Composites: Part B 60 (2014) 14–20

Contents lists available at ScienceDirect

Composites: Part B

journal homepage: www.elsevier.com/locate/compositesb

Influence of activated drinking-water treatment waste on binary cement-based composite behavior: Characterization and properties

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ARTICLE INFO

Article history:
Received 28 October 2013
Received in revised form 15 November 2013
Accepted 12 December 2013
Available online 23 December 2013

Keywords:
A. Recycling
B. Chemical properties
B. Mechanical properties
B. Microstructures
Blended cement

ABSTRACT

Drinking water treatment plants regularly dispose of large volumes of industrial sludge in landfill sites, which often has negative environmental consequences. The calcination products of these kaolinite-based sludges have properties that could make them appropriate supplementary cementing materials in the production of blended binary cements.

This research analyses the pozzolanic and thermodynamic properties of a Venezuelan drinking water sludge activated at 600 °C for 2 h and its behavior in blended cement matrices prepared with 15% Activated Waste (AW) and 85% Ordinary Portland Cement (OPC). Our results show that this activated drinking water sludge presents high pozzolanic properties, mainly during the first 24 h of reaction. The XRD, SEM/EDX and thermodynamic studies confirm the formation of C_2ASH_8, C–S–H gels and C_4AH_{13} as the hydration products from the pozzolanic reaction. The binary mixture of 15% AW/85% OPC complied with the physical and mechanical specifications contained in current European cement standards.

1. Introduction

Over recent years, fewer high-quality limestone quarries and clays pits have been supplying raw materials to the cement industry, due fundamentally to the environmental policies introduced in developed countries. This reduction coupled with an imperative need to limit the CO_2 emissions of the cement industry, has prompted the search for supplementary cementing materials extracted from industrial waste and its related sub-products [1–10]. In consequence, research into binary and ternary cement-based composites is a priority research line in the cement sector at present, due to energetic, economic and technical advantages, stoked mainly by the present global economic crisis [11–14].

In this area, scientific interest has recently been focused on kaolinite-based industrial waste, because it can be converted into a highly pozzolanic product (metakaolinite-based pozzolan), having undergone a process of thermal activation [15–22]. The sludges generated in drinking water treatment plants are among this class of waste, generating significant quantities of drinking water sludges, which are normally taken to landfills for disposal, with the ensuing environmental problems [23]. In general, a drinking-water treatment plant of 1 m^3/s of volume generates about 8300 kg/day of sludge [24], which means that the material is available in abundance, bearing in mind that there are 160,000 public water systems in the United States alone. In some European countries, only 25% of drinking water sludges are re-used, mainly as raw materials in the manufacture of Portland clinker as well as in various other industrial sectors [25–28].

In a previous work by Frías et al. [29], the scientific bases were established for the use of these siliceous–aluminous sludges as a pozzolanic material in activated waste systems/$Ca(OH)_2$, which highlighted suitable activation conditions at 600 °C and 2 h retention in a laboratory furnace to transform this inert kaolinite-based sludge into a metakaolinite based pozzolan.

However, there is a large gap in scientific and technical knowledge of the properties of binary cement-based composites prepared with these activated sludges. Hence, this present study reports a novel study and a full characterization of industrial sludge activated at 600 °C, its pozzolanic behavior, the evolution of its mineralogical phases and their influence on the properties of the new eco-cement composites. The results obtained from this research are fundamental for the establishment of scientific -technical knowledge bases for the manufacture of future commercial composites.

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http://dx.doi.org/10.1016/j.compositesb.2013.12.020

2. Materials and methods

2.1. Materials

The Starting Waste (SW) for this research came from a Venezuelan drinking water treatment plant (Embalse La Mariposa), located at 8 km from Caracas. Its water content was initially around 92%. After drying, the SW was activated at 600 °C for 2 h of retention in an electric laboratory furnace at a heating rate of 20 °C/min, following the indications of a previous paper, [29] in which these conditions were selected as the suitable activation conditions from an economic and energetic point of view. The activated waste (AW), when cooled to room temperature in a desiccator, showed a reddish coloration (Fig. 1). The sample was ground in an agate mortar and pestle and then sieved through a 63 μm sized mesh. According to the laser granulometry analysis [30], 50% of the particles were of a size below 9.8 μm, 60% below 12 μm and 97% passed by 45 μm.

2.2. Blended cements

CEM I 52.5 R Ordinary Portland Cement (OPC) supplied from the Lafarge Cement Company's plant at Villaluenga de la Sagra (Toledo, Spain) was used. All the cement particles were under 63 μm and 47.41% passed through a 12 μm sieve mesh. The chemical composition and mineralogical of the OPC is given in Table 1.

The blended cements were prepared in a high-speed powder mixer to guarantee homogeneity. The blends were calculated by weight, with AW/OPC ratios of 0/100 and 15/85. This replacement level corresponds to the standardized ratios for type II/A cements (6–20%) [31].

2.3. Pozzolanic and thermodynamic methods

Pozzolanic activity method: the pozzolanic behavior in a pozzolan/calcium hydroxide (lime) system was studied using the solid sludge waste after applying an accelerated chemical method. After each period of 1, 7, 28 and 90 days of reaction, the sludge was washed with acetone and dried in an electric oven at 60 °C for 24 h, in order to stop the pozzolanic reaction. The content of fixed lime was calculated as the difference between the CaO concentration (mmol/l) in the original saturated lime solution (17.68 mmol/L) and the content of this compound in the solution at each established time. Extra pure calcium hydroxide Ph Eur, USP, BP chemical reagent was used.

PHREEQC geochemical software program version 2.18 was used to evaluate the evolution of the hydrated phases formed in this study, in terms of their thermodynamic behavior [33]. The samples entered an aqueous species concentration -AW/$Ca(OH)_2$- at different ages (1, 7, 28 and 90 days of reaction). Even though the pH values were optimized with the geochemical PHREEQC code, due to the various uncertainties of experimental analyses, rather than using the PHREEQC database, our simulation used the THERMODDEM database [33] that lists all the minerals presented in this study.

The saturation index of the strätlingite ($Ca_2Al_2SiO_2(OH)_{10}{\cdot}2.5H_2O$), C–S–H phases with Ca/Si ratios 0.8, 1.2 and 1.6 ($Ca_{0.8}SiO_{2.8}{\cdot}1.54H_2O$, $Ca_{1.2}SiO_{3.2}{\cdot}2.06H_2O$ and $Ca_{1.60}SiO_{3.6}{\cdot}2.58H_2O$), C_3AH_6 ($Ca_3Al_2(OH)_{12}$) and C_4AH_{13} [$Ca_4Al_2(OH)_{14}{\cdot}6H_2O$], C_3AH_6 and portlandite $Ca(OH)_2$ were calculated with the simulation at different ages (1, 7, 28 and 90 days of reaction), in order to study the stability and evolution of the minerals (dissolution/precipitation) over time. The simulation also allowed us to calculate the activities of the aqueous species. The concentrations of aqueous species measured in the solution at different times were introduced in the model at pH = 12. The aqueous carbonate (not experimentally determined in solution) was equilibrated with calcite in the model.

Table 1
Chemical and mineralogical composition of OPC.

Compositions	Chemical (%)	Mineralogical (%)
SiO_2	20.16	
Al_2O_3	4.36	
Fe_2O_3	2.52	
CaO	63.41	C_2S = 8.95
MgO	2.21	C_3S = 64.75
Na_2O	0.35	C_3A = 7.29
K_2O	0.91	C_4AF = 7.65
TiO_2	0.21	
P_2O_5	0.14	
$S0_3$	3.57	
LOI	1.99	

Fig. 1. Appearance of AW activated at 600 °C for 2 h.

2.4. Standardized methods

The rheological behavior of the blended cement pastes was assessed as described in standard EN 196-3 [34], using a Vicat apparatus to determine normal consistency and setting times. The soundness of the blended cement pastes was tested with Le Chatelier apparatus, following the procedure specified in the current European standard [34]. The effect of this addition on the mechanical behavior of new cements was ascertained as per standard EN 196–1[35], which describes the methodology for testing mortar components, and their preparation, curing and strength. Blended cement mortar specimens measuring 4 × 4 × 16 cm were prepared with a sand/binder ratio of 3/1 and a water/binder ratio of 0.5.

2.5. Characterization techniques

Different techniques were used for chemical, physical, mineralogical, morphological and microporosity characterization of the sample. Its chemical composition was studied with a Philips PW-1404 780 X-ray fluorescence analyzer fitted with a Sc–Mo anticathode tube. Particle size was analyzed by laser ray diffraction (LRD) on a Sympatec Helos 12 KA spectrometer using isopropyl alcohol as the non-reactive liquid. Material mineralogy was determined with X-ray diffraction (XRD) using random powder mounts for the bulk sample and oriented slides for the <2-μm fraction. The samples were analyzed with a SIEMENS D-500 Cu anode diffractometer operating at 30 mA and 40 kV (2-mm divergence slit; 0.6-mm reception slit; 2θ goniometer; step size: 0.04; count time: 3 s). The morphological observations and microanalysis of the samples were performed with a SEM/EDX, by using an INSPECT FEI