



Research paper

Lime-calcined clay materials with alkaline activation: Phase development and reaction transition zone

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ABSTRACT

The research aim was to investigate phase development and reaction transition zone of alkaline activated lime-calcined clay materials. Locally available china clay mainly supplied metakaolin (MK) after calcination. MK and calcium hydroxide (CH) were used to supply SiO₂ and CaO, respectively. The CH to MK ratio of 0.4 with CaO/SiO₂ of 1.18 was selected to coincide with the theoretical CaO/SiO₂ of calcium silicate hydrate in tobermorite group (Ca₅Si₆O₁₆(OH)₂). Phase development was investigated using X-ray diffraction and Fourier transform infrared spectroscopy. Compressive strength and density were also investigated to confirm binding properties of the pozzolanic reaction products. The reaction of mixture was dependent on the NaOH concentration. At low concentration of NaOH (<1 M), the pozzolanic reaction was dominant while the zeolitic reaction and geopolymerization became dominant at medium NaOH concentration (>1 M) and at high NaOH concentration, respectively. The activations of CH:MK mixtures with 0.01 and 0.1 M NaOH promoted semicrystalline calcium silicate hydrate (CSH (I)) and crystalline calcium aluminosilicate hydrate (CASH) formations. The mixture with 0.01 M NaOH gave the highest compressive strength of 19.0 MPa. With 3 and 5 M NaOH activations, sodium aluminosilicate hydrate (NASH) and sodium calcium silicate hydrate (NCSH) compounds were formed instead of CSH (I) gel and crystalline CASH phase. At 10 M NaOH, NCSH disappeared and only NASH was formed and resulted in a relatively low compressive strength of 6.7 MPa.

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1. Introduction

Pozzolans have been receiving high attention as their use as supplementary cementing material to react with calcium hydroxide (CH), so called “pozzolanic reaction” to form compounds possessing binding properties resulting in concrete strength enhancement (ASTM C125, 2011). Uses of pozzolans as supplementary cementing material from various sources such as volcanic ash, clay minerals, and coal ashes aim to reduce cost and overall environmental impact according to CO₂ emission. Calcium silicate hydrate (CSH) gel is a pozzolanic reaction product for strength improvement together with porosity reduction (Chindaprasirt and Pimraksa, 2008; Frías et al., 2000; García et al., 2009 and García et al., 2009; Kakali et al., 2001; García et al., 2009; Siddique and Klaus, 2009; Sabir et al., 2001). The CSH gel formed at ambient temperature exists in both amorphous and semicrystalline phases at which a distorted semicrystalline phase referred as CSH (I) is normally found as hydration product. Its composition varies considerably depending on parameters such as the component materials (CaO/SiO₂

ratio) and the pH of the surrounding medium (Chen et al., 2004; García et al., 2008; Yip et al., 2005). CSH gel has been found to be compatible to other hydrated products such as sodium aluminosilicate hydrate gel (NASH) which is a new family of aluminosilicate polymers (geopolymers) (García et al., 2008, 2010; Yip et al., 2005). However, CSH and/or calcium aluminosilicate hydrate (CASH) compounds could also precipitate as well-crystalline solids. Geopolymers are usually precipitated by reacting active aluminosilicate materials such as metakaolin (MK) and fly ash, with an appropriate proportion of alkali metals (Na, K, Ca) under very high alkalinity conditions in which the water content is limited (Davidovits, 1989, 1991; Khale and Chaudhary, 2007; Steveson and Sagoe-Crentsil, 2005; Verdolotti et al., 2008).

The mechanism of alkaline activated CH and MK materials are quite close to geopolymer cement (Khale and Chaudhary, 2007; Yip et al., 2005). Geopolymer cement is formed by 2 main steps; dissolution of reactive starting materials and polycondensation of reaction products. For alkaline activated CH and MK materials, the second step includes the precipitation of the pozzolanic reaction products in addition to the polycondensation. Therefore, chemical structures of alkaline activated CH and MK materials compose of several forms of products ranging from highly alkaline products such as geopolymer, zeolite material

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and hydration gel products of CSH and CASH. Not many works explored the relation between CSH and CASH/MASH gels ($M =$ alkali metals) by alkaline activation, to their mechanical properties (Alonso and Palomo, 2001a,b; Yip et al., 2005). However, the coexistence of geopolymeric and CSH gels obtained from using ground granulated blast furnace slag and MK as starting material is responsible for the strength enhancement as geopolymeric binder works as micro-aggregate, thus resulting in the homogeneous and dense structures (Yip et al., 2005). In synthesizing CSH gel including pozzolanic reaction and sol–gel procedures, the CSH gel was produced cooperating with alkaline aluminosilicate product at high alkalinity (Alonso and Palomo, 2001a,b; Bondar et al., 2011; Granizo et al., 2002; García et al., 2008, 2010). Sol–gel procedure was used to synthesize both CSH and NASH gels. pH level was found to play a determinant role as $\text{pH} > 11$ and > 12 resulted in CSH and NASH gels, respectively (García et al., 2008).

This study, therefore, proposed an investigation of alkaline activated CH and MK materials in terms of their phase development and reaction transition zone. The attention to explore pozzolanic reaction of MK was due to the advantages of abundantly local availability and its highly reactive nature. Locally available clay is used as starting material to obtain MK in this study. Not only does such clay contain kaolinite (Kaol), but also muscovite and quartz. With calcination during 500–800 °C, Kaol is transformed to MK by dehydroxylation at which bound hydroxyl groups located at octahedral sites of Kaol are dispelled resulting to a disruption of Kaol structure (Sabir et al., 2001; Siddique and Klaus, 2009; Vizcayno et al., 2010). However, some clay minerals are much less reactive although they undergo dehydroxylation due to their crystallinity are not all disrupted, for example, illite or muscovite and montmorillonite (Fernandez et al., 2011). Quartz is also inert to pozzolanic reaction (Carroll and Starkey, 1971; Deschner et al., 2012; Fennis et al., 2009; Mechti et al., 2012; Yock, 2009). Many researchers reported some inert minerals also influenced on mechanical properties of material structure due to filling effect (Deschner et al., 2012; Fennis et al., 2009; Jaturapitakul et al., 2011; Mechti et al., 2012). With alkaline activation, such inert minerals have been found to be dissolved. For example, the findings from dissolution of aluminosilicate minerals in alkaline solutions at low and high concentrations, found that minerals composed of crystalline phases (cristobalite, feldspar, K-alunite, quartz, Kaol, illite, zeolite) could be dissolved to be aluminate and silicate ions in high concentration of alkaline activation (Panagiotopoulou et al., 2007). The pozzolanic reaction of MK under alkaline activation was, therefore, studied in term of mineralogical development in order to figure out the reaction transition zone of the formation between calcium based hydrate products and sodium based hydrate products using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) spectroscopy and the related mechanical properties. The reaction of secondary minerals such muscovite and quartz was also investigated. This finding would no doubt lay a solid ground work to explain the uses of locally available clay instead of pure MK.

2. Materials and experimental methods

2.1. Raw materials

Kaolin in this study was obtained from Ranong Province in southern Thailand supplied by Sibelco Mineral (Thailand) Co., Ltd. Its chemical composition characterized by X-ray Fluorescence (XRF) using a Horiba Mesa-500W with principle of energy dispersive XRF Analyzer and XEROPHY high-purity silicon used as detector, the results are shown in Table 1. Mineralogical composition was identified by XRD using a Rigaku Miniflex with $\text{CuK}\alpha$ radiation and K β -filter ($\lambda = 1.540 \text{ \AA}$), the current and voltage intensity applied to the generating X-ray tubes were 15 mA and 30 kW, the analysis was performed over the diffraction angle range $5^\circ \leq 2\theta \leq 70^\circ$ with a 12 degree min^{-1} and step width of 0.015° , as shown in Fig. 1 and in Table 1. The calcination temperature of kaolin was investigated by thermal differential analysis and thermal

Table 1
Chemical and mineralogical compositions of kaolin.

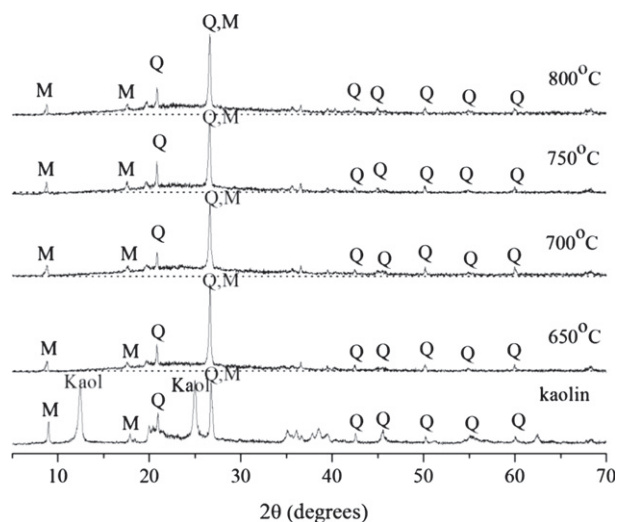
Characteristics	
Chemical composition (mass %):	
SiO ₂	53.08
Al ₂ O ₃	30.69
Fe ₂ O ₃	1.51
CaO	0.08
K ₂ O	2.46
MnO	0.11
Y ₂ O ₃	0.07
LOI	12.00
Mineralogical composition (mass %)	
Kaolinite	53.70
Muscovite	14.70
Quartz	31.60
Volume mean diameter, D[4,3] (μm)	20.01
Specific surface area (m ² /g)	21.07
Specific gravity	2.62
SiO ₂ /Al ₂ O ₃ molar ratio	2.93

gravimetric analysis (DTA/TGA) using a Seiko SSC-5000 analyzer with temperature range of room temperature to 1000 °C and heating rate of 10 °C/min. The DTA/TGA curves are shown in Fig. 2. From the DTA/TGA result, kaolin was calcined at 750 °C for transforming Kaol into MK phase (dehydroxylation). XRD was used to confirm phase formation of MK. The mineralogical compositions of Kaol were quantitatively calculated by Rietveld method refinement using X'pert high score plus software to report the degree of Kaol structure disorder.

Particle sizes and specific surface areas of clays were measured by Laser diffraction and by Brunauer–Emmett–Teller method (BET), respectively. The results are shown in Table 1. A commercial grade CH and analytical grade sodium hydroxide (NaOH) were used in this study.

2.2. Solubility of kaolin and MK in alkaline solutions

The solubility of amorphous phase contained MK due to phase transformation from Kaol to MK was studied using 0.500 g of kaolin and MK mixed with 20 mL of NaOH solutions at various concentrations (0.01, 0.1, 1, 3, 5 and 10 M). The solutions were filtrated by Whatman filter paper (no. 5) and 5 mL of solutions were diluted into 250 mL and adjusted to $\text{pH} < 1$ by hydrochloric acid. Atomic absorption spectrometer (AAS, SHIMADZU AA-6200) was used to analyze the dissolved Si and Al ion concentrations (Panagiotopoulou et al., 2007).



M = muscovite, Kaol = kaolinite, Q = quartz

Fig. 1. XRD patterns of kaolin and calcined kaolin at 650–800 °C.

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