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Alkaline activation of ceramic waste materials

L. Reig¹, M.M. Tashima², L. Soriano², M.V. Borrachero², J. Monzó², J. Payá²

¹ EMC, Universitat Jaume I, Av. Sos Baynat s/n 12071 Castelló de la Plana, Spain

² Instituto de Ciencia y Tecnología del Hormigón (ICITECH), Universitat Politècnica de València, Camino de Vera s/n 46022 Valencia, Spain.

Corresponding author: L. Reig; lreig@uji.es

Tel.: +34 96 472 9163

Fax: +34 96 472 81 06

E-mail addresses: lreig@uji.es; maumitta@hotmail.com; lousomar@gmail.com; vborrachero@cst.upv.es; jmmonzo@cst.upv.es; jjpaya@cst.upv.es

Abstract

Ceramic materials represent around 45% of construction and demolition waste, and originate not only from the building process, but also as bricks and tiles rejected from the industry. Despite the fact that these wastes are mostly used as road sub-base or construction backfill materials, they can also be employed as supplementary cementitious materials, or even as raw material for alkali-activated binders. The aim of this research was to investigate the properties and microstructure of alkali-activated cement pastes and mortars produced from ceramic waste materials of various origins. Sodium hydroxide and sodium silicate were used to prepare the activating solution. The compressive strength of the developed mortars ranged between 22 and 41 MPa after 7 days of curing at 65°C, depending on the sodium concentration in the solution and the water/binder ratio. These results demonstrate the possibility of using alkali-activated ceramic materials in building applications.

Keywords: Ceramic waste, Waste management, Alkaline activation, Compressive strength.

1 Introduction

The Portland cement clinker is the dominant binder used in concrete, however, its production requires approximately 850 Kcal and involves the emission of near 0.8-1.0 kg of CO₂ per kg of cement produced [1]. The cement industry, together with the scientific community, is actively seeking alternatives to reduce the energy involved in the cement production, produce low-CO₂ binders and reuse waste materials from other industries.

There is a large amount of ceramic wastes in Spain, and they are generated not only by the industry, but also by the construction sector. According to [2], in Spain approximately 950 kg per person/year were originated in the construction sector in 2007, and this amount decreased in subsequent years due to the crisis (520 kg per person/year in 2009). About 45% of the construction and demolition wastes are ceramic in nature. Regarding the production of ceramic materials, different categories can be distinguished in accordance with the source of raw materials: structural ceramic products (i.e. bricks, roofing tiles, vaults...), ceramic tiles and sanitary ware. As reported by HYSPLIT, the Spanish Association of Manufacturers of Bricks and Clay Roofing Tiles, the manufacture of structural ceramics increased progressively from 1994 to 2006, when almost 30 million tonnes were manufactured. The production rate dramatically decreased since then, and only 7.7 mill tonnes were made in 2010. On the other hand, the Ceramic World Review survey [3] reported a world tile production of 9515 billion square meters in 2010, being 96.0% of them (9170 Sq.m Bill.) covered by the 30 major manufacturing countries. Although the Spanish industry recorded a decrease in production close to 40% from 2006 to 2010 (608 to 366 Sq.m Mill., respectively), it still ranked seventh on the list of manufacturers in year 2010, with 3.8 % of the total world production. Due to the consumption of the Spanish market diminished by 54 % since 2006, two thirds of the manufactured tiles were exported.

Although a huge part of the ceramic wastes is used in landfills, with low added value, prior research has proved its suitability in concrete and as cementitious materials. In the studies performed by Medina et al. [4], up to 25% of the natural coarse aggregates were replaced by ceramic sanitary ware wastes to obtain concrete with structural purposes. Similarly, Pacheco-Torgal and Jalali [5] observed a slight increase in water absorption and permeability when replacing traditional coarse aggregates by ceramic wastes, and a superior durability when the traditional sand was replaced. On the other hand, the potential of ceramic wastes to produce pozzolanic cements was also confirmed in several studies [6-9]. Among them, Puertas et al. [7] not only successfully used up to 35% of certain types of ceramic wastes as pozzolan admixtures, but also proved their suitability as raw materials for the manufacture of Portland cement clinker.

Although ceramic materials can be used as cement admixtures and concrete aggregates, in these applications only a portion of the cement is replaced (usually 10 to 35%) so, it is interesting to develop binders made entirely or almost entirely from waste materials [10]. This can be achieved by the alkali activation process. A conceptual model of the reaction processes involved was proposed by van Deventer et al. [11] for the metakaolin system. An aluminosilicate-based material is dissolved by a highly concentrated alkali hydroxide and silicate solution, originating sodium or potassium silicate and aluminate monomers. These precipitate and form an alkali-aluminosilicate gel (amorphous) and sites for the nucleation of zeolitic type phases (nanocrystalline), originated by the transformation of the gel. As Deventer et al. pointed out [11], the reaction mechanism is modified depending on the chemistry of the raw material.

The success of converting waste materials to useful products following this process has been extensively proved in materials such as silicoaluminous fly ash, metakaolin or blast furnace slag [12-14], and its suitability has also been confirmed for other waste materials, such as hydrated-carbonated cement [15], glass [16] or ceramic materials [17-19]. In the study performed by Puertas et al. [17], six different ceramic wastes were mixed with NaOH and sodium silicate solution, giving a maximum compressive strength of 13 MPa for pastes cured for 8 days at 40 °C. Mortars with similar compressive strengths (14 MPa) were obtained by Reig et al. [18,19] by mixing red hollow bricks powder with a NaOH solution and curing the samples for 7 days at 65°C. However, further research must be done in order to understand the influence of the alkali activator on the alkali activation process of different ceramic materials. From an environmental point of view, the cement industry has been considered unfriendly and highly pollutant. This is because Portland cement clinker production requires a lot of energy (850 Kcal per kg of clinker) and involves the emission of large amounts of greenhouse gases into the atmosphere (near 0.8-1.0 ton of CO₂ per ton of produced clinker) [1]. Different solutions have been proposed by the scientific community [1-5] to reduce both the damage to the environment and the emission of polluting gases. Among them, the alkali activation process [6-8] has been successfully employed to develop binders by a reaction between aluminosilicate based materials and highly concentrated alkali hydroxide and silicate solutions.

A conceptual model of the reaction processes involved in geopolymerisation was proposed by van Deventer et al. [9] for the metakaolin system. As explained, the aluminosilicate source is dissolved by the activating solution during the polycondensation reaction, originating sodium or potassium silicate and aluminate monomers. These precipitate and form an alkali-aluminosilicate gel (amorphous) and sites for the nucleation of zeolitic type phases (nanocrystalline), originated by the transformation of the gel. As pointed out by the authors, the reaction

~~mechanism is modified depending on the chemistry of the raw material.~~

~~The success of the geopolymerisation process has been extensively proved in materials such as silicoaluminous fly ash, metakaolin or blast furnace slag [7,10,11], and its suitability has also been confirmed for other waste materials [6,12-14]. In this sense, the construction sector originates an important volume of wastes, which has been estimated to be 800 kg per person/year in 2007 [15]. Building wastes are generated not only by industry, but also during the building process, and are about 45% ceramic in nature [15,16]. Despite most of them being used as road sub-base filling materials with low added value, prior research works [3,5,12,13,17] have proved their suitability as cementitious materials. However, there is a large amount of ceramic products whose properties and microstructure depend mainly on clay composition and the sintering temperature.~~

~~To that purpose, In this research,~~ two different ceramic products, with very different sintering temperatures and chemical compositions, have been selected: red clay bricks, and porcelain stoneware. While the former are sintered at temperatures ranging from 800°C to 1000°C [179], porcelain tiles are usually **sintered burnt** at between 1190°C and 1220°C [1820]. According to Baronio and Binda [1921], powder from bricks is expected to present pozzolanic activity due to the destruction of the crystalline network when the structural hydroxyl groups of clay minerals (phyllosilicates or sheet silicates) are lost (600°C -900°C). [According to the study performed by Zanelli et al. \[22\], which analysed 93 porcelain stoneware samples,](#) ~~p~~Porcelain tiles are also presumed to react [according to the study performed by Zanelli et al. \[2022\], which analysed 93 porcelain stoneware samples.](#) Their mineralogy is composed of some crystalline phases, such as quartz, mullite or feldspars, which are dispersed through a main vitreous phase whose proportion varies from 40% to 80% depending on the sample.

The aim of this research was to develop ~~geopolymeric~~ binders by the alkali activation of two different ceramic waste materials (porous red clay brick and porcelain stoneware) and to analyse the influence of the alkali activator concentration on the mechanical strength and microstructure of the binders formed.

2 Experimental

2.1. Materials

Two different ceramic waste materials were used for the ~~geopolymerisation-alkaline activation~~ process: red clay brick (B) and porcelain stoneware (P). The materials were crushed in a jaw crusher to obtain a particle diameter

less than 4 mm. This granulated material was then ground in a laboratory-type ball mill (alumina medium, 40 min). Particle size distribution was measured using a laser analyzer (Mastersizer 2000, Malvern Instruments). Figure 1 presents both cumulative curves. As shown, both powders present a similar particle distribution, with particles ranging from 0.2 to 100 μm , 90% in volume under 50 μm , and almost 7% had a diameter under 1 μm . Despite both ceramic materials presenting a mean particle diameter close to 20 microns, a slightly larger amount of thinner particles (under 10 micron) was observed in the red clay brick powder.

In Figure 2, both ground materials were examined by scanning electron microscopy (JEOL JSM-6300). The irregular shape of the milled particles is observed and particles showed no significant porosity.

The chemical composition of the milled samples was determined by X-ray fluorescence analysis (XRF). As shown in Table 1, the amount of SiO_2 is larger in the porcelain waste (71% versus 51%), while the presence of other compounds, such as CaO , K_2O , MgO and Fe_2O_3 , is barely noticeable. In fact, 94% of the porcelain stoneware is composed of SiO_2 , Al_2O_3 and Na_2O . For red clay brick waste, the sum of silica, alumina and sodium oxide is less than 70%. In both cases, loss on ignition (LOI) is less than 2%.

The mineralogical composition of the raw materials was determined by XRD in a Philips diffractometer PW1710 with $\text{Cu K}\alpha$ radiation under the routine conditions of 40 Kv and 20 mA, from 5-55° (2 θ). As shown in Figure 3, the major crystalline phase is quartz (SiO_2 , PDFcard 331161), which was found in both waste materials. Other compounds previously reported in the mineralogy of ceramic materials [53,172], such as mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$, PDFcard 150776), anortite ($\text{CaAl}_2\text{Si}_2\text{O}_8$, PDFcard 100489), wollastonite (CaSiO_3 , PDFcard 350755), gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$, PDFcard 350755) or celite ($\text{Ca}_3\text{Al}_2\text{O}_6$, PDFcard 320148), were found in minor quantities. Mullite, an important constituent in porcelain material [223], was found in the porcelain stoneware powder.

2.2. Preparation of paste and mortar samples

In order to develop the alkali-activated binders, the ceramic waste materials were mixed with an alkaline solution. The activating solution was prepared by dissolving sodium hydroxide pellets (Panreac, 98% purity) with water and a sodium silicate solution (Merck, Waterglass $\text{SiO}_2=28\%$, $\text{Na}_2\text{O}=8\%$, $\text{H}_2\text{O}=64\%$).

Paste samples were obtained by mixing ground ceramic with the required alkaline solution for 4 min and were

cast in plastic containers. Mortar samples were prepared by mixing the ceramic material with the activating solution for 2 min. Siliceous sand (4.36 modulus fineness and maximum particle diameter of 2 mm) was then added and the mixing process was continued for an additional 3.5-min period. The formed mortar samples were placed into a mould and were vibrated for 4 min. Both pastes and mortars were stored in a thermostatically controlled bath at 65°C at 100% relative humidity for 7 days.

The mix proportions used in this study are summarised in Table 2. Mixes are coded as 'x/ω/m/r-c', where x is the type of ceramic waste (binder: B=brick and P=porcelain), ω is the amount of water per 100g of binder, m is the molality (mol/kg) of Na⁺ in the activating solution, r is the SiO₂/Na₂O molar ratio in the activating solution and -c is the percentage of Ca(OH)₂ (93% purity) used as a replacement of ceramic waste.

A water/binder (w/b) ratio of 0.45 was used for the samples made with brick, which was lowered in samples 'B/40/8.0/1.60' and 'B/35/9.0/1.60' to analyse the influence of this parameter (w/b). Due to the reduced water absorption of the porcelain stoneware (less than 0.5%) [2324], the w/b ratio was lowered to 0.35 for all the porcelain waste mixes. A binder/sand (b/s) ratio of 1:3 was used for all the mortars tested in this paper (see Table 2).

2.3. Sample testing

Compressive strength was determined on the alkali-activated mortars following the UNE EN 196-1 standard. The microstructure was examined on paste samples using SEM-EDX (JEOL JSM-6300) and mineralogical phases were identified by X-ray diffraction XRD. Thermogravimetry (TG, TGA-850 Mettler-Toledo thermobalance) was done to determine the mass loss of samples in an N₂ atmosphere using sealed pinholed aluminium crucibles at a heating rate of 10°C min⁻¹. Tests were run from 35°C to 600°C to assess the mass loss related to bonded water molecules or hydroxyl groups in the pastes. Samples were taken at 7 days of curing at 65°C at 95-100% relative humidity.

3 Results and Discussion

3.1. Alkali activation of porcelain stoneware waste: Preliminary study

Alkali-activated cement pastes and mortars using NaOH and sodium silicate solutions as activators were

prepared by employing porcelain stoneware powder and after taking into account that the water demand for this residue was lesser than that found for red clay brick. Thus, the water/binder ratio was fixed as 0.35. Sodium molality and the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio varied within the ranges of 6.5-8.5 and 1.12-2.13, respectively. Table 3 summarises the behaviour of the fresh pastes developed with the porcelain waste. ~~In some mixtures, an extra amount of calcium hydroxide (93% purity) was used.~~ As regards the setting of pastes, a strong dependence on the amount of $\text{Ca}(\text{OH})_2$ was observed so that only those mortars with 2% calcium hydroxide (replacing the porcelain stoneware powder) set during the first 24 hours. While mortars without calcium hydroxide did not harden, the setting time for those whose calcium hydroxide contents were higher than 5% was so low that samples could not be placed into the mould. The presence of soluble calcium in the binding material was necessary to produce a stable matrix after curing, which is in agreement with [2425,265], who observed that deficiencies in the CaO content of the raw material can be compensated by adding mineral additives.

3.2. Compressive strength development

3.2.1. Effect of Na^+ concentration on the alkali activation of ceramic waste

The compressive strength of the mortars mixed at a constant ' $\text{SiO}_2/\text{Na}_2\text{O}$ ' ratio (1.60) and different Na^+ concentrations (6.0 to 9.0 mol.kg⁻¹) is depicted in Figure 4. For the activation of the porcelain stoneware-based mortars, and according to Section 3.1, 2% of the waste material was replaced with $\text{Ca}(\text{OH})_2$. Furthermore, the presence of $\text{Ca}(\text{OH})_2$ was not necessary for the alkali-activated red clay brick based mixtures. The mortars containing B waste presented the highest compressive strength for a sodium concentration in the 6-7 mol/kg range. However, the mechanical strength of porcelain mortars increased with alkali concentration. These results agree with the studies reported by Provis et al. [276], who observed that the optimum activator concentration depends on the precursor, and that this must be the case to balance the charges of tetrahedral Si and Al, thus avoiding the presence of unreacted sodium or silica. Duxson et al.[287] and Tashima et al. [298] also found an optimal concentration for the alkali activation of metakaolin and the fluid catalytic cracking catalyst residue, respectively.

3.2.2. Influence of Na^+ concentration and the water/binder (w/b) ratio on alkali-activated red clay brick waste

In order to assess the effect of the amount of water on the activating solution, clay brick-containing mortars were

prepared with a w/b ratio within the 0.45-0.35 range. Although low workability was observed when reducing the quantity of water, it was sufficient to allow the mortars to be cast into the mould. As observed in Figure 5, compressive strength increased by more than 40% when the w/b ratio lowered from 0.45 to 0.35, meaning that the amount of water was still sufficient to effectively wet the brick particles. According to Komnitsas et al. [2930], enhanced compressive strength may be motivated by the lesser available amount of free water after the hydration process, which is expected to diffuse or evaporate, leading to pores and cracks.

Good compressive strength behaviour when lowering the w/b ratio also implies an improvement from the environmental point of view since better mechanical behaviour is obtained while keeping the 'Na⁺/binder' and 'SiO₂/binder' ratios constant (3.15 mol of Na⁺ and 2.53 mol of SiO₂ per kg of ceramic waste).

3.3. Scanning electron microscopy studies

The microstructure of pastes obtained by the alkali activation of bricks and porcelain stoneware powders is represented in Figure 6. Both matrixes look denser for larger amounts of sodium, and porcelain is more compact for a given sodium molality. However, brick pastes presented areas with a high sodium concentration (detected by EDS), which became more frequent in sample 'B/45/9/1.60' (9 mol/kgmolal). These results are connected with the mechanical properties of brick mortars, suggesting that excess sodium is provided for concentrations higher than 7 mol/kg. Conversely, porcelain pastes looked denser with increasing sodium contents, which is consistent with the compressive strength presented by mortars. This suggests that even higher sodium concentrations may develop a denser microstructure, leading to higher compressive strength values.

Furthermore, all the pastes presented unreacted particles surrounded by hydration products. According to the results obtained by Kourti et al. [416], porcelain particles are expected to influence the mechanical properties of the matrix more positively as they are stronger and better bonded to the matrix than the red clay brick particles.

3.4. X-Ray diffraction studies

The diffraction patterns of the pastes obtained by the alkali activation of brick and porcelain wastes are presented in Figures 7 a and b, respectively. The XRD data of the ground material were plotted for comparison purposes. As observed, the identifiable crystalline phases in the raw material were not completely dissolved by the alkaline solution, and most remained in the activated binder. Only wollastonite and gehlenite, found in minor quantities in ground brick, were not identified in the activated pastes. Moreover, the amount of amorphous phases slightly

increased in the porcelain binder when compared to the raw material, whose content increased with the highest sodium concentration (9 ~~mol/kg~~molal).

Minor quantities of sodium carbonate (natrite, Na_2CO_3) were identified only in brick paste 'B/45/9/1.60'. This corroborates that a concentration of 9 ~~mol/kg~~molal provides brick samples with excess sodium which, according to Provis et al. [2627], can lead to the formation of carbonate salts from atmospheric carbonation.

3.5. Thermogravimetric analysis of pastes

The differential thermogravimetric curves and the total mass loss of alkali-activated brick and porcelain pastes are represented in Figure 8. As observed, all the pastes presented a similar total mass loss, which increased with a higher sodium molality in the solution. According to Bernal et al. [3031], this behaviour can be attributed to a stronger presence of OH^- groups provided by the NaOH in the activating solution.

All the pastes showed a single peak centred at approximately 130°C, which was attributed to the loss of the bound water of the pastes in [2829,312]. Despite several authors [911,139,319,332] having identified zeolitic reaction products in alkali-activated binders, no zeolitic signals were recognised by thermogravimetry as, according to Bernal et al. [319], they tend to overlap with the peak centred at 130°C. Likewise, the TG analyses were unable to identify sodium carbonates because their decomposition occurs at temperatures higher than 600°C [319]. Additionally for the porcelain stoneware containing pastes, no $\text{Ca}(\text{OH})_2$ decomposition was detected at a high temperature (500-600°C), suggesting that this reagent was totally consumed during matrix formation.

4. Conclusions

Alkali-activated binders have been obtained through the alkali activation of two different ceramic waste materials. During the alkali activation process of porcelain stoneware, the addition of $\text{Ca}(\text{OH})_2$ proved an essential ~~parameter~~constituent, and only samples with 2% of this reagent could be obtained. The optimum mix for the alkali-activated porcelain stoneware was 'P/35/9/1.60-2' (9 ~~mol/kg~~molal), which gives mortars with compressive strengths close to 30 MPa after 7 curing days at 65°C. Conversely for the red clay brick powder, the best compressive strength was obtained for mortar 'B/45/7/1.60' (7 mol/kg), which diminishes for higher sodium concentrations. A great influence of the w/b ratio on compressive strength was observed for brick mortars as it

increased by 40% (29 to 41 MPa) when the w/b ratio lowered (from 0.45 to 0.35) and the 'activator/binder' ratio remained constant. Further research must be conducted in order to completely understand the influence of calcium on the properties of the binder developed by the alkali activation of porcelain waste and to obtain mixtures with settings at room temperature.

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