

# Utilization of ceramic wastes as pozzolanic materials

Edgardo Irassar\*, Viviana Rahhal\*, Alejandra Tironi\*, Mónica Trezza\*,  
Zbyšek Pavlík\*\*, Milena Pavlíková\*\*, Milos Jerman\*\*, Robert Cerný\*\*

\*Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires,  
B7400JWI Olavarría, Argentina. firassar@fio.unicen.edu.ar

\*\*Faculty of Civil Engineering, Czech Technical University in Prague,  
Thákurova 7, CZ-166 29 Prague, Czech Republic

## ABSTRACT

The possible applicability of ceramic waste powder as partial portland cement replacement in concrete production is studied in this paper. The cement industry is responsible for about 7% of all CO<sub>2</sub> generated and the cost of cement represents more than 45% of the concrete cost. Several by-products are used as portland cement replacement. In this research, the use of two wastes ceramic and two portland cements was analyzed. The replacements in weight were of 8, 16, 24, 32, and 40%. The chemical and mineralogical compositions of raw materials, were determined using XRF and XRD analysis. For the all blended cement, the pozzolanic activity, the heat released rate and the hydrated compounds identification by XRD were determined. The results showed that both ceramic wastes have pozzolanic activity with both portland cements.

**Keywords:** portland cement, ceramic waste, heat of hydration, XRD-ray.

## 1 INTRODUCTION

In the cement industry, the manufacture of one ton of portland clinker requires 1.7 tons of raw materials that causes a large consumption of non-renewable mineral resources and serious depletion of quarrying areas. Furthermore, the high temperature process requires high energy consumption and also releases a large volume of CO<sub>2</sub> to the atmosphere as a result of decarbonation of limestone in the kiln and the combustion of fossil fuels.

Additionally, the growth of industrial activity also produced a large volume of solid waste that annually increases in several industrial sectors, becoming an environmental issue its final deposition. Among this industrial sector, the ceramic brick industry grows due to its high heat-efficient envelope for building. In Europe, the amount of wastes from different production stages of the ceramic industry reaches to 3-7 % of its global production, meaning millions of tons of calcined-clays per year [1]. The same values of scrap are reported for the Latin-American ceramic industry.

The cement production companies have begun to implement a series of measures to reduce their environmental impact and transform the portland cement in

a material with sustainable development. To find economic, technological and environmental friendly solutions, the use of industrial by-products or waste material has been widespread [2-5] in the manufacture of portland cement.

In this paper the potential of using ceramic wastes as partial replacement of portland cement is studied.

## 2 MATERIALS AND METHODOLOGY

Two portland cements (ArgPC and CzPC) and two ceramic wastes (ArgCW and CzCW) were used. The characteristics of all materials, chemical and mineralogical composition, density and specific surface (Blaine) are given in Table 1. The chemical composition was determined by XRF and the mineralogical composition of cements was calculated by Bogue's formula and the main crystalline minerals of ceramic waste was determined by XRD.

**Table 1:** Characteristic of materials

Parameters	Portland Cements		Ceramic Wastes	
	ArgPC	CzPC	ArgCW	CzCW
SiO <sub>2</sub> , %	21.5	18.9	64.6	51.3
Al <sub>2</sub> O <sub>3</sub> , %	3.8	4.2	17.0	20.0
Fe <sub>2</sub> O <sub>3</sub> , %	3.8	3.8	5.6	6.0
CaO, %	64.3	62.4	2.5	11.5
MgO, %	0.8	1.0	1.5	4.5
SO <sub>3</sub> , %	2.6	2.3	-	1.0
Na <sub>2</sub> O, %	0.1	0.0	4.2	1.3
K <sub>2</sub> O, %	1.1	0.0	2.9	3.2
TiO <sub>2</sub> , %	-	0.8	0.7	0.8
Loss on ignition	2.1	1.5	0.6	1.1
Density	3.15	3.10	2.70	2.72
SS Blaine, m <sup>2</sup> /kg	315	330	590	512

The ArgPC were constituted by 60% C<sub>3</sub>S, 16.4% C<sub>2</sub>S, 3.8% C<sub>3</sub>A, 11.5% C<sub>4</sub>AF and 5.5% gypsum and the CzPC were constituted by 50.5% C<sub>3</sub>S, 19.2% C<sub>2</sub>S, 8.8% C<sub>3</sub>A, 11.6% C<sub>4</sub>AF and 7.2% gypsum. Both cements have limestone filler as minor component. The main crystalline mineral phases of ArgCW were quartz, feldspar (especially anorthite) and hematite. The CzCW is constituted by quartz, feldspar, mica, akermanite and hedenbergite.

Regarding the mineralogical composition of cements, ArgPC has more  $C_3S$  than the CzPC, but the last-one has more  $C_3A$  and more gypsum than the ArgPC; with respect to their  $C_2S$  and  $C_4AF$  contents, they are similar. The ceramic wastes have a similar mineralogical composition with high content of mica in the CzCW. The CW was incorporated to blended cement with 8, 16, 24, 32 and 40 % of replacement by weight of cement. For all blended cements, the pozzolanic activity, the heat liberation rate and hydrated compounds identification by XRD were determined.

The pozzolanic activity of blended cement was determined by Frattini test. The method consists in the determination of the amount of  $Ca^{2+}$  and  $OH^-$  in the water of contact with the samples stored at 40 °C at 2, 7 and 28 days. The blended cements may be considered as pozzolanic when the  $[CaO]$  and  $[OH^-]$  of their solution are located below the solubility isotherm of calcium hydroxide. The heat released rate was determined for 48 hours in an isothermal calorimeter operating at 20 °C, the amount of blended cement was 20 g and the water-to-cementitious ratio was 0.50. The hydration of cement pastes curing in sealed condition at 2, 7 and 28 days. To identify the crystalline hydrated phases, XRD analysis on powdered samples of paste was performed using a Philips PW 3710 diffractometer, with  $Cu K\alpha$  operating radiation 40 kV and 20 mA using carbon monochromator

### 3 RESULTS AND DISCUSSION

Figures 1 shows the results of Frattini test at 2, 7 and 28 days on the  $[CaO]$  vs  $[OH^-]$  plot for ArgPC-ArgCW and CzPC-CzWC blended cement, respectively.

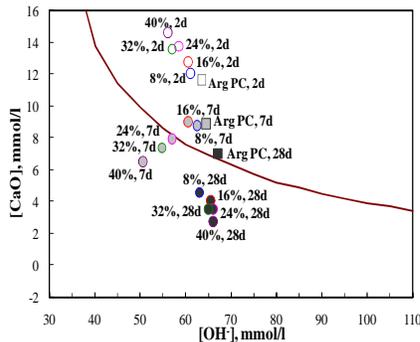


Figure 1: Frattini test of ArgPC with ArgCW

At 2 days, blended cements with 8 to 40 % of ceramic waste have not pozzolan activity: all points are above the calcium solubility isotherm at the super saturation zone. The  $[CaO]$  increases when increase the level of replacement showing the stimulation effect on the hydration of cement. At 7 days, the reduction of  $[OH^-]$  and  $[CaO]$  shows that ceramic wastes have pozzolanic reactivity and the blended cement with high replacement level became below the solubility isotherm at the calcium sub saturation zone. At 28 days, all blended cements present good pozzolanic

activity and this is more evident when the replacement level of CW increases.

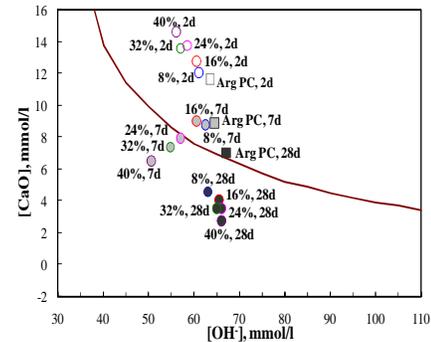


Figure 2: Frattini test of CzPC with CzCW

Figures 3 and 4 show the results of calorimetric test for ArgPC-ArgCW and for CzPC-CzWC blended cements, respectively. For both systems, it can be observed that the increase of replacement level from 8 to 40 % produces a reduction in the heat liberation rate and in the accumulated heat. This observation can be attributed to the dilution effect [4]. For the ArgPC-ArgCW blended cements, the acceleration slope of the second peak in the calorimetric curve is reduced and it remains with slight changes for the CzPC-CzWC blended cements.

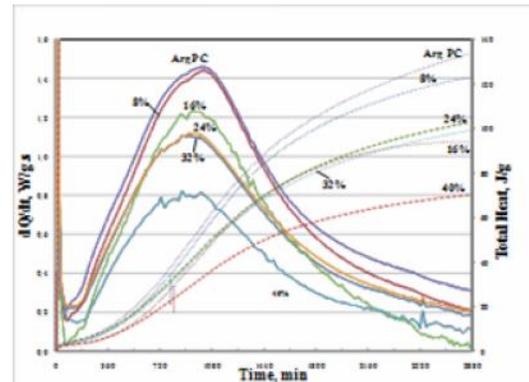


Figure 3: Heat released rate and accumulated heat of ArgPC-ArgCW blended cements

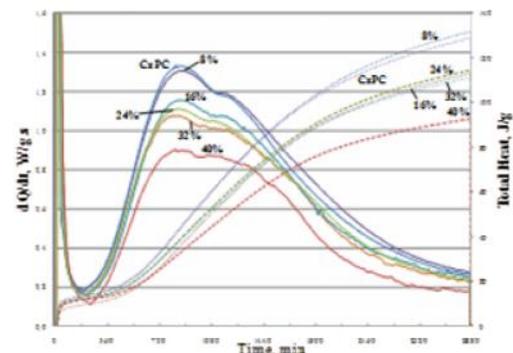


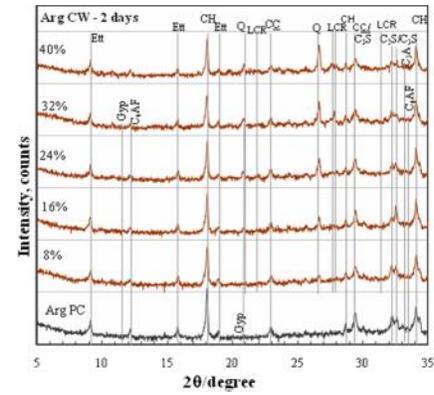
Figure 4: Heat released rate and accumulated heat of CzPC-CzCW blended cements

The high C<sub>3</sub>A content of the CzPC produces the third peak, which is not revealed in pastes with the ArgPC (low C<sub>3</sub>A). For the CzPC-CzCW system, it can be observed that the CzCW stimulates the cement hydration, specially the aluminic phase, because the intensity of the second peak decreases more than the intensity of the third peak when the replacement level of CzCW increased.

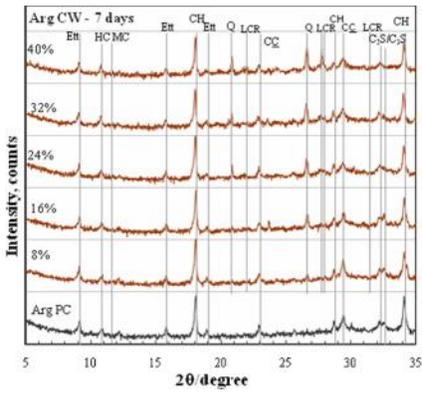
All blended cements develop the maximum of the hydration heat at approximately 14 hours revealing that CW does not interfere in the cement hydration.

Therefore, the kinetics of the early hydration reaction for both systems behaves in similar way. From the practical point of view, this behavior could produce a reduction of hydration heat that is beneficial for casting and production of high volume structures, but it could a shortcoming for the early strength development of these blended cements.

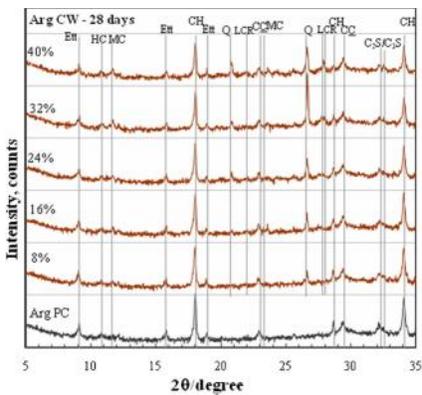
Figures 5 and 6 show the XRD patterns for the hydrated paste at 2, 7 and 28 days of ArgPC-ArgCW and CzPC-CzWC blended cements, respectively.



(a)

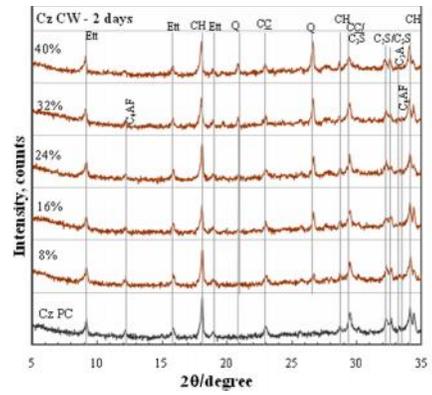


(b)

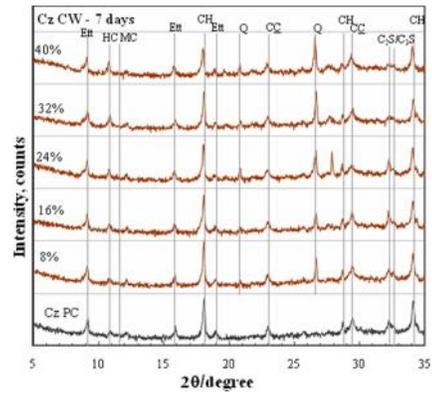


(c)

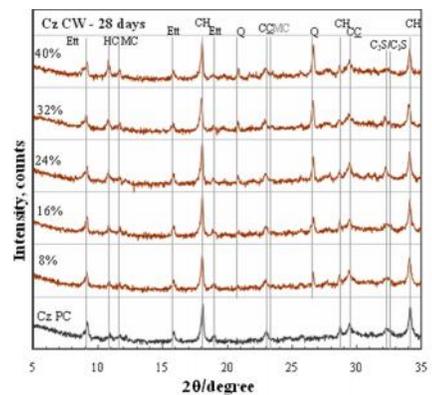
**Figure 5:** XRD pattern for hydrated paste of ArgPC –ArgCW blended cement: (a) 2 days, (b) 7 days and (c) 28 days



(a)



(b)



(c)

**Figure 6:** XRD pattern for hydrated paste of CzPC –CzCW blended cement: (a) 2 days, (b) 7 days and (c) 28 days

At 2 days (Figs. 5a and 6a), the plain cements (ArgPC and CzPC) show the presence of ettringite (Ett) and calcium hydroxide (CH). For all blended cements (8 to 40% ArgCW and CzWC), the intensity of Ett and CH peaks have similar value to those of corresponding PCs instead of the dilution effect caused by CW-addition. These observations indicates that the stimulation of cement hydration is caused by the incorporation of CW due to the filler effect, the heterogeneous nucleation and the large amount of free water [7]. In blended cements, quartz (Q) is identified from ceramic wastes and consequently its peak intensity increases when increasing the replacement level.

At 7 days (Figs 5b and 6b), the Ett and CH are accompanied by hemicarboaluminate (HC) and the incipient formation of monocarboaluminate (MC). The HC and MC formation is promoted by the limestone present as minor component in the PCs.

At 28 days, the intensity of CH and Ett peaks decreases and the peaks intensity of MC increases. This effect appears more remarkable for blended cements with high replacement level. The significant decrease of the CH peak is attributed to the progress of the pozzolanic reaction of CW as commented in results of Frattini test. The transformation of HC into MC is attributed to the presence of limestone filler.

Summarizing, both CW combinations with different PC showed a similar behaviour. At early ages, the incorporation of CW produces the dilution of PC and the 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 [4]. According to the Frattini test results at 2 days, the [CaO] increases for incremental levels of CW replacement. It was corroborated in the calorimetric test because the characteristic peaks on the heat released curve do not reveal advances or delays for all blended cement tested and the cumulative heat is higher than the proportional to cement reduction. Finally, the XRD patterns show a similar intensity of CH peak at 2 days. At later ages, the CW blended cements shows thier pozzolanic activity in the Frattini test and it can be corroborated by the decrease of CH peaks in the XRD patterns at 7 and 28 days.

## 4 CONCLUSIONS

Based on the results present here, it can be concluded that:

The ceramic wastes providing from the brick ceramic industry have a very good pozzolanic activity at 28 days. However, ceramic wastes can be classified as a slow reactive pozzolan.

The addition of ceramic waste (from 8 to 40 %) does not produce significant changes on the mechanisms and kinetics of PC hydration at early ages as showed the calorimetric curve. At later ages, the hydrated compounds

identified by XRD are the same for all blended cements indicating no change in the hydration mechanism of portland cement.

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