Portland blended cements: demolition ceramic waste management

M.A. Trezza, S. Zito, A. Tironi, E.F. Irassar, V.F. Rahhal
Facultad de Ingeniería, CIFICEN (CONICET –UNCPBA), (Buenos Aires, Argentina).
mtrezza@fi o.unicen.edu.ar

ABSTRACT: Demolition ceramic wastes (DCWs) were investigated in order to determine their potential use as supplementary cementitious materials in Portland Blended Cements (PBCs). For this purpose, three ceramic wastes were investigated. After characterization of the materials used, the effect of ceramic waste replacement (8, 24 and 40% by mass) was analyzed. Pozzolanic activity, hydration progress, workability and compressive strength were determined at 2, 7 and 28 days. The results showed that the ground wastes behave as filler at an early age, but as hydration progresses, the pozzolanic activity of ceramic waste contributes to the strength requirement.

KEYWORDS: Portland cement; Demolition ceramic waste; Pozzolane; Characterization

RESUMEN: Cementos Portland con adiciones: manejo de residuos cerámicos de demolición. Se estudiaron residuos cerámicos de demolición (DCWs) a fin de determinar su potencial uso como materiales cementicios suplementarios en cementos mezcla (PBC). Para este propósito, se investigaron tres residuos cerámicos. Luego de la caracterización de los materiales a utilizar, se analizó el efecto del reemplazo por residuos cerámico (8, 24 y 40% en peso). Se estudió la actividad puzolánica, el progreso de la hidratación, la trabajabilidad y la resistencia a compresión a 2, 7 y 28 días. Los resultados mostraron que los residuos molidos se comportaron como fillers a edades tempranas, pero con el progreso de la hidratación, la actividad puzolánica de los residuos cerámicos contribuye a los requerimientos de resistencia.

PALABRAS CLAVE: Cemento Portland; Residuos cerámicos de demolición; Puzolana; Caracterización

ORCID ID: M.A. Trezza (http://orcid.org/0000-0002-4192-0066); S. Zito (http://orcid.org/0000-0002-7356-8612); A. Tironi (http://orcid.org/0000-0002-2583-2043); E.F. Irassar (http://orcid.org/0000-0003-4488-0014); V.F. Rahhal (http://orcid.org/0000-0001-7710-1203)

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1. INTRODUCTION

Currently, environmental concern and energy reduction have become two major topics under discussion. Portland cement (PC) industry does not remain unaware of these topics and many changes have occurred in the last decades, one of which promotes the use of natural materials, waste and industrial by-products in its manufacturing process. Consequently, energy demand in clinker production has been significantly reduced over the last years.

The raw materials for clinker production are primarily based on limestone, clay or its natural mixture. In many cases, alternative raw materials are mostly used as corrective materials (1). Typical examples are fly ash, calcium fluoride, sludge, etc. The future challenge of the cement industry is to use more alternative raw materials originated as byproducts from other industries or directly from other waste streams. Regarding resource efficiency along the value chain, concrete recycling as coarse aggregate source is already in an advanced state (1).
On the other hand, the most efficient alternative for Portland cement materials replacement is pozzolans such as calcined clays. ASTM C618 (2) defines a pozzolan as "a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties".

Clay minerals in their natural state, due to their crystalline structure will not have pozzolanic properties. However, they have good pozzolanic activity when calcined at temperatures between 600 and 900 °C and ground to cement fineness (3, 4). The ceramic industry generates a large volume of calcined clay wastes (up to 3% of production depending on producer and country). These products, discarded as scrap, are generally crushed to be used as aggregate or as landscaping material, reducing the volume available. Nevertheless, another more interesting source is demolition scraps where ceramic materials are the largest components due to the traditional building habits and old-line production technology in Argentina.

Construction and Demolition (C&D) wastes contribute to the largest volume of wastes worldwide (75%), and ceramic materials contribute to the highest percentage of wastes within the C&D wastes (54%) (5).

These C&D wastes are mainly composed (75%) by bricks, slabs, tiles, ceramic floors and other materials as concrete and lime and / or cement mortar (6).

In recent years, the literature on construction and demolition waste management has grown (7, 8). Construction waste, or C&D waste, is generally defined as a mixture of inert and non-inert materials arising from construction, excavation, renovation, demolition, roadwork and other construction-related activities (9).

Some proposals promote the use of waste from the ceramic industry, which has already gone through a process at high temperature, particularly waste from roof tiles (10–15), bricks (16–19) and floors tiles (20) as pozzolan. It is worth classifying this waste in terms of its potential as active pozzolanic capability and Portland cement additions.

In this study, three demolition ceramic wastes (DCWs) originated in different industrial processes were characterized and the potential pozzolanic activity was determined in order to investigate the potential use of ground DCWs as supplementary cementitious materials in Portland Blended Cements (PBC).

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Portland cement (IRAM 50000) (21) was used to prepare paste and mortar specimens. This cement is equivalent to CEM I of EN 197:1(22) containing up to 5% of limestone filler as minor constituent. The chemical composition was provided by the producer and the mineralogical composition was calculated by Bogue’s formulas based on clinker chemical composition. The specific gravity and Blaine fineness are 3.14 and 315 m²/kg, respectively (Table 1).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Portland cement (PC)</th>
<th>Industrial Ceramic Block (CB)</th>
<th>Mud Brick (MB)</th>
<th>Sanitary Ware (SW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂, %</td>
<td>21.5</td>
<td>64.4</td>
<td>62.2</td>
<td>70.8</td>
</tr>
<tr>
<td>Al₂O₃, %</td>
<td>3.8</td>
<td>17.0</td>
<td>17.1</td>
<td>19.0</td>
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<tr>
<td>Fe₂O₃, %</td>
<td>3.8</td>
<td>5.6</td>
<td>5.7</td>
<td>0.9</td>
</tr>
<tr>
<td>CaO, %</td>
<td>64.3</td>
<td>2.5</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>MgO, %</td>
<td>0.8</td>
<td>1.4</td>
<td>1.8</td>
<td>0.3</td>
</tr>
<tr>
<td>SO₃, %</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O, %</td>
<td>0.1</td>
<td>4.2</td>
<td>5.2</td>
<td>2.7</td>
</tr>
<tr>
<td>K₂O, %</td>
<td>1.1</td>
<td>2.9</td>
<td>2.3</td>
<td>4.6</td>
</tr>
<tr>
<td>TiO₂, %</td>
<td>-</td>
<td>0.7</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Loss on ignition, %</td>
<td>2.1</td>
<td>0.6</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>C₃S, %</td>
<td>60.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineralogical composition</td>
<td></td>
<td>Quadrat</td>
<td>Quadrat</td>
<td>Quadrat</td>
</tr>
<tr>
<td>C₃S, %</td>
<td>16.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃A, %</td>
<td>3.8</td>
<td>Feldspar</td>
<td>Feldspar</td>
<td>Mullite</td>
</tr>
<tr>
<td>C₄AF, %</td>
<td>11.5</td>
<td>Hematite</td>
<td>Hematite</td>
<td></td>
</tr>
<tr>
<td>Gypsum, %</td>
<td>5.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Three DCW originated by different industrial processes were used: mud-brick (MB), industrial ceramic block (CB) and sanitary ceramic ware (SW). DCWs were obtained in coarse aggregate particle size. Their particle size was further reduced to passing 4.75-mm sieve (#4) and, finally, ground in ball mill until 100% pass through 75 μm sieve (#200). For ground DCWs, the Blaine specific surface area (BSS) (23) and the particle size distribution (PSD) were determined. The PSD was determined using Malvern Mastersizer 2000 laser particle size analyzer, and the d_{50}, d_{90}, and d_{10} diameters were calculated. The chemical composition of different ceramic wastes is given in Table 1 and it was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis in an external laboratory (ALS, Argentina). The mineralogical composition of DCWs was identified by X-ray diffraction (XRD) and FT-IR spectroscopy (FT-IR). XRD analysis was performed using a Philips PW 3710 diffractometer operating with Cu Kα radiation at 40 kV and 20 mA and the FT-IR spectra were performed on NICOLET Magna 500 using KBr technique.

2.2. Blended cements

Nine PBCs were prepared replacing 8, 24 and 40% of each DCW by mass of Portland cement. The PBCs are identified using the replacement level and the type of ceramic waste used (CB, MB and SW). Table 2 shows the nomenclature used in this study.

2.3. Frattini test

Pozzolanic activity was determined by Frattini test according to the procedure described in EN196-5 at 2, 7 and 28 days (24). This test evaluates the pozzolanic activity of DCW measuring its reaction with the Ca(OH)₂ released during the PC hydration. The result is considered positive when the points are located below the calcium hydroxide solubility isotherm at 40 °C.

2.4. Flow and strength of mortar

Mortars were made with standard siliceous sand using a sand/cement ratio of 3 and a water-to-cementitious material ratio (w/cm) of 0.50. It was mixed using the standard procedure. The workability of mortar was determined using the flow table test according to ASTM C1437 (25). For each mortar batch, the flowability was determined as the diameters of spread mortar measured along four lines in mm. Mortars were cast in 40 x 40 x 160 mm specimens moulds and then compacted in two layers, smoothed and covered with plastic sheet to prevent water loss at 20 ± 2 °C. After 24 h, specimens were removed from the molds and cured in water until the test age. From different blended cements, the compressive strength was determined on prisms at 2, 7 and 28 days. The reported results are the average of six compression tests. The compressive strength index (CS Index) was calculated as the ratio between the compressive strength of the blended cement and the strength of the PC at the same test age.

2.5. Hydration products

To study the progress of hydration, blended cement pastes were prepared using a w/cm of 0.50 and cured in sealed plastic bags in water-bath at 20 °C during 2, 7 and 28 days. At this time, fragments of paste samples were carefully ground to particle size lower than 45 μm (#325) and the crystalline hydration phases were identified using XRD analyses. Determination was performed on Philips PW 3710 diffractometer operating with Cu Kα radiation at 40 kV and 20 mA using carbon monochromator.

2.6. Demolition ceramic wastes characteristics

The XRD patterns and FT-IR spectra od DCWs are shown in Figure 1. The mineralogical composition of the ceramic wastes obtained by XRD (Figure 1-a) includes quartz (SiO₂), anorthite (CaAl₂Si₂O₈) and hematite (Fe₂O₃) for CB and MB, while SW is composed by quartz (SiO₂) and mullite (Al₆Si₂O₁₃). The XRD patterns of DCWs show a small but evident diffuse band ranging from 20 to 30, 2θ deg., indicating the presence of amorphous materials (26). According to the XRD data, DCWs contain weak crystalline minerals and amorphous phase. Judged by the XRD diffuse band intensity, the proportion of non-crystalline phases is broader in the SW sample.

FTIR spectra of DCWs (Figure 1-b) confirm the phase identification by XRD. The quartz in all wastes is identified through the strong band at 460 cm⁻¹, corresponding to deformation of Si-O⁻. Stretching bands of Si-O are placed at 695 cm⁻¹ (m), doublet 780–800 cm⁻¹ (s) and 1080 cm⁻¹ (vs) and 1170 cm⁻¹ (s) (27). In addition, CB and MB samples present assignable bands to feldspars (anorthite in this case) at 1100 cm⁻¹ range (1095, 948 cm⁻¹), which deform and widen the quartz band, and the additional band at 571 cm⁻¹ is also observed.
The physical characteristics of all materials (density, particle size distribution -d_{10}, d_{50}, and d_{90}- and the BSS) are given in Table 3. According to Table 3, three DCW have lower density, larger specific surface area and particle size distribution with large volume (d_{10} and d_{90} are low) of particles, smaller than the corresponding to Portland cement. This is evident for MB and SW samples.

3. RESULTS AND DISCUSSION

3.1. Pozzolanic activity

Figure 2 shows the results of Frattini test for the PBCs at 2, 7 and 28 days. At 2 days, results for all blended cements were above the calcium solubility isotherm, showing pozollanic activity did not occur. For the three DCWs, the [CaO] increased when the level of replacement in blended cement increased, showing the stimulation effect on the hydration of Portland cement phases. In addition, it can be observed that the dilution effect caused by the replacement of PC by DCWs produced a decrease of [OH−] when the DCW replacement level increased.

At 7 days, the reduction of [OH−] and [CaO] showed that PBCs with high replacement level (40% for all DCWs) have a pozollanic activity and the test-points are located below the saturation curve. For 24CB blended cement, the point is on the saturation curve, indicating the early reaction of this DCW. At 28 days, all blended cements presented proper pozollanic activity.

According to Frattini test results, MB has a slower pozollanicity than SW, although both have similar specific surface area and particle size distribution.

### Table 3. Physical characteristics

<table>
<thead>
<tr>
<th>Material</th>
<th>d_{10}, μm</th>
<th>d_{50}, μm</th>
<th>d_{90}, μm</th>
<th>Density</th>
<th>BSS, m²/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>2.741</td>
<td>18.991</td>
<td>63.469</td>
<td>3.15</td>
<td>315</td>
</tr>
<tr>
<td>CB</td>
<td>2.265</td>
<td>18.369</td>
<td>91.833</td>
<td>2.5</td>
<td>590</td>
</tr>
<tr>
<td>MB</td>
<td>1.956</td>
<td>13.094</td>
<td>54.935</td>
<td>2.6</td>
<td>530</td>
</tr>
<tr>
<td>SW</td>
<td>1.979</td>
<td>12.719</td>
<td>50.591</td>
<td>2.6</td>
<td>534</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)  
**Figure 1.** Mineralogical composition by DRX and FT-IR methods. Q: quartz, M: mullite, F: feldespar, α: α alumina, H: hematite.

![Figure 2](image2.png)  
**Figure 2.** Frattini test at 2, 7 and 28 days.
It can be exclusively attributed to the surface characteristics of the particles and the glass content.

3.2. Flow test

The results of mortar flow tests for different blended cements are shown in Figure 3. It can be observed that the flow of mortar slightly decreases as the DCW replacement increases in blended cement.

The flow of mortar using 8CB (128%) was approximately the same than that of the control mortar (PC = 127%). For mortars 24CB and 40CB, the flow decreases 14 and 22% when compared to the control, respectively. For blended cements 8MB and 8SW, the flow was higher than that of control and their reduction was 3 and 10% for mortars 40% MB and 40SW, respectively.

The high flow reduction for CB blended cements is attributable to the large BSS (see Table 3) of this ceramic waste when compared with the specific surface of MB or SW ceramic wastes. For blended cement with low replacement (8%), the increase of flow compared with the control mortar may be attributable to the reduction of water fraction used to fill the inter-grains voids due to the better packing of blend that compensates the water needed to wet the large specific surface of DCWs. When the percentage of DCW increases, the flow decreases due to the increase mortar viscosity caused by the high specific surface area and the large volume occupied by solid fraction in paste due to the lower density of DCWs.

3.3. Compressive strength

For each ceramic waste, the evolution of compressive strength (CS) of blended cements up to 28 days is shown in Figure 4. Additionally, the figure includes the evolution CS Index. For all DCWs, the compressive strength increases with the curing age and it decreases when the replacement level increases.

At 2 days, CS of all blended cements was less than that of the control mortar and its reduction increased when increasing the replacement level due to the dilution effect caused by the incorporation of ceramic waste. Dilution effect reduces the volume of PC available to react at early age increasing the effective w/c (0.54, 0.66 and 0.83 for 8, 24 and 40% replacement, respectively) that could not be compensated by the stimulation of PC hydration.

At 7 days, the CS of blended cements with 8% replacement was similar to that corresponding to PC, indicating that the stimulation of PC hydration compensates the dilution effect. On the other hand, the CS of mortars with 24% and 40% of replacement is lower than control, but its reduction is lower than the percentage of DCW replacement.

At 28 days, the CS of blended cement was lower than the control. For 8 and 24% replacement, the compressive strength is comparable to the control mixture, but it was low for blended cement with 40% replacement.

For PBCs containing 8, 24 and 40% DCW, the CS Index was higher than 0.92; 0.74 and 0.60 at 7 and 28 days, respectively. In all cases, the CS Index was higher than the replacement level in the PBCs. At 28 days, the CS index ranged from 0.93 to 1.00 for 8 and 24% DCW indicating that blended cements could be classified at the same strength class.

3.4. Hydration at early age, XRD analysis

The study of the hydration progress of PC and PBCs by XRD at 2, 7, and 28 days showed a similar behavior. The hydration phases were identical at the same hydration times and the variation of intensity of peaks was only observed due to the different percentages of DCW replacement. As a consequence, Figure 5 only shows the XRD patterns of PC and PBC with 24% replacement of different ceramic wastes at 2, 7 and 28 days.

At 2 days, the PC showed the presence of calcium hydroxide (CH) and ettringite (Et). In all blended cements, the intensity of Et and CH peaks had a similar value to PC despite the dilution effect caused by ceramic addition. These observations reveal that stimulation of PC hydration occurred due to the filler effect, the heterogeneous nucleation and the large amount of free water in the system (28). Quartz (Q) is identified in PBCs from ceramic waste.

At 7 days, the Et and CH were accompanied by hemicarboaluminate (Hc), and the incipient formation of monocarboaluminate (Mc). The Hc and Mc
formation was promoted by the calcium carbonate (CC) present in PC as a minor component.

At 28 days, the intensity of CH and Ett peaks decreased in PBCs. The peak intensity of Mc increased and the intensity of Hc peaks decreased. The reduction of CH peak was attributed to the pozzolanic reaction generated by the addition of ceramic wastes, according to the Frattini test results. Similar trends were observed for the three materials.

4. ENVIRONMENTAL BENEFITS

In addition to the technological properties, the use of DCWs saves a large amount of raw materials and generates other environmental benefits, such as the reduction of energy consumption due to the decrease in grinding time (16), and the reduction of CO₂ emissions by ton of PC with equivalent compressive strength at 28 days for low or medium replacement level (29).

Raw materials for clinker production are primarily based on limestone, clay or its natural mixture. During the clinkering process, the CaCO₃ in the limestone is transformed into CaO(s) and CO₂(g), the latter being emitted into the atmosphere. Considering the chemical composition of PC used and estimating a complete transformation, 505 g CO₂ by kg of clinker are emitted due to CaCO₃ dissociation, plus approximately 400 g of CO₂ emitted by fuel combustion (30).

Since CB, MB and SW have similar reactivity and considering the replacement level (8, 24 and 40% w/w) by ceramic waste, in general, the emission in 72, 216 and 360 g CO₂ / kg cement could be reduced, respectively.

**FIGURE 4.** Compressive strength (MPa) and CS Index.
In 2014, according to the Association of Portland Cement Manufacturers in Argentina (AFCP) (31), 11,438,165 t of cement were exported to the domestic market. Considering that 20% of the annual production will be carried out with the proposed technology and a replacement of 24% w/w by DCWs, CO₂ emissions will be reduced by approximately 3.8 \times 10^8 t CO₂ / year to obtain the same strength class cement.

5. CONCLUSIONS

The behavior of three demolition ceramic wastes was analyzed as a partial replacement of PC in the manufacture of PBCs, and the following conclusions were drawn:

- At early ages, the incorporation of ceramic wastes shows the dilution and stimulation of PC hydration due to the increase of effective water to cement ratio in the system and their role as nucleation sites for calcium hydrated products. This can be observed in the Frattini test results at 2 days where the CaO concentration increases for incremental levels of waste ceramic replacement.
- At later ages, the XRD shows that ceramic wastes incorporation develops its pozzolanic reaction as revealed by the Frattini test and it can be corroborated by the decrease of CH peaks in XRD patterns at 7 and 28 days. Likewise, the CS Index for blended cements with 8 and 24% of replacement ranged from 0.93 to 1.00 indicating the pozzolanic contribution of ceramic waste addition to the CS.
- The hydration products detected by XRD revealed that hydration mechanisms of PC and the PCBs are the same.
- The experimental results presented here show that ceramic wastes from the construction demolition process have pozzolanic activity. The three DCWs studied have similar reactivity despite their different origins. However, they must be classified as slow pozzolana.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial supports received from the FONCYT, MINCYT Argentina under project PICT 2012-0160.
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