



Research article

Reduction of CO₂ diffuse emissions from the traditional ceramic industry by the addition of Si-Al raw material

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ABSTRACT

The fabrication of ceramics can produce the emission of several gases, denominated exhaust gases, and also vapours resulting from firing processes, which usually contain metals and toxic substances affecting the environment and the health of workers. Especially harmful are the diffuse emissions of CO₂, fluorine, chlorine and sulphur from the ceramics industry, which, in highly industrialized areas, can suppose an important emission focus of dangerous effects. Concerning CO₂, factories that use carbonate-rich raw materials (>30% carbonates) can emit high concentrations of CO₂ to the atmosphere. Thus, carbonate reduction or substitution with other raw materials would reduce the emissions. In this contribution, we propose the addition of Al-shales to the carbonated ceramic materials (marls) for CO₂ emission reduction, also improving the quality of the products. The employed shales are inexpensive materials of large reserves in SW-Spain. The ceramic bodies prepared with the addition of selected Al-shale to marls in variable proportions resulted in a 40%–65% CO₂ emission reduction. In addition, this research underlines at the same time that the use of a low-price raw material can also contribute to obtaining products with higher added value.

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1. Introduction

The European ceramics industry is highly committed to achieving the targets set by the European Climate Change policies because these are some of the most important challenges faced by the energy sector. Improving environmental quality is a priority of the EU. In recent years, there have been a variety of specific programs of policy and action in relation to the environment, to address greenhouse gases causing global warming. Within these programs, the allowances for emitting tons of CO₂ in the EU countries were assigned according to the commitments made under the Kyoto Protocol. Among the industrial sectors involved in this assignment are ceramic bricks and tiles, and the clinker industries. Therefore, one of the main challenges for the future of research in ceramics is the protection of the environment in its entirety. To meet this objective, some studies have determined the amounts of harmful gases derived from the raw materials that can be emitted during the firing processes, as well as the factors that

may be involved in these emissions (Fabbri, 1991; Galán et al., 2002; García-Ten et al., 2006; González et al., 2006, 2008; 2009, 2011; 2014; Bonvicini et al., 2006; Mezquita et al., 2009; Monfort et al., 2008, 2010; 2011; Vicente et al., 2012). Studies proposing other alternatives to reduce these emissions are still necessary for environmental protection.

In Spain, most ceramics companies do not exceed the pollution thresholds for CO₂ emissions. Only 36 ceramics plants are part of the emissions trading system, including 8 exceeding the thresholds required for the firing process of ceramic products, and the rest of them for having combustion plants exceeding 20 MW (Mezquita et al., 2009). The problems of CO₂ diffuse emissions in structural ceramics factories are linked to the high carbonate content derived from some raw materials (process emissions). Some of them, such as marl and clay, which are traditionally used for structural building materials, can contain high percentages of carbonates; when the content is over 20%, they can be problematic due to the high CO₂ emissions during the firing processes (González et al., 2011). Emissions from the decomposition of carbonates vary according to their contents in the raw material, being 62 kg CO₂/t in materials for tiles, 15 kg CO₂/t for glazed tile, and 1 kg CO₂/t in porcelain tile (Mezquita et al., 2009).

According to this, it is necessary that the structural ceramics

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sector join efforts to reduce CO₂ emissions in the manufacturing process of their products to meet their emission reduction commitments for the period 2013–2020 (Gabaldón Estevan et al., 2014). The options will be focused on changing the type of fuel, on recovering cooling gases (Mezquita et al., 2014) or in using new formulations of the raw materials. In the first case, an effective measure was to replace coal by natural gas (Peng et al., 2012).

Concerning the use of new formulations, it was found that when adding 257.7 t CaSiO₃ (wollastonite) to the manufacturing process, 44 t CO₂ was not emitted (Del Águila, 2013). The problem arises because of the high price of this mineral, which makes it economically not profitable to use these mixtures. Other researches propose the addition of Mg, Ca, Sr or Ba carbonates (García-Ten et al., 2011). In all cases cited, the addition of new components to the raw material involves a high cost for the companies. Other cheaper solution is to incorporate some appropriate wastes to the ceramic body. For instance, Faria et al. (2012) showed that CO₂ emissions decrease when sanitary ware mass wastes were incorporated into red clays.

This research studied the Neogene marine sediments of the Guadalquivir Basin used in Andalucía (S. Spain) for the production of structural ceramics, which are usually clays and marls that can emit very high amounts of CO₂ during the firing processes. The environmental problem can become serious in areas where there is a high concentration of industries and the production exceeds 75 t/day (González et al., 2011). With the aim of reducing these emissions, new formulations are proposed in this paper based on the addition of non-contaminating raw materials, consisting of Paleozoic Al-shales from southwest Spain, which do not contain carbonates (Galán and Martín Vivaldi, 1974; Mesa, 1986). The purpose of these formulations was also to obtain competitive ceramic products from such mixtures. The new formulations were prepared on the basis of the chemical-mineralogical knowledge of the raw materials.

2. Materials and methods

2.1. Previous studies on the raw materials

In a preliminary study (González et al., 2016), a composed marl sample, which is representative of most of the Andalusian industries, was selected (sample M) and characterized. The sample consists of quartz (~15–20%), carbonates (30–35%), and phyllosilicates (50–55%). The fine fraction (<2 µm) is composed of kaolinite, illite and smectite in equivalent proportions. Marls of the Seville province, and the Guadalquivir basin, have been previously studied (González et al., 1998; García Valdecasas et al., 1980; González García y García Ramos, 1966).

Concerning the Al-shales, two non-mined quarries, Alange and Zarza de Alange (Badajoz), were sampled, and because of the large lateral facies variation, several samples were collected from each. The Alange samples are composed of 70% phyllosilicates as major minerals. The fraction less than 20 µm is composed of kaolinite (50–60%), sericite (16–50%), pyrophyllite (<5%), and quartz and feldspar in smaller proportions. The shales from Zarza de Alange have lower contents of phyllosilicates (30–45%), and higher quartz (40–60%) and feldspar (<5%). In some samples, alunite was determined up to 15%. The mineralogy of the fine fraction is composed of sericite (15–40%), kaolinite (10–15%) and pyrophyllite (5–20%). These materials were classified as sericitic/kaolinic shales (Galán and Martín Vivaldi, 1974; Mesa, 1986) or pyrophyllite shales by Sánchez-Soto and Pérez Rodríguez (1998).

In González et al. (2016), 5 mixtures of these marls and shales were tested, according to three premises: a) the percent of Al-clay in the mixture should not exceed 50% to avoid increasing the cost of

the final product due to its refractory nature, b) the samples should have optimal plasticity to ensure good moulding behaviour, and c) the chemical and mineralogical compositions should be suitable based on the theoretical diagrams. After testing their possibilities it was advisable to use the mixtures to fabricate monoporosa or white (mixtures X1, X2 and X3) or red (mixtures X4 and X5) birapida fired products.

The emissions of those mixtures during heating were studied in the present research, particularly the CO₂ ones.

2.2. Determination of CO₂, F, Cl and S

The determinations of CO₂, F, Cl and S were made in the raw materials and mixtures fired at different temperatures. The carbonate content was measured by a Bernard calcimeter, following UNE 103-200-93 modified by the addition of FeCl₂·4H₂O to HCl to prevent interference between organic materials and inorganic carbonates (Allison and Moodie, 1965). Triplicate measurements were taken after 30 s for determining the content of calcite and after 30 min for total inorganic carbon (calcite + dolomite). Because calcite and dolomite coexist in the beginning, both minerals are reacting and the amount of each mineral cannot be calculated exactly. However, although the contents of calcite and dolomite may vary slightly, the final result as wt% of CO₂ remains constant. This technique was selected because there is a high correlation ($r^2 = 0.93$) between the results obtained by the Bernard calcimeter and elemental microanalysis provided for the determination of carbon in samples of similar characteristics (González et al., 2011).

The content of organic matter was determined in selected samples of shale by the method of Walkley-Black (1934). This method is based on the oxidation of organic matter with potassium dichromate. The excess of oxidant was titrated with ferrous-ammonium sulphate (Mohr's salt), and the amount of organic carbon is calculated from the amount of dichromate reduced. The reaction is basically an oxidation of organic carbon, which becomes carbon dioxide. The stirred sample in the presence of H₂SO₄ allows oxygen to come in contact with the organic matter, and the heat coming from sulphuric acid dissolution supplies the energy needed for the oxidation. The method has a detection limit of approximately 0.10% in homogeneous materials, and it is generally reproducible with errors as low as 8% (Nelson and Sommers, 1982). The determinations were made in triplicate to obtain the mean value.

F and Cl were determined by X-ray fluorescence (XRF) in samples prepared in pressed powder pearls (12 g sample/wax 3 g), and S was determined by preparation of glass disks (0.8 g sample/7.2 g of lithium metaborate/lithium tetraborate in proportions of 34–66%).

Emission values have been obtained by differences among emissions at different temperatures.

2.3. Chemical and mineralogical composition

The chemical of the new formulations was carried out by XRF in an AXIOS equipment, at the I+D+I laboratories of Seville University (CITIUS). Uncertainties, detection and quantification limits can be extracted from <https://investigacion.us.es/scisi/sgi/servicios/area-de-rayosx/areas-aplicacion>.

The mineralogical characterization of the new formulations and the fired products were performed by X-ray diffraction (XRD) with a Bruker D8 Advance instrument (using Cu-K α radiation and nickel filter, with 40 kV and 20 mA). The total sample was analysed by the powder method; the samples were mounted in a side-holder to avoid preferred orientations. The qualitative mineralogical composition was completed by the study of orientated aggregates of the <2 µm and <20 µm fractions with the following treatments:

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