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Research paper

Influence of gibbsite and quartz in kaolin on the properties of metakaolin-based geopolymer cements

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ABSTRACT

Three different kaolins (K1, K2, K3) from sources in Cameroon were applied for producing geopolymer cements. The kaolins differ significantly in their gibbsite and quartz contents. Thermal transformation (700 °C, 4 h) into their metakaolins MK1, MK2, MK3 shows the total loss of crystalline kaolinite and reveal the typically rather broad bump in the X-ray pattern. Gibbsite becomes dehydrated into γ and χ-Al_2O_3. Geopolymer cements (GP1, GP2, GP3) were obtained using freshly prepared sodium silicate solutions (NWG) with a ratio NWG/MK = 0.87. It could be observed that the initial (60/80/90 min) and final (90/140/160 min) setting time increases and their 28 day compressive strength (49/39/30 MPa) decreases in the course GP1/GP2/GP3. It is discussed that the higher content of quartz in K1 (up to 22 wt.%), compared to K2 (10 wt.%) and K3 (8 wt.%) promotes higher strength values and decreased setting times. Gibbsite was not present in K1, but up to 11 wt.% in K2 and 28 wt.% in K3, transformed in its dehydrated forms remains unreacted during geopolymerization. Therefore, the higher content of gibbsite in the kaolinite could be related to a lower strength. The reacted volumes and compositions of the geopolymer become almost the same in all three cases. A content of 30–50% of unreacted metakaolin was proved in all cases.

1. Introduction

A better knowledge for the production of geopolymer cements based on raw materials (calcined kaolin, volcanic scoriae) and waste materials (slag, fly ash) becomes more and more important to improve the local economy (Provis and van Deventer, 2009; Kriven, 2011). Many previous studies show that geopolymers possess advanced properties compared to ordinary Portland cements, such as fast setting time, high compressive strength, long-term durability, good fire resistance (Elimbi et al., 2014) and acid resistance (Bakharev, 2005). Due to such properties, geopolymers have the potential to be used in several industrial applications. The most important advantage of geopolymers is their low manufacturing energy consumption and low CO_2 emission (Duxson et al., 2007), which make them a "green material" (Essaidi et al., 2013).

Geopolymers are X-ray amorphous three dimensional aluminosilicate networks that can be synthesized at room- or slightly higher temperature by alkaline activation of suitable aluminosilicate source materials from industrial wastes (Oh et al., 2010), or with metakaolin (Elimbi et al., 2011, 2014), volcanic scoriae (Tchakoute et al., 2012, 2013a,b,c), etc. Among these precursors, metakaolin has a high reactivity and relatively simple composition compared to other materials and has been extensively studied to understand the mechanisms of geopolymer formation (Rowles and O'Connor, 2003, 2009; Duxson et al., 2005a,b; Rüscher et al., 2010a,b,c). It has been shown that the mechanical properties of metakaolin based geopolymer cements rather sensitively depend on the chemical compositions given with the waterglass/metakaolin ratio and also depend on the curing behavior. The role of silica source material on the geopolymerization rate or the degree of metakaolin dehydroxylation has been investigated in some detail by Autef et al. (2012, 2013a,b). In this sense details of the composition of the used kaolinite seems to be important, for example the positive effect of the presence of quartz in the natural source (Rüscher et al., 2013). Kaolinite, $Al_2Si_2O_5(OH)_4$, is a simple layer silicate consisting of alternate layers of silica and alumina in tetrahedral and octahedral coordination, respectively. The natural source kaolin is usually composed of kaolinite as the major mineral with other minerals such as quartz, illite, hematite, goethite, gibbsite, halloysite, anatase, etc. Previous researches have shown that some secondary minerals such as illite, quartz and halloysite present in kaolin influence the morphology, reaction process and final properties of geopolymers (Zibouche et al., 2009; Zhang et al., 2012; Rüscher et al., 2013). Among these secondary minerals, the effect of gibbsite has been paid less attention. It is a crystalline aluminum trihydroxide and is a very common component of clays (Santos et al., 2005).

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The aim of this work was to investigate and compare the properties of metakaolin-based geopolymer cements, using three kaolins with different contents of gibbsite and quartz. The starting materials were characterized by their chemical and mineralogical compositions and Fourier Transform Infrared (FTIR) spectroscopy. The effects of gibbsite in kaolin on geopolymerization reaction, structure and mechanical properties have been studied using setting times, X-ray diffractometry (XRD), thermal analysis (DTA/TGA), Fourier Transform Infrared spectroscopy and compressive strength.

2. Experimental

2.1. Materials

The kaolins were extracted from Dibamba (K1, Littoral Region of Cameroon) and also provided by the group Nubru Holding (K2, K3) which is involved in the valorization of certain local raw materials in Cameroon. The starting materials were crushed in a mortar and then sieved to 90 μm followed by calcination (Nabertherm, Mod. LH 60/14) for 4 h at 700 °C (heating/cooling rate of 1°/min) obtaining metakaolin samples MK1, MK2, MK3. The heating rate of 1°/min was chosen according to the conclusion of the work of Kenne et al. (in press). Commercially available gibbsite was dehydrated (4 h at 700 °C) used as reference material (Merck, F1148393 306) and the commercial available quartz was also used.

The alkaline solution was prepared by mixing aqueous solution of sodium hydroxide (10 M, 99% NaOH dried pellets in distilled water) and commercial sodium silicate solution with a mass ratio of 1.6. This solution was sealed to prevent reaction with CO_2 from the atmosphere and then stored for at least for 24 h at ambient temperature before use to allow full silica dissolution, cooling and equilibration. The nominal composition of the sodium water glass (NWG) had a composition by weight of 28.7% SiO_2, 8.9% Na_2O, 62.4% H_2O and the bulk density of 1400 kg/m^3.

Pastes were prepared by adding NWG gradually to each metakaolin in a Hobart mixer (M & O model N50-G) and mixed for 10 min, obtaining the series of samples GP1, GP2, GP3. The liquid/solid mass ratio was kept constant at 0.87 obtaining a suitable workability. The fresh geopolymer paste samples were rapidly molded into cubic molds (edge = 20 mm) and were vibrated for 5 min on an electrical vibrating table (M & O, type 202, No. 106) to remove entrapped air bubbles. During hardening of the geopolymer paste samples, the samples were covered with a thin film of polyethylene for 24 h at the ambient atmosphere before demolding. To ensure reproducibility, six duplicate specimens were prepared for each geopolymer paste.

2.2. Characterizations

The chemical composition of the kaolins was determined using ICP-AES (Inductive Coupled Plasma-Atomic Emission Spectrometry). Thermo Gravimetric Analysis (TGA) of kaolins was performed with the samples held in a Pt crucible between 25 and 975 °C using a NETZSCH STA-449F3. The samples were heated at 20 °C min^{-1} in a dry air flow. TGA of crushed geopolymer cements was performed using alumina crucible between 25 and 600 °C (technical air with flow 20 ml/min, 5 °C/min heating/cooling rate, Setaram Setsys Evolution 1650). XRD-patterns of powders of kaolins, metakaolins, quartz, geopolymer cement, gibbsite and dehydrated gibbsite were taken using CuKα radiation between 5 and 80° in 20 h in steps of 0.02° (Bruker D8). Infrared (IR) absorption spectra were taken by the KBr method (200 mg KBr, 1 mg sample, Bruker Vertex 80 V, 2 cm^{-1}, 32 scans).

The initial and final setting times were measured with fresh geopolymer pastes using the Vicat apparatus according to the EN 196-3 standard. The needle used was 1.00 ± 0.05 mm in diameter. Each metakaolin was placed in the mixer bowl successively. Then, the Hobart mixer was operated at gear 1 for 5 min. Within the 5 min, the prepared amount of activator (liquid/ solid of 0.87) was poured into the mix on two separate times. Geopolymers were cast into the 40 mm height, 40 mm diameter conical mold in two layers. Each layer was tamped with a rod for 25 times. For every 10 minute interval, the specimen was placed on the Vicat apparatus to measure the initial and final setting times. These setting times were measured at room temperature (25 ± 3 °C).

The compressive strength of the geopolymers was measured after 28 days staying under ambient temperature of the laboratory using an electro-hydraulic press (M & O, type 11.50, No. 21). Six samples of each synthesized geopolymer paste were tested with average compressive strength values reported as the result. The specimens were subjected to a compressive force at average rate of 3 mm/min until the specimen failed (refer to ASTM C 109 standard test methods). Before the compressive strength test, each specimen was polished by sand paper to obtain flat and parallel surfaces to avoid non-loading.

3. Results

3.1. Characterization of kaolins and metakaolins

The results of ICP AES analysis of the kaolins K1, K2, K3 show high total Al_2O_3 plus SiO_2 contents, between 78 and 83% (Table 1). Other contributions (K_2O, Na_2O, Fe_2O_3, TiO_2, MgO CaO, etc.) sum up to 2.85%, 1.6% and 2.31% for K1, K2, and K3, respectively (values < 0.1 disregarded). The Fe_2O_3 content is responsible for the reddish color observed for the metakaolins. The amount of TiO_2 indicates the presence of anatase as detected below in the XRD pattern (Figs. 2, 3). The presence of K_2O is attributed to minor amounts of micaceous or K-feldspar mineral, and in combination with Na_2O as for K_1 probably to traces of Na-feldspar (Monteiro et al., 2004). Feldspar, however, did not show up in our X-ray analysis (see below). Kaolins K_1 and K_2 are characterized by a high loss of ignition of about 15%. K3 even lost 18%. This loss is mostly due to the presence of kaolinite and gibbsite (see below).

The details of mass loss observed in TGA measurements (Fig. 1) enable a rather easy and accurate estimate of the content of kaolinite available suggesting that the mass loss of kaolinite is always close to 13.96 wt.% in relation to the ideal composition $Al_2Si_2O_5(OH)_4$. Therefore, the total loss obtained between 320 °C and 800 °C reveal 76.3%, 80.9% and 64.5% of kaolinite for K1, K2 and K3, respectively. For K1 the effect of dehydroxylation of kaolinite is centered around 570 °C whereas for K2 and K3 this effect is about 510 °C. Such a difference could be related to the different shapes of kaolinite grains or sizes. It has been reported that the mass loss is shifted to lower temperatures with decreasing grain size, depending on the area to thickness ratio of the sheet type crystals and also with increasing crystal defects (Huertas et al., 1997; Pérez-Rodriguez et al., 2006). A further step feature centered around 300 °C is related to the dehydrating effect of gibbsite, $Al(OH)_3$, in K2 and K3, estimating their contents to around 11.3% and

Table 1
Chemical composition of the kaolins (K_1, K_2 and K_3) in mass percent.

Oxide	K_1	K_2	K_3
SiO_2	44.10	47.2	39.09
Al_2O_3	33.90	35.1	39.44
Fe_2O_3	0.99	0.46	0.74
K_2O	0.42	0.46	0.30
TiO_2	0.83	0.49	1.14
MgO	0.20	0.19	0.13
Na_2O	0.20	<0.1	/
CaO	0.21	<0.1	/
SO_3	<0.02	< 0.01	/
P_2O_5	0.03	/	0.06
Cr_2O_3	0.02	/	/
MnO	0.01	/	/
LOI	14.75	14.94	18.48

LOI: loss on ignition at 1000 °C.