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Research paper

Potassium-rich biomass ashes as activators in metakaolin-based inorganic polymers

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ABSTRACT

The use of biomass ashes as an alkaline activator in the synthesis of metakaolin-based inorganic polymers was investigated in the present work. Maize stalk and maize cob ashes reached the highest pH after mixing with water, 13–14, and contained the largest amount of potassium, 30–32 wt.% K_2O. Of these two, the maize cob ashes showed a higher reactivity and reaction extent when mixed with water and metakaolin calcined at an optimized temperature of 700 °C. A maximum reaction enthalpy of −372 J/g was reached with a mixture with an ash to metakaolin mass ratio of 0.9. In attenuated total reflection Fourier-transformed infrared spectroscopy, the wavenumber shift of the Si–O–T (T: Si, Al) stretching band upon activation proved to be linearly related to the compressive strength of pressed samples, cured with all surfaces exposed at 80 °C or 60 °C for 48 h. A maximum strength of 27 MPa and a wavenumber shift of the Si–O–T stretching band of 52 cm^{-1} were observed for samples with a maize cob ash to metakaolin mass ratio of 0.9 cured with an open surface at 80 °C. This shift and increase in strength is explained by a larger reaction extent, which was also observed using calorimetric techniques, and confirmed by electron probe micro-analysis. The curing conditions were altered to optimize the microstructure. The temperature was lowered to 60 °C, the samples were wrapped in plastic to avoid water evaporation, or the samples were subjected to a pre-cure of 24 h at 20 °C before curing at 80 °C. The latter resulted in the maximum compressive strength of 40 MPa.

1. Introduction

Driven by an ecological motivation, research into alternative cementitious binders is rising in importance, as 5–8% of the total antropogenic emissions of CO_2 are attributed to Portland cement production (Olivier et al., 2012). Past studies have shown that inorganic polymers obtained from alkali activation of a silicate source are good alternatives in terms of CO_2 emissions (McLellan et al., 2011; Melado et al., 2014). However, taking into account other influences on the environment, the inorganic polymers do not always show themselves as environmentally friendly alternatives (Habert et al., 2011). The latter is mainly attributed to the alkaline activating solution (Habert et al., 2011; Melado et al., 2014). Therefore, to reduce the environmental impact of inorganic polymers, it is beneficial to reduce the amount of activating solution, to find another way to produce the solution or to search an alternative activator.

Alternative ways to produce alkali silicate solutions have been investigated, e.g. by Bouzon et al. (2014). The challenge in present paper is to replace these pure chemicals completely with a natural strong alkali. The use of a natural source of alkalis is not only beneficial for the processing cost and environmental impact, but also enlarges the accessibility of the precursors for people in less developed regions or allows higher volumes of production in the more developed world. Biomass ashes are selected for this purpose. From biomass ashes a solution can be obtained with high alkalinity, commonly called a lye (Liodakis et al., 2005). An overview of the chemical composition of biomass ashes from different sources has been collected by Vassilev et al. (2013, 2014). The chemical composition is discussed in detail in the referred articles, only general trends relevant to inorganic polymer synthesis are mentioned here. The most abundant elements in biomass ashes are calcium, potassium and silicon (Vassilev et al., 2013). Different sources of biomass deliver different compositions. In wood ashes calcium is most abundant, while herbal ashes mainly consist of potassium and silicon (Vassilev et al., 2013). Therefore, herbal ashes can be investigated for use as activator in geopolymer-like inorganic polymer synthesis. Wood ashes can be investigated for use in calcia rich, C–A–S–H type (Macphee and Garcia-Lodeiro, 2011) binders.

Metakaolin is selected as aluminosilicate source. It is a widely used precursor for inorganic polymer synthesis and can therefore be considered as a model system. Kinetics and formation mechanism have been studied by numerous authors (Duxson et al., 2005; Rahier et al., 2007; Bell et al., 2009) and nowadays metakaolin is used on its own (Temuujin et al., 2009; Cheng et al., 2012) or as a blend (Soleimani et al., 2013; Zhang et al., 2014) in applied research studies on inorganic

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polymerization. The calcination temperature that is used for transforming kaolin into metakaolin is an important factor for inorganic polymer synthesis. Its influence on inorganic polymer properties has been investigated by Rahier et al. (2000). However, no direct relation between inorganic polymer strength and calcination temperature has been developed, as the relation is complex and depends on the genesis of and impurities in the kaolin clay (Medri et al., 2010; Autef et al., 2013).

The present paper investigates first the optimal temperature for calcination of the kaolin, by studying the influence of the calcination temperature on the compressive strength after 7 days at room temperature. The biomass ash with the highest potential for alkali activation was selected from a range of herbal ashes and tree ashes by measuring their alkalinity by pH measurements and alkali content by X-ray fluorescence (XRF). The reactivity of the biomass ash–metakaolin mixture upon addition of water is investigated by calorimetric techniques, after which inorganic polymers were synthesized. The influence of the ash to metakaolin ratio and curing conditions on the compressive strength is investigated. Using scanning electron microscopy (SEM), attenuated total reflectance Fourier-transformed infrared spectroscopy (ATR-FTIR), and electron probe micro-analysis (EPMA), the inorganic polymers were structurally investigated, providing an explanation for the relative strengths.

2. Experimental

2.1. Materials

The kaolin used in this study originated from the UK and was provided by Imerys. Metakaolin was synthesized by heating the kaolin in a furnace at temperatures of 700, 750, and 800 °C, as at 650 °C the extent of dehydroxilation was observed to be too low according to thermogravimetry. The samples were heated in a muffle furnace with static air atmosphere at about 15 K/min after which the temperature was kept constant for 1 h.

Two families of biomass ashes were investigated, wood ashes and plant ashes. The wood ashes originated from a mixture of oak and beech wood, burnt in a Contura 560 T wood stove at maximum air supply. The plant ashes originated from the combustion of agricultural waste in Cameroon. Maize ashes (from the cob and the stalk), and cotton ashes (from the shell and the stalk) were investigated. To ensure full decarbonization, the ashes were put in a furnace for 8 h at 750 °C (other parameters the same as for the kaolin). For lowest environmental impact it would be best to use a regional aluminosilicate also from Cameroon (like volcanic ash), but the chemistry and mineralogy of the precursor and inorganic polymer will be easier to understand with the more pure UK kaolin selected.

The composition of the inorganic polymer mix is expressed in molar ratios in Table 1. The activating solution is characterized by $SiO_2/(Na_2O + K_2O)$ and $H_2O/(Na_2O + K_2O)$ ratios. With respect to the solid precursors, only the phases that are considered reactive are taken into account. For metakaolin this is the amorphous metakaolinite phase. For the ashes, everything is considered to be reactive. The samples are named “ash-X”, with “ash” the type of ash used in the synthesis and X the mass ratio of ash to metakaolin. The maize ash mixes are designed to deliver a geopolymer binder with a ratio of $(Na_2O + K_2O)/Al_2O_3$ of 1. By estimating the dissolved amount of metakaolinite from the Na-silicate activated metakaolin (about 45 wt.%) and assuming different possible dissolution extents for the maize ashes (100 wt.%, 75 wt.%, 50 wt.%), the different mixes from 0.3 to 0.9 are calculated. The sample with a mass ratio of 1.2 is performed afterwards to find the optimum strength value. Metakaolin is assumed to dissolve in the same extent for every mix, which will be proven to be invalid in the continuation of this paper.

Using a Hobart mixer, mortars for compressive strength testing were prepared with a sand to clay (kaolin or metakaolin) ratio of 1.5, as this was showed optimal in preliminary tests, and binder compositions as presented in Table 1. Speed 1 was used when gradually adding the clay or clay–ash blend to the sand and activating solution or water. Quartz sand with standardised particle size distribution (EN 196-1) was used. The mixing procedure was completed by mixing 1 min on speed 1 and 3 min on speed 2. For shaping, a Nannetti press was used. A uni-axial pressure of 59 MPa was maintained for 30 s for the synthesis of 4 samples per batch. The samples synthesized to obtain the optimal calcination temperature of the kaolin, were cured at room temperature (20 °C, 60% relative humidity). For the ash activated metakaolin, curing took place in a drying oven at 80 °C for 48 h with all surfaces of the samples freely exposed if not mentioned otherwise. This curing conditions have been found optimal by Slaty et al. (2013). The samples were stored before testing in a chamber under controlled conditions of 20 °C and 60% relative humidity.

2.2. Methods

2.2.1. XRF

Semi-quantitative wavelength dispersive X-ray fluorescence (XRF) spectrometry on a Philips, model PW 2400 spectrometer, was used for the chemical analysis.

2.2.2. XRD

The X-ray diffraction (XRD) analysis was performed on a Philips PW 1830 diffractometer. To be able to perform the analysis quantitatively, 10 wt.% of ZnO as an internal standard was used. For clay samples, this was mixed with the samples in a McCrone Micronizing mill for 5 min. Quantification was performed by Quanta. In this method, the spectrum is fitted with previously obtained experimental data. For clays, this method has shown to be accurate (Omotoso et al., 2006). The ashes were treated differently. Because they are very reactive, the preparation was executed without contact with moisture. The samples were mixed with the ZnO using mortar and pestle until visually observed to be homogeneous. Afterwards, the samples are put in a Turbula mixer for 4 h for further homogenisation. The analysis of the XRD patterns is performed using the Rietveld method and Topas software.

Table 1
Composition of the activating solution and the chemically active system expressed as molar rations, and the solid to water (S/W) content as mass ratio.

Sample name	$SiO_2/(Na_2O + K_2O)$	$H_2O/(Na_2O + K_2O)$	$(Na_2O + K_2O)/Al_2O_3$	SiO_2/Al_2O_3	S/W
MK700	0.88	15.64	0.27	2.24	3.22
MK750	0.88	15.64	0.27	2.24	3.22
MK800	0.88	15.64	0.27	2.24	3.22
Maize stalk 0.3	/	∞	0.31	2.31	3.20
Maize stalk 0.6	/	∞	0.33	2.27	3.20
Maize stalk 0.9	/	∞	0.62	2.61	3.20
Maize cob 0.3	/	∞	0.65	2.54	3.20
Maize cob 0.6	/	∞	0.92	2.90	3.20
Maize cob 0.9	/	∞	0.97	2.81	3.20
Maize cob 1.2	/	∞	1.28	3.07	3.20