



Review article

Geopolymer from kaolin in China: An overview

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ABSTRACT

The use of kaolin and calcined kaolin (metakaolin: MK) to manufacture geopolymer has attracted worldwide interests. The aim of this paper is to present an overview on the progress of the geopolymer research and development in China in the last 25 years. The works on geopolymerisation mechanisms, microstructure development, properties and the application development of geopolymers as green building material, thermal resistant material and advanced inorganic composites and ceramics are reviewed. Most of these works have been published, many of which are in Chinese, and have made significant contribution to the progress of geopolymer science and technology, as a whole from a global view. The latest experimental results of efflorescence and phase transformation are discussed as two key issues regarding to the application of MK-based geopolymers.

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1. Introduction

In the late 1970s, Professor Joseph Davidovits carried out the research on fireproof polymers and introduced the concept of *geopolymer*, which was coined to describe a family of alkali activated aluminosilicate binders (Davidovits, 2008). The formation of geopolymer was based on the reaction between the two parts of materials: alkali activator and reactive aluminosilicate precursor, which was mainly MK at the very early age of the research development. The geopolymer based on alkali-activation of MK has gained worldwide interests in the past 40 years, not only because of its excellent thermal stability, which is much better compared with conventional polymer material, but also due to its comparable mechanical properties to cements, which make it being considered as a green alternative to Portland cement (Duxson et al., 2007). In recent years, the rapid research and development of geopolymer has shifted from the early interests of thermal resistant applications towards construction and building materials (Pacheco-Torgal et al., 2008a, 2008b). And because of this, the raw materials used for large volume geopolymer manufacture has been significantly broadened, including heated low quality clays and a variety of Si- and Al-bearing waste materials and by-products sourced from different industries.

Despite the fact that fly ash and slag become the two major materials used in today's limited commercial geopolymer products, MK is

probably still the most promising feedstock materials for geopolymer in the future. This is because MK has more consistent chemical compositions than fly ash and slag, and is expected to result in more consistent and predictable products. In fact, fly ash and slag are becoming less available in many countries because of their effective usage in the manufacture of blending cements and concrete (Malhotra and Mehta, 1996; Joshi and Lohta, 1997), in addition to the cost and technical challenges of supply chain (van Deventer et al., 2012). Therefore, from a long term of view, the use of MK (perhaps with other Al- and Si-bearing minerals together) as raw materials is becoming more attractive and realistic.

MK is a thermally treated product from kaolin, which is one of the naturally occurring abundant minerals in the earth's crust. Kaolin refers to a family of kaolinitic clays that consist of a 1:1-type clay mineral with one tetrahedral sheet and one octahedral sheet (Bergaya et al., 2006; Zhou and Keeling, 2013), depending on the geological and weathering conditions. Kaolin has been historically used in the production of Portland cement. To produce 1 tonne of clinker, the most important ingredient in cement, it requires about 0.3 tonnes of clay to mix with 1.5 tonnes of limestone and other iron-bearing minerals and calcination at 1450 °C (Zhang et al., 2014a). Kaolin can also be used in another form as the supplementary cementitious material in concrete mixing. This utilization requires a thermal treatment process, usually at a temperature ranging between 500 °C and 800 °C, to convert kaolin into metakaolin (MK). MK is a pozzolan, which in itself possesses little or no cementitious property but will react chemically with calcium hydroxide (Ca(OH)₂) to form compounds in the presence of water to possess cementitious

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properties. Theoretically, the replacement, usually 5–20% in mass, contributes to a slight reduction of CO₂ emission due to the less intensive thermal and grinding treatment required in obtaining MK compared with cement clinker. In practice, however, MK is not commonly used in most construction cases due to the relatively large specific surface area, which may demand high water/binder ratio to achieve satisfying workability. This means that such a family of abundant resource is not utilized in large volume in concrete, the largest manmade materials used in the world. In comparison, geopolymer can be made with 100% MK, and this type of binder has shown great reduction (can be up to 70–80%) in CO₂ emissions.

With the worldwide interests of geopolymer, the number of scientific publications is increased exponentially in recently years as well as the research organizations, with three milestone technical books by Shi et al. (2006), Provis and van Deventer (2008) and Pacheco-Torgal et al. (2014), in addition to the contributions by Davidovits. The research topics of MK-based geopolymer cover from the reaction mechanisms and kinetics (Granizo and Blanco, 1998; Provis and van Deventer, 2007a, 2007b; Sagoe-Cretnsil and Weng, 2007; Weng and Sagoe-Cretnsil, 2007; White et al., 2012) to the molecular structure and microstructure (Duxson et al., 2005; Bell et al., 2008; White et al., 2010, 2011), the effects of raw materials (Granizo et al., 2000; Xu and van Deventer, 2003; MacKenzie et al., 2007; Zibouche et al., 2009; Kuenzel et al., 2013), the chemical, thermal and mechanical properties (Wang et al., 2005a; De Silva and Sagoe-Cretnsil, 2008; Bell and Kriven, 2009; Temuujin et al., 2009; Kamseu et al., 2011, 2012; Delair et al., 2012) and too many other aspects.

The aim of this paper is to present an overview on the progress of the MK-based geopolymer research and development in China in the last 25 years. Most of these works have been published, many of which are in Chinese, and have made significant contribution to the progress of geopolymer science and technology, as a whole from a global view. In addition, the latest experimental results by the authors in regarding to the critical parameters of geopolymer manufacture are also presented. The key issues regarding to the development and application of MK-based geopolymers are discussed for the future research.

2. Geopolymerisation mechanisms and products

2.1. Geopolymerisation mechanisms

Although there has been a significant progress on the research and development of alkali-activated slag and alkali-activated fly ash since the 1980 in China (Yang, 1996a, 1996b), the reported research on MK-based geopolymerisation mechanisms was started from the 2000. A very brief summary of the research on alkali activated MK systems for the period of 2003–2009 was presented by Pan and Yang (2010) at the First International conference on Advances in Chemically-Activated Materials held in 2010, Jinan, China.

Zhang et al. (2003) used environmental scanning electron microscopy (ESEM) to understand geopolymerisation process. It was observed that the MK grains packed loosely at 10 min after being mixed, leading to many large voids. As reaction proceeded, a large amount of gels were formed and gradually precipitate on the surface of MK grains, which were covered by thick gel layers at later stage, with reduction of large voids. Terminologically, *hydration* was still used to refer *geopolymerisation* at that time, which misleadingly brought the concept of conventional hydration of cement in mind. Duan et al. (2006) reported the reaction process of alkali activation of MK by monitoring the thermal history of MK mixed with modulus (SiO₂/Na₂O molar ratio) Ms = 2.41 sodium silicate at a Na₂O concentration of 20%. Only one exothermic peak was observed in 24 h at 25 °C. In combination with the zeta potential measurement, the authors tried to divide the geopolymerisation into initial, induce, accelerate, decelerate and stable stages, which were adopted from traditional cement hydration but endowed with new meanings.

In fact, there are many other factors that affect the number and shape of exothermic peak. When the MK is activated with the silicate solution of Na₂O·1.4SiO₂·10H₂O, the exothermic peak is affected by its specific surface area (Rahier et al., 2003), which has been verified by the mathematical modelling (Provis et al., 2005a, 2005b). Weng and Sagoe-Cretnsil (2007) studied the NaOH solution activation of MK as well as the sodium silicate activation of MK (Sagoe-Cretnsil and Weng, 2007). They found the exothermic peak shape to be significantly affected by the concentration of Na₂O and the formation of dissolved silica. It is worthy to highlight their valuable work of understanding the stability of alumina, silicate and aluminosilicate species by using nuclear magnetic resonance (NMR) technique and the speciation prediction with the partial charge model. They found that the condensation process in sodium silicate activated systems occurred in two stages: (a) quick condensation between aluminate and silicate species; followed by (b) a slow condensation stage solely involving silicate species. Zhang et al. (2009c) studied the reaction energy of every possible reorientation pathway using computational chemistry method with semi-empirical AM1 calculation, and made further attempt to understand geopolymerisation process, although there were some issues with the proposed states of alumina and silicate species, which were discussed in more details by Provis et al. (2010). Zhang et al. (2007, 2009b) also investigated the dissolution of MK and polymerization of alumina and silicate oligomers using semiempirical AM1 calculation method and reported that MK was more reactive in NaOH solution than in KOH due to the stronger ionic coordination of Na⁺.

Because of the complexity of reaction paths and the difficulty of quantifying the amorphous products entangled with amorphous raw materials, only a few techniques can provide quantitative and in-situ information of geopolymerisation. Calorimetric characterization technique is one of them, which can provide heat exchange during the reaction process. However, the traditional isothermal or non-isothermal measurements used for monitoring Portland cement hydration usually cannot monitor the very beginning of the reaction because it needs time to transfer the fresh mixture. The errors are shown to be large (Rahier et al., 2003; Weng and Sagoe-Cretnsil, 2007). Considering the irreplaceable advantages of calorimetry over other intermittent methods and the limitations of previous calorimetric methods, Zhang et al. (2009e) started, for the first time, to use the internal mixing technique. By using the equipment of 3114/3236 TAM Air isothermal calorimeter, which has inner mixing devices, they were able to equilibrate the MK and alkaline solution separately in the reaction ampule to a target reaction temperature (from 20 up to 60 °C) and monitored the reaction without gaps between mixing and measuring (Fig. 1).

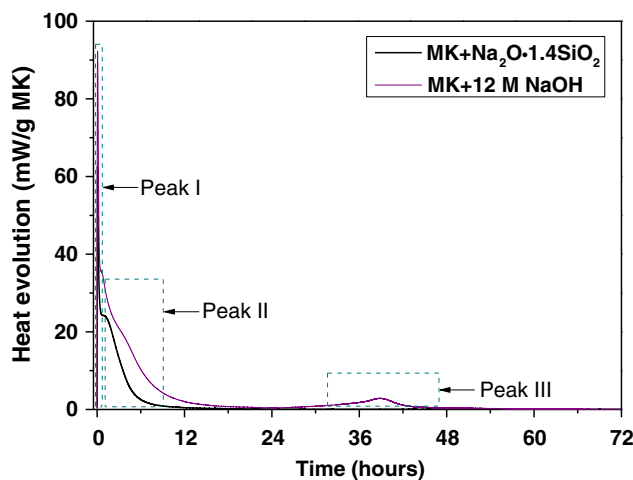


Fig. 1. Heat evolution rate of MK geopolymerisation activated by NaOH solution and sodium silicate solution (Na₂O·1.4SiO₂) at 40 °C. The peaks I, II and III correspond to different reactions (Zhang et al., 2012a, 2013a).

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