



## Hydrothermal synthesis and characterization of alkali-activated slag–fly ash–metakaolin cementitious materials

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### ABSTRACT

In the present work, the alkali-activated slag–fly ash–metakaolin cementitious materials were prepared by hydrothermal method. The as-synthesized products were characterized by X-ray diffraction (XRD), fourier transform-infrared spectrum (FT-IR), scanning electron microscopy (SEM), mercury porosimetry and universal testing machine. The results showed that the main mineral phases of the products were zeolite NaP1, analcime and aluminosilicate gel (zeolite precursor) when Si/Al/Ca molar ratio of the starting materials was 1.7:1.0:0.25. While Si/Al/Ca molar ratio of the system changed to 2.3:1.0:0.45, zeolite NaP1 transformed to analcime, and a tobermorite phase appeared. The quantities and types of zeolites synthesized depended on the Si, Al and Ca molar ratio of starting materials. The average compressive strength of the products was more than 60 MPa after hydrothermal process. And the products exhibited a porosity of less than 36% and a median pore diameter (area) of approximately 12 nm. The reaction degree results indicated that about 75% of starting materials transformed to zeolitic structure and aluminosilicate gel after alkaline activation and hydrothermal process.

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### 1. Introduction

The alkaline activation of active aluminum–silicon materials is a chemical reaction process that transforms glassy structures (amorphous and metastable phases in raw materials) into compact cementitious material [1–9]. These active aluminum–silicon materials are metakaolin, fly ash, pozzolan, lime and slag. The alkali activators are composed of sodium/potassium hydroxide solution, water glass or their mixtures. The resultant materials are probably an amorphous alkaline aluminosilicate gel [10–12], cement hydration products (hydrated calcium silicate (C–S–H) and tobermorite) [13,14], even some crystallized zeolitic materials [15–19] at elevated temperatures or hydrothermal conditions. The final mineral phases of products relies on the synthesis conditions such as the nature of starting material, temperature, aging and curing time, content and concentration of activators, etc.

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In recent years, metakaolin has been widely used in cement and concrete industries. As well known, metakaolin is a kind of disordered nature or amorphous structure, which results in high reactivity in favorable conditions such as alkaline activation and hydrothermal process. Besides, as a kind of active aluminum–silicon material, fly ash is also successfully applied to synthesize various zeolites [20–24]. Owing to its glassy phase and spherical shape, fly ash has potential activity in the presence of alkali and under the hydrothermal circumstance. Studies show that, when metakaolin or mixtures of metakaolin and fly ash were treated by alkaline activation and hydrothermal process, they can synthesize hydroceramics [25–27] and zeoceramics [15]. However, the lower strength of the products possibly restrains their application. If the mechanical strength and zeolites contents of these resultant materials were improved, they would be well used as an alternative for processing nuclear wastes with high contents of alkalis and salts. Researches find that the hydration products of alkali activated slag are mainly amorphous C–S–H gel and products which are similar to zeolites [28–30]. Furthermore, the alkali-activated slag cements have excellent mechanical strength, which have been widely used in many fields. Therefore, the properties of alkali slag cements provide an idea for us to prepare cementitious materials from mixtures of slag–fly ash–metakaolin by alkaline activation

and hydrothermal process. So far, this kind of cementitious material has not been studied consistently.

In this work, the alkali-activated slag–fly ash–metakaolin cementitious materials were synthesized by hydrothermal method. The mineralogy, microstructure, porosity, compressive strength and reaction degree of the products were investigated. In order to ensure that the cementitious materials have sufficient mechanical properties and zeolitic structure, we took measures by adding slag in the mixtures to improve strength, and varied the curing time and temperature of hydrothermal process to promote formation of zeolites in the products.

## 2. Experimental method

### 2.1. Raw materials

The samples were prepared using metakaolin, type F fly ash and blast-furnace slag as raw materials. Metakaolin was prepared by calcining kaolinite (kaolinite were supplied by Weiyuan Porcelain Factory in Sichuan Province, China) at 800 °C for 3 h at a heating rate of 4.5 °C/min. Type F fly ash was taken from Bashu power station at Jiangyou (Sichuan province, China) and blast-furnace slag was purchased from Chengdu Iron & Steel Co. Ltd. (Chengdu, China). All these raw materials were ground with planetary mill until particle size was less than 74 μm. The activator was water glass (the modulus was 3.11), and sodium hydroxide was used to adjust the modulus of water glass. The compositions of raw materials and water glass are listed in Table 1.

### 2.2. Synthesis

According to the chemical compositions of raw materials, the proportion design for samples was mainly controlled by adjusting molar ratio of Si/Al/Ca of starting materials. The specific formulas of samples are shown in Table 2. Accordingly, the sample pastes were prepared by mixing raw materials and water glass. The modulus of water glass was adjusted to 1.0 by dissolving sodium hydroxide (NaOH) in water glass, and the ratio of water to solid was regulated to about 0.35. A thorough mixing in a cement paste mixer was done to get uniformity. After that, the pastes were molded in a stainless steel mold with a size of 20 mm × 20 mm × 20 mm, and then they were compacted on a vibrating table and scraped flat. Afterward, the specimens were precured at room temperature for 24 h until the sample pieces get hard. After demolding, all samples were transferred into teflon vessel in a hydrothermal reactor, sealed and cured at 180 °C for 72 h. After hydrothermal curing, all products were taken out and dried at 105 °C for 3 h, then ground using a mortar and pestle.

### 2.3. Chemical attack

According to the literatures [15,16], after alkali and hydrothermal process (at 180 °C), the alkali activated materials were subjected to an acid attack with a 1:20 HCl (by volume) to determine the “reaction degree”. Namely, the powders of products were attacked with acid to determine the amount of raw materials

that had been converted to “cements and zeolitic materials” and the portion that had not reacted with the alkaline solutions. Since this attack provokes the dissolution of the chief reaction products (alkaline aluminosilicate gel and zeolites) in the acid, while the fraction not activated by the alkalis remains in the insoluble residue. The 1:20 HCl solution was prepared using a concentrated reagent HCl (37%).

The experimental method of reaction degree used by Fernández-Jiménez et al. [16] was adopted as follows: 1 g powders of product were added to a beaker containing 250 ml of (1:20) HCl. The mixture was stirred with a plastic rotor for 3 h, after which it was filtered and washed with de-ionized water to a neutral pH. The insoluble residue was first dried at 100 °C and then calcined at 1000 °C; the reaction degree was obtained by determining weight loss. These trials were repeated at least three times to guarantee reproducibility.

### 2.4. Characterization

The products were examined by the X-ray diffraction (XRD) with Cu K $\alpha$  radiation at a scanning speed of 0.8 min<sup>-1</sup> between 2 $\theta$  = 5° up to 60° (Rigaku D/max-RB X-ray diffractometer, Japan). FT-IR spectra were scanned in the range of 400–4000 cm<sup>-1</sup> (Nicolet 380 IR spectrophotometer, USA). Morphology of the products was investigated using a scanning electron microscopy (SEM) (Leica Cambridge S440, Germany). Porosity was measured by mercury intrusion porosimetry from pressure 0.1 to 30,000 psia (Micromeritics AutoPore IV 9500, USA), and compressive strength was tested using universal testing machine at a rate of 0.2 kN/min (Sansi Instruments WDW 1000, China).

## 3. Results and discussion

### 3.1. Mineralogical analysis

Fig. 1(a) shows XRD patterns of the products with Si/Al/Ca molar ratio of 1.7:1.0:0.35, 2.0:1.0:0.35 and 2.3:1.0:0.35, respectively (see Table 2, sample J1735, J2035 and J2335). It can be seen that, after alkaline activation and subsequent hydrothermal processing, the major mineral phases of these products are analcime (JCPDS, 19-1180) and zeolite NaP1 (JCPDS, 39-0219), the minor mineral phases are quartz (JCPDS, 65-0466), tobermorite (JCPDS, 19-1364) and other amorphous phases. When Si/Al/Ca molar ratio of starting materials is 1.7:1.0:0.25, zeolite NaP1 coexists with analcime to constitute the main phases of product. Furthermore, with the increase of Si/Al molar ratio, zeolite NaP1 and quartz disappear and the main crystalline phases transform to analcime and tobermorite. In the previous study, the similar conclusion has been drawn [17,18].

Fig. 1(b) represents data for products with Si/Al/Ca molar ratio of 2.0:1.0:0.25, 2.0:1.0:0.35 and 2.0:1.0:0.45, respectively, (see Table 2, sample J2025, J2035 and J2045) obtained by hydrothermal processing at the same temperature. In this instance, analcime is the main mineral phase in all products, and the diffraction peaks of tobermorite become stronger gradually with increasing Ca/Al molar ratio from 0.25:1.0 to 0.45:1.0.

**Table 1**  
Chemical compositions of raw materials (wt%).

| Raw materials | Loss | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO   | MgO  | MnO  | K <sub>2</sub> O | Na <sub>2</sub> O | SO <sub>3</sub> | H <sub>2</sub> O | Total |
|---------------|------|------------------|--------------------------------|--------------------------------|------------------|-------|------|------|------------------|-------------------|-----------------|------------------|-------|
| Metakaolin    | 1.23 | 54.70            | 41.33                          | 1.17                           | 0.70             | 0.08  | 0.18 |      | 0.25             | 0.13              | 0.14            |                  | 99.89 |
| Fly ash       | 4.69 | 54.27            | 22.94                          | 6.44                           | 1.26             | 2.46  | 3.79 |      | 3.55             | 0.30              | 0.21            |                  | 99.91 |
| Slag          | 1.28 | 29.80            | 12.47                          | 2.70                           | 1.97             | 35.06 | 8.16 | 0.73 | 0.66             | 0.33              | 2.14            |                  | 95.30 |
| Water glass   |      | 25.82            |                                |                                |                  |       |      |      |                  | 8.55              |                 | 59.34            | 93.71 |

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