clay, foundry sand dust and Waelz slag (Coronado et al., 2014a). Test specimens were prepared by wet mixing and formed as previously explained for the as-received raw materials: uniaxial pressing at 10 MPa, oven-drying at 110 °C for 24 hours and firing in a laboratory electric furnace using the industry firing cycles for wall bricks (850 °C), roof tiles (950 °C) and facing bricks (1050 °C). The chemical analysis of the unfired mixtures and fired ceramic specimens were determined as previously described and the percentage of reduction for each element calculated

3. RESULTS AND DISCUSSION

3.1 Thermal behaviour of the as-received raw materials

Figure 1 shows the thermal behaviour (DSC curves) during firing (10 °C/min) of the clays (C₁, C₂, C₃) and the foundry waste (FSD and WS) up to 1200 °C. Five endothermic peaks and two exothermic peaks are observed for the clays (Figure 1a). The first two endothermic peaks (at 120 and 150 °C) are due to the release of absorbed water. The third endothermic peak (at 250-300°C) corresponds to the evolution of interlayer-bound water and

water from the dehydration of hydroxides. The small fourth endothermic peak at ~ 575 °C is attributed to the α - β quartz structural transition while the fifth endothermic peak (at ~ 600 °C) is related to the dehydroxylation of kaolinite and other clay minerals. Finally, the endothermic peaks at temperatures between 750 and 850 °C are due to carbonate decomposition (dolomite and calcite) (Serra et al., 2013). The decomposition of calcite is associated with a sharp peak at 827 °C for C₁ and a weak peak at 850 °C for the non-calcareous clays (C₂ and C₃). The larger peak observed for clay C₁ at this temperature is due to the higher CaO and total carbon content (10.04% and 2.25%) compared to clays C₂ (0.62% and 0.04%) and C₃ (0.52% and 0.11%) (see Table 1).

The first exothermic peak observed between 300 and 400 °C for clays C₁ and C₃ is due to combustion of organic matter. This peak is not observed in the case of clay C₂. The second exothermic peak results from the crystallization of new mineral phases, as anorthite, wollastonite and gehlenite start to appear above 880 °C.

The DSC curve of FSD (in Fig. 1b) shows an endothermic event at 127 °C due to the evolution of physically adsorbed surface water. Despite the high SiO₂ content of FSD the endothermic peak related to the α - β quartz structural transition is not observed due to possible masking by exothermic reactions. Exothermic events are related to oxidation and combustion of carbonaceous matter and volatile compounds. Fig. 1 does not show an endothermic peak related to dehydroxylation of clay minerals contained in FSD but this may be masked by exothermic processes.

The DSC curves of WS (in Fig. 1b) exhibits three exothermic events. The first small peak (at 475 °C) is related to combustion reactions. The second peak (at 628 °C) is related to combustion and oxidation processes. Finally, the third small peak (at 776 °C) is due to ferrous oxidation of wustite (FeO) to form hematite (Fe₂O₃) and magnetite (Fe₃O₄), which was also confirmed by the XRD analysis (Fig. 3). WS gains weight during thermal treatment between 450 and 750 °C due to the oxidation of Fe present in WS in the form of wustite (FeO) to form hematite (Fe₂O₃) (Quijorna et al., 2014). This weight gain may compensate for the weight loss due to volatile compounds.

3.2 *Changes in crystalline phases during firing raw materials*

Mineral changes in the clays (C₁, C₂, C₃) upon heat treatment to the sintering temperatures used to manufacturing wall bricks (C₁, 850 °C), roof tiles (C₂, 950 °C) and facing bricks (C₃, 1050 °C) are shown in Figure 2. The unfired clays mainly contain quartz, illite and kaolinite while pyrite was not detected. The presence of dolomite in clay C₂

indicates higher MgO content. C₁ also contains calcite as a major phase as expected from the calcareous nature of this clay. During firing the intensity of the XRD peaks associated with illite, k-feldspars and plagioclase decrease while other crystalline phases such as anorthite and wollastonite are formed. CaO from the decomposition of CaCO₃ reacts to promote the formation of these new minerals. The strong fluxing effect of CaO reduces the sintering temperature and this is why clay C₁, used in the production of wall bricks, is fired at a lower temperature (850 °C).

Mineral changes in the FSD and WS during heating to the temperatures used to manufacturing wall bricks (850 °C), roof tiles (950 °C) and facing bricks (1050 °C) are shown in Figure 3. The main components in FSD are quartz, bentonite and mica (Fig. 3a). However, at higher temperatures the high intensity peaks are not visible. Mineral phase transformations occurs as temperature increases to form anorthite as indicated by the triple characteristic peak observed at 28.03 2-theta value and taking into account the content of CaO and SiO₂ in FSD. The quartz peaks remain after heating to the highest temperature (1050 °C). As can be seen in Figure 3b, WS consists primarily of iron oxide (magnetite and wustite). The strong reducing conditions that exist during the Waelz process form wustite in WS. Furthermore, the presence of magnetite (Fe₂O₃) has been confirmed using a permanent magnet. Calcium silicate (Ca₂SiO₄) and various mixed Fe, Ca and Mg oxides are also present. Despite the high S content in WS (1.46 %), pyrite, gypsum or other sulphur bearing minerals that might be present were not detected by XRD (Figure 3). Firing WS results in complete oxidation of wustite to magnetite, with hematite peaks also present in fired specimens. Anhydrite (CaSO₄) is also present in WS fired at the three temperatures (850 °C, 950 °C and 1050 °C) while it is not observed in the as-received WS. There is also a decrease in the total content of CaO containing phases.

According to Gredmaier et al., (2011), the most likely compound of Ca and S in heavy clay ceramics is calcium sulphate or anhydrite (CaSO₄) and several options exist for its formation, which involves a variety of chemical reaction paths (Tourneret et al. 1999). The most simple is the reaction between the evolved CaO from the CaCO₃ decomposition at high temperatures and the SO₂ to form CaSO₄ (Tullin and Ljungstrom 1989) in the presence of oxygen (Eq. 2). The SO₂ liberated during firing migrates from the core towards the surface of the brick where in presence of oxygen from the atmosphere and the evolved CaO forms CaSO₄. This reaction requires an oxygen as oxidizing agent, which is only available close to the brick surface. XRD data for WS clearly indicates the formation of anhydrite.



3.3 Evolved gas analysis of the as-received raw materials.

Figure 4 shows the gas evolution profiles of water and the acid gases HCl, HF and SO₂ from powder samples of the clays (C₁, C₂, C₃) fired up to 1200 °C at 10 °C/min with a dwell time at peak temperature of 1 hour. Gas evolution profiles in Fig. 4 shows qualitative information of the gas emissions during heating the materials expressed as emission intensity in absorbance units.

H₂O emissions: Three major emission peaks are observed in the gas evolution profiles of H₂O. The first emission peak (150-200 °C) is due to the release of absorbed water. The second emission peak (350-400 °C) is attributed to the dehydration of hydroxides. The third emission peak (at ~ 600 °C) is related to the dehydroxylation of kaolinite and other clay minerals. These results are in good agreement with the thermal behaviour of the clays previously showed in Figure 1 (DSC curves).

HCl emissions: The emission peak in the gas evolution profiles of HCl at 575 °C can be attributed to the decomposition of organic compounds that contain chlorine or to the loss of crystalline water during the clay mineral dehydroxylation which promotes the release of fluorine contained in the hydroxyl-bearing minerals jointly with the hydroxyl groups (García-Ten et al. 2011). The emissions at higher temperature starts at 1140 °C for C₁, 950 °C for C₂, and 1100 °C for C₃, increasing progressively throughout the firing cycle up to the peak firing temperature (1200 °C) due to decomposition of chlorine-containing mineral salts (Monfort et al., 2011).

HF emissions: In the gas evolution profiles of HF the emission peak at 575 °C is related to the loss of crystalline water during the clay mineral dehydroxylation which promotes the release of fluorine contained in the hydroxyl-bearing minerals (García-Ten et al. 2011). This is in good agreement with the temperature at which the release of crystalline water was observed in the DSC results (Fig. 1). An additional HF emission peak is observed at higher temperature for the three clays with these emissions starting at 1030 °C for C₁, 940 °C for C₂, and 1020 °C for C₃. These emissions are attributed to the decomposition of fluorite (CaF₂) formed by the chemical reaction of the fluorine released during the clay mineral dehydroxylation with the CaO liberated from the decomposition of carbonates (eq. 3) (García-Ten et al., 2006).



SO₂ emissions: a single emission peak is observed for the clays in the gas evolution profiles of SO₂. The SO₂ emissions start at 1120 °C for C₁, 850 °C for C₂, and 930 °C for C₃, increasing progressively throughout the firing cycle up to a peak temperature (1200 °C for C₁, 1114 °C for C₂, and 1170 °C for C₃). This indicates the presence of alkaline and alkaline earth sulphates (Na₂SO₄, K₂SO₄, CaSO₄, MgSO₄) or complex sulphates containing these alkaline and alkaline earth sulphates (Dondi et al., 1997) that decompose at lower temperatures. These results also confirm the absence of pyrite, which decomposes in the temperature range between 400 and 550 °C. The high temperature at which the SO₂ emissions are observed for clay C₁ reveals the presence of CaSO₄ which is also confirmed by the previous XRD analysis (see Fig. 2) and by the presence of efflorescence in some areas of fired specimens. The low temperatures at which the SO₂ emissions are observed for clays C₂ and C₃ (850 and 950 °C) suggests the presence of other alkaline sulphates that decompose at lower temperatures.

Figure 5 shows the gas evolution profiles of HF, HCl and SO₂ from powder samples of foundry sand dust (FSD) and Waelz slag (WS), fired up to 1200 °C with a dwell time at peak temperature of 1 hour. In the case of HCl and SO₂ two firing rates, slow firing (2 °C/min) and fast firing (10 °C/min), were used. The gas evolution profiles of HF were obtained using only the fast firing (10 °C/min) because the FTIR analysis can only carry out short-term fluorinated emission measurements from thermal processes due to technical reasons.

HF emissions: The emissions of HF start at about 800 °C for the FSD with a single emission peak at about 1100 °C. HF emissions for WS are observed at temperatures above ~900 °C, increasing progressively during the firing cycle and therefore the firing peak cannot be observed within this firing temperature interval. This can be related to the presence of cuspidine which is more stable than fluorite (García-Ten et al. 2011). Cuspidine begins to crystallise above 850 °C increasing in content up to a maximum around 1100 °C in mixtures with high CaO content. The appearance of this crystalline phase in the temperature range in which the CaF₂ content decreases (900-1100 °C) fixes the fluorine and reduces fluorine compound emissions into the atmosphere in this temperature range. Thermal treatment of FSD and WS at 10 °C/min does not show the characteristic HF emission peak at 575 °C observed for the clays but the second emission of HF moves towards lower temperatures (820 °C for the FSD and 900 °C for the WS).

HCl emissions: The emissions of HCl from FSD start at 850 °C when firing at 2 °C/min and shows a single peak at 1090 °C. However, when using a faster firing rate (10 °C/min) a delay in the emissions is observed with the emissions starting at 950 °C and showing a firing peak at 1114 °C. HCl emissions for WS are observed at temperatures above 950 °C showing a

peak at about 1200 °C during firing using the two firing rates. The thermal treatment of FSD and WS at 10 °C/min do not show the HCl emission peaks at low temperatures observed for the clays. The second emission of HCl appears at temperatures similar to the emission peak temperature observed for clay C₂ (~ 950 °C). However, the HCl emissions of the FSD and the WS are found at lower temperature compared to clays C₁ and C₃ (~1100 °C).

SO₂ emissions: two emission peaks are observed for the FSD in the gas evolution profiles of SO₂. The first emission peak at ~ 550 °C for the two heating rates might be related to oxidation of sulphur-bearing carbonaceous compounds at this temperature. The SO₂ emissions for FSD are affected by the firing rate. A delay of 200 °C is observed in the second SO₂ emission when using faster firing (emission is observed at 950 °C) compared to the slow firing rate (emission is observed at 1180 °C). SO₂ emissions for WS are observed above ~1100 °C. An emission peak at 1200 °C is observed when firing at 2 °C/min but a peak is not observed when firing at 10 °C/min. The formation of barium sulfate (BaSO₄), calcium aluminosulfate (3CaO·3Al₂O₃·CaSO₄) and calcium silicate sulfate (Ca₅(SiO₄)₂SO₄) that can encapsulate CaSO₄ and prevent it from decomposing at high temperatures (Cheng et al. 2003) could be the reason for the absence of the peak when firing at slower firing rate. Nevertheless the high-temperature behaviour of the WS matrix during firing is complex and therefore identification of complex phases containing sulphur and the clarification of the reaction mechanisms during firing at different rates is particularly challenging. Further investigation will be undertaken in future works. The thermal treatment of FSD at 10 °C/min shows a SO₂ emission peak at low temperature (550 °C). This is not observed for clays which show SO₂ emission that start at temperatures above 850 °C (clay C₁), 930 °C (Clay C₂) and 1120 °C (clay C₃). The starting temperature for the SO₂ emissions is higher when firing WS (1115 °C) compared to clays C₁ and C₂.

Small differences in the temperatures of reactions observed using DSC and EGA may be attributed to differences in the mass sample that can result in temperature gradients in the crucible. This means that decomposition of the compounds is not instantaneous at the corresponding temperature. As a result the emission peaks move towards higher temperatures in the EGA which uses a larger sample mass than used in DSC analysis.

3.4 *Mass balance analysis of pressed samples of raw materials*

The emission of the pollutants (HF, HCl, and SO₂) for the clays (C₁, C₂, C₃), FSD and WS fired to three temperatures (850 °C, 950 °C and 1050 °C) simulating the industrial

processes (higher firing time) described in previous works (Coronado et al., 2014a) and estimated by mass balance [eq. 1] are summarized in Table 3.

HF and HCl emissions for the FSD are high (~ 800 mg/kg for the F and 1000-1100 mg/kg for the Cl) and they do not present significant differences between the three firing processes. This is because these emissions are primarily conditioned by the Cl and F content in the as-received FSD rather than by the firing temperature of the ceramic process. The low content in CaO of the FSD do not promote the formation of CaF₂ which is a compound that avoid HF emissions below its decomposition temperature (900-950 °C)". According to the EGA data in Fig. 5 HF and HCl emissions for the FSD start at temperatures close to 850 °C and increase up to 1100 °C. However, the higher dwell time (3-4 h) of the industrial processes means that all the F and Cl are emitted.

Results from the mass balance (Table 3) show that HF and HCl emissions for WS are low (< 160 mg/kg) when simulating the industrial process for the manufacturing of wall bricks at 850 °C due to the formation of CaF₂ although they increase from ceramic processes using higher temperatures. The emissions of F are 842 mg/kg at 950 °C and 1263 mg/kg at 1050 °C and the emission of Cl are 2159 mg/kg at 950 °C and 28~9 mg/kg at 1050 °C. These results are in good agreement with those obtained from the EGA (Fig. 5) which show that HF and HCl emissions for WS start at 900 and 950 °C respectively.

Despite the high S content in the WS compared to FSD, higher SO₂ emissions are observed for the FSD. High values of SO₂ emissions are observed even using the lowest temperature (850 °C) and are higher in processes using higher temperatures (950 and 1050 °C). This is in agreement with the EGA data that showed a first SO₂ emission for the FSD at 550 °C and a second emission starting at 950 °C. The emissions of SO₂ for the WS are low in all three firing processes due to the formation of CaSO₄. This is confirmed by the EGA test which show SO₂ emissions for the WS at temperatures above 1100 °C are controlled by the formation of CaSO₄ which results in low S emissions.

3.5 *Acid gas emissions from fired ceramic samples*

The reduction in content of a pollutant during firing can give a good estimate of the gas emissions due to volatilization of the element. In this work the emissions during three firing processes of ten mixtures (M₁ to M₁₀) containing the clays, FSD and WS fired using the corresponding firing cycle of each clay to obtain wall bricks (clay C₁, 840 °C), roof tiles (clay C₂, 950 °C) and facing bricks (clay C₃, 1050 °C) have been assessed by calculating the reduction in pollutant content resulting from firing. The initial content of F, Cl and S in mixes

was calculated from the content in as-received materials (Table 1) and the mix proportions (Table 2). The content of F, Cl and S in the fired mixtures was analysed with the same methods used to analyse the as-received materials. Equation 4 was used to assess the potential emissions during firing these mixtures.

$$\% \text{ Reduction in content} = \frac{\text{Initial content,ppm} - \text{Final content,ppm}}{\text{Initial content,ppm}} * 100 \quad [4]$$

Fig. 6 shows that the reduction or loss in the content of a pollutant depends on the firing temperature. In general, mixes fired at higher temperatures exhibit higher reduction or loss of the pollutants and higher potential emissions. Negligible values of the reduction in the initial content of S are observed for mixtures fired at the lowest temperature (850 °C) used to manufacture wall bricks. The SO₂ emissions at 850 °C may be low compared to the emissions from firing at 950 °C and 1050 °C during the manufacturing of roof tiles and facing bricks respectively. Similar behaviour was found for F and S contents during firing where two different zones (I and II) can be distinguished. In zone I are mixes with high proportions of FSD (M₄₋₅ and M₈₋₉) and therefore high F content. Zone II contains mixes with a high proportion of WS (M₁₋₂ and M₆₋₇) and therefore a high content of S. In zone I higher contents of F and S in the mixes before firing results in greater reduction in content and therefore higher HF and SO₂ emissions. An inverse trend is found in zone II, where lower reductions in the content of the pollutants occur and thus lower emissions are found. This is associated with the presence of high amounts of CaO from the WS which allows formation of CaF₂ and CaSO₄ favouring retention of S and F. Binary mixes containing clay and Waelz slag (M₁, M₂) and ternary mixtures with low contents in FSD (M₇) show the lowest reduction of initial content after firing.

Cl loss in fired mixtures is around 50% at 850 °C (wall bricks), 75% at 950 °C (roof tiles) and between 80-100 % at 1050 °C and this is not related to the proportions of the different components in mix.

4. CONCLUSIONS

This work have characterised the acid gas emissions from three ceramic processes, containing FSD and WS as alternative raw materials, at laboratory scale by the combination of different analytical techniques such as DSC, XRD, EGA, FUS-ICP, ISE, INAA and FUS-IR that traditionally have been used in materials characterization. Key parameters in analytical measurements such as the limit of detection (LOD), limit of quantification (LOQ), the standard deviation and the accuracy quantified by the estimation of the uncertainty of the analytical measurements have been quantified in this work. Mass balance approach has been applied to estimate these emissions and no direct measurement of the emissions have been performed. Taking into account the boundaries of the study, it is concluded that the combination of these techniques and the use of mass balance is able to provide improved understanding of the acid gas emissions during ceramic processes. The combination of DSC and XRD allows determination of the main mineral phases responsible for emissions. EGA allows the temperature of the emissions during heating using different firing rates to be determined. Results from the mass balance confirmed the temperature of the gaseous emissions of the pollutants previously established using the EGA and estimates the values of these emissions.

Results highlight a clear relationship between emissions of HF and SO₂ and the CaO content in the raw materials. However, the emissions of HCl were controlled by the firing temperature because CaCl₂ decompose below the firing temperatures (850-1050 °C) promoting its emission. The firing parameters, firing rate (°C/min) and firing temperature (°C), also have an important role. In general, lower temperatures and faster firing decreases emissions. The mass balance was applied to compacted samples fired using dwell times similar to industrial firing cycles. The dwell time at peak temperature allows extensive decomposition of the chlorine-bearing minerals, fluorite and sulphates.

The percentage reduction in the content of the pollutants during firing was assessed in the clay-FSD-WS mixes fired to simulate the industrial firing cycles used to obtain wall bricks (850 °C), roof tiles (950 °C) and facing bricks (1050 °C). It is concluded that binary mixtures containing high amounts of WS show the lowest reduction in S and F despite containing high levels of S and F. This is due to the formation of CaF and CaSO₄. Binary mixtures containing a high level of FSD contain low amounts of F and S but show higher percentage reduction during firing. This indicates that even low initial contents of F and S in these mixtures have a relevant effect on the emissions of F and S. The reduction in Cl content is mainly controlled by the firing temperature and the mineral phases in the raw materials.

It is remarkable that significant adsorption of sulphur compounds in the WS occurs which reduces SO₂ emissions. WS is able to adsorb sulphur up to high temperature and it might be a potential new raw material in the ceramic processes used to obtain wall bricks, roof tiles and facing bricks. The absorption of F by WS is observed below the temperature at which CaF₂ decomposes (900-950 °C). This has an important role in reducing F emissions from manufacturing wall bricks.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support for this research granted by the Spanish Education and Science Ministry (Project CTM2009-11303) and F.P.I. Fellowship awarded to M. Coronado. The authors are also grateful to Professor Ana María Segadães from the Centre for Research in Ceramics and Composite Materials (CICECO) of the University of Aveiro (Portugal) for her interest and helpful suggestions in this work.

REFERENCES

Actlabs, 2015a. Activation Laboratories Ltd. <http://www.actlabs.com/page.aspx?page=506&app=226&cat1=549&tp=12&lk=no&menu=64>. Accessed 10th October 2015

Actlabs, 2015b. Activation Laboratories Ltd. <http://www.actlabs.com/page.aspx?page=528&app=226&cat1=549&tp=12&lk=no&menu=64>. Accessed 10th October 2015.

Actlabs, 2015c. Activation Laboratories Ltd. <http://www.actlabs.com/page.aspx?page=735&app=226&cat1=549&tp=12&lk=no&menu=64>. Accessed 10th October 2015.

Anderson, M., Elliott, M., Hickson, C. 2002., Factory-scale proving trials using combined mixtures of three by-product wastes (including incinerated sewage sludge ash) in clay building bricks, *J. Chem. Technol. and Biotechnol.* 77, 3, 345-351.

- Basegio, T., Berutti, F., Bernardes, A. Bergmann, C.P., 2002., Environmental and technical aspects of the utilisation of tannery sludge as a raw material for clay products. *J. Eur. Ceram. Soc.* 22, 2251-2259.
- Coronado, M., Blanco, T., Quijorna, N. Alonso-Santurde, R., 2014b. Chapter 7, 129-188 Types of waste, properties and durability of waste-based fired masonry bricks, in: WP Wood head Publishing in materials (elservier). F. Pacheco-Torgal, P.B. Lourenco, J.A. Labrincha, V.M. John, N.P. Rajamane, *Eco-efficient Masonry Bricks and Blocks: Design, Properties and Durability*. ISBN: 978-1-78242-305-8
- Coronado, M., Segadães, A.M., Andrés, A., 2014a. Combining mixture design of experiments with phase diagrams in the evaluation of structural ceramics containing foundry by-products. *Applied Clay Science*. 101, 390-400.
- Coronado, M., Segadães, A.M., Andrés, A., 2015. Using mixture design of experiments to assess the environmental impact of clay-based structural ceramics containing foundry wastes. *Journal of Hazardous Materials*. 299, 529–539.
- Dondi M., Ercolani G., Fabbri B., 1995. Concentration of pollutant elements (F, S, Cl) into the clays used by the Italian brick industry in: G.J. Churchman, R.W. Fitzpatrick and R.A. Eggleton (editors), *Clays: Controlling the Environment*. Proc. 10th Int. Clay Conf., Adelaide, Australia, 1993, CSIRO Publishing, Melbourne, 79-83.
- Dondi, M., Ercolani, G., Guarini, G., Raimondo, M., Ruffini, A., 2002. Orimulsion fly ash in clay bricks-part 3: chemical stability of ash-bearing products. *J. Waste Manag. and the Environ.* 22, 11, 547-556.

Dondi, M., Fabbri, B., Guarini, G., Marsigli, M., & Mingazzini, C., 1997. Soluble salts and efflorescence in structural clay products: a scheme to predict the risk of efflorescence. *Bol. Soc. Esp. Ceram. Vidrio*, 36, 6, 619-629

Galán, E. González, I., Fabbri, B., 2002. Estimation of fluorine and chlorine emissions from Spanish structural ceramic industries. The case study of the Bailén area, Southern Spain. *J. Atmos. Environ.* 36, 5289–5298.

García-Ten, J., Monfort, E., Gómez-Tena M.P., Sanz, V., 2011. Use of coatings to minimise acid emissions during ceramic tile firing, *J. Clean. Prod.* 19, 9-10, 1110-1116.

García-Ten, J., Gómez, M.P., Zumaquero, E., Monfort, E. and Machi, C., 2008. Use of TGA-EGA technique in studying acid emissions during ceramic tile firing. Study of the test variables 11th Mediterranean Congress of Chemical Engineering, Expoquimia, Barcelona, Spain.

Garcia-Ubaque, C.A, Gonzales Hässig A., Acosta Mendoza, C., 2010. Stack emissions tests in a brick manufacturing Hoffmann kiln: firing of municipal solid waste. *Waste Manag Res.* 28, 7, 596-608.

Gómez, M.P, Gazulla, M.F, Zumaquero, E., Orduña, M., 2007. Utilización de técnicas acopladas de análisis térmico TG-DSC-QMSFTIR en la caracterización de arcillas y composiciones cerámicas utilizadas en la fabricación de baldosas cerámicas. Cuantificación de compuestos de carbono. *Bol. Soc. Esp. Ceram. Vidr.* 46, 5, 259-266.

González, I. Aparicio, P., Galán, E., Fabbri, F., 2002. Proposal for reducing F and Cl emission in the brick industry using new formulations. *J. Appl. Clay Sci.* 22, 1-7.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

González, I. Galán, E., Miras, A. 2006., Fluorine, chlorine and sulphur emissions from the Andalusian ceramic industry (Spain)-Proposal for their reduction and estimation of threshold emission values. *J. Appl. Clay Sci.* 32, 153-171.

Gredmaier, L., et al., 2011. Calcium and sulphur distribution in red clay brick in the presence of a black reduction core using micro X-ray fluorescence mapping. *Construction and Building Materials*, 25(12), 4477-4486.

Hamer, K., Karius, V., 2002. Brick production with dredged harbour sediments. An industrial-scale experiment. *J. Waste Manag.* 22, 521-530.

Junkes, J.A., Carvalho, M.A., Segadães, A.M. and Hotza, D., 2011. Ceramic tile formulations from industrial waste', *InterCeram: Int. Ceram. Rev.* 60, 1, 36-41.

Monfort, E., García-Ten, J., Celades, I., Gazulla, Ma.F., Gomar, S., 2008. Evolution of fluorine emissions during the fast firing of ceramic tile. *J. Appl. Clay Sci.* 38, 250–258.

Monfort, E., Gomar, S., Celades, I., Gómez, P., Moro, E., Márquez, E., 2010a. Reducción de las emisiones de azufre de un horno túnel. *Bol. Soc. Esp. Ceram. Vidr* 49, 5, 343-350.

Monfort, E., García-Ten, J., Celades, I., Gomar, S., 2010b. Monitoring and possible reduction of HF in stack flue gases from ceramic tiles. *J. Fluorine Chem.* 13, 6–12.

Monfort, E., Celades, I., Gomar, S., Rueda, F., Martínez, J., 2011. Characterisation of acid pollutant emissions in ceramic tile manufacture. *Bol. Soc. Esp. Ceram. Vidr.* 50, 4, 179-184.

Parsons, A.J, et al., 1997. Evolved gas analysis (EGA) of brick clays. *J. Thermal Analysis*, 48, 49-62.

- Quijorna, N., Coz, A. and Andrés A., 2012. Recycling of Waelz slag and waste foundry sand in red clay bricks. *J. Resour. Conserv. and Recycl.* 65, 1-10.
- Quijorna, N., Miguel, G.S. and Andrés, A., 2011. Incorporation of Waelz slag into commercial ceramic bricks: A practical example of industrial ecology. *J. Ind. and Eng. Chem. Res.* 50, 9, 5806-5814.
- Quijorna, N. De Pedro, M., Romero, M., Andrés, A., 2014. Characterisation of the sintering behaviour of Waelz slag from electric arc furnace (EAF) dust recycling for use in the clay ceramics industry. *Journal of Environmental Management.* 132, 278–286.
- Safiuddin, M.D., Mohd Zamin Jumaat, Salam, M. A., Islam, M.S., Hashim, R., 2010. Utilization of solid wastes in construction materials. *Int. J. Phys. Sci.* 5, 13, 1952-1963.
- Serra, M. F., Conconi, M.S, Suarez, G., Agietti, E.F, Rendtorff, N. M., 2013. Firing transformations of an argentinean calcareous commercial clay. *Cerâmica.* 59, 254-261.
- Segadães, A.M., 2006. Use of phase diagrams to guide ceramic production from wastes. *Adv. Appl. Ceram.* 105, 1, 46–54
- Souza, V.P., Toledo, R., Holanda, J.N.F., Vargas, H. and Faria JR., R.T., 2008. Pollutant gas analysis evolved during firing of red ceramic incorporated with water treatment plant sludge. *Cerâmica.* 54, 331, 351-355.
- Toledo, R., Dos Santos, D.R., Faria, Jr. Carrió, J.G., Auler, L.T. and Vargas, H., 2004. Gas release during clay firing and evolution of ceramic properties. *Appl. Clay Sci.* 27, 151- 157.
- Tourneret, L., et al., 1999. Efflorescence - study of the formation of calcium sulphate during firing of ceramic ware. *Ziegelindustrie International*, 6, 15- 25.

Tullin C., and Ljungstroem, E. 1989. Reaction between calcium carbonate and sulfur dioxide. *Energy & Fuels*, 3(3), 284-287.

UNE-EN 14899, 2007. Characterization of waste - Sampling of waste materials - Framework for the preparation and application of a sampling plan.

Vieira, CMF., Monteiro, S.N., 2009. Incorporation of solid wastes in red ceramics- an updated review. *Revista materia*, 14, 3, 881-905.

Table 1 Chemical composition of the three clays (C₁, C₂, C₃), foundry sand dust (FSD) and Waelz slag (WS).

Table 2. Mixture compositions of the three clays (C₁, C₂, C₃), foundry sand dust (FSD) and Waelz slag (WS) expressed as weight fractions.

Table 3. Emission values of the pollutants (HCl, HF and SO₂) calculated using mass balance data on compacted samples of clays (C₁, fired at 850 °C, C₂ fired at 950 °C, C₃ fired at 1050 °C), and foundry sand dust (FSD) and Waelz slag (WS) fired at all three temperatures.

Fig. 1. Thermal behaviour (DSC) from clays (C₁, C₂, C₃), foundry sand dust (FSD) and Waelz slag (WS) fired up to 1200 °C at 10 °C/min.

Fig. 2. XRD data clays: (a) C₁, (b) C₂ and (c) C₃ before and after firing at their firing temperatures (C₁ = 850 °C, C₂ = 950 °C, C₃ = 1050 °C respectively). An=anorthite; Ka=kaolinite; I=illite; Q=quartz; Ca=calcite; K-fel=Kfeldspar; Pl=Plagioclase; Do=dolomite; H=hematite; Wo=wollastonite; Ge=gehlenite; S=anhydrite.

Fig. 3. XRD data of (a) foundry sand dust (FSD) and (b) Waelz slag (WS), before and after firing at 850 °C, 950 °C and 1050 °C. Mi= mica; Be=bentonite; Q=quartz; An=anorthite; W=wustite; H=hematite, M=magnetite; S=anhydrite; CS=calcium silicate; C=Calcium oxide.

Fig. 4. Gas evolution profiles of HF, HCl, SO₂ and H₂O from the clays (C₁, C₂, C₃) fired up to 1200 °C at 10 °C/min and a dwell time of 1 hour.

Fig. 5. Gas evolution profiles of HCl, and HF from the foundry sand dust (FSD) and Waelz slag (WS) fired up to 1200 °C at fast firing (10 °C/min) and at slow firing (2 °C/min) during a dwell time of 1 hour.

Fig.6. Percentage of reduction in the content F, Cl and S resulting from firing the ten mixes (M₁ to M₁₀) given in Table 1 containing clays (C₁, C₂, C₃), foundry sand dust (FSD) and Waelz slag (WS) using the industrial firing cycles for three different clay ceramic products.

Table 1 Chemical composition of the three clays (C₁, C₂, C₃), foundry sand dust (FSD) and Waelz slag (WS)

Major oxide, wt.%								
	Analytical method	(LOQ, %) ¹	Uncertainty ²	C ₁	C ₂	C ₃	FSD	WS
SiO ₂	ICP/OES	0.03	0.01% + 3.45 %	46.55±5.19	56.35±3.15	64.22±5.78	51.02±4.39	7.15±1.45
Al ₂ O ₃		0.01	0.01% + 4.85%	15.28±1.94	16.92±1.48	16.93±2.11	12.36±1.27	3.47±0.90
Fe ₂ O ₃ **		0.01	0.01% + 2.71%	5.21±0.31	5.94±0.45	5.91±0.81	3.47±0.09	56.02±6.38
MnO		0.01	0.01% + 7.22%	0.07±0.01	0.07±0.01	0.06±0.01	0.09±0.01	2.60±0.08
MgO		0.01	0.01% + 7.94 %	2.14±0.45	4.15±0.59	0.89±0.48	2.31±0.61	3.24±0.91
CaO		0.01	0.01 + 3.48%	10.04±3.03	0.62±0.21	0.52±0.13	2.07±0.87	15.92±3.41
Na ₂ O		0.01	0.01% + 10.84%	0.59±0.11	1.11±0.24	0.58±0.15	1.93±0.15	0.78±0.12
K ₂ O		0.01	0.01% + 19.6%	3.25±0.65	3.75±0.75	3.03±0.71	0.47±0.14	0.20±0.09
TiO ₂		0.01	0% + 2.58%	0.63±0.10	0.82±0.16	0.83±0.12	0.39±0.10	0.18±0.06
P ₂ O ₅		0.02	0.01% + 65.41%	0.11±0.01	0.18±0.02	0.08±0.01	0.06±0.01	0.30±0.03
Total carbon		0.06	0.01% +3.51%	2.25±0.03	0.04*±0.00	0.11±0.01	14.54±0.20	2.54±0.50
Acid pollutants content, mg/kg								
	Analytical method	Limit of quantification (LOQ, mg/kg) ¹	Uncertainty ²	C ₁	C ₂	C ₃	FSD	WS
Total sulphur (TS)	FUS-IR	600	0.01% +3.48%	5400±455	300*±45	650±50	1900±151	14600±223
F	ISE	600	0.01% + 4.98%	350*±47	400*±47	100*±50	600±48	5150±403
Cl	INAA	100	0.01% + 4.6	350±47	250±5	250±47	1000±125	4550±309
LOI	Weight difference before and after firing ³			14.50±0.06	9.77±0.04	5.78±0.03	25.61±0.42	-1.77±0.05

**Total iron oxide content expressed as Fe₂O₃, ⁽¹⁾LOQ was calculated as 10* standard deviation of n blanks. ⁽²⁾ Uncertainty: + (x + U) of analyte value for all elements is 0.01 % except for TiO₂ (LOD= 0.001 %). ⁽³⁾ LOI was measured as the weight difference before and after firing the clays at their corresponding temperatures (C₁ at 850 °C, C₂ at 950 °C, C₃ at 1050 °C) and the wastes (FSD and WS) at all temperatures. * Values below the limit of quantification (LOQ).

Table 2. Mixture compositions of the three clays (C_1 , C_2 , C_3), foundry sand dust (FSD) and Waelz slag (WS) expressed as weight fractions.

Mixture	C_i	FSD	WS
M1	60	0	40
M2	80	0	20
M3	100	0	0
M4	80	20	0
M5	60	40	0
M6	60	20	20
M7	66.66̂	6.66̂	26.66̂
M8	86.66̂	6.66̂	6.66̂
M9	66.66̂	26.66̂	6.66̂
M10	73.33̂	13.33̂	13.33̂

Table 3. Emission values of the pollutants (HCl, HF and SO₂) calculated using mass balance data on compacted samples of clays (C₁, fired at 850 °C, C₂ fired at 950 °C, C₃ fired at 1050 °C), and foundry sand dust (FSD) and Waelz slag (WS) fired at all three temperatures.

Material	Temperature °C	Final content, mg/kg			Emissions, mg/kg		
		F	Cl	S	F	Cl	S
Limit of detection (LOD)		100	100	100			
Limit of quantification (LOQ)⁽¹⁾		600	100	600			
C ₁	850	350±50	300±48	4850±153	62	112	2929
C ₂	950	100±0.00	200±34	200*±21	362	79	265
C ₃	1050	<LOD	200±29	200*±37	≤112	67	979
FSD	850	<LOD	400±26	1600±236	≤849	971	1906
	950	<LOD	300±39	1500±113	≤849	1074	2106
	1050	<LOD	250±80	700±113	≤849	1125	3074
WS	850	5000±478	4400±287	14400±2255	158	154	300
	950	4350±245	2450±141	14400±2134	842	2159	400
	1050	3950±82	1750±150	14100±1943	1263	2879	1000

⁽¹⁾ LOQ was calculated as 10* standard deviation of n blanks.

* Values below the detection limit (LOD)

Figure 1

[Click here to download high resolution image](#)

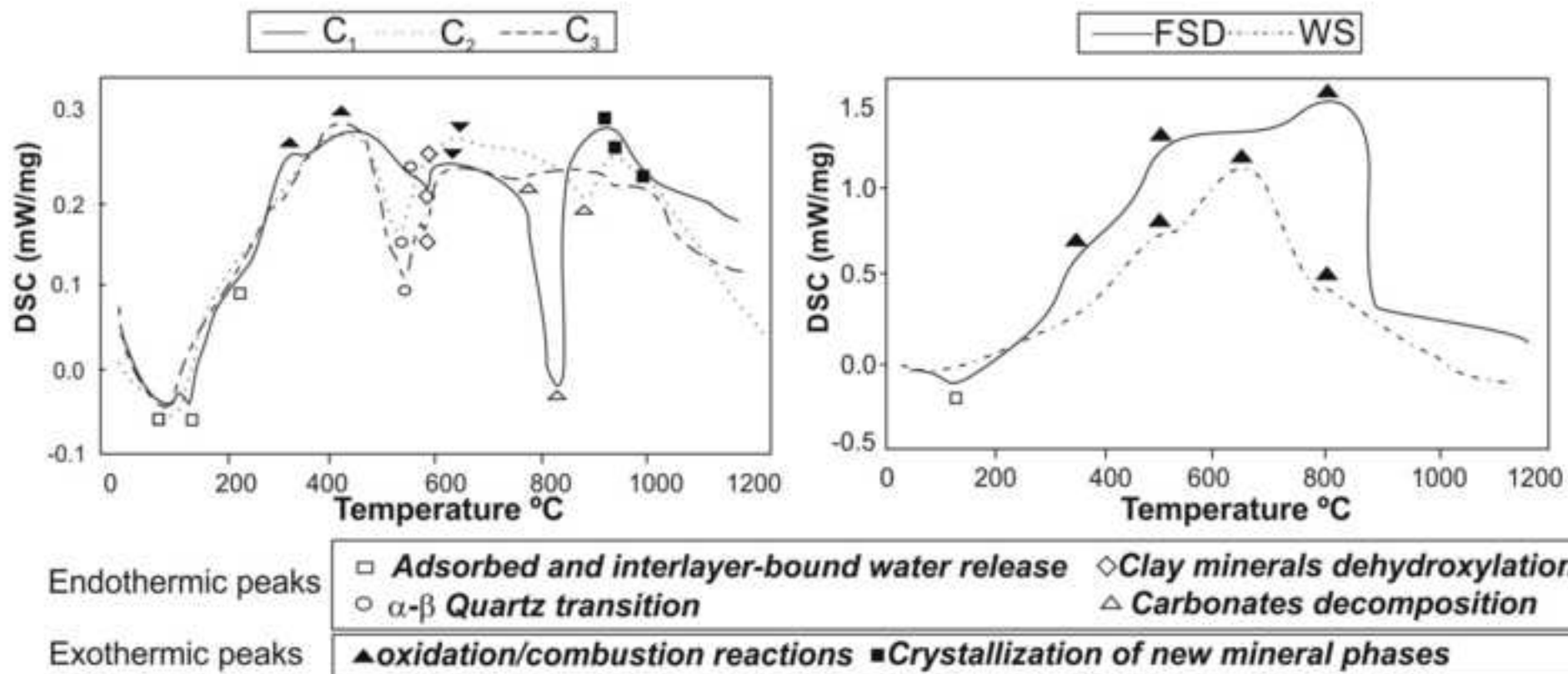


Figure 2
[Click here to download high resolution image](#)

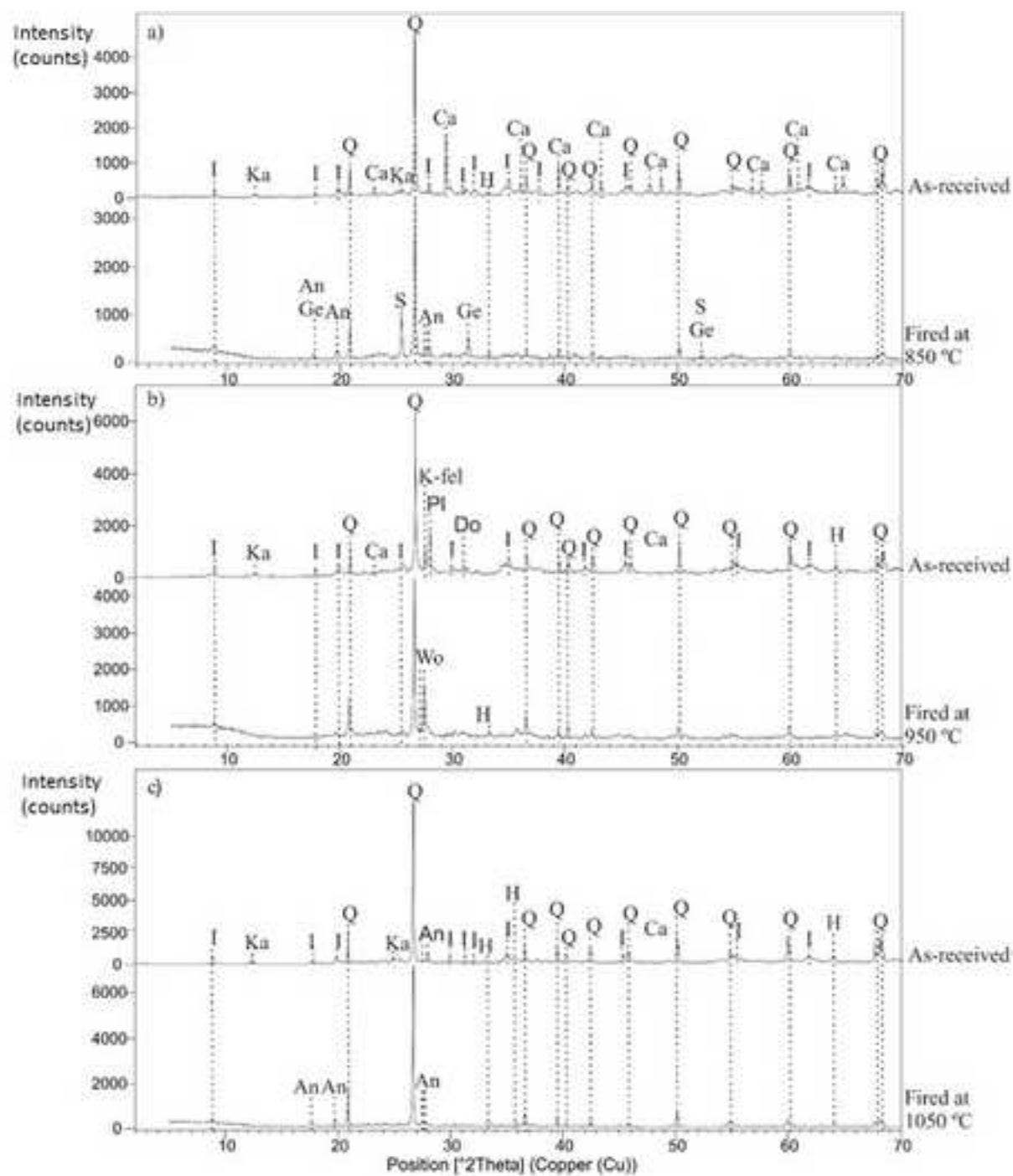


Figure 3
[Click here to download high resolution image](#)

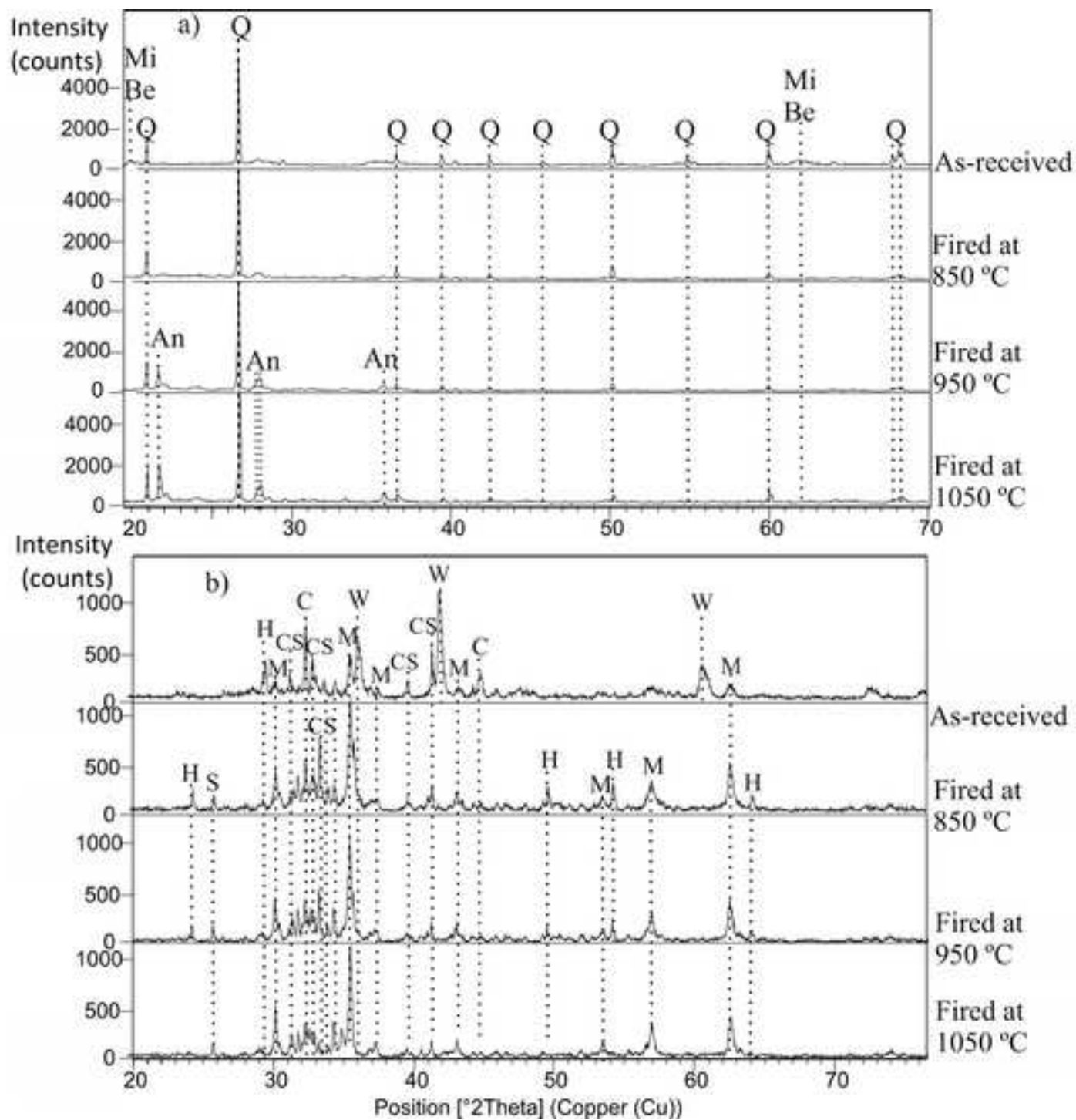


Figure 4
[Click here to download high resolution image](#)

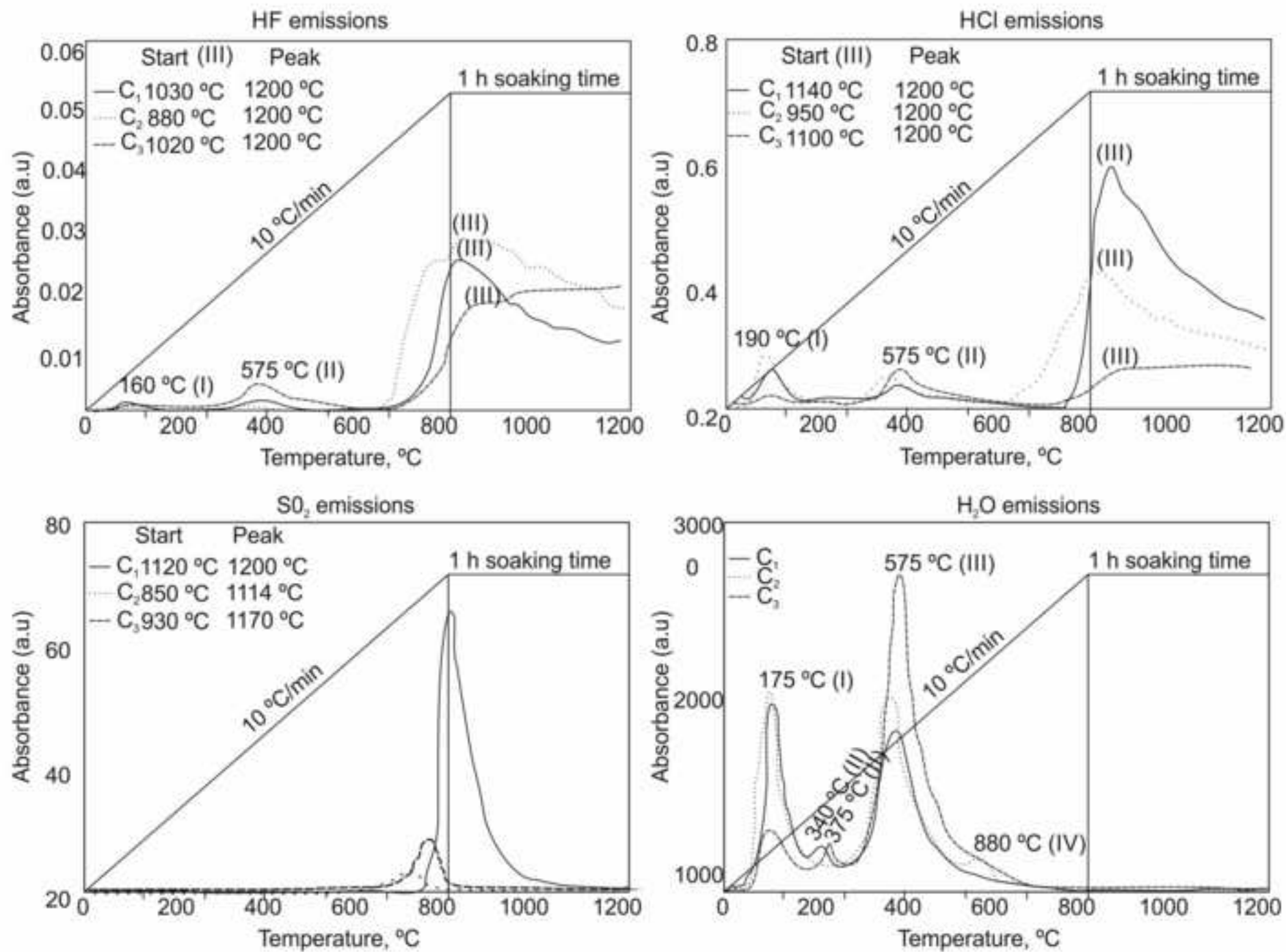


Figure 5

[Click here to download high resolution image](#)

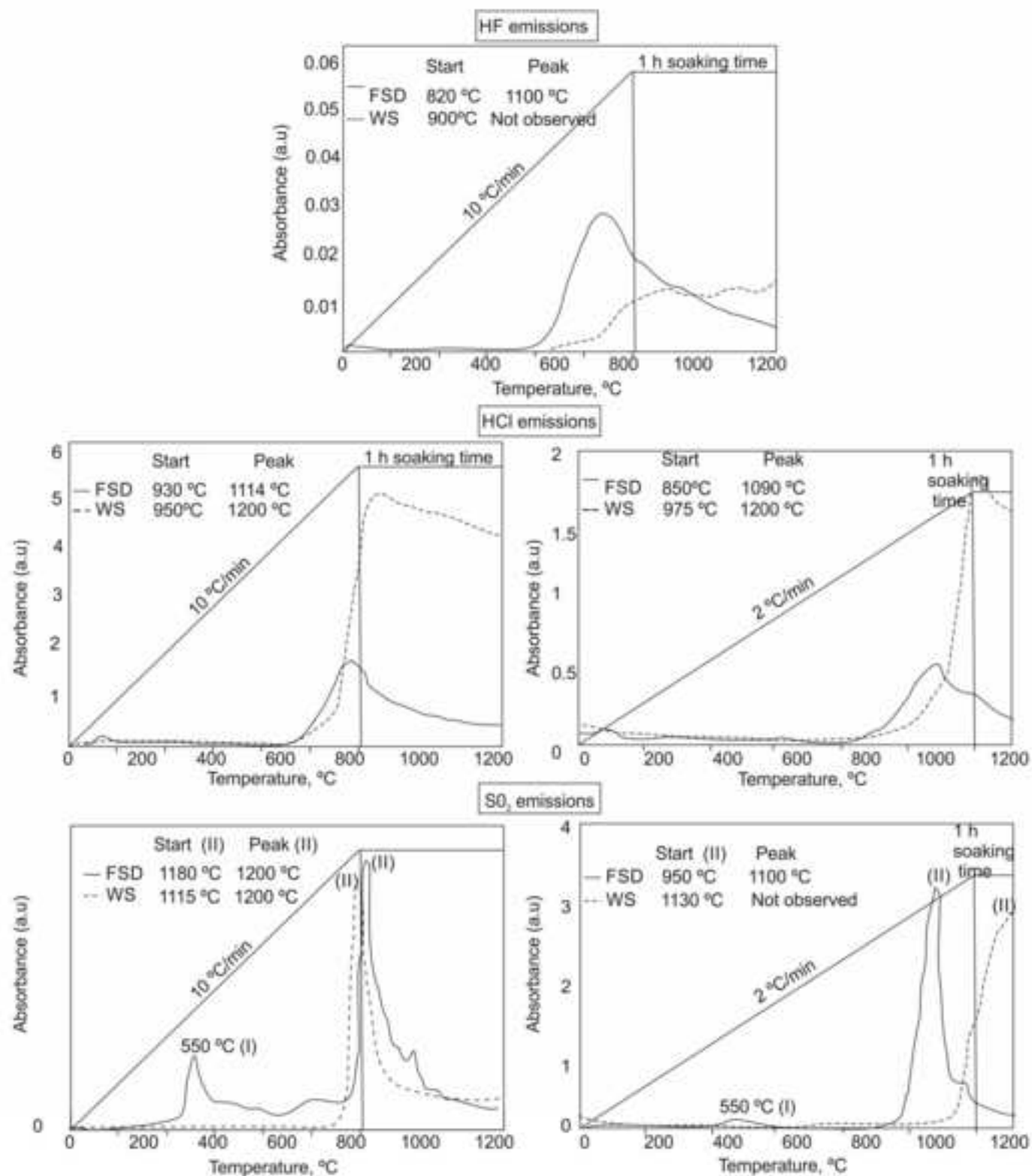
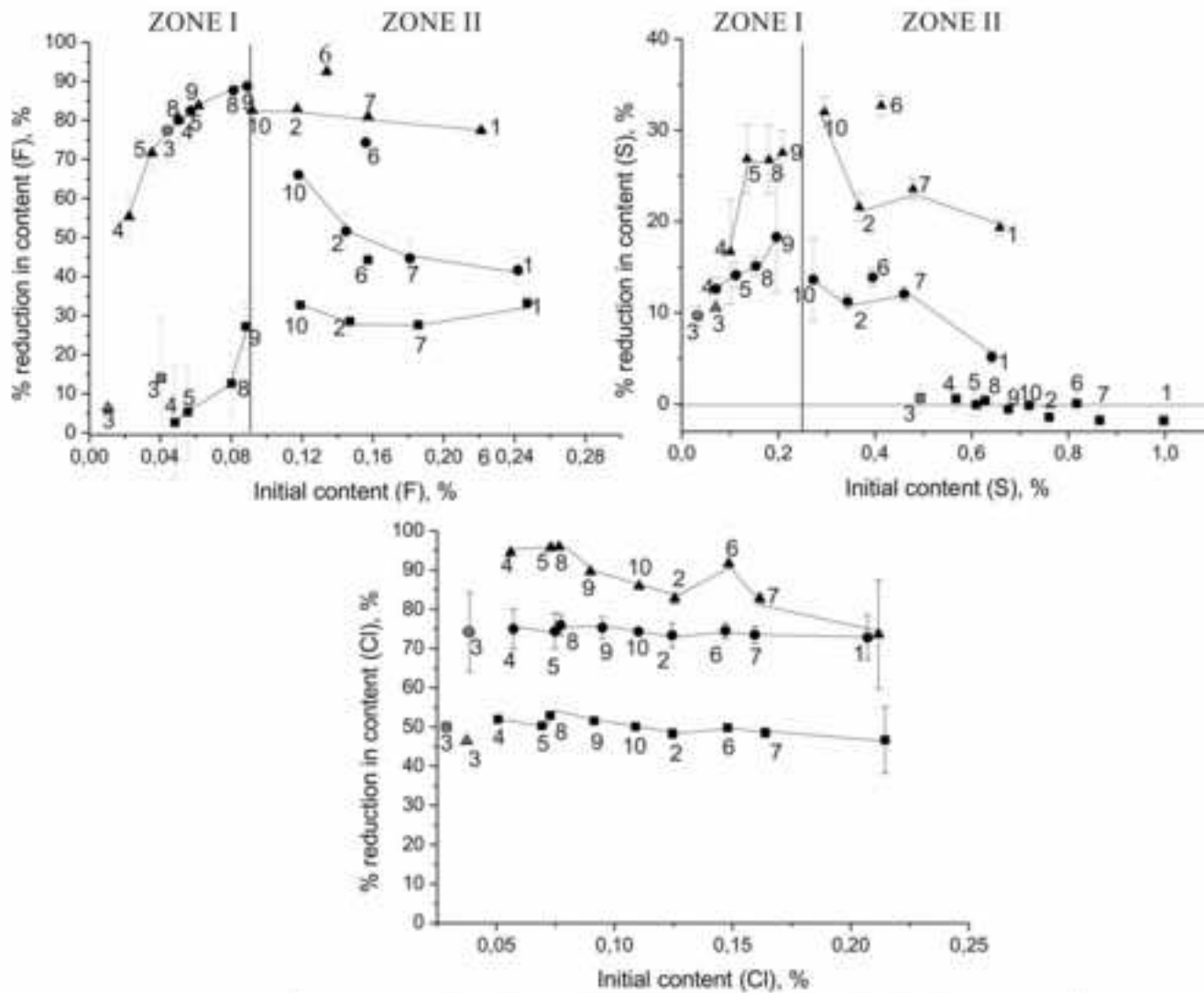


Figure 6
[Click here to download high resolution image](#)



■ Wall bricks (850 °C) ● Roof tiles (950 °C) ▲ Facing bricks (1050 °C)

	M3	Pure clay
I	M(4,5)	Binary mixtures clay-foundry sand dust (FSD)
	M(8,9)	Ternary mixtures clay-WS-FSD (High porcentaje of FSD)
II	M(1,2)	Binary mixtures clay-Waelz slag (WS)
	M(6,7)	Ternary mixtures clay-WS-FSD (High porcentaje of WS)
	M(10,6)	Ternary mixtures clay-WS-FSD (same proportion FSD-WS)