ROLE OF THE SYNTHESIS METHOD ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF METAKAOLIN-BASED POTASSIUM GEOPOLYMERS

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The synthesis method used has an important effect on the development of the compressive strength of a material. This work aims to research the effect of synthesis temperature (30°C and 70°C), curing condition (dried and sealed curing) and alkaline solutions (S_c commercial alkaline solution and S_l laboratory alkaline solution) on the development of compressive strength. The microstructure of these geopolymers was characterized using thermal analysis as well as porosity and microscopic observations, and the results were discussed. The total porosity was found to play a negative role on the compressive strength. Synthesis at a lower temperature demonstrated a better compressive strength due to the lower porosity and smaller pore sizes. The Sl geopolymers showed a better compressive strength than the Sc geopolymers due to their lower porosity. It was also found that the reaction was hindered when the samples were cured under a dried curing condition.

INTRODUCTION

The notion of activated alkalis as inorganic binders was first proposed by Glukhovsky [1] in the 50s, and these materials were later designated by Davidovits as "geopolymers" [2]. Geopolymers are usually obtained using alkali silicates, which activate an aluminosilicate powder (such as metakaolin or fly ash), forming a three-dimensional structure based on AlO_4 and SiO_4 units, with alkaline ions balancing the charge [2, 3]. Geopolymers have many attractive features that make them a good alternative to traditional, ordinary Portland cement, with the potential for use in specific environments.

One of the main attractive properties of geopolymers is their mechanical properties. Mechanical properties are important indices to evaluate a geopolymer as they provide the basic information to decide the utility of materials in the construction industry. Factors influencing the mechanical properties of geopolymers can be attributed to both internal and external properties. The internal properties, which include the composition of the raw materials (such as metakaolin, fly ash, and slugs), the Si/Al ratio in the mixture, and the presence of alkali cations and chemical impurities, have been well discussed and summarized in the literature [4-9].

The external properties include factors involved in the synthesis method, such as synthesis temperature and curing condition [4-9]. Other parameters can also play an important role in the increase of compressive strength. However, although there have been many discussions regarding the effect of temperature on this process, it seems that there is no consensus. Khale and Chaudhary [9] summarized the literature and concluded that curing at an elevated temperature (between 30°C and 90°C) has a more significant contribution to the geopolymeric reaction. Guo et al. [10] tested a fly ash-based geopolymer with a range of curing temperatures from 60 to 90°C and found that the best compressive strength was observed when cured at 75°C. Similarly, Muñiz-Villarreal et al. [11] concluded that curing at 60°C showed the highest compressive strength. These conclusions were based on experiments that were conducted by varying the curing temperature while keeping the reaction time constant. It is well known that curing at an elevated temperature can accelerate the geopolymerization reaction and decrease the setting time, but curing for longer periods at elevated temperature will break down the structure, inducing dehydration and excessive shrinkage, thus leading to a loss of mechanical strength [12, 13]. Therefore, research involving the temperature effect should not

simply be limited to the same reaction time but should also consider the state of consolidation and degree of geopolymerization.

The geopolymerization process is sensitive to moisture [14, 15] due to the role that water plays in the polymerization process [16], which includes dissolution and hydrolysis of raw materials as well as the condensation of dissolved species. The first stage involves the dissolution of the raw materials into the silicate species $[SiO_2(OH)_2]^{2-}$ and $[SiO(OH)_3]^-$ and the aluminate species $[Al(OH)_4]^-$. This stage consumes water and results in a decrease of free water. Then, the silicate and aluminate species react to produce aluminosilicate species as well as water. This condensation stage leads to an increase of water. These two stages can occur simultaneously once the raw materials are mixed with an alkaline activator. However, little information is available on the effect of moisture on the development of compressive strength.

A silicate solution is used as the adhesive in the synthesis of geopolymer binders. The commonly used silicate solution, named "waterglass", is a commercial product synthesized by melting sand and soda ash or potash. The high price and high content of water in this commercial silicate solution inhibits its use as a construction material. Thus, our laboratory developed an alternative to produce a silicate solution through the dissolution of amorphous silica in an alkaline solution. This synthesis solution has similar properties as the commercial waterglass, but it contains more of the reactive components $Q^0(Si)$ and $Q^1(Si)$ in the solution, which has a higher reactivity at the beginning of the geopolymerization reaction [17-19].

This article aims to study the influence of the synthesis method on the evolution of metakaolin-based potassium geopolymers. Specifically, the evolution of compressive strength was researched by varying the reaction temperature and curing condition. Moreover, two sources of silicate solution were compared (a commercial and a self-made silicate) to complete this research. The microstructure was studied through thermal analysis, and the porosity and microstructural morphology were observed using microscopy.

EXPERIMENTAL

Sample preparation

The geopolymer paste S_c (obtained from a commercial silicate solution) was prepared from a solution containing metakaolin (Table 1) and KOH pellets (85.7% purity) dissolved in potassium silicate (Si/K=1.66, density 1.33). The geopolymer paste S_l (fabricated from a laboratory self-made silicate solution) was prepared from a solution containing metakaolin and a mixture of KOH solution (KOH pellets dissolved in water, approximately 8 M/L) and silica supplied by Cabot, USA. The reactive mixture was then placed in a sealed polystyrene mold in an oven at 30°C for 18 h or at 70°C for 2 h. These samples were labeled as S_c-30°C, S_c-70°C, S_l-30°C and S_l-70°C, respectively. Two different curing conditions were used with these samples: (i) a dried cure method was performed under 43% RH after demolding at time points of 1, 7 and 28 days; (ii) a sealed cure method was applied to the specimens maintained inside the molds until the time points of 7 and 28 days. The variation of mass was observed with time. For the samples cured under dried conditions, an initial value was measured when the sample was removed from the oven and a stable mass was maintained in air. For the samples cured under sealed conditions, the total mass of the mold and samples was taken. The results allowed for the determination of the weight loss of the closed system.

Compressive strength

The compressive tests were performed at room temperature on a LIoyd Instrument EZ20 machine. Specimens were cylindrical, with an aspect ratio of 2 (15 mm in diameter; 30 mm in length). Specimen end surfaces were polished to obtain good parallelism. The samples were tested with a crosshead displacement rate of 0.50 mm/min. All values presented in the current work were an average of six samples.

Characterization

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out on a SDT Q600 apparatus in a Pt crucible from 30 to 800°C with a heating rate 10°C/min under a dry air flow of 100 mL/min.

Mercury intrusion porosimetry (MIP) tests were performed with a Micrometrics Autopore IV 9510 porosimeter, which is able to detect a diameter range of 3 nm ~ 360 μm, with a mercury intrusion and extrusion volume of 0.1 μL. The mercury pressure was raised from 0.0007 to 413.69 MPa. The samples were loaded into a penetrometer, which consists of a sample cup connected to a metal-clad precision-bore glass capillary stem. The penetrometer was then sealed and placed in a low-pressure port, where the sample cup was evacuated to remove air and moisture. The penetrometer cup and capillary stem were then automatically backfilled with mercury. The total porosity (open pores in the material) was calculated by multiplying the volume of mercury intruded at the maximum experimental pressure per gram by the bulk density of the material [20].

The morphology of the products was observed with a Cambridge stereoscan S260 scanning electron microscope (SEM). Prior to the observations, the samples were Pt-coated.

Table 1. Chemical analysis of metakaolin.

	SiO$_2$	Al$_2$O$_3$	K$_2$O+Na$_2$O	Fe$_2$O$_3$	TiO$_2$	CaO+MgO
Mass %	55	40	0.8	1.4	1.5	0.3

RESULTS

Compressive strength

Figure 1 shows the effects of synthesis temperature, curing condition and silicate solution used on the compressive strength of geopolymers. Regardless of the sample type and the curing condition, the results show that the metakaolin-based geopolymers acquire a compressive strength at an early time point. The compressive strength of a geopolymer at day 1 (22 MPa; Figure 1a) synthesized at 30°C reaches approximately 70% of the maximal value (33 MPa), which is obtained from the cured samples under the sealed conditions after 28 days. Therefore, the "basic" geopolymer network was built and the main compressive strength was obtained after 1 day of consolidation. Along with time, the compressive strength tends to increase as the geopolymerization continues. However, the two curing conditions show different states of evolution. Under the dried curing condition, an increase of 18% is found at the end of 28 days, while under the sealed curing condition,

the value is up to 47%. The increase of compressive strength under the dried condition is weak compared to that under the sealed condition. A similar effect of curing condition is observed for the S_l solution (Figure 1b) as for the S_c solution. Under the dried curing condition, little change is observed after 28 days, whereas, under the sealed curing condition, an increase of up to 43% is observed.

The variation of synthesis temperature (70°C compared to 30°C) is shown in Figure 1c, d. At a higher synthesis temperature, the formation of a geopolymer network is accelerated, and the time necessary for the consolidation decreases drastically from 18 h at 30°C to 2 h at 70°C. Because the longer reaction time at an elevated temperature could destroy the geopolymer network [12,13], the geopolymers synthesized at 70°C were not maintained in the oven for the same amount of time as the geopolymer synthesized at 30°C. Both of these geopolymers were removed from the oven once the initial consolidation was complete and then cured at ambient temperature. Although the reaction is accelerated at
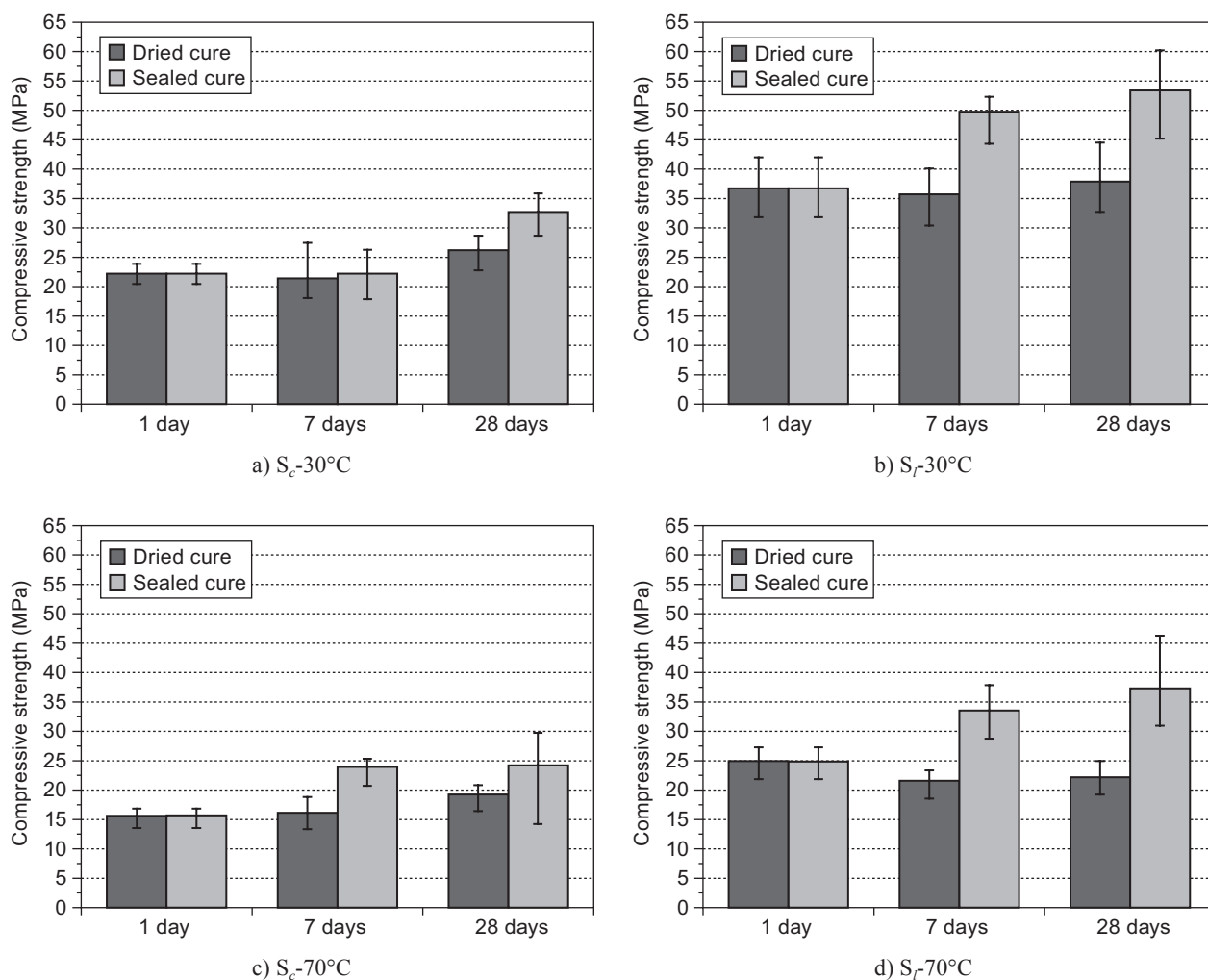

Figure 1. Compressive strength values for geopolymer synthesized from S_c (a, c) and S_l (b, d) alkaline solution at 30 and 70°C respectively, and then cured under dried and sealed condition respectively at ambient temperature.

70°C, the consolidated material does not show better mechanical properties. For example, the S_c geopolymer demonstrates a lower compressive strength at 70°C (16 MPa) than at 30°C (22 MPa) after 1 day (Figure 1a,c). Although the compressive strength increases along with time, after 28 days of curing under the sealed condition, the compressive strength obtained for S_c-70°C (24 MPa) is still lower than that for S_c-30°C (33 MPa). Similar effects of synthesis temperature were observed for the both the S_l and S_c silicate solutions.

Comparing the effects of the alkaline solutions, the S_l geopolymers show better mechanical properties than the S_c geopolymers. An increase of 39% was evidenced for the maximal values obtained at 30°C and cured under the sealed condition for 28 days.

The mass evolution for the samples cured under dried and sealed conditions was observed, as shown in Figure 2. For S_c-30°C, a rapid loss of mass is shown at the beginning of the dried cure (until 7 days; Figure 2a). However, after 7 days, this trend is no longer observed, and the mass does not change with time. In the end, 27 % of the initial mass was lost during the experiment. This loss of mass is likely due to the evaporation of free water in the pores when the samples were exposed to the drying condition. Taking into account the initial water content of the S_c geopolymers (38.4 %), it can be deduced that approximately 70 % of the initial water content is lost during the dried curing condition. For S_c-70°C, the rate of weight loss is more rapid than that of S_c-30°C. The maximal value is achieved after 2 days. However, the same weight loss of 27 % is found for S_c-70°C. This phenomenon signifies that the water in the S_c-70°C samples is more easily lost than that in S_c-30°C. For the samples cured under the sealed condition (Figure 2a), a slight variation of mass is detected, which demonstrates that no loss of water happens in the closed system. For the S_l solution (Figure 2b), the rate of weight loss was also faster at 70°C than at 30°C, as observed in the case of the S_c solution. The weight loss is approximately 23 %, losing approximately 70 % of the initial water content in the S_l geopolymers (32 %), which is in agreement with the S_c solution.

In summary, the compressive strength obtained at an early stage (1 day) is approximately 70 % of that at 28 days. No obvious evolution of compressive strength is found for the samples that were dried cured, but for the samples that were sealed cured, there was a drastic improvement of the compressive strength with time. At the same time, 70% of the initial water is lost for the samples that were dried cured, whereas no loss of weight is observed for the sealed cured system. The geopolymerization is likely to be inhibited when the samples are exposed to the dried condition, thus leading to a slight improvement of the compressive strength. The compressive strength is better at a lower synthesis temperature (30°C) compared to a higher temperature of 70°C. Otherwise, at 30°C, the loss of water under the dried cure condition is slower than that at 70°C. These phenomena demonstrate that the microstructure of these geopolymers is most likely different as a result of the different reaction temperatures. The S_l geopolymers show a better compressive strength than the S_c geopolymers. This difference is likely to be attributed to the different compositions of the solutions, which leads to the variations in the microstructure.

Microstructure characterization

To understand and explain the phenomena referred to above, the microstructure of the samples was characterized by thermal analysis as well as by porosity and microscopic observation.
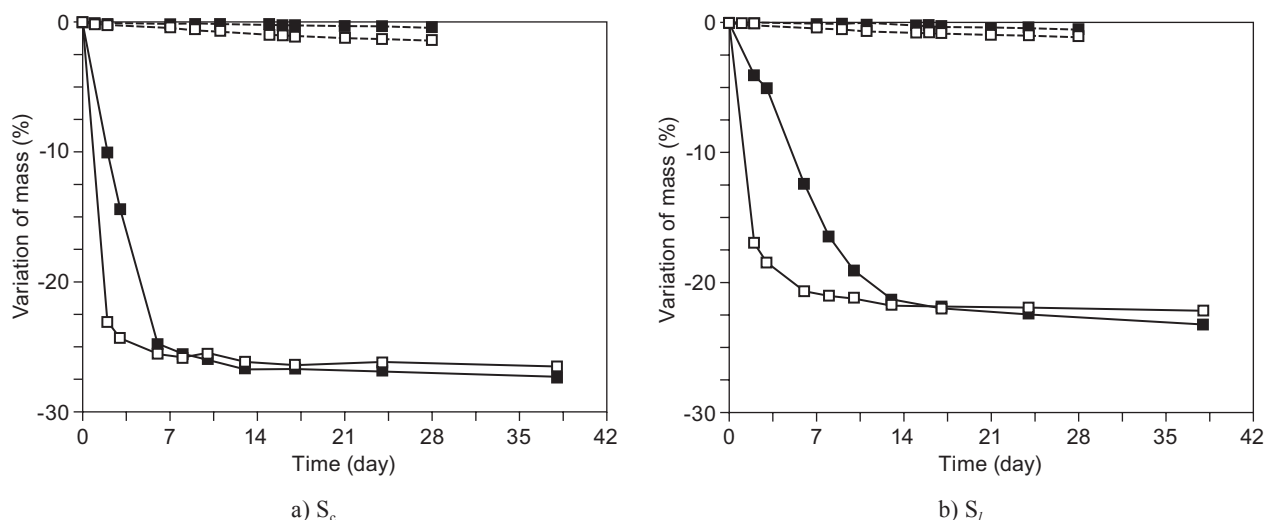

Figure 2. Variation of mass for geopolymer synthesized from S_c (a) and Sl (b) alkaline solution at 30 (■) and 70°C (□) respectively, and then cured under dried (—) and sealed condition (---) respectively at ambient temperature.

Thermal analysis

TG-DTA was performed on all the samples and is reported in Figure 3. As the curves show little difference between S_c-30°C, S_c-70°C, S_l-30°C and S_l-70°C, only the curve for the S_l-30°C geopolymer is shown. The curves are typical of a geopolymer compound, and the weight loss can be attributed to the loss of water. The heat flow (Figure 3a) was characteristic of the stability of these compounds in the range of considered temperatures, in accordance with the literature [18]. A significant loss of weight is found before 200°C (Figure 3b), which corresponds to a large endothermic peak centered at 80°C in the heat flow curves. The curing conditions influence the evolution of the curves with time. Under the dried curing condition, the shape of the weight loss curves, along with the heat flow curves, changes with time, and a drastic decrease of weight loss is evidenced. This phenomenon is in agreement with the variation of mass (Figure 2). When the samples were exposed to controlled humidity (~ 43 % RH), a significant amount of water was evaporated, and the amount of water remaining in the samples decreased. Under the sealed curing condition, the weight loss and heat flow curves maintain the same shape with time, and the total loss of mass decreases gradually.

Porosity

A mercury intrusion porosimetry test was performed to determine the pore size distributions in the geopolymers. Figure 4 presents the pore structure in terms of cumulative pore volume for S_c-30°C, S_c-70°C, S_l-30°C and S_l-70°C under the sealed curing condition at a time point of 21 days. The pore size distribution for the S_c-30°C samples is on average 15 nm, with a range

of 5-40 nm. With an increase in the synthesis temperature, the peak shifts to a larger pore size of 55 nm, with a wider range of 15-85 nm. For the S_l solution, S_l-30°C shows a higher pore size distribution near 95 nm, with a broader range of 15-255 nm. With the increase of the synthesis temperature, the peak moves to a larger size of approximately 120 nm, with a wider range of 10-1000 nm.

According to the IUPAC classification [21], these pore sizes can be attributed to mesopores (2-50 nm) and flow-through pores (>50 nm). These pores can be filled with migrated molecules, which are different from pores formed in the gel structures (micropores, <2 nm) [22, 23]. Regardless of the solution, larger pores and a greater contribution of pore size are found for the samples synthesized at 70°C. Geopolymer synthesis at a higher temperature (70°C) led to the rapid
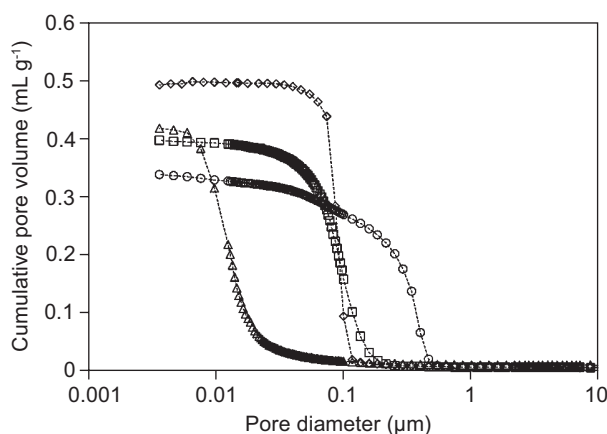
Figure 4. Pore distribution of S_c-30°C (Δ), S_l-30°C (□), S_c-70°C (◊) and S_l-70°C (○) geopolymer cured under sealed condition for 21 days.
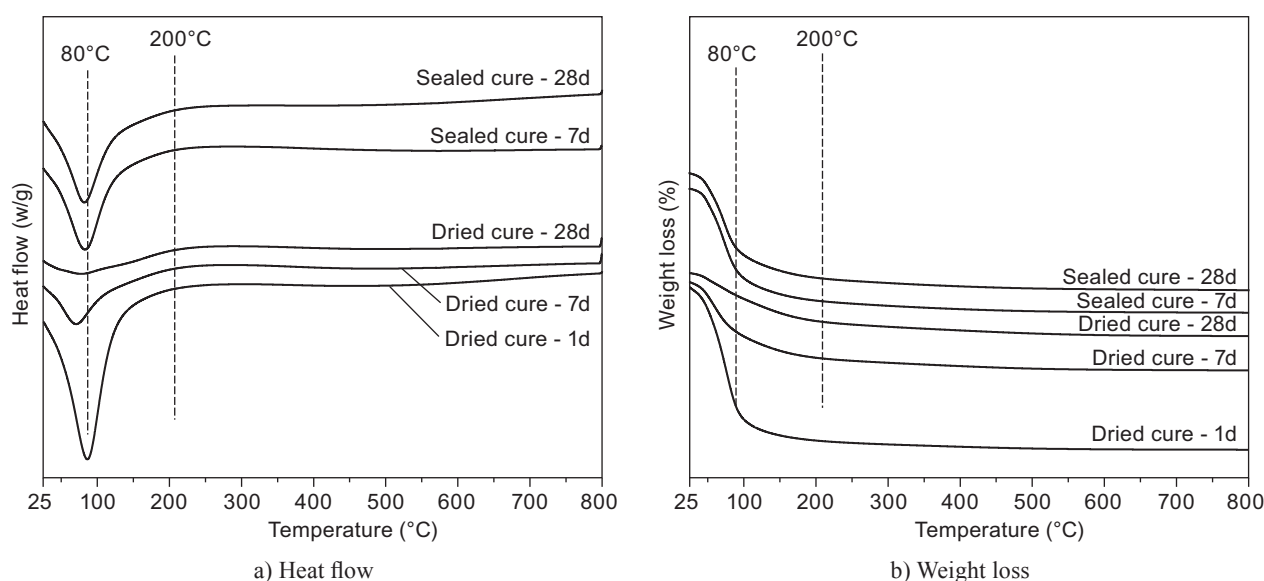
a) Heat flow

b) Weight loss

Figure 3. Heat flow (a) and Weight loss (b) curves of S_l-30°C geopolymer under dried and sealed cure respectively for 1, 7 and 28 days.

formation of a geopolymer network with a less ordered structure, which produced a poor quality material with larger pores. On the contrary, synthesis at a lower temperature (30°C) gradually filled the pores and thus narrowed the pores [24]. Additionally, the pores in the S_l geopolymers are found to be larger than those in the S_c geopolymers. According to [25], the S_l solution contains the more reactive composites $Q^0(Si)$ and $Q^1(Si)$ than the S_c solution. These reactive species result in the fast formation of a geopolymer network, leading to a poorer quality but larger pores compared to the geopolymers fabricated at 70°C.

SEM observations

All of the samples display a uniform, flake-like, layered microstructure, which is typically identified with metakaolin-based geopolymers (as shown in Figure 5).

Although these geopolymers have different mechanical properties due to the synthesis method (temperature, curing condition and alkaline solutions, as described above), they displayed a similar morphology with a homogeneous network of Si, Al and K, which is in accordance with the literature [26].

DISCUSSION

The results clearly show that the synthesis temperature, curing condition and alkaline solution influenced the compressive strength. These influences can be attributed to the formation of different microstructures in the geopolymer materials. Thus, the correlation between the characteristics of pore structure, thermal analysis and the compressive strength are depicted and discussed in Figure 6 and 7. Because the density of the S_c and S_l
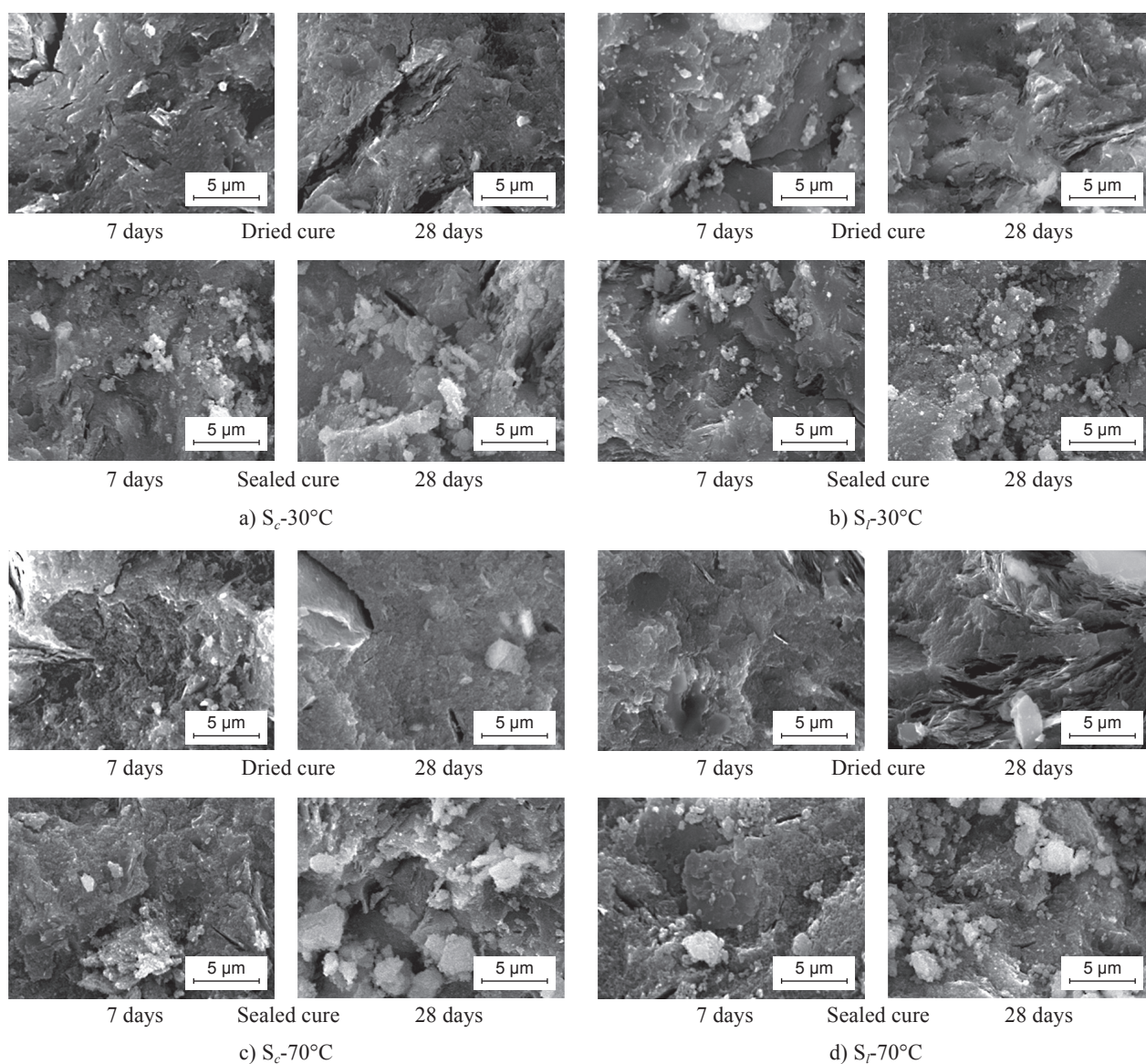

a) S_c-30°C

b) S_l-30°C

c) S_c-70°C

d) S_l-70°C

Figure 5. SEM of geopolymers synthesized from S_c (a, c) and S_l (b, d) alkaline solution at 30 and 70°C respectively and then cured under dried and sealed condition for 7 days and 28 days.

geopolymers varies slightly, this parameter cannot be taken into account to compare their compressive strength. Figure 6 relates the compressive strength with the total porosity, which takes into account the continuous pores and the ink-bottle pores. It can be seen that the compressive strength decreases with an increase in total porosity. It makes sense that the different methodologies of synthesis lead to the variations of pore structure, and as expected, the porosity induces a negative effect on the compressive strength.

Synthesis at 70°C produced larger pores and a greater total porosity compared to synthesis at 30°C, regardless of the solution used. The entire geopolymerization reaction is an exothermic reaction [2, 11]. A considerable amount of heat is generated during the formation of the samples. The geopolymerization reaction can be accelerated at a higher synthesis temperature. The acceleration of the geopolymerization reaction leads to the rapid formation of a geopolymer network as well as the release of a significant amount of

heat. The released heat results in a high local temperature and, consequently, the evaporation of local water. This evaporation of water during the consolidation process is important when the synthesis temperature is 70°C, which can explain the large pore size and high total porosity. The S_l geopolymers demonstrated larger pores but a lower total porosity compared to the S_c geopolymers, regardless of the synthesis temperature. These changes in the microstructure can be attributed to the different compositions of the alkaline solutions: the S_l alkaline solution contains more of the reactive components $Q^0(Si)$ and $Q^1(Si)$ than the S_c solution. These Q^n species are more highly reactive at the beginning of the geopolymerization reaction [17-19], which accelerates the geopolymerization and finally results in the rapid formation of a geopolymer network and larger pores, as shown at 70°C. However, the total porosity for the S_l geopolymers is lower than that for the S_c geopolymers. This can be attributed to the S_c geopolymers' greater Si/Al ratio. The initial Si/Al ratio is higher for the S_l geopolymers (1.75) than for the S_c (1.65) geopolymers. The low Si/Al ratio leads to a highly porous microstructure [3, 5, 6].

Figure 7 relates the compressive strength of the samples to the thermal analysis to study the evolution of the polymerization process under the different curing conditions. The weight loss deduced from TG-DTA represents the water content maintained in the samples. The compressive strength decreases with the increase of water content in the samples. This phenomenon is observed for both of the curing conditions but is less evident for the dried curing condition (Figure 7a). When the samples were exposed to the dried condition (controlled humidity: 43% RH), surface dehydration occurred, and water was taken away from the surface and open pores. The loss of water prevents the geopolymerization process and thus hinders the development of
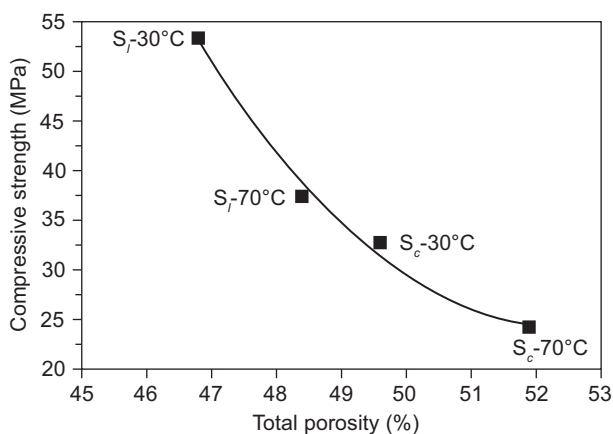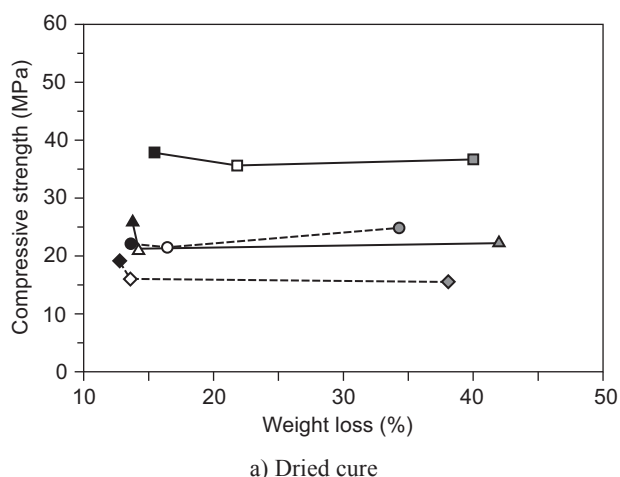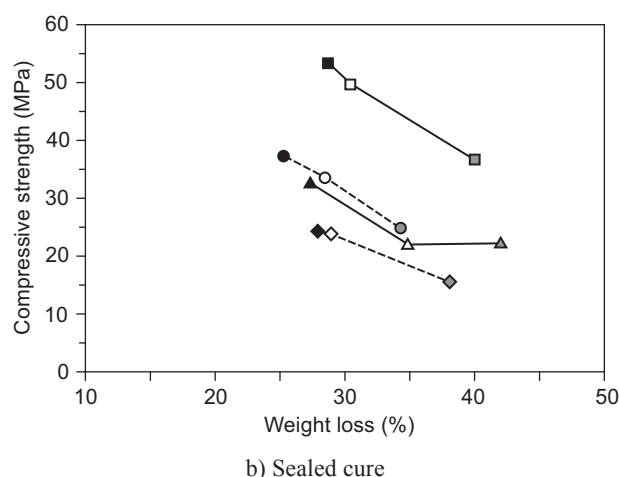

Figure 6. Relationship of mechanical property and total porosity deduced from MIP results for geopolymer samples.

a) Dried cure

b) Sealed cure

Figure 7. Relationship of mechanical property and weight loss deduced from TG-DTA analyses for S_c-30°C (Δ), S_c-70°C (◊), S_l-30°C (□) and S_l-70°C (○) geopolymer cured under dried (a) and sealed (b) condition respectively for 1 (black), 7 (white) and 28 days (grey).

compressive strength. However, when the samples were exposed to the sealed curing condition, no water was lost in the environment. The decrease of water content in the samples is likely caused by the consumption of water during the geopolymerization process. The advancement of geopolymerization leads to an increase of compressive strength.

CONCLUSION

This work studies the effect of synthesis methods on the evolution of the compressive strength of metakaolin-based geopolymers. The results were discussed based on the microstructure as follows:

1) reaction at a higher temperature (70°C compared to 30°C) leads to the fast formation of a geopolymer network as well as a significant amount of water evaporation during the geopolymerization reaction, which causes the formation of larger pore sizes and higher total porosity and consequentially a lower compressive strength;

2) the S_l geopolymers (fabricated with a self-made silicate solution) showed better compressive strength than the S_c geopolymers due to the lower total porosity produced, which is likely caused by the lower Si/Al ratio of the geopolymers.

The compressive strength is hindered under the dried curing condition due to the loss of water from surface and pores. Under the sealed curing condition, the water content in the pores or surface is consumed during the geopolymerization process, and thus, the compressive strength improves.

REFERENCES

1. Glukhovsky V.D., Soil silicates. Gosstroyizdat, Kiev, p154, 1959.
2. Davidovits J. (Eds.), Geopolymer Chemistry & Applications, 2nd ed., Institut Gépolymère, Saint-Quentin, France 2008.
3. Provis J.L., Van Deventer J.S.J. (Eds.), Geopolymers structure, processing properties and industrial applications, Woodhead, UK, Cambridge, 2009.
4. Komnitsas K., Zaharaki D., Miner. Eng. *20*, 1261 (2007).
5. Duxson P., Provis J.L., Lukey G.C., Mallicoat S.W., Kriven W.M., van Deventer J.S.J., Coll. Surf. A *269*, 47 (2005).
6. Duxson P., Fernández-Jiménez A., Provis J.L., Lukey G.C., Palomo A., van Deventer J.S.J., J. Mater. Sci. *42*, 2917 (2007).
7. Duxson P., Lukey G.C., van Deventer J.S.J., J. Mater. Sci. *42*, 3044 (2007).
8. Duxson P., Mallicoat S.W., Lukey G.C., Kriven W.M., van Deventer J.S.J., Coll. Surf. A *292*, 8 (2007).
9. Khale D., Chaudhary R., J. Mater. Sci. *42*, 729 (2007).
10. Guo X., Shi H., Dick W.A., Cem. Concr. Comp. *32*, 142 (2009).
11. Muñiz-Villarreal M.S., Manzano-Ramírez A., Sampieri-Bulbarela S., Ramón Gasca-Tirado J., Reyes-Araiza J.L., Rubio-Ávalos J.C., Pérez-Bueno J.J., Apatiga L.M., Zaldivar-Cadena A., Amigó-Borrás V., Mater. Lett. *65*, 995 (2011).
12. Van Jaarsveld J.G.S., Van Deventer J.S.J., Lukey G.C., Chem. Eng. J. *89*, 63 (2002).
13. Bakaharev T., Cem. Concr. Res. *35*, 1224 (2005).
14. Perera D.S., Uchida O., Vance E.R., Finnie K.S., J. Mater. Sci. *42*, 3099 (2007).
15. Zuhua Z., Xiao Y., Huajun Z., Yue C., Appl. Clay Sci. *43*, 218 (2009).
16. Wang L., Sagoe-crentsil K., J. Mater. Sci. *42*, 2997 (2007).
17. Prud'homme E., Michaud P., Joussein E., Peyratout C., Smith A., Rossignol S., Appl. Clay Sci. *51*, 15 (2011).
18. Prud'homme E., Michaud P., Joussein E., Clacens J.M., Rossignol S., J. Non-Cryst. Solids *357*, 1270 (2011).
19. Prud'homme E., Michaud P., Joussein E., Rossignol S., J. Non-Cryst. Solids *358*, 1908 (2012).
20. Ma Y., Hu J., Ye G., Fuel *104*, 771 (2013).
21. Urban J., Eeltink S., Jandera P., Schoenmakers P.J., J. Chromaogr. A *1182*, 161 (2008).
22. Moro F., Bőhni H., J. Colloid Interf. Sci. *246*, 135 (2002).
23. Kumar R., Bhattacharjee B., Cem. Concr. Res. *34*, 321 (2004).
24. Rovnaník P., Constr. Build. Mater. *24*, 1176 (2010).
[25] Prud'homme E., Autef A., Essaidi N., Michaud P., Samet B., Joussein E., Rossignol S., Appl. Clay Sci. *73*, 26 (2013).
26. Gao X.X., Autef A., Prud'homme E., Michaud P., Joussein E., Rossignol S., J. Sol-Gel Sci. Technol. *65*, 220 (2013).