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Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures

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Abstract

This paper presents the results of a study on the effect of elevated temperatures on geopolymers manufactured using metakaolin and fly ash of various mixture proportions. Both types of geopolymers (metakaolin and fly ash) were synthesized with sodium silicate and potassium hydroxide solutions.

The strength of the fly ash-based geopolymer increased after exposure to elevated temperatures (800 °C). However, the strength of the corresponding metakaolin-based geopolymer decreased after similar exposure. Both types of geopolymers were subjected to thermogravimetric, scanning electron microscopy and mercury intrusion porosimetry tests. The paper concludes that the fly ash-based geopolymers have large numbers of small pores which facilitate the escape of moisture when heated, thus causing minimal damage to the geopolymer matrix. On the other hand, metakaolin geopolymers do not possess such pore distribution structures. The strength increase in fly ash geopolymers is also partly attributed to the sintering reactions of un-reacted fly ash particles.

Keywords: Geopolymer; Metakaolin; Fly ash; Thermal analysis; SEM

1. Introduction

Geopolymer is a term used to describe inorganic polymers based on aluminosilicates [1] and can be produced by synthesizing pozzolanic compounds or aluminosilicate source materials with highly alkaline solutions [2]. Due to their ceramic-like properties, geopolymers are believed to possess good fire resistance. Therefore, concretes produced using geopolymers may possess superior fire resistance compared to conventional concretes produced with Ordinary Portland Cement (OPC). OPC concretes are generally considered to provide adequate fire resistance for most applications. However, OPC concrete degenerates at elevated temperatures due to chemical and physical changes [3]. Further, spalling of conventional concrete occurs in fire which causes a rapid layer-by-layer loss of concrete cover, potentially leading to the exposure of the main reinforcements within the concrete to fire [4].

Elevated temperature performance of various geopolymers are investigated and presented in this paper with a view to produce an alternative construction material with superior fire resistance compared to OPC-based concrete. This paper presents experimental research data on metakaolin and fly ash-based geopolymers and establishes some parameters that affect their behavior under elevated temperature.

Geopolymers based on metakaolin are produced by thermal processing of aluminosilicates derived from kaolin sources at a relatively low temperature (600 °C to 800 °C) compared to the calcining temperatures of OPC. Alternatively, geopolymers can also be synthesized with fly ash which does not require high temperature processing. Fly ash used for this purpose is typically Class F type, an industrial by-product from coal-fired power stations [5]. The production of raw materials for geopolymers does not require a high level of energy consumption.

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Table 1
Chemical composition of metakaolin and fly ash precursor

Chemical	Component (wt.%)	
	Metakaolin	Fly Ash
Al_2O_3	37.2	27.0
SiO_2	55.9	48.8
CaO	0.11	6.2
Fe_2O_3	1.7	10.2
K_2O	0.18	0.85
MgO	0.24	1.4
Na_2O	0.27	0.37
P_2O_5	0.17	1.2
TiO_2	2.4	1.3
BaO	0.05	0.19
MnO	–	0.15
SrO	0.03	0.16
SO_3	0.02	0.22
ZrO_2	–	–
LOI [a]	0.8	1.7

[a] Loss on ignition.

The energy consumption is calculated to be approximately 60% less than that required by OPC [6].

2. Source materials and mixture proportions

2.1. Materials characterization

Metakaolin used in this study was a product of kaolin (china) clay calcined at 750 °C in accordance to methods described by Davidovits [7]. The kaolin was of HR1-F grade with an average particle size of 38 µm and was procured from Unimin Australia Ltd. The fly ash was sourced from Gladstone Power station in Australia. The fly ash was of low calcium fly ash (class F) and generally glassy with some crystalline inclusions of mullite, hematite and quartz. The fineness of the kaolin and fly ash was 100% and 89% respectively passing through a 45 µm sieve. The chemical composition of the aluminosilicate precursors was determined by X-ray Fluorescence (XRF) and are given in Table 1.

Alkaline activators in the investigation consisted of alkali silicate and hydroxide solutions. Alkali silicate source was Grade D sodium silicate solution (Na_2SiO_3) supplied by PQ Australia with a specific gravity of 1.53 and a modulus ratio (M_s) equal to 2 (where $M_s = SiO_2/Na_2O$, $Na_2O = 14.7\%$ and $SiO_2 = 29.4\%$). The hydroxide solution needed for activation was prepared to a concentration of 7.0 M using potassium hydroxide (KOH) flakes of 90% purity and distilled water.

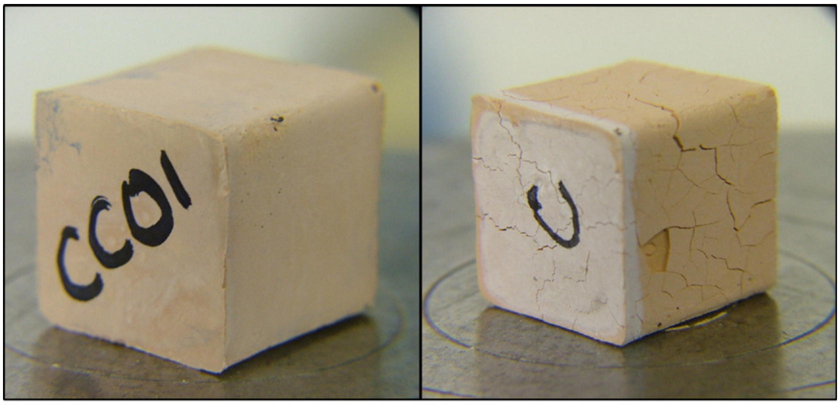
2.2. Mixture compositions

A large number of samples with various SiO_2/M_2O and solids-to-liquids ratios were investigated, both at room temperature and after elevated temperature exposures. Two sets of geopolymer paste mixes, one based on fly ash and the other based on metakaolin, were investigated for this paper. Both mixes had the same SiO_2/M_2O ratio of 1.2 and were both activated using the same alkaline solutions, namely, Na_2SiO_3 and KOH.

The metakaolin-based geopolymer paste had a solids-to-liquids ratio of 0.8, whereas the fly ash-based geopolymer had a ratio of 3.0. Among the many trial mixes studied, these two respective ratios provided near optimum strength and workability. When the solids-to-liquids ratio exceeded these values, the workability of the pastes decreased, causing difficulties in compaction and loss of strength. Metakaolin has higher liquid demand compared to fly ash due to its finer particle size as mentioned in Section 2.1. Further, fly ash with its spherical shape particles increases workability, when compared to metakaolin with its plates-like structure. As a result, higher solids-to-liquids ratios were achievable in fly ash mixes compared to metakaolin mixes.

2.3. Specimen preparation

The geopolymeric precursor (either metakaolin or fly ash) and alkaline silicate solution were mixed by hand for 10 min and a further 5 min with a mixer before being cast into cubic molds. The dimensions of the geopolymer cubic specimens prepared were 25 mm × 25 mm × 25 mm. The samples were then



(a) Before exposure **(b) After temperature exposure**

Fig. 1. Photographs of metakaolin geopolymer specimens. (a) Before exposure (b) after temperature exposure.

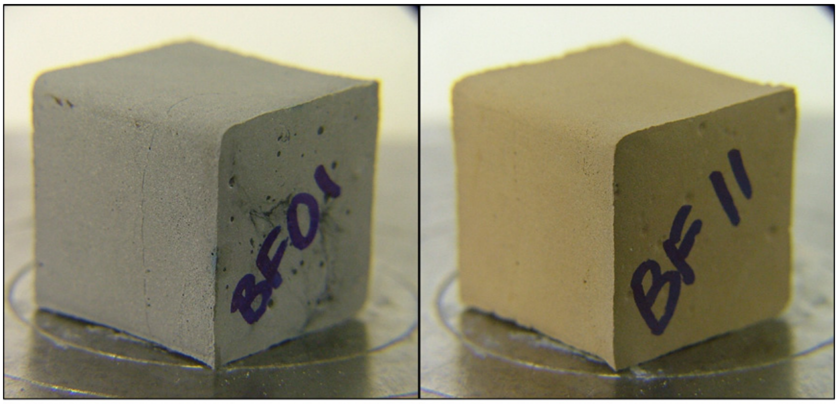

(a) Before exposure **(b) After temperature exposure**

Fig. 2. Photographs of fly ash geopolymer specimens. (a) Before exposure (b) after temperature exposure.

vibrated to release any residual air bubbles. Subsequently, the molded samples were sealed with a film and transferred to an air-tight container to prevent moisture loss. Each sample batch was prepared in duplicates. Six samples were prepared for each study (i.e. 3 unexposed and 3 for elevated temperature exposure).

2.4. Curing regime and elevated temperature exposure

All specimens were cured undisturbed for 24 h at room temperature before being subjected to high temperature curing at 80 °C for a further 24 h. At the end of the curing regime, the specimens were removed from their molds and allowed to cool before initial physical properties were recorded.

Specimens were subjected to temperatures of up to 800 °C at an incremental rate of 4.4 °C/min from room temperature. Once the desired temperature (800 °C) was attained, it was maintained for 1 h before the specimens were allowed to cool naturally to room temperature inside the furnace. Meanwhile, the unexposed samples were left undisturbed at ambient temperature.

3. Results and discussions

3.1. Qualitative observations

After exposure to elevated temperature, there appeared to be a slight lightening of color in the metakaolin geopolymer. Macro-cracks in the order of 0.1 to 0.2 mm were noticeable on the surface of the specimens after the temperature exposure (Fig. 1). The fly ash geopolymer paste samples did not have any cracks on the surface after the temperature exposure (Fig. 2). However, there was significant change of color in fly ash specimens after the temperature exposure.

3.2. Strength results

The compressive strength of the geopolymer cubes were measured using a Mohr and Federhaff AG mechanical testing machine in a load control regime with a loading rate of 20 MPa/min. The specimens were tested for 3-days strengths after casting. Strength results before and after temperature exposures for the geopolymer pastes are summarized in Table 2.

As presented in Table 2, the metakaolin geopolymer suffered strength loss after temperature exposure. However, the fly ash geopolymer gained strength after the same high temperature exposure. Results show a strength drop of 34% in metakaolin-synthesized specimens while fly ash-synthesized counterparts had a strength increase of 6% after elevated temperature exposures. The next section of this paper proposes some of the possible causes of this phenomenon.

3.3. Thermogravimetric analysis results

Thermogravimetric analysis (TGA) was conducted using a Settaram TGA92 device to accurately measure mass loss while the specimens were gradually exposed to elevated temperatures. Powdered specimens were used in the tests to ensure uniform heating of the samples during transient heating.

Fig. 3 shows the differential thermogravimetric (DTG) curve for the metakaolin and fly ash-based geopolymer pastes. Both geopolymers experienced mass reductions with temperature increase. An average mass reduction of 11% after temperature exposures was recorded for the fly ash geopolymer; which was significantly lower than that of the metakaolin geopolymer (30% mass reduction). This mass reduction is assumed to be due to loss of evaporable water.

Exposure to high temperatures leads to changes in chemical structure and the dehydration of free and chemically-bound water. As the external temperature increases, moisture within the specimen rapidly migrates towards the surface of the specimen and escape. This in turn causes surface-cracking and internal damage in the overall structure of the geopolymer.

Table 2
Geopolymer pastes strength results

Binder type	Compressive strength (MPa)	
	Unexposed	Temperature exposed
Metakaolin	38.5	25.4
Fly ash	59.0	62.8

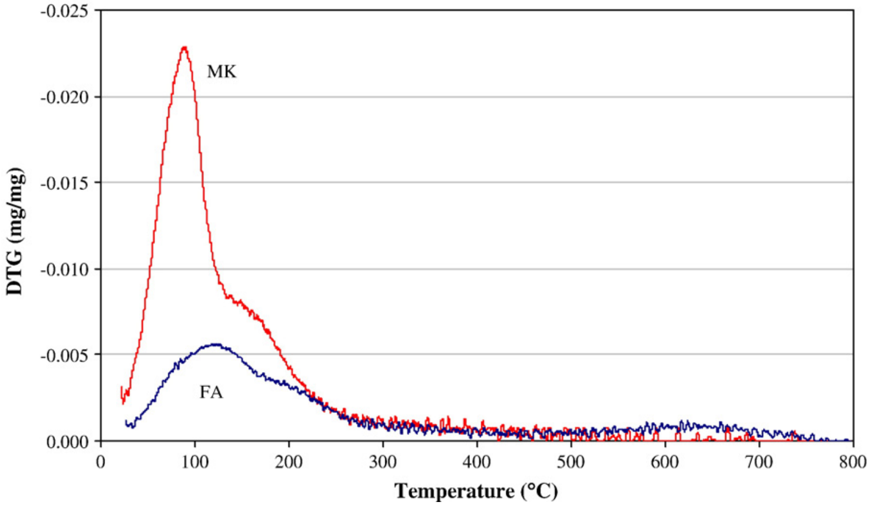


Fig. 3. DTG curve of metakaolin and fly ash-based geopolymer paste.

Since the metakaolin-to-liquids ratio was 0.8 while the fly ash-to-liquids ratio was 3.0, there was more moisture within the metakaolin geopolymer system compared to the fly ash-based geopolymer system. Thus, as depicted in Fig. 3, at lower temperature, the metakaolin geopolymer underwent a higher rate of water loss than the fly ash geopolymer. This is believed to be one of the causes for the poorer performance of metakaolin geopolymer strengths after elevated temperature.

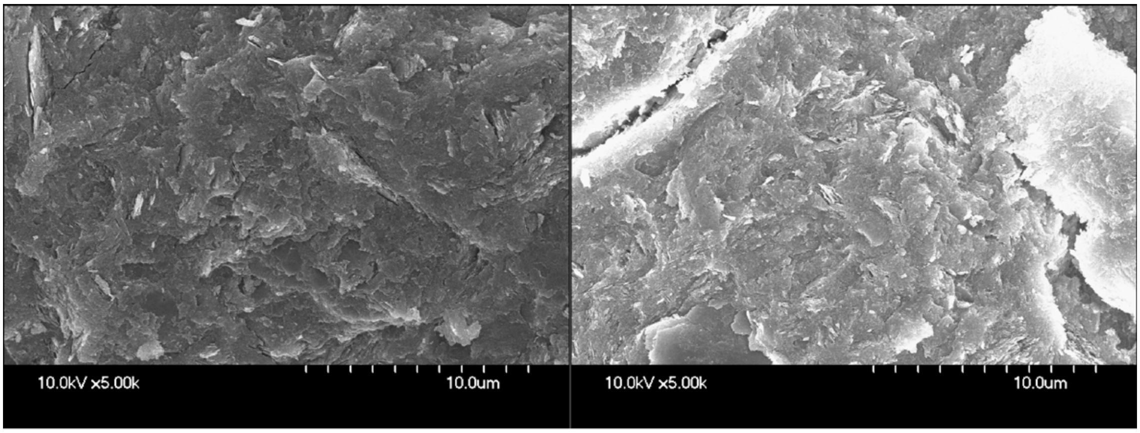
3.4. Scanning electron microscopy results

Microstructural images of both geopolymers were obtained using scanning electron microscopy (SEM). Images were obtained from samples cut from a 25 mm diameter cylindrical specimen using a diamond saw and polished down gradually to a 0.1 μm diamond paste finish. The samples were vacuum-dried overnight prior to SEM. The samples were then mounted on the sample stubs and sputter-coated with gold-palladium alloy. Imaging was conducted using a Hitachi S-4700 SEM.

From the SEM images, the metakaolin particles appeared as plates forming a layer-like structure as seen in Fig. 4. Some macro-cracks developed on the surface of the specimen after exposure to elevated temperature; however, under SEM at micro level, no cracks were visible. The uniform layered structures with angular edges have been previously reported by Steveson and Sagoe-Crentsil [8]. Notably, much fewer layers were observed in the temperature-exposed specimens.

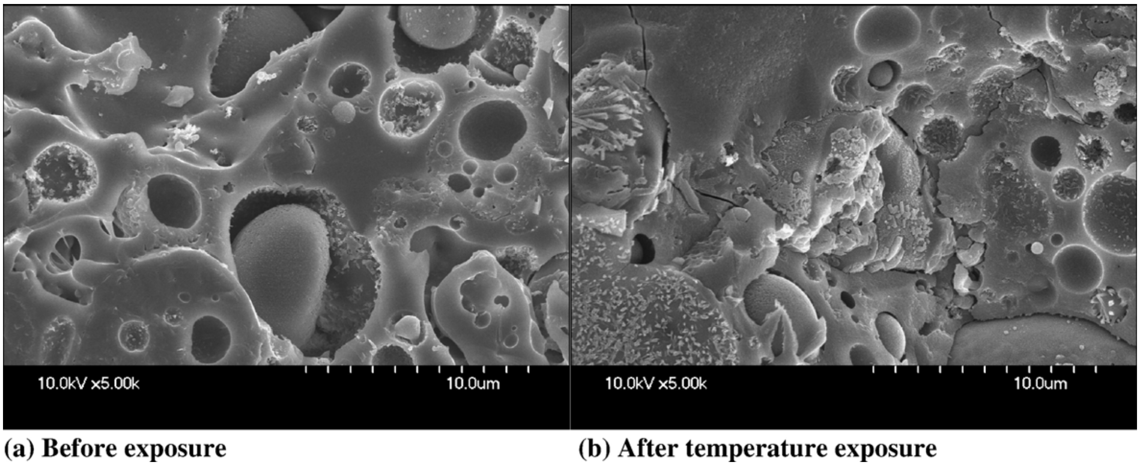
Comparatively, fly ash geopolymer images showed heterogeneous elements and contained far more un-reacted particles. Fly ash is known to contain significant proportion of particles with hollow spheres. When these hollow spherical particles are partially dissolved they create porosity in the matrix containing highly dispersed small sized pores. These un-reacted particles were found in hollow cavities as shown in Fig. 5. The hollow cavities seen in the images are possibly due to the spaces left behind by dissolved fly ash particles. The authors hypothesize that this porous system of the fly ash geopolymer provides escape routes for moisture during heating without significantly damaging the geopolymer matrix.

In addition, the development of porosity is caused by different developments of microstructural skeletons in the geopolymers. Since the difference in solids-to-liquids ratio are



(a) Before exposure **(b) After temperature exposure**

Fig. 4. Photographs of metakaolin geopolymer before and after temperature exposure. (a) Before exposure (b) after temperature exposure.



(a) Before exposure **(b) After temperature exposure**

Fig. 5. Photographs of fly ash geopolymer before and after temperature exposure. (a) Before exposure (b) after temperature exposure.

different between the two studied, there would be a considerable difference in soluble silica and hence leading to dissimilarity in microstructure. However, fly ash and metakaolin-based mixes with similar solids-to-liquids ratio are not achievable due workability limitations. Metakaolin has a higher water demand compared to fly ash for reasons previously in Section 2.2. A plot of compressive strength for varying solids-to-liquids ratio using metakaolin is shown in Fig. 6. The solids-to-liquids ratio affects the volume of voids and porosity in the pastes which directly influences the strength of geopolymer. Geopolymers based on metakaolin lost strength at least of the order of 17% after elevated temperature exposure for all formulation covering the different solids-to-liquids ratios investigated.

3.5. Mercury intrusion porosimetry results

Mercury intrusion porosimetry (MIP) has been widely used to study porous materials including cementitious material. This technique provides the cumulative pore volume as a function of applied pressure based on the mercury intrusion under increasing pressures. For the purpose of this study, small sample cubes measuring approximately 15 × 15 × 15 mm were cut out from the larger specimens using a diamond saw. The samples were left in a vacuum oven overnight to ensure removal of moisture in the samples. MIP tests were done on these samples using a Micromeritics 9420 Autopore III high-pressure mercury-intrusion porosimeter.

MIP tests were performed on metakaolin and fly ash geopolymer samples at the sample age of 3 days. The pore size distributions obtained from the 3-day old samples are shown in Fig. 7. MIP tests were also performed on 1-year old samples to identify how pore size distribution changed with age. Fig. 8 shows the pore size distribution of 1-year old samples. The comparison between Figs. 7 and 8 shows that the pore size distributions are almost identical between 3-day and 1-year samples. Unlike cement pastes which hydrate with time, the strength of the geopolymer samples remain virtually the same after the initial curing period. Geopolymers have a relatively slower post-

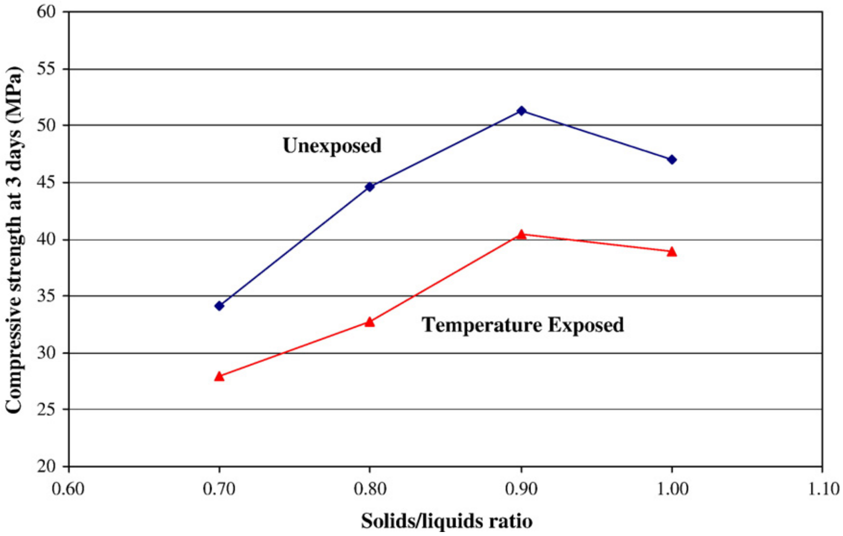


Fig. 6. Effect of the solids-to-liquids ratio on metakaolin-based geopolymer.

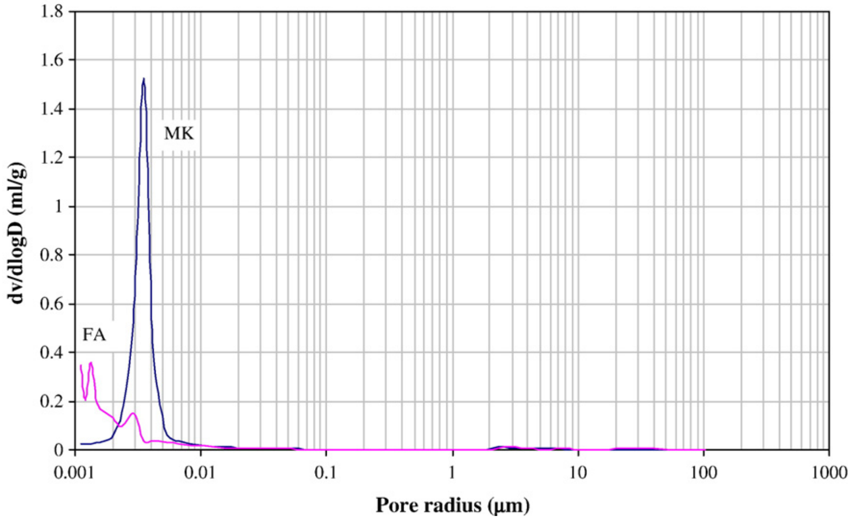


Fig. 7. Pore size distribution of metakaolin and fly ash geopolymers at the age of 3 days.

curing strength development when compared with conventional cement paste. This is also confirmed by compressive tests on 3-day and 1-year old samples that showed almost identical results.

Application of MIP tests for cement and concrete has been widely criticized as inappropriate in the literature. However, the MIP results may be appropriate for comparing the two different geopolymers studied here, rather than for establishing the actual pore sizes in these samples. Previous researchers [9], who compared pores observed in SEM and MIP tests of cementitious materials, concluded that pore sizes computed based on MIP results are about three orders of magnitude smaller than the pore sizes observed in SEM images. Therefore, in this study, MIP results will only be used for comparative purposes.

A summary of pore size percentages categorized in accordance to the IUPAC classification system is presented in Table 3. The total porosities of the metakaolin geopolymer samples are significantly higher than the porosities of the fly ash based geopolymers. This is expected since the metakaolin geopolymers contain much higher liquids than fly ash based geopolymer. The pore system left behind by liquid in the system tends to be larger than the pores created by partially dissolved hollow fly ash particles. This can be clearly seen from the break down percentages of various pore size ranges presented in Table 3. Fly ash geopolymer pores contain much higher proportion (19.3 to 24.6%) of pores in the micropores size than the metakaolin geopolymer pores (0.7 to 0.5%).

4. Conclusions

1. The TGA results showed that metakaolin-based geopolymers had significantly higher moisture loss than the fly ash-based geopolymers. The smaller amount of moisture having to escape from fly ash matrix may be the reason why there is less damage to the matrix. Both types of geopolymers were made to the same SiO_2/M_2O ratio.

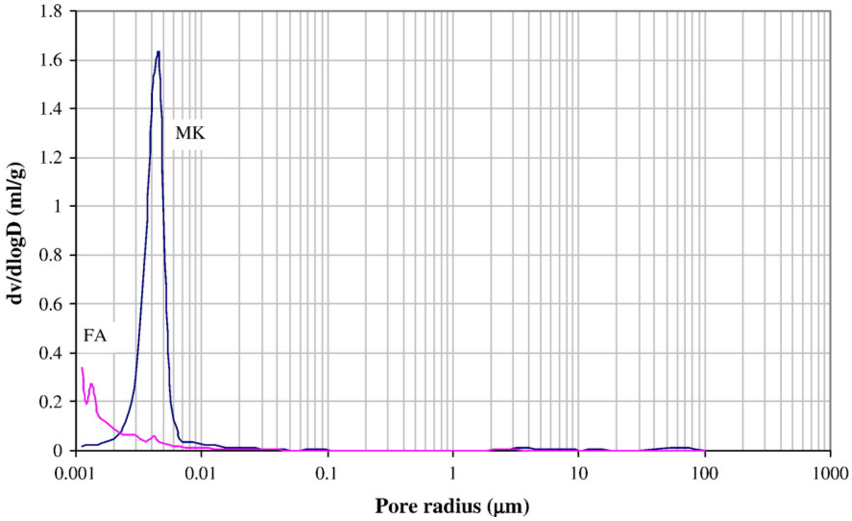


Fig. 8. Pore size distribution of metakaolin and fly ash geopolymers at the age of 1 year.

Table 3
Pore size percentages (based on IUPAC classification)

Pore classification and radius	Metakaolin geopolymer (%)		Fly ash geopolymer (%)	
Age of sample	3 days	1 year	3 days	1 year
Total porosity	40.4	44.6	21.7	15.4
Micropores (<1.25 nm)	0.7	0.5	19.3	24.6
Mesopores (1.25–25 nm)	96.3	94.2	74.7	71.3
Macropores (25–5000 nm)	2.3	1.8	3.2	2.6
Air voids/cracks (5000–50,000 nm)	0.7	3.5	2.8	1.5

2. From the SEM images, un-reacted fly ash particles shaped like hollow spheres were observable. When these shells are partially dissolved in geopolymer matrix, they appear to create a matrix with a large number of small highly dispersed pores. At elevated temperatures, these pore spaces provide escape routes for moisture in the matrix thereby decreasing the likelihood of the damage to the matrix.
3. Some degree of sintering appears to occur at elevated temperatures, thus increasing the strength. By contrast, the plate-like structures of residual metakaolin particles do not provide similar moisture escape routes at elevated temperatures causing damage to the matrix.
4. The fly ash geopolymer achieved significantly higher solids-to-liquid ratios compared to the metakaolin geopolymer. This is mainly attributed to the spherical shapes and fineness of fly ash particles, which greatly increases workability.
5. Mercury Intrusion Porosimetry (MIP) results confirm that the fly ash geopolymer has significantly higher proportion of micropores compared to metakaolin geopolymers.
6. The main difference between fly ash and metakaolin geopolymers is that the metakaolin geopolymer pores are predominantly composed of mesopores whereas fly ash pores contain higher proportion of micropores than metakaolin geopolymer.

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