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EXPERIMENTAL STUDY OF THE CHEMICAL DEFORMATION OF METAKAOLIN BASED GEOPOLYMER

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Abstract
Chemical deformation is an important material property which influences the autogenous deformation of the materials. While geopolymer is emerging as an eco-friendly alternative to ordinary Portland cement (OPC), few studies have been conducted on the chemical deformation of this material. In this paper, the chemical deformation of a metakaolin (MK) based geopolymer is studied. Unlike OPC paste which exhibits monotonous chemical shrinkage, metakaolin-based geopolymers can show chemical shrinkage and chemical expansion at different stages of curing. X-ray diffraction (XRD) and Fourier transform Infrared Spectrophotometer (FTIR) tests were conducted to characterize the geopolymer paste cured at different ages in order to explain the mechanisms of different chemical deformation behaviors. It was confirmed that the early age chemical shrinkage was mainly due to the dissolving of MK, where the density of MK plays an important role. The chemical expansion taking place in the second stage was mainly associated with the formation of Al-rich products. The chemical shrinkage in the late age was related to the formation of Si-rich products in literature, but this finding was not confirmed in this study. The understanding of chemical deformation of geopolymers is helpful to explain the autogenous deformation of geopolymers.

1. Introduction
Geopolymer has emerged as an eco-friendly alternative to OPC. OPC has been widely utilized in construction for many centuries with stable properties but the CO_2 emission produced by cement industry is becoming a serious issue hindering the application of this material. Geopolymer, in contrast, can be made from industrial by-products or other inexpensive aluminosilicate materials, to which little or no CO_2 footprint is usually attributed. To serve as a qualified binder in construction, geopolymer needs to have good volume stabilities. However, the autogenous deformation property of geopolymers remains an unsolved issue. To better understand the autogenous deformation of geopolymers, research attention needs to

be paid on the chemical deformation, since it essentially influences the driving force of autogenous deformation [1]. Li et al. [2] have studied the chemical deformation evolution and mechanism of a geopolymer made from a highly reactive MK with a typical Si/Al ratio around 1. They found that the metakaolin based geopolymer (MKG) experiences three stages of chemical deformation, i.e. chemical shrinkage in the first stage which was mainly due to dissolution of the precursor, chemical expansion in the second stage which was strongly associated with the formation of Al-rich (nano-) zeolites and chemical shrinkage again in the final stage due to the reorganization and polymerization of the Al-rich products to form Si-rich gels. To verify the applicability of their theories in explaining geopolymers synthesized from different precursors, this paper concentrates on the chemical deformation of a geopolymer made of MK with different reactivity and a different Si/Al ratio. The reaction products of the MKG paste are characterized.

2. Materials and experiments

2.1 Materials

The MK used as precursor was from Argeco (France), with a particle size range of 0.15-142 μm and a d_{50} of 69.4 μm. The chemical compositions of MK determined by X-ray fluorescence spectrometry (XRF) are shown in Tab. 1. The reactive SiO_2 and Al_2O_3 contents in MK were determined by chemical dissolution treatment. The MK was dissolved in dilute hydrochloric acid solution and were afterwards treated with boiling solution of sodium carbonate. The obtained residue was rinsed, heated up to 950 °C and then was cooled to room temperature in a desiccator before subject to XRF test. The dissolved fraction corresponding to the mass loss after chemical dissolution treatment is determined as the amorphous phase content. The amount of reactive SiO_2 and Al_2O_3 was shown in Tab. 2. The mole ratio of SiO_2/Al_2O_3 in the reactive part of MK is 0.65.

The activator was prepared by mixing solid NaOH and liquids (sodium silicate and distilled water) in a closed plastic bottle to prevent evaporation. The solution was then allowed to cool for 24 hours before mixing with MK. The mixture proportions of the MKG paste are presented in Tab. 3.

Table 1: Chemical compositions of MK and insoluble residue.

Oxide weight (%)	**SiO_2**	**Al_2O_3**	**CaO**	**Fe_2O_3**	**K_2O**	**TiO_2**	**ZrO_2**
MK	55.14	38.43	0.55	2.60	0.17	1.12	0.05
Insoluble residue	83.65	12.61	0.12	0.79	0.23	2.43	0.11

Table 2: Reactivity of MK (wt%).

Components (%)	**I.R.**	**Reactive content**	**Total SiO_2**	**Reactive SiO_2**	**Total Al_2O_3**	**Reactive Al_2O_3**
MK	51.23	48.77	55.14	12.29	38.43	31.97

Table 3: Mixture proportions of MKG paste.

	SiO_2 (mol)	Al_2O_3 (mol)	Na_2O (mol)	H_2O (g)
MK	1.23	1.88	--	--
Activator	1	--	1.5	350
MKG	2.23	1.88	1.5	350

2.2 Experiments

The densities of MK and the insoluble residue were measured by pycnometer. The chemical deformation of the paste was measured from casting till 2 weeks according to gravimetry method, with the detailed procedure described elsewhere [2]. The chemical deformation value was described as the absolute volume change of the paste per gram of the reactive part of the precursor. XRD was conducted by using a Philips PW 1830 powder X-ray diffractometer, with Cu Kα (1.5406 Å) radiation, tube setting to be 40 kV and 40 mA, a step size of 0.030°, and a 2θ range of 5–70°. FTIR was performed by using a Spectrum TM 100 Optical ATR-FTIR spectrometer over the wavelength range of 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1 Chemical deformation evolution

The evolution of chemical deformation of MKG is shown in Fig.1 (a). For the convenience of comparison, the chemical deformation of the geopolymer synthesized from another kind of MK (denoted as MKG2) studied in [2] is shown in Fig.1 (b). It can be seen that the chemical deformations of the two MKGs both experience three stages of evolutions, i.e. chemical shrinkage in the first few hours, chemical expansion in the subsequent stage and chemical shrinkage again in the third and final stage. No evident change was observed after 2 weeks of curing. These results indicate that the three-stage evolution of chemical deformation seems an intrinsic behavior of MKGs rather than a phenomenon dependent on the properties of precursors. The development of chemical deformation of geopolymers is essentially different from that of OPC, where OPC always exhibits a monotonous chemical shrinkage in the whole age of curing. The absolute volume change of OPC is called chemical shrinkage, but the one of geopolymers can only be called chemical deformation due to the expansion observed.

Despite of the same trend followed by the chemical deformations of the two MKGs, the magnitudes of the first-stage chemical shrinkages of these two mixtures differ a lot. This difference will be emphasized in next section.

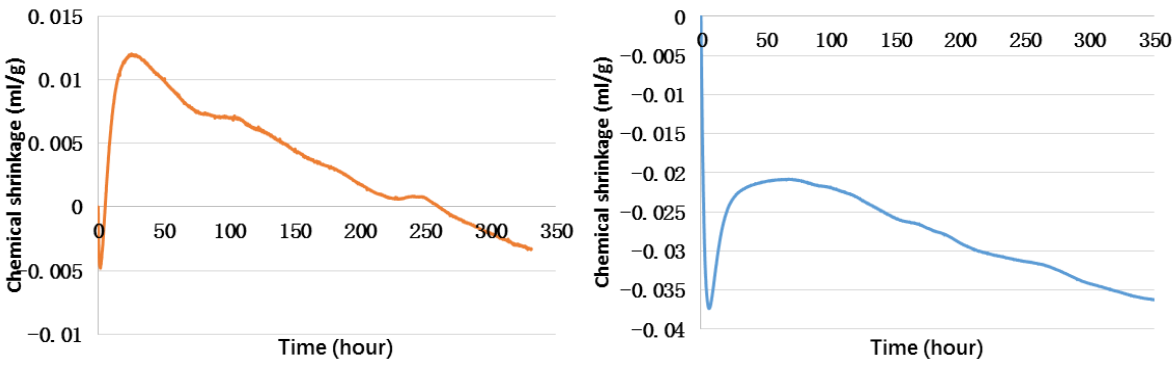

Figure 1: Comparison of chemical deformations of MKG from this study (a) and MKG2 from [2] (b).

3.2 Explanation of the chemical deformations in different stages

3.2.1 Chemical shrinkage in the first stage (the first few hours after casting)

According to [2], the first stage chemical shrinkage of MKG was mainly due to the dissolution of the precursor. To verify this hypothesis, 120g of MK was mixed with 1200g of alkali activator with continuous stirring. The volume change of the suspension during mixing was measured according to Le Chatelier method. The volume change (ml) divided by the mass (g) of the reactive part of MK is shown in Fig.2.

It can be seen that the volume of the suspension decreased in the first half an hour of mixing. Due to the low concentration of MK in the solution, the dissolution of MK should be the dominant reaction in this period. After half an hour of mixing, the volume of the suspension began to increase, indicating that the concentrations of the dissolved species reached a threshold and the polymerization among them began to occur. Therefore, the volume reduction of 0.0044 ml/g at the time 0.5 hour can be considered as an approximation of the chemical shrinkage caused by dissolution of MK. In fact, the value of 0.0044 ml/g is quite close to the chemical shrinkage of MKG in the first stage which is 0.0048 ml/g as shown in Fig.1 (a). This result supports the hypothesis proposed in [2] that the early age chemical shrinkage of MKGs is mainly due to the dissolution of MK.

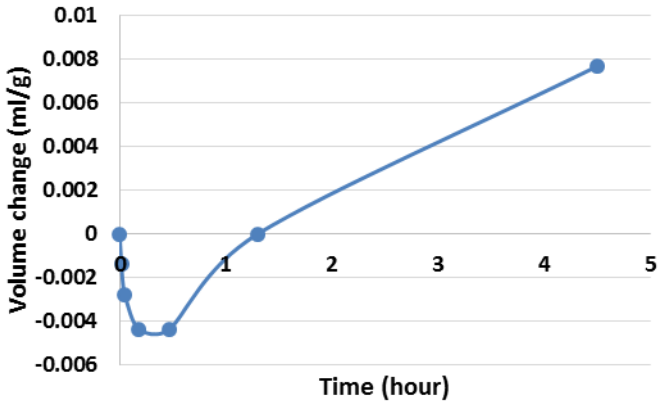

Figure 2: Volume change during dissolution of MK.

Moreover, the chemical shrinkage due to dissolution of MK can also be approximated by calculation. If we assume the reaction products after dissolving of MK are simply monomers, $Si(OH)_4$ and $Al(OH)_3$, without considering the ionization or the polymerization of these species, the dissolution of MK can be described as Eq. (1). The chemical formula of MK is expressed as $(SiO_2)0.65{\bullet}Al_2O_3$ because the SiO_2/Al_2O_3 ratio of the reactive part of MK is 0.65.

$$(SiO_2)0.65{\bullet}Al_2O_3 + 4.3\ H_2O + 2\ OH^- \longrightarrow 0.65\ Si(OH)_4 + 2Al(OH)_4^- \quad (1)$$

The chemical deformation associated with Eq.(1) can be calculated based on the density of reactive MK and the molar volumes of H_2O, OH^-, $Si(OH)_4$ and $Al(OH)_3$. Based on the densities of MK and insoluble residue measured by pycnometer method, the density of the

reactive part of MK can be calculated to be 2.37 g/ml. The molar volumes of $Si(OH)_4$ and $Al(OH)_3$ are assigned as 58.68 ml/mol and 42.3 ml/mol, respectively, according to the data in literatures [3–5]. The chemical deformation associated with Eq. (1) is calculated to be -0.034 ml/g, i.e. chemical shrinkage of 0.034ml/g. This is qualitatively consistent with the experiment results which also show chemical shrinkage in the first stage. However, the value 0.034ml/g is much higher than the measured chemical shrinkage of MKG in the first stage which is 0.0048 ml/g. This is because the calculation above assumes the precursor was 100% dissolved while in real alkali activation only a part of the MK was dissolved in the first hours. Even though the dissolution of MK proceeded with elapse of time, the chemical shrinkage induced by later dissolution was compensated by the chemical expansion which occurred in the second stage, hence the experimentally measured chemical shrinkage in the first stage reached only 0.004 - 0.005 ml/g.

The calculation also indicates that a key parameter influencing the early age chemical shrinkage of MKG is the density of the reactive part of the precursor, which determines the volume of the reactants before reaction. The big difference between the densities of the precursors used in this study and in [2], which are 2.37 g/ml and 2.09 g/ml, respectively, explains the big difference between the first-stage chemical shrinkages of the two MKGs shown in Fig.1.

3.2.2 Chemical expansion in the second stage (from 3 to 50 hours curing)

The FTIR spectra of the MKG pastes at different curing times are shown in Fig.3. The main band of the spectrum of raw MK located at around 1045 cm^{-1} is assigned to the asymmetric stretching vibration of Si-O-T bonds (T= tetrahedral Si or Al). After 4 hours of activation, the main band shifts to around 940 cm^{-1}, which is attributed to the formation of NASH gels [6], indicating that the MK was largely dissolved and the reaction products began to form in this period. At the curing age of 16 hours and 30 hours, the humps at 680 cm^{-1}, 740 cm^{-1} and 860 cm^{-1}, which represent the vibrations of Al-O bonds in AlO_4 tetrahedral groups, become apparent, indicating that a large amount of Al was incorporated into the polymerized structures. These reaction products are normally denoted as "Al-rich" products [7]. The formation of Al-rich products corresponds to the chemical expansion occurring in this stage, indicating that the finding proposed in [2] that the chemical expansion occurring in the second stage of geopolymerization is associated with the formation of Al-rich products is also applicable to the present MKG.

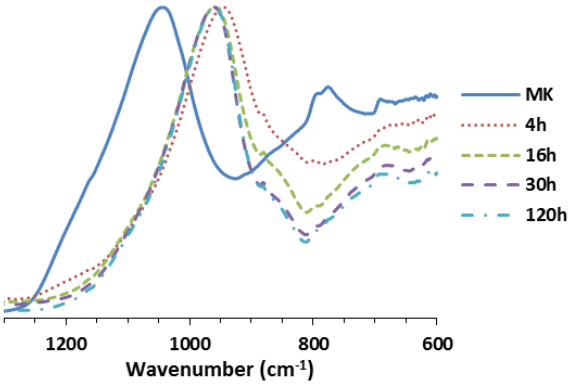

Figure 3: FTIR spectra of MK and MKG pastes cured for 4 hours, 16 hours, 30 hours and 120 hours.

3.2.3 Chemical shrinkage in the final stage (after about 50 hours curing)

The formation of Si-rich gels was reported to be responsible on the chemical shrinkage happening in the final stage of geopolymerization [2]. However, this hypothesis cannot be confirmed in this study by only the FTIR results. As shown in Fig.3 (a), the spectra of 30h and 120h are indistinguishable, although the reactions were ongoing and the chemical shrinkage was continuously developing in this period. It is suggested that techniques like nuclear magnetic resonance (NMR) need to be utilized to detect the Si coordination environments of the MKG pastes cured at different ages.

3.3 Perspective

In [8], the autogenous deformation of the MKG paste with the same mixture design as in this study was investigated. Autogenous expansion after final setting time (2.3 hours after mixing) and subsequent autogenous shrinkage after 1 day of curing were observed, but the mechanisms behind these behaviors were not clearly understood. The chemical expansion and the chemical shrinkage observed in this study may help to explain the autogenous expansion and autogenous shrinkage of MKG, respectively.

4. Conclusions

The MKG experienced three stages of chemical deformation regardless of the reactivity of the precursor. The chemical shrinkage in the first stage was mainly due to the dissolving of precursor. MK with higher density of the reactive part was supposed to have lower chemical shrinkage in this period. The chemical expansion occurred subsequently was associated with the formation of Al-rich products, which may consist of nano-zeolites that cannot be detected by X-ray. The chemical shrinkage in the late age may be due to the reorganization and polymerization of the previously formed entities, where further research is needed.

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