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Recycling of hydrated cement pastes by synthesis of α'_H-C_2S

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ABSTRACT

Hardened cement paste in concrete wastes can be a valuable precursor material for the production of recycled cements. In the reported study, X-ray diffraction data of cementitious materials obtained by thermal processing of hardened pastes were quantitatively analyzed using Rietveld refinement to explain the effect of process parameters on their hydration reactivity and on the strength gain of pastes made with them. The parameters studied were annealing temperature, residence time, and cooling rate. Across the annealing temperature range explored C_2S polymorphs were found to comprise the larger fraction of the resulting materials. However, their relative concentrations varied. Results indicate alpha'$_H$-C_2S formed at low temperature is highly reactive and remains stable on cooling due to its smaller crystallite size, whereas at higher temperatures most of it converts to the less reactive beta-C_2S on cooling. Accordingly, materials obtained at lower temperatures exhibited higher heats of hydration and much higher strength gain rates.

1. Introduction

Even though concrete is not a particularly contaminating material, it has a large impact on the environment due to the large quantity being produced every year. Recycling has the potential to reduce all of the main aspects of concrete environmental impact: the consumption of natural resources and energy, the emissions of carbon dioxide and the generation of solid wastes. Production of recycled aggregates has already been shown to effectively reduce the pressure of concrete manufacturing on natural aggregate sources and the pressure of construction and demolition wastes on available landfills. However, the largest part of energy consumption and CO_2 emissions are associated with the cement production [1]. Considering Portland cement is the higher costing component of concrete, both in economic and environmental terms, significant benefits could be achieved by recycling the hydrated cement fraction of the concrete wastes. Hydrated cement paste (HCP) remains partly adhered to crushed concrete aggregates and concentrates in the finer sized fraction due to the higher surface to volume ratio of the smaller aggregate particles. Since residual HCP in the recycled aggregates degrades the performance of new concrete, several crushing steps are usually implemented to improve the separation. The byproduct is crushed concrete fines with a high concentration of HCP.

In practice, different recycled materials can be developed based on different degrees of processing of the fines, with higher degrees requiring higher energy input. At the lower energy end of the range, the fines can be used as a low value filler material. At the opposite end, the fines can be used as a raw material for the production of new Portland cement Clinker [2–4]. Unless original concrete has been exposed to severe chemical attack or environmental weathering, the oxide composition of the HCP should match that of the cement it was made with. Major constituents of HCP are cement hydration products: calcium silicate hydrates (C-S-H), Portlandite and hydrated calcium sulfates, plus any unreacted cement remaining. Analogously as in the case of clinker raw materials, when powdered HCP is heated, Belite (C_2S) is the first calcium silicate formed in solid state reactions occurring below 1200 °C. However, whereas in the materials resulting from heating of clinker raw meals to 800 °C beta-C_2S is the most abundant polymorph of C_2S present [5], a significant fraction of alpha'-C_2S was identified in materials obtained by heating of HCP to the same temperature [6]. Due to the presence of this more reactive polymorph of C_2S, materials obtained by heating and annealing HCP to around 800 °C display significant cementitious behavior [7,8]. This behavior opens up the possibility of recycling the cement fraction of concrete wastes producing reactivated cementitious materials by thermal processing of HCP at temperatures much lower than those required to produce clinker.

In a previous study it was shown that the relationship between annealing temperature and cementitious behavior of the reactivated materials correlated with the relative concentration of alpha'-C_2S in them [6]. Qualitative analysis of X-ray diffraction (XRD) profiles of the reactivated materials showed alpha'-C_2S related peaks increased in

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intensity with increasing annealing temperature in the range 600 to 800 °C. Above 800 °C the peaks were seen to change in position and intensity towards the pattern of beta-C_2S. Concurrently, mortars made with reactivated materials annealed at 800 °C achieved higher 28-day strengths. Regression models for 7-day strength of the mortars predicted somewhat lower optimal annealing temperatures, but this was considered as due to larger variance of the 7-day strength results. The study did not distinguish between the two main forms of alpha′-C_2S observed in pure C_2S: alpha′$_H$-C_2S stable above 1160 °C and alpha′$_L$-C_2S, stable above 630–680 °C. Although the XRD pattern best fitting the observed profile was from a phosphate stabilized form of alpha′-C_2S, the precise cause for the stabilization at room temperature of this high temperature polymorph could not be determined from the results of the qualitative analysis.

The study reported in this manuscript focused on quantitatively characterizing the effect of additional parameters of the thermal process on the relative abundance and crystal structure characteristics of the phases in the resulting materials. Considering phase formation and polymorph transformations are thermodynamically controlled processes, in addition to annealing temperature, residence time and cooling rate were considered, as they are expected to affect the phase composition of the reactivated materials. By simultaneously characterizing the effect of the said process parameters on the cementitious behavior of the materials, the study aimed at stablishing stronger relationships between phase composition and material performance. Phase composition and crystal structure characteristics were studied by quantitative analysis of powder X-ray diffraction (QXRD) by whole pattern fitting using the Rietveld method [9]. Cementitious behavior was studied by isothermal conduction calorimetry of hydration reactions up to 7 days, and by compressive strength testing of neat pastes made with the resulting materials up to 90 days of hydration. A new method for the mixing of reactivated material pastes was developed that avoids the negative effects of rapid free Lime hydration and allows mixing at lower effective water to cement ratios.

2. Experimental design, materials and methods

2.1. Experimental design

The experimental region of interest was defined to partly encompass the combination of factor levels that had been explored in previous studies. The ranges of experimental levels for the annealing temperature, residence time and cooling rate, were thus centered at 800 °C, 90 min and − 10 °C/min, respectively. Response surface methodology was selected to explore the experimental region around this central point. The combinations of factor levels in the experiment were defined using a rotatable central composite design for 3 factors which enables efficient use of least squares regression to produce second order response surface models [10] (Fig. 1). The core of the design is a full factorial experiment in two levels that allows estimation of the linear effects of factors and factor interactions. This core is augmented with two axial cases for each factor (at factor levels exceeding the range covered in the factorial part) which allow estimation of the second order effects of the factors, and multiple replications of a central case (at the center level of all factors) which allow estimation of the experimental variance. In response surface models derived from rotatable designs, the variance of the predicted response is a function of the distance from the center of the design only. This is a desirable feature when the behavior of the response in the experimental region is not known in advance. In central composite designs each factor is applied in five coded levels: $-\alpha$, -1, 0, 1, α, where α is the coded level of the factor at the axial cases. Choosing $\alpha = (n_f)^{1/4}$, where n_f is the number of factorial cases in the design, a rotatable design is obtained. Therefore, in the selected design $\alpha = 1.682$. The coded and experimental levels of the factors, annealing or maximum temperature (factor X1: m_temp), residence time (X2: r_time) and cooling rate (X3: c_rate) for all cases in

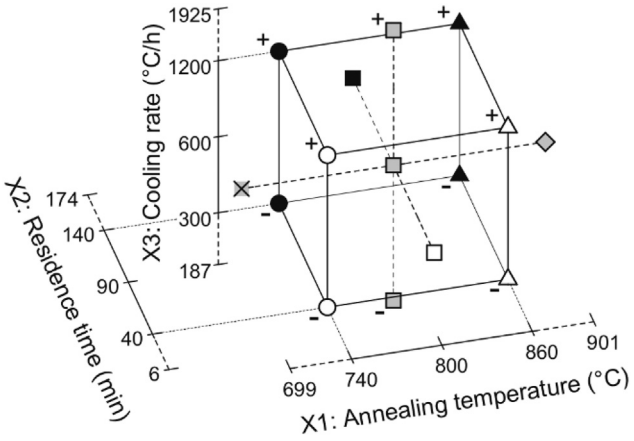

Fig. 1. Central composite experimental design defined for the study, showing the range and combination of factor levels explored across the experimental region. The symbols displayed at every design point provide a key to identify cases or groups of cases having specific factor levels in the result plots shown in the following figures.

the experimental design are shown in Table 1. Cooling rate levels where based on a logarithmic scale, with the central level set to match the rate applied during heating (10 °C/min). The experiment was divided in two blocks: Block A, comprising the factorial cases and three central case replicates, were executed first followed by Block B, comprising the axial case and two central case replicates. Execution of cases within each block was randomized.

2.2. Precursor materials and thermal treatments

For the purposes of this study, precursor materials for the thermal reactivation process were obtained from a single batch of cement paste produced using ordinary (type I) Portland cement and distilled water. Elemental composition of the Portland cement was determined by X-ray fluorescence, using a Bruker S8 Tiger wavelength dispersive spectrometer. Cement samples were cast in Lithium-Borate glass beads using a Claisse M4 gas fluxer. The paste was mixed at a 0.5 water to cement ratio (by weight) and molded into slab-like forms approximately 600 by 400 by 40 mm in size. The hardened cement paste obtained was unmolded after 24 h and placed under lime-saturated water to cure. After 28 days of curing, the hydrated cement paste (HCP) slabs were crushed into irregular pieces of 40 mm maximum dimension. Hydration was stopped by drying the material at 105 °C until constant weight was achieved. The pieces were then reduced in size using a jaw crusher and then powdered in a ball mill in batches of 2.5 kg each. The number of mill revolutions required to achieve a material with 90% of particles under 100 μm in size (equivalent volume sphere diameter) was determined by sampling the first batch at fixed intervals. Samples were analyzed in a Malvern Mastersizer 2000 laser diffraction particle size analyzer, dispersed in water and using sonication to improve dispersion. The number of revolutions thus determined was applied to all subsequent batches. Powdered precursor material was kept in a sealed container until the time of thermal processing.

Thermal treatments according to the experimental design were carried out in a Nabertherm HT-16/40 programmable electric furnace equipped with motorized exhaust flap and drought fan that enables controlled forced cooling. Every process involved heating, annealing and cooling of 640 g of precursor material, distributed in 8 crucibles of 150 ml capacity (80 g of precursor material in each), arranged in two lines of four roughly centered in the oven chamber (both horizontally and vertically). A type K (chromel-alumel) thermocouple embedded in the material of one of the centermost crucibles was used to monitor the temperature evolution of the charge in each of the thermal processes applied (Fig. 2). The maximum temperature and cooling rate set values in the thermal process programs were adjusted according to results