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# Geopolymer matrices with improved hydrothermal corrosion resistance for high-temperature applications

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**Abstract** Ceramic matrix composites have to overcome two major barriers for applications in aircraft and stationary turbines/engines. One is the unacceptably high processing cost to obtain sufficient mechanical properties and the other is their poor corrosion resistance under hydrothermal oxidizing conditions typical of engines and turbines. Functional geopolymer composites provide possible solutions to the above two problems since they can be formed by technologically simple processing routes and the hydrothermal corrosion resistance can be improved by tailoring material compositions. In this paper geopolymer matrix materials with superior hydrothermal corrosion resistance were processed from the selected geomimetic compositions. The effects of processing parameters, such as particle size, extent of dissolution, and firing temperature on the compressive strength and microstructures were examined and specimens with a compression strength as high as ~99 MPa were fabricated. Hydrothermal test experiments on KOH-derived geopolymer specimens showed that all of potassium-bonded geopolymer specimens have minimal mass change or dimensional change during hydrothermal exposure in spite of the phase change.

## Introduction

Ceramic matrix composites (CMCs) have been developed extensively over the last two decades and they are attractive for many aerospace turbine engine applications [1]. CMCs retain strength to much higher temperatures than metals and they offer overall lower densities. However, there are significant problems that need to be addressed before their high temperature applications become practical, such as the extremely high processing cost to achieve sufficient mechanical properties [2] and poor corrosion resistance of SiC based continuous fiber ceramic composites (CFCC) to hydrothermal oxidizing conditions typical of engines and turbines [3, 4].

One type of material that has recently shown significant promise as a potential low-cost matrix material for CMCs is the geopolymer system, which is amorphous or semi-crystalline with three-dimensional networks formed by reaction of aluminosilicates with highly concentrated alkaline solutions [5]. It has been shown that geopolymer materials can be processed in net-shape at very low temperatures from various aluminosilicates and they have use-temperature up to 1,000 °C and tailored physical properties, such as strength and CTE, varying as a function of Si/Al ratio [5]. One tremendous advantage that geopolymers offer for CMC processing is the potential to infiltrate a ceramic slurry into a fiber prepreg to form a near net shape matrix, thus avoiding excessive processing costs due to technologically complex infiltration process such as chemical vapor infiltration or post infiltration densification steps. Flexural strengths as high as 380 MPa at room temperature and approximately 180 MPa at 1,000 °C for geopolymer/SiC-fiber reinforced composites have been reported [6].

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For engine and turbine applications geopolymer based CMCs have to be stable under hydrothermal oxidizing conditions besides their potential to obtain excellent mechanical properties through low-cost processing route. There is no systematic study regarding the relative stability of various geopolymer-derived materials under high-temperature hydrothermal exposure. In this paper the geopolymer matrix materials were processed from the selected geomimetic compositions, i.e. synthetic aluminosilicates. Their compressive strength, microstructure, and the stability under hydrothermal exposure conditions were reported.

## Experimental

### Materials

Sodium hydroxide (NaOH, 50 wt.%) and potassium hydroxide (KOH, 45 wt.%) solution were procured from J. T. Baker Chemical. Alumina, calcium hydroxide, barium hydroxide powders, and silica gel were procured from Alfa Aesar. The silica gel was first crystallized by firing to 1,400 °C to ensure that all the organics were removed such that the batching weights accurately represented the amount of silica incorporated into the aluminosilicate and milled to sub-micron particle size.

### Geopolymer sample fabrication

To form geopolymer samples, six geomimetic compositions were selected as the precursors, which is shown in Table 1. Table 1 also shows the raw materials and calcination conditions used to form these precursor powders by the solid-state reaction route. Sintered pellets with the same six compositions for comparison purposes were also made by pressing the mixed powders into small discs at a pressure of 7,000 psi and then sintering at different temperatures, which are also shown in Table 1. All the calcination temperatures were selected based on XRD results to ensure formation of the desired phases.

To form geopolymer specimens, the alkali solutions (either KOH or NaOH) were mixed with the six geomimetic precursor powders at different ratios, cast into molds on a vibrating table for 15 min, made to gel for 4 h by keeping the mold covered, and then allowed to dry for another 6 h at room temperature by removing the mold covers. The specimens were then fired in air for 8 h either at 200–250 °C in a drying oven or at 800 °C in a furnace. Table 2 shows some typical compositions of the geopolymer specimens prepared for hydrothermal corrosion tests.

### Crystalline phase identification

The crystalline phases of the samples were identified by a Philips X'Pert X-ray diffraction (XRD) system using Cu K$\alpha$ radiation (1.5416 Å). A typical scan is from 10° to 90° with a scan rate of 0.02°/s.

### Measurement of compressive strength

Compression specimens were fabricated by cutting samples to approximate dimensions of 4 mm × 4 mm × 6 mm using a diamond saw. This small dimension of

**Table 1** Geomimetic compositions for geopolymer sample fabrication

| Composition | Raw materials used | Calcination condition to form geopolymer precursor powders | Calcination condition to form sintered pellets |
|---|---|---|---|
| Mullite ($3Al_2O_3{\cdot}2SiO_2$) + 2 vol.% $Al_2O_3$ | Alumina, silica gel | 1,600 °C/8 h | 1,550 °C/8 h |
| Mullite ($3Al_2O_3{\cdot}2SiO_2$) + 10 vol.% $Al_2O_3$ | Alumina, silica gel | 1,600 °C/8 h | 1,550 °C/8 h |
| Anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) + 2 vol.% $Al_2O_3$ | Calcium hydroxide, alumina, and silica gel | 1,275 °C/8 h | 1,275–1,300 °C/8 h |
| Anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) + 10 vol.% $Al_2O_3$ | Calcium hydroxide, alumina, and silica gel | 1,275 °C/8 h | 1,275–1,300 °C/8 h |
| Celsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) + 2 vol.% $Al_2O_3$ | Barium hydroxide, alumina, and silica gel | 1,550 °C/8 h | 1,550 °C/8 h |
| Celsian ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) + 10 vol.% $Al_2O_3$ | Barium hydroxide, alumina, and silica gel | 1,550 °C/8 h | 1,550 °C/8 h |

**Table 2** Typical compositions for geopolymer specimens used for hydrothermal corrosion tests

| Sample ID | Precursor | Alkaline solution (45 wt.% KOH solution) (mL) | Curing temperature (°C) |
|---|---|---|---|
| AnK000 | 5 g of (Anorthite + 2 vol.% $Al_2O_3$) | 2 | 220 |
| AnK001 | 7.5 g of (Anorthite + 2 vol.% $Al_2O_3$) | 2 | 220 |
| AnK002 | 7.5 g of (Anorthite + 2 vol.% $Al_2O_3$) | 2 | 800 |
| CeK001 | 7.69 g of (Celsian + 2 vol.% $Al_2O_3$) | 2 | 220 |
| CeK002 | 7.69 g of (Celsian + 2 vol.% $Al_2O_3$) | 2 | 800 |
| MuK002 | 5.7 g of (Mullite + 2 vol.% $Al_2O_3$) | 2 | 800 |

compression specimens was chosen in order to obtain relatively larger number of testing samples (8–10) for each type of specimen. The 4 mm × 4 mm ends of the specimen were polished to be nearly perfectly parallel to each other by mounting and polishing using a special aligning fixture. The test was done using an Instron mechanical testing apparatus. The equipment was modified with an appropriate fixture, to help align the faces of the specimen perfectly with the pistons so as to prevent any localized stresses that may arise due to practical limitations in achieving perfectly parallel specimens. The maximum stress to failure under compression conditions was calculated.

### Characterization of microstructure

The microstructures of the samples were observed by a JEOL JSM-5900LV SEM equipped with the EDS system for composition identification. All samples were mounted by epoxy resin, polished, and sputtered with carbon before SEM observations.

### Hydrothermal corrosion test

Before hydrothermal corrosion testing, samples were cut into thin slices to increase the surface area exposed to steam. Then the specimens were first annealed in flowing air at 1,000 °C for 13 h to burn off any debris and water accumulated on the samples during the cutting process. Following the annealing step, XRD patterns were obtained from the specimens. Subsequently, the specimens were put into the reactor for hydrothermal corrosion tests at 1,200 °C, $pH_2O = 0.15$ atm, $P = 1$ atm, gas flow rate of 0.7 L/min, with anneal times up to 100 h. The water vapor pressure was controlled by a water bath, which was at a temperature that fixed the vapor pressure at the desired level for the experiment. Specimens were characterized by surface XRD and monitored every 25 h for mass change.

## Results and discussion

### Geopolymer sample fabrication

Figure 1 shows some of the specimens through geopolymerization experiments. It was identified that a precursor powder to alkali ratio of 5 g to 1–1.5 mL (of concentrated alkali solution) was optimal to obtain high-quality specimens. The KOH-based specimens in general, had higher ''green-strength'' as evidenced by the fact that the specimens could be retrieved in near net-shape from the molds with very little damage near the edges as shown in Fig. 1. Another observation was that the specimens with 2 vol.% alumina fared much better than the specimens made with 10 vol.% alumina. This trend was observed for both KOH and NaOH-based specimens, but was more significant for the NaOH based specimens.

After firing at 200 and 800 °C, these specimens were very strong and could not be broken by hand. However, generally speaking the KOH-based specimens have much higher compressive strength than the NaOH based specimens after 200 and 800 °C firing, which is shown in Fig. 2. It should be pointed out that the comparison of the effectiveness of K and Na based alkaline solutions to make higher quality parts is not conclusive [7, 8]. But within the material and processing scopes of the current

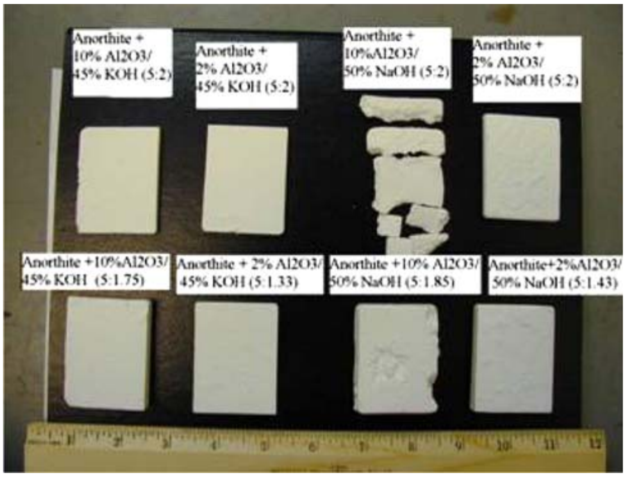


**Fig. 1** Anorthite-based geopolymer specimens fabricated with using different processing parameters and fired at 200 °C. The ratio indicated in brackets for each specimen is the ratio of the weight of powder (g) to the volume of concentrated alkali solution (mL)

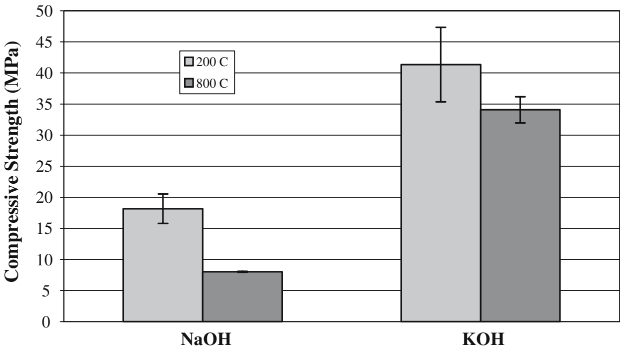


**Fig. 2** Compression test data on geopolymer specimens fabricated using the anorthite-based alumina silicate powders reacted with NaOH and KOH at 200 and 800 °C

study, KOH is better than NaOH to form stronger specimens. XRD shows that the precursor compositions are almost completely broken down under these conditions to form a number of other phases. Scanning electron microscopy was performed on anorthite-based specimens bonded with NaOH and KOH, and fired to 200 and 800 °C (Fig. 3). These specimens had a complex microstructure that consisted of unreacted particles of the aluminosilicate dispersed relatively uniformly in a secondary phase, which presumably was the gel phase prior to solidification. High-resolution back-scattered imaging, combined with energy dispersive spectroscopy, revealed that the solidified gel-phase itself consists of a two-phase mixture of a Na/K rich phase and an Al/Si rich phase dispersed on a micrometer-scale. Firing to a higher temperature of 800 °C seems to result in significant densification for the KOH-based geopolymer specimens.

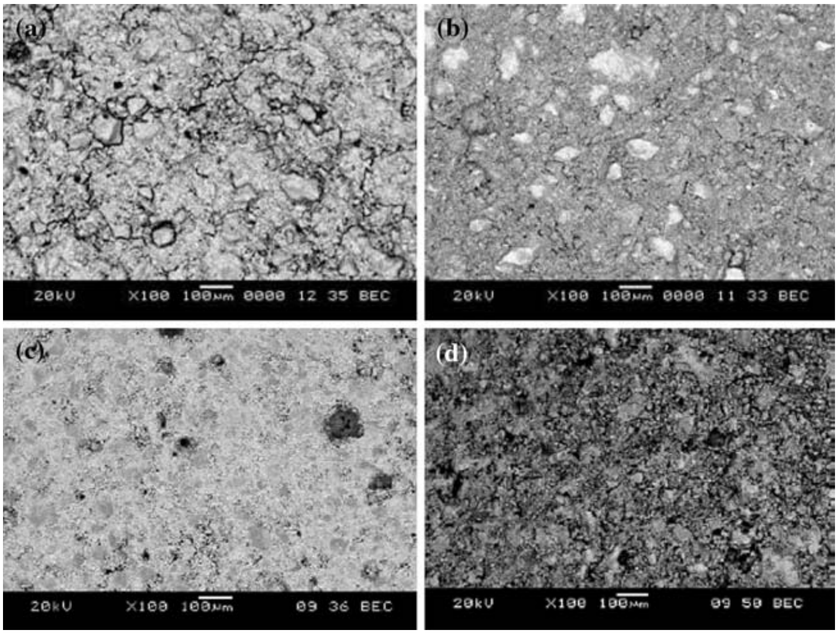
## Effects of processing parameters on strength and microstructure

### *Effect of particle size on compressive strength of geopolymers*

The effect of particle size on compressive strength of geopolymers was studied on anorthite based geopolymer specimens. The mean compressive strength increased from 28 ± 9 to ~46 ± 10 MPa when the particle size of precursor powders (anorthite + 2 vol.% alumina) was lowered from 327.1 to 6.8 μm (Fig. 4). To the best of our knowledge, this study is the first to directly demonstrate an increase in compressive strength of geopolymer materials with decreasing particle size. The result is not an obvious one, since the particle size is not expected to be a major contributor to the compressive strength as it would be to the tensile or flexural strength. In the case of flexural and tensile strength, strength is directly linked to the grain-size since failure is usually initiated at the grain-boundaries and the defect size is intimately linked to the grain-size of the materials. In compression, however, the relationship is not quite as obvious as compressive stress can close grain-boundary cracks or open them depending on the relative orientation of the defects.

Another factor that complicates the issue in the case of geopolymeric materials is that a finer powder is expected to generate a proportionately higher reaction product during geopolymerization due to the increased surface area of the powder, which is supported by the work done by Rahier et al. They found that the

**Fig. 3** SEM images of anorthite based geopolymer samples (**a**) anorthite powder reacted with KOH solution and fired to 200 °C, (**b**) anorthite powder reacted with NaOH solution and fired to 200 °C, (**c**) anorthite powder reacted with KOH solution and fired to 800 °C, (**d**) anorthite powder reacted with NaOH solution and fired to 800 °C



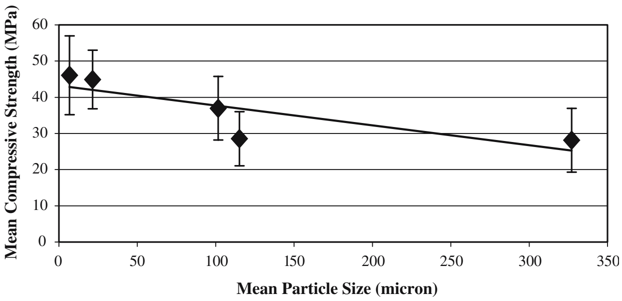


**Fig. 4** Compression test data on geopolymer specimens fabricated from anorthite + 2 vol.% alumina powders with various mean particle sizes and KOH solution showing a trend of increasing compressive strength with decreasing particle size

geopolymerization rate increased with decreasing particle size of precursor powders [9]. Figure 5a, b shows back-scattered electron micrographs of geopolymer compositions with mean particle sizes of 327.1 and 6.8 μm, respectively. One clear observation from the SEM examination was that the geopolymer material with the higher particle size seems to have higher porosity than the material with the finer particle size. Conceivably, the greater amount of the gel phase formed during the geopolymerization of finer precursor powders is enough to fill the inter-particular voids and result in a denser material, which may explain the increase in compressive strength.

### *Effect of the extent of dissolution on compressive strength of geopolymers*

Figure 6 shows the variation of the compressive strength of geopolymer specimens made from anorthite based precursor powders with KOH of various concentrations while keeping the powder weight to alkaline solution volume constant. The strength of the anorthite based geopolymers increases with increasing alkali concentration in the test range studied from 25 to 45% KOH. This alkaline concentration effect on the compressive strength of geopolymers is consistent with the previous studies on the water content effect [7, 8, 10]. There higher compressive strength is obtained for the system with higher $M_2O/H_2O$ ratio (M is either K or Na) or lower water content. Forty-five percent KOH is the highest concentration of KOH that could be obtained commercially, and it is close to the solubility limit of KOH in water. However, it is anticipated that if higher dissolution could be obtained by using even stronger alkali solutions, this trend of increasing strength will eventually be reversed. This is because the optimal microstructure is believed to be a composite structure with the gel phase coating the aluminosilicate particles. If the extent of dissolution is very high and most of the structure is the gel phase, then the strength is expected to be lower than that of the composite structure.

Another set of experiments was carried out to study the effect of the extent of dissolution on the compressive strength of geopolymer specimens by varying the precursor powder to alkali ratio. Figure 7a shows the variation of mean compressive strength of geopolymer specimens fabricated by reacting anorthite + 2 vol.% alumina samples (mean particle size: 6.8 μm) with 45% KOH solution. The result clearly demonstrates that there is an optimal ratio, close to a 1:1 mol ratio of anorthite to KOH, for maximal compressive strength. The maximum strength obtained, 99 MPa, compares favorably with the highest strengths obtained in geopolymer systems. The bell shape curve in Fig. 7a makes sense based on the earlier assertion that the optimal microstructure would be one of aluminosilicate particles embedded in a gel phase. When the anorthite to KOH ratio is very low (i.e. below 0.8), the strength of the geopolymer becomes characteristic of the gel phase (~28 MPa). When the anorthite to KOH ratio is very high, the extent of reaction is low and there is not enough gel phase to give good bonding between the aluminosilicate particles. This is also evidenced by the standard deviation change shown in Fig. 7b. In the low anorthite to KOH ratio range (0.2–0.4) the standard deviation of the compressive strength is about 10% of the strength value itself. This deviation shows the influence of defects inherited from the material system, such as the geopolymerization extent, and/or introduced by the processing methods, such as the casting

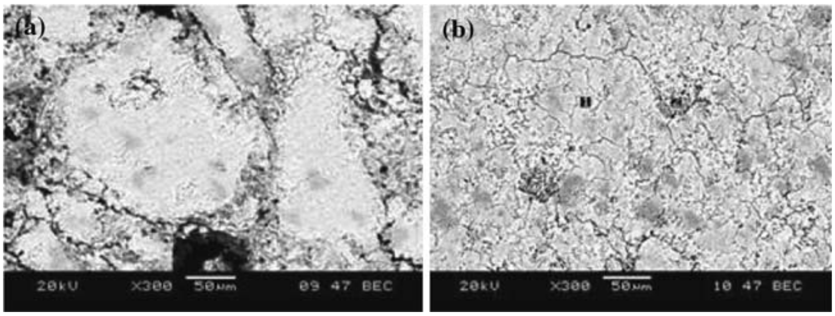


**Fig. 5** Back-scattered electron images of geopolymers formed by reaction of anorthite + 2 vol.% alumina with 45% KOH solution and fired at 220 °C. (**a**) Mean particle size 327.1 μm; (**b**) mean particle size 6.8 μm

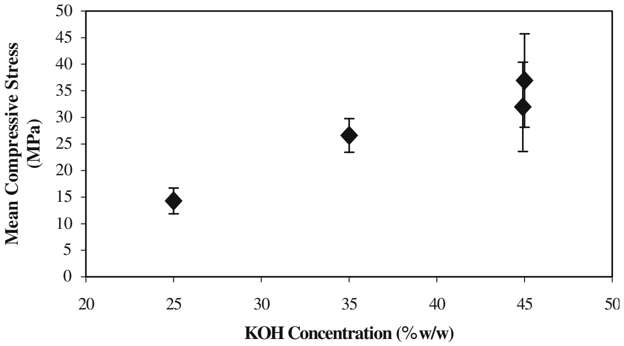


**Fig. 6** Effect of KOH concentration on the compressive strength of anorthite based geopolymeric materials

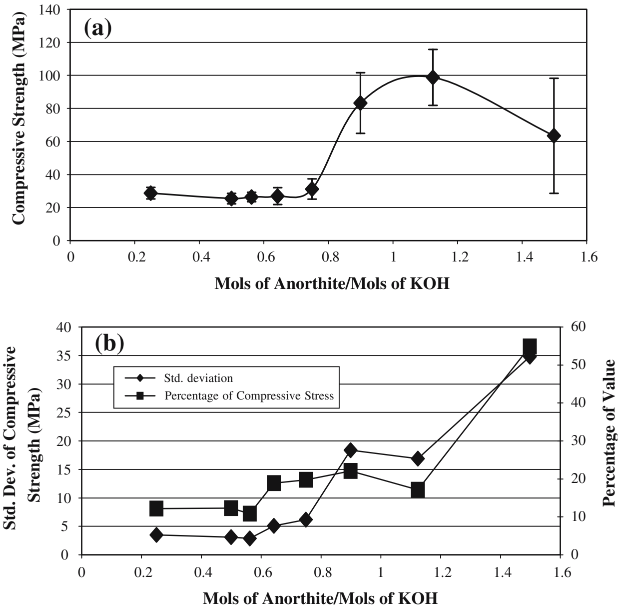


**Fig. 7** Effect of powder to KOH ratio on the compressive strength of anorthite based geopolymeric materials. (**a**) Mean compressive strength variation; (**b**) variation of standard deviation

technique and the post-machining. However, at the very high anorthite to KOH ratio (~1.5) end the standard deviation of the compressive strength is close to 55% of the strength value itself. Since the casting and post-machining techniques are the same, this significant increase in standard deviation should come from the variation on the extent of geopolymeric reaction.

### *Effect of firing temperature on compressive strength of geopolymers*

A study of anorthite based geopolymer specimens fired at various temperatures seems to indicate that there is an optimal firing temperature in the range of 300–600 °C, as shown in Fig. 8, to result in optimal room temperature strength, which is consistent with the results from Jaarsveld et al. [11]. However, it is not clear at this point if the trend will also be affected by other parameters such as the extent of dissolution. Further compression test experiments and SEM studies has to be performed to gain more information on this effect.

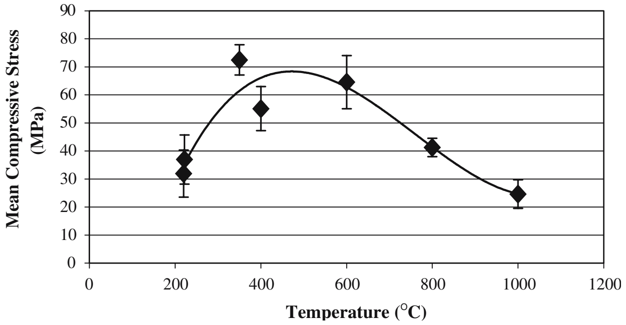


**Fig. 8** Effect of firing temperature on the compressive strength of anorthite-based geopolymeric materials

### Hydrothermal stability of geopolymer samples

Under hydrothermal exposure in 15% $H_2O$ at 1,200 °C in flowing air, the behavior of the KOH- and NaOH-polymerized specimens is notably different. The KOH-polymerized specimen retained its dimensional stability while the NaOH-polymerized specimen demonstrated notable, non-uniform shape change—related both to sintering and to slumping (i.e., creep under the influence of its own weight).

The results of mass change during hydrothermal corrosion test for sintered and geopolymerized specimens are presented in Table 3. In general there was

**Table 3** Mass change of geopolymer specimens after hydrothermal exposure

| Sample | Initial mass (g) | Mass change (g) | Mass change (%) |
|---|---|---|---|
| Sintered pellets | | | |
| Anorthite + 2 vol.% $Al_2O_3$ | 1.12673 | 0.00106 | 0.1 |
| Celsian + 2 vol.% $Al_2O_3$ | 0.50400 | 0.00069 | 0.1 |
| Mullite + 2 vol.% $Al_2O_3$ | 0.80903 | 0.00785 | 1.0 |
| Anorthite + 10 vol.% $Al_2O_3$ | 0.78242 | 0.00330 | 0.4 |
| Geopolymer specimens | | | |
| AnK000 | 0.56093 | –0.00516 | –0.92 |
| AnK001 | 0.88601 | –0.00475 | –0.54 |
| AnK002 | 0.66468 | –0.00420 | –0.63 |
| CeK001 | 0.74853 | –0.02432 | –3.25 |
| CeK002 | 0.55055 | –0.00901 | –1.64 |
| MuK002 | 0.90385 | –0.02470 | –2.73 |

little mass change at high temperatures with steam, both for sintered samples and for the geopolymerized samples. All the sintered samples registered a small mass gain from the hydrothermal exposure. It is presumed that the small mass gain is due to the formation of hydrated phases such as $Si(OH)_4$, combined with the fact that the testing flow rates may not be sufficient to initiate volatilization of these hydrated phases. A comparison between the various sintered materials tested indicates that celsian showed the highest stability gaining less than 0.1% of weight in 100 h of steam exposure at 1,200 °C. In contrast, all the geopolymer specimens lost a small quantity of mass during hydrothermal exposure. Based on the mass change study, the anorthite-based geopolymer specimens seem to have fared best during hydrothermal exposure. The anorthite based geopolymer specimens lost less than 1% of mass after 100 h of exposure. The celsian based samples lost between 1.6 and 3.2% and the mullite-based samples lost 2.7% of weight. The possible reasons for this mass change include silica volatilization from potassium aluminosilicate glass compositions, which may have higher silica activities than the starting materials.

For all anorthite-based geopolymer specimens, XRD studies indicate substantial gehlenite formation both during the high-temperature drying/crystallization step and subsequent hydrothermal treatment at 1,200 °C. This comes from two reasons: (1) with the loss of the silica when forming silicic acid under hydrothermal conditions, the reaction makes anorthite phase moving towards the direction to form gehlenite. (2) Because of the limited solubility range of potassium into anorthite, one potassium and one silicon ion displace one calcium and one aluminum ion. The potassium ions will then exist on the calcium ion sites, whereas the silicon ions will exist on the tetrahedrally coordinated aluminum ion sites. Therefore, by doping anorthite with potassium, gehlenite formation is facilitated. Figure 9 shows that some gehlenite is formed even after the initial drying/

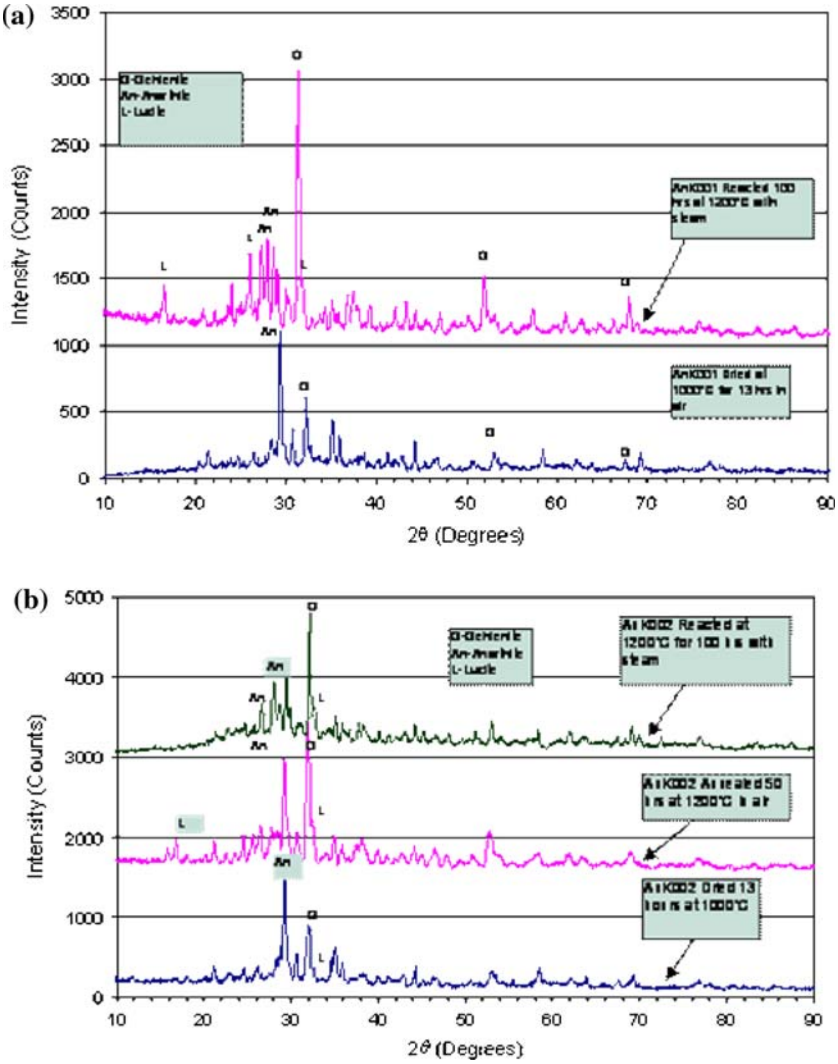


**Fig. 9** X-ray diffraction analysis of (**a**) AnK001 and (**b**) AnK002 specimens subjected to a drying/crystallization step at 1,000 °C/13 h and subsequently subjected to hydrothermal exposure at 1,200 °C in 15% $H_2O$/air

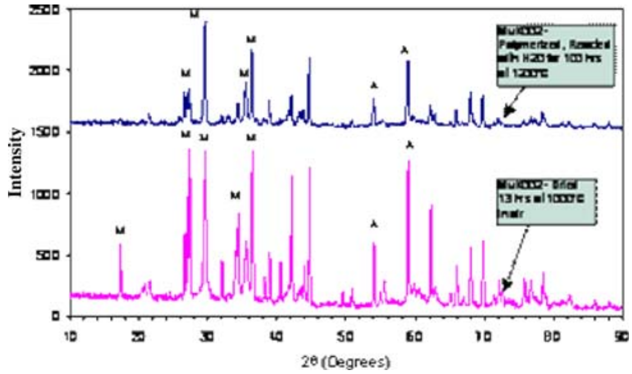


**Fig. 10** X-ray diffraction analysis of MuK002 specimens subjected to a drying/crystallization step at 1,000 °C/13 h and subsequently subjected to hydrothermal exposure at 1,200 °C in 15% $H_2O$/air

crystallization step at 1,000 °C, but the sample is still predominantly anorthite. After thermal exposure, the sample is predominantly gehlenite, with some anorthite and leucite. This phenomenon is confirmed by the phase diagram of $CaO–SiO_2–Al_2O_3–H_2O$ system [12], which clearly indicates that under high water pressure and high temperature conditions multiple phases (gehlenite + anorthite + wollanstonite) are more thermodynamically stable than anorthite single phase.

Figure 10 shows the phase changes in the mullite-based geopolymer composition exposed to hydrothermal environments. The only significant difference observable in the specimen between being dried/crystallized at 1,000 °C and after hydrothermal exposure at 1,200 °C is a change in the relative peak heights of the mullite and alumina phases. At the higher temperature, excess mullite seems to be crystallizing out from the gel phase.

The data for chemical changes occurring in the polymerized celsian samples CeK001 and CeK002 during hydrothermal exposure is presented in Fig. 11. The only difference in processing between CeK001 and CeK002 is that CeK001 was fired at 220 °C and that CeK002 was fired at 800 °C after geopolymerization. Intriguingly, the phase composition of CeK001 and CeK002 after identical thermal treatments in air at 1,000 °C are substantially different. This suggests that the lower temperature thermal treatments at 220 and 800 °C have an impact on phase stability on subsequent thermal exposure. CeK001 has a mixture of monoclinic para-celsian (P), hexa-celsian (H) and a potassium aluminosilicate phase ($K_4Al_{12}Si_2O_9$) after 1,000 °C firing, while CeK002 has virtually no para-celsian, and has a mixture of hexa-celsian, orthoclase (O, $KAlSi_3O_8$) and some other phases not yet identified. This suggests that at 1,000 °C, the equilibrium phase formation is still prevented by diffusion kinetics. Presumably, the firing step at the higher temperature in CeK002 stabilizes the H–O phase mixture, which cannot fully convert to the equilibrium composition at 1,000 °C due to slow kinetics. After the 1,200 °C hydrothermal treatment, both CeK001 and CeK002 have only the celsian and orthoclase phases.

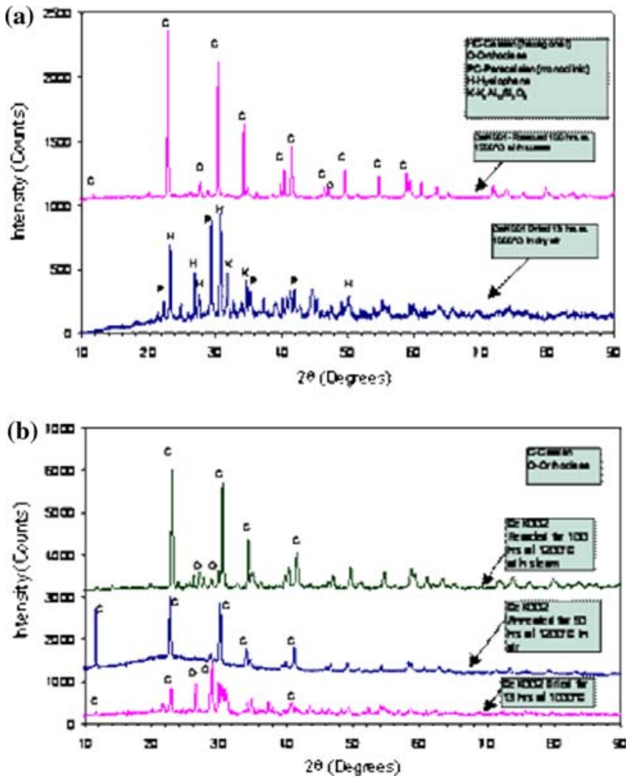


**Fig. 11** X-ray diffraction analysis of (**a**) CeK001 and (**b**) CeK002 specimens subjected to a drying/crystallization step at 1,000 °C/13 h and subsequently subjected to hydrothermal exposure at 1,200 °C in 15% $H_2O$/air

Future work will focus on the investigation of microstructure change during the hydrothermal exposure and optimize the geopolymer compositions for further improved phase stability under hydrothermal conditions.

## Conclusion

Geopolymer materials can be processed from the selected geomimetic compositions with alkali solutions. For anorthite based geopolymer specimens the compressive strength increases as the particle size of precursor powders decreases. Higher concentration KOH solution (45 wt.%) results in higher compressive strength compared to lower concentration KOH solution (25 wt.%), and there is an optimal ratio, close to a 1:1 mol ratio of anorthite to KOH, for maximal compressive strength (~99 MPa). The optimal firing temperature to obtain high compressive strength is in the range of 300–600 °C. The hydrothermal test experiments on KOH-derived geopolymer specimens showed that all of the geopolymer specimens have minimal mass change or dimensional change during hydrothermal exposure in spite of the phase change.

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