Applied Clay Science 135 (2017) 386–393

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

The influence of alkali activator type, curing temperature and gibbsite on the geopolymerization of an interstratified illite-smectite rich clay from Friedland

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ARTICLE INFO

Article history:
Received 21 August 2016
Received in revised form 8 October 2016
Accepted 13 October 2016
Available online 19 October 2016

Keywords:
Alkaline activation
Illite-smectite
Geopolymers
NaOH
KOH
Gibbsite

ABSTRACT

Illitic clays, such as the interstratified illite-smectite clays, are one of the most abundant aluminosilicates on Earth's surface and are widely available for geopolymer production. Geopolymers are a group of alkali-activated materials, which are gaining increasing attention as low-CO_2 binders with some advantageous properties compared to ordinary Portland cement. In this study, high strength geopolymers were formed from a calcined and ground interstratified illite-smectite clay, which was mixed with 6 M NaOH or KOH and cured at 25, 50 and 75 °C. We furthermore tested the effect of increasing Al content of the precursor by adding gibbsite to the metaclay. The temperature dependent reactivity of the precursor, i.e. the Si and Al solubility of the metaclay and gibbsite is shown. It is revealed that the geopolymerization of the meta-illite-smectite clay was favored by KOH-activation at 50 °C. Adding 10 wt% gibbsite by solid mass increased the strength of the geopolymers by ~20% from 38 to 45 N/mm^2, which is partly attributed to increased formation of an amorphous aluminosilicate gel. NaOH-activation was not affected by gibbsite addition and increased strength only at 75 °C, which was related to phillipsite (zeolite) crystallization. Na-geopolymers showed lower strength of ~30 N/mm^2 and abundant capillary pores.

1. Introduction

Since the 1990's and in a time of increased awareness of the effects of global warming and climate change, geopolymers are becoming more important as alternative construction materials to traditional Portland cement due to their potential as low-CO_2 cements (Davidovits, 1976; Pacheco-Torgal et al., 2008). Geopolymers are alkaline activated binders with low calcium and moderate to high Al concentrations, which are produced by the reaction of hydroxide solutions with reactive aluminosilicate materials (Provis and van Deventer, 2009; Yung-Ming et al., 2016). Aluminosilicates are derived from industrial wastes such as fly ash or from calcined clays, especially metakaolin. Due to the low concentration of carbonate phases in these precursor materials and the relative lower energy consumption during their processing, CO_2 emissions during production can be significantly less compared to the production of Portland cement (Van Deventer et al., 2012, Ouellet-Plamondon and Habert, 2014; Provis et al., 2015). Illitic clays and rocks constitute some of the most abundant materials formed in surface and near surface enviroments in both marine and continental settings and are common to sedimentary rocks, soils and argillaceous sediments (Meunier and Velde, 2004). Thus, illitic clay minerals such as the interstratified illite-smectite offer great potential as high quality and low cost raw material for geopolymer synthesis.

The effect of calcination temperature on illite-smectite minerals of different compositions, i.e. a synthetic NH_4^+-bearing and a natural, smectite-rich illite-smectite to form a highly reactive and amorphous meta-illite-smectite precursor has been well studied (He et al., 2000; Buchwald et al., 2009; Garg and Skibsted, 2016; Dietel et al., 2016). However, it has not yet been possible to synthesize meta-illite-smectite-based geopolymers of high strength (>20 Nmm^2) without the addition of cement additives. As the alkaline activator type and curing temperature are well known parameters that control geopolymerization and need to be optimized for producing high strength binders (Duxson et al., 2007), in this study we addressed 1) the reactivity (Si and Al solubility) of a calcined and ground meta-illite-smectite clay from Friedland (NE Germany) in 6 M NaOH or KOH, which was cured at 25, 50 and 75 °C and 2) the development of the mineralogy, microstructure and the mechanical properties of the resulting 28 days old geopolymers. Due to the high SiO_2 content and relatively low Al_2O_3 content of the Friedland clay (Si/Al = 2.8) and the assumption that adequate reactive Al is required for irreversible chemical hardening (Duxson et al., 2007), we

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http://dx.doi.org/10.1016/j.clay.2016.10.021
0169-1317/

furthermore investigated the effect of increasing Al content of the precursor by adding a synthetic gibbsite ($Al(OH)_3 \cdot nH_2O$) to the metaclay. Our results demonstrate that geopolymer binders of significantly higher strength (up to 45 N/mm^2) can be produced by alkali activation of Friedland metaclay, as long as adequate attention is given to the type of alkali activator and the curing temperature used.

2. Materials and methods

To synthesize illite-smectite metaclay-based geopolymers we used a raw clay material (Batch No. 101693/43) from a local supplier in Friedland (Mineralische Rohstoffmanagement GmbH), which is located in Mecklenburg-West Pomerania (NE Germany). The Friedland clay of late Eocene age (~56 million years) is comprised of a mixture of fluvial and marine transported detritus derived from the weathered crust of the Baltic Shield and Bohemian Massif, together with diagenetic clay minerals formed during subsequent burial of the sediment (Henning and Kasbohm, 1998). The illite-smectite clay was calcined at 850 °C for 1 h in a muffle furnace (Nabertherm-N11) to produce a reactive and partly amorphous meta-illite-smectite clay (referred to as metaclay) precursor for geopolymer synthesis (Figs. 1, 2) and subsequently ground for 2 h in an agate ball mill (Retsch-PM4) to significantly increase its reactive surface area and decrease its grain size (Fig. 3). 850 °C has been observed to obtain an optimum amount of a reactive and amorphous aluminosilicate precursor material (~50 wt%) from the Friedland clay (Buchwald et al., 2009). Calcination at higher temperatures would form spinel and γ-Al_2O_3, which incorporates Al in its crystal structure and in return will decrease the amount of reactive Al from the amorphous precursor (Buchwald et al., 2009; He et al., 2000). Synthethic gibbsite ($Al(OH)_3 \cdot nH_2O$) from Merck was mixed with the metaclay to vary the Si/Al ratio of selected precursor materials. Four mixtures were studied comprised of 1) the metaclay with no gibbsite, 2) the metaclay with 5 wt% gibbsite of solid precursor mass (MG5), 3) the metaclay with 10 wt% gibbsite of solid precursor mass (MG10) and 4) the metaclay with 15 wt% gibbsite of solid precursor mass (MG15), which exhibit molar Si/Al ratios of 2.8, 2.4, 2.0 and 1.8, respectively (Table 1).

The mineral phases of the raw clay, the metaclay, gibbsite and the alkali-activated cements were identified by using a Siemens-D5000 X-ray diffractometer equipped with a Cu-K_α source (Ni-k_β filter) and a scintillator detector. The XRD patterns of randomly oriented powder samples were aquired at 40 kV and 30 mA over a 2-Theta range from 5 to 50° with a step-size of 0.02° and 2 s/step dwell time (Fig. 1). The mineral phases were identified with help of the software DIFFRAC^{PLUS} Basic Evaluation Package Release 2008 EVA V14 from Bruker AXS. For this

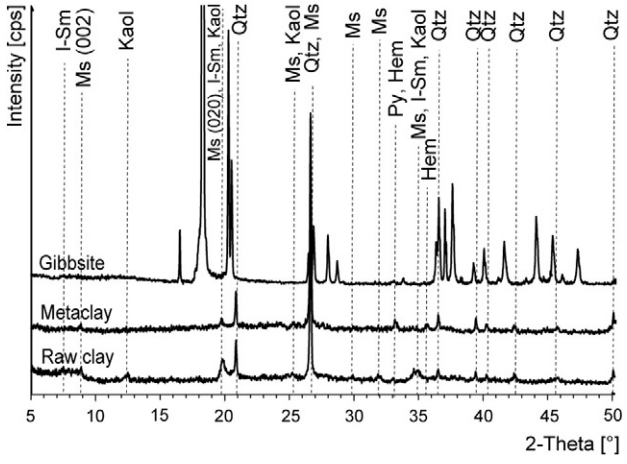

Fig. 1. X-ray diffraction patterns of precursor materials: raw clay, calcined and ground metaclay and gibbsite. I-Sm: illite-smectite, Ms: muscovite, Kaol: kaolinite, Qtz: quartz, Py: pyrite, Hem: hematite.

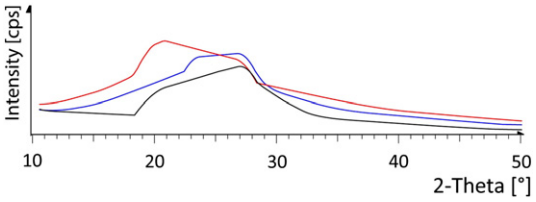

Fig. 2. XRD background broadening of the raw illite-smectite clay (black), the calcined (blue) and the subsequent ground metaclay (red). The reflections of the crystalline phases were substracted from the diffratogram by using the EVA software evaluation program.

purpose, the following data files from the Inorganic Crystal Structure Database ICSD were used: muscovite (#063123), kaolinite (#008697), quartz (#063532), hematite (#066756), pyrite (#000316), phillipsite (#023902) and zeolite L (#067031). The illite-smectite was characterized with the help of calculated patterns of Moore and Reynolds Jr. (1997). To compare qualitatively the relative amount of amorphous phases in the raw clay and the metaclay, the areas of the elevated XRD backgrounds of the samples were measured by fitting with parabola function after first removing the X-ray reflections of crystalline phases (Fig. 2). Here, the background evaluation method of the software EVA was applied, using the enhanced method with a curvature function and a threshold of 1.

The chemical composition (Table 1) of the precursor materials was determined using a X-ray fluorescence spectrometer (Phlips-PW 2404) equipped with a Rh target X-ray tube, LiF spectrometer crystals and scintilation and sealed gas detectors. Analyses were carried out at 60 kV and 50 mA after the powder samples were mixed with $LiBO_2$, $Li_2B_4O_7$ and I_2O_5 and solubilized at ~1100 °C in a propane flame.

Morphological imaging of the cement particles and determination of their chemical composition was undertaken using a focused ion beam - secondary electron microscope (Zeiss - Auriga) coupled with an energy dispersive X-ray spectrometer (Oxford Instruments – 80mm^2 X-Max®). The cathode of the SEM is a Schottky field emission cathode and secondary electron images were recorded using an inlens detector with a resolution of 1 nm at 15 kV. Semi-quantitative determinations of the chemical compositions were conducted by machine calibration to Cu-metal and internal calibration by the Oxford INCA Instrumental software. Spot test of mineral phases of known chemical composition produced results of <5% precision for the main cations present (Si, Al, Na, Fe, Mg, K and Ti). 5–6 repeat analyses of each phase were measured to determine the mean oxide concentrations (Table 3), which were normalized to 100 wt%. Fe_2O_3 concentrations were calculated from FeO values by multiplying FeO by a factor of 1.111.

Sample surface area was measured by nitrogen adsorption at − 196,15 °C using a Quantachrome Autosib-1-c. Prior to analyses, the samples were degassed in vacuum at 105 °C for 12 h. The sample specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938).

In order to study the relation between the dissolution behaviour of the ground metaclay precursor and its geopolymerization, reactivity tests were conducted at three different temperatures. The ground metaclay was dissolved in 6 M NaOH or KOH at a solution/solid ratio of 1000 (as used by Buchwald et al., 2009). The tests were conducted at 25, 50 and 75 °C for 6, 24, 72 and 168 h. The amount of dissolved Si and Al was determined on aliquots by a flame atomic absorption spectroscope (Analytik Jena - AAS – contr AA®) equipped with a xenon lamp. A gas mixture of N_2O-C_2H_2 produced the flame. The primary Si line (251.61 nm) and the primary Al line (396.15 nm) were used for analysis. 6 repeat analyses of each sample were measured to determine the mean Si and Al concentration.

Geopolymers were synthesized by mixing 210 g precursor material with 105 g 6 M NaOH or KOH at a solution/solid ratio of 0.5 using a shear mixer (IKA - Eurostar 20) at 500 rpm for 10 min. 25 g binder