Preliminary Study of Lime-Pozzolan Based Cement after Exposed to High Temperatures

Hyuk Lee, Vanissorn Vimonsatit, Prinya Chindaprasirt, and Kornkanok Boonserm

***Abstract*—**This paper presents a preliminary study on the properties of lime-pozzolan based cement and the effect of high temperatures on these properties. Conventional lime-pozzolan cements (LPC), alkali-activated LPC and hybrid alkali-activated LPC pastes were experimentally investigated. Microstructural analyses were performed based on XRD and SEM tests to identify the hydration products. Based on the results, the strength improvement of hybrid alkali-activated LPC cement, where ordinary Portland cement (OPC) was used to enhance the early age strength, could be due to (i) the dissolution of $Ca(OH)_2$ in the mixtures, and (ii) the pozzolanic effect of pozzolanic materials, which interacted with the free $Ca(OH)_2$ during hydration. The residual strength results indicated that the materials lost the strength gradually when exposed to the temperature up to 400°C, except for hybrid cement which showed a slight increase in strength. The microstructure analysis results indicated that the deterioration of the materials was due to the decomposition of hydration products at high temperature.

***Keywords*—**alkali activated, cement, lime, high temperature, hybrid, pozzolan

I. INTRODUCTION

LIME-POZZOLAN cement is one of the earliest building materials, widely used in the masonry construction during Roman times. Slow strength development with ambient temperature curing condition is one of the disadvantages of lime- pozzolan cement (LPC). In 19th century, its use was significantly reduced because of the invention of ordinary Portland cement (OPC) which was the faster setting and had higher early strength development.

LPC has been used for manufacturing construction products because of low cost and excellent durability than OPC in the past 50 years [1]. The advantageous properties of pozzolans consisted of the reduction of cost, heat evolution, alkali-aggregate expansion, concrete drying shrinkage and permeability as well as the improvement of the properties of fresh concrete and chemical resistance [2].

A number of researches [3-7] presented that alkali-activator was potentially possible to accelerate the early strength development. Shi [8] recommended that sodium sulfate (Na_2SO_4) was the most effective activator in LPC and the optimization content of chemical was 4%. He also showed that alkali-activator in LPC could increase its early strength development. Despite the improved early strength, alkali-activated LPC was not strong enough for the application in structural uses compared to OPC pastes. With the concern of the environmental problems caused by the worldwide production of Portland cement, efforts are therefore made to reduce some parts of Portland cement with supplementary cementing materials (SCM). Hybrid cement is a possible solution to solve this problem. Adding OPC to alkali-activated LPC is the concept of hybrid alkali-activated LPC, which early strength development is improved [9]. Another recent study [10] on conceptualization of Alkali Pozzolan Cement is conducted by adding chemical activator and scaffolding materials into fly ash and quicklime mixtures.

According to literature reviews [11-14], the hydration products of OPC is formed when the OPC reacts with water. The main hydration products of cementing compound are "*calcium silicate hydrate (CSH), calcium hydroxide (Portlandite* $Ca(OH)_2$*), AFt (ettingite,* $C_3A{\cdot}CaSO_4{\cdot}32H_2O$*), AFm (monosulfate,* $C_3A{\cdot}CaSO_4{\cdot}12H_2O$*)*".

The reaction mechanism of LPC is well described by Shi et al. [1].When $Ca(OH)_2$ mixes with pozzolan in water, the solution reaches a high pH values is approximately 12.5 at 20°C quickly. In a High pH solution under OH^-, pozzolan is dissolved and depolymerized into the solution such as Ca^{2+}, K^+, and Na^+. As Ca^{2+} ions and contact those dissolved or depolymerized monosilicate and aluminate species, hydration products form as follows:

$$Ca(OH)_2 + \text{Pozzolan} + \text{Water} \rightarrow \text{Hydration products} \qquad (1)$$

Concrete can expose to high temperature during fire or when it is near to furnace and reactions. During its exposure to high temperature, the mechanical properties such as strength, elastic modulus deteriorates decrease significantly quality of structural concrete [15]. Physical deterioration process that affects the durability of concrete structure is one of most

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important issue during high temperature exposure. The harmful effects of high temperature on concrete can be minimized by taking preventive measure such as choosing the right materials [16]. When exposed to high temperature, spalling of OPC binder concrete could occur resulting in a rapid loss of concrete cover layer by layer and potentially exposing the main still reinforcement. Therefore, it will be beneficial to find an alternative binder cement which carries good resistance of high temperature in term of spalling resistance and strength loss [17]. Many research papers show that using pozzolan as partial cement replacement lead to an improvement in temperature resistant properties. Xi et al. [18] studied the influence of high temperature on pulverized fly ash (PFA) in which OPC was replaced with 0%, 25% and 55% PFA. The residual strength of concrete samples after exposed to 250°C to 800°C were determined and found a dosage of 55% PFA showed high residual strength than other dosages PFA samples. Mendes et al.[19] used slag at 35%, 50% and 65%, and determined the residual strength after exposing to 100°C to 800°C. It was found that the samples with slag showed less damage under elevated temperatures.

Although number of research papers studied the LPC and effect of exposure high temperature on blended cement pastes, there is not enough information on hybrid LPC and the effect of high temperature exposures on the materials.

The aims of this research are to determine the properties of mechanical, chemical and microstructure properties of LPC based pastes.

II. EXPERIMENTAL PROGRAM

A. Raw Materials

In this experiment, commercial cementitious material from Western Australia, Class F (Low calcium) fly ash, manufactured hydrated lime, OPC are used to prepare LPC based pastes.

TABLE I
TYPICAL CHEMICAL COMPOSITION OF RAW MATERIALS

Composition	Fly ash	OPC	Hydrated lime
SiO_2	51.80	21.1	3
Al_2O_3	24.40	4.7	4
CaO	1.61	63.6	-
Fe_2O_3	13.20	2.9	0.25
MgO	1.70	2.6	-
SO_3	-	2.5	-
$Ca(OH)_2$	-	-	87.5

B. Ratios of Constituent Materials

Water to cementitious material ratio of 0.35 was used to prepare paste specimens. Shi [8] recommended that the optimum content of hydrated lime in LPC mixtures was 20%. Therefore, 20% of hydrated lime was adapted to this study. Table II shows the mixture proportions of the constituent materials in the tested mixes.

TABLE II
RATIOS OF CONSTITUENT MATERIALS

Index	Fly ash	Hydrated lime	Na_2SO_4	OPC
P-L	80	20	-	-
P-A	76.8	19.2	4	-
P-H	53.76	13.44	2.8	30

C. Mixing, Casting and Curing

A Hobart mixer was used to mix all of the materials. The appropriate amount of materials was weighed on electrical scales. The *ASTM C305* was adapted for mixing pastes [20]. Specimens were cast in the cubic mold of size 50 mm × 50mm × 50 mm. The specimens were cured in the curing room at 23°C until testing.

D. High Temperature

The specimens were selected after 56 days curing then dried in oven at 105 ± 5°C for 24 hours. After drying, the specimens were placed in the kiln to the selected heating regime up to reaching maximum temperature were 200, 400, 600 and 800°C and holding at this temperature for 2 hours. The specimens were exposed to temperature in electric furnace with the heating rate of 10°C per minute. The specimens were allowed to cool gradually to room temperature after exposed to temperature.

III. RESULTS AND DISCUSSION

A. Lime-Pozzolan Cement

Fig. 1 shows the compressive strength development of P-L pastes. The results indicate that the compressive strength development of P-L pastes is very low. X-ray diffraction (XRD) pattern is presented in Fig. 2. At 7 and 28 days, the main phases of P-L pastes indicate SiO_2 (Quartz), $Ca(OH)_2$ (Portlandite), AFt (ettringite) and CAH (calcium aluminate hydrate). The difference between AFt and CAH phases at 7 and 28 days is not observable. It seems that at the age of 7 days, the covalent bonds of Si-O-Si and Al-O-Al in fly ash was not efficiently broken down and ionization of $Ca(OH)_2$ in P-L pastes was also not efficient. Scanning Electron microscope (SEM) micrographs show no evidence of hydration products of P-L pastes as shown in Fig. 3.

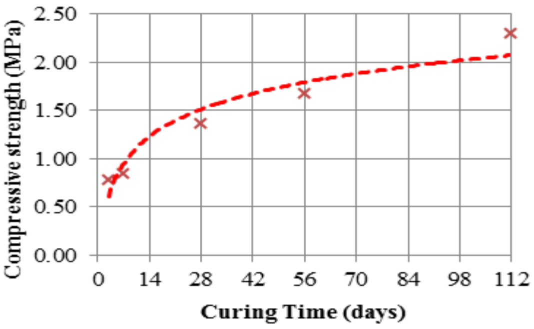


Fig. 1 Compressive strength development of P-L pastes

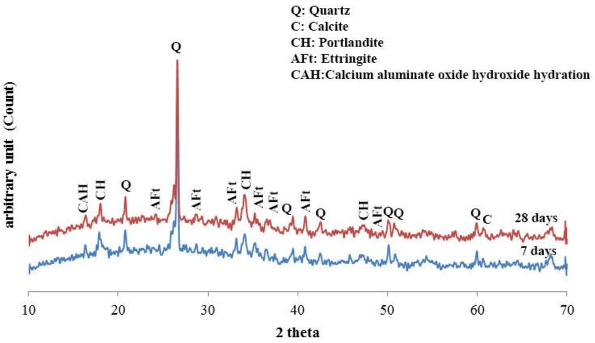
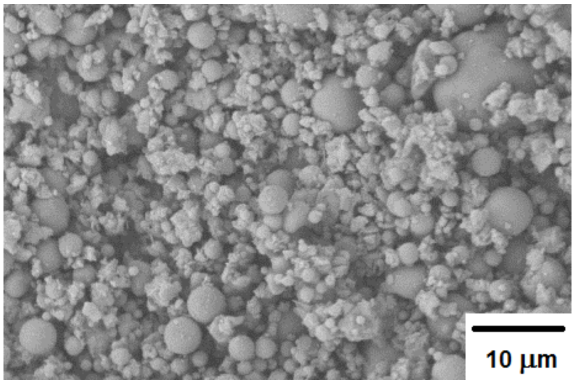
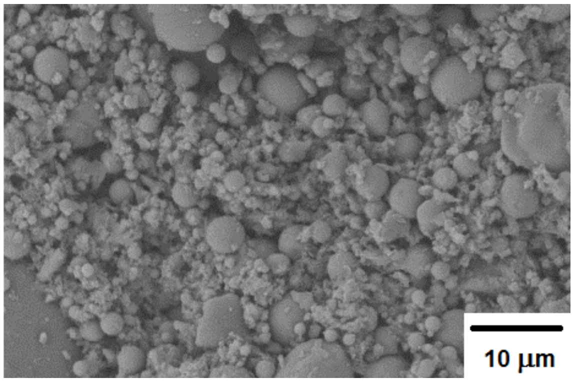


Fig. 2 XRD pattern of P-L pastes



(a) 7 days



(b) 28 days

Fig. 3 SEM micrographs of P-L paste

B. Alkali-Activated Lime-Pozzolan Cement

The alkali-activators create pH environment which allows the covalent bond Si-O-Si and Al-O-Al in pozzolan to breakdown with pH. Shi et al. [9] report that using alkaline activator can increase pozzolan reactivity in the mixtures. The most important pozzolan reaction between reactive silica and calcium hydroxide is the produced hydrated calcium silicates. The reaction between $Ca(OH)_2$ and Na_2SO_4 can be expressed by:

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow + 2NaOH \qquad (2)$$

As a result, sodium hydroxide (NaOH) increases the rate of hydration product in LPC.

Fig. 4 shows the strength development of P-A pastes in the presence of 4% Na_2SO_4. The rate of strength gains of P-A pastes is increased dramatically between 3 to 28 days. XRD pattern indicates the formation of CSH and AFt phases at 7 and 28 days, as shown in Fig. 5. CSH phases and some of AFt phases increase between 7 and 28 days. SEM micrographs as illustrated in Fig. 6 show the development of hydration products at 7 and 28 days. As curing time increases, the phase of hydration products is richly developed to form fabric structures.

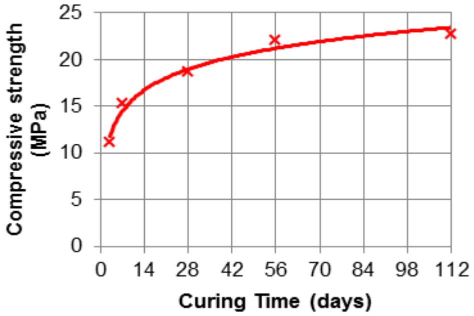


Fig. 4 Compressive strength development of P-A pastes

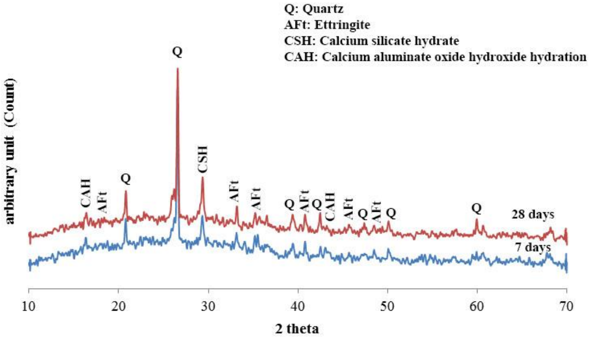
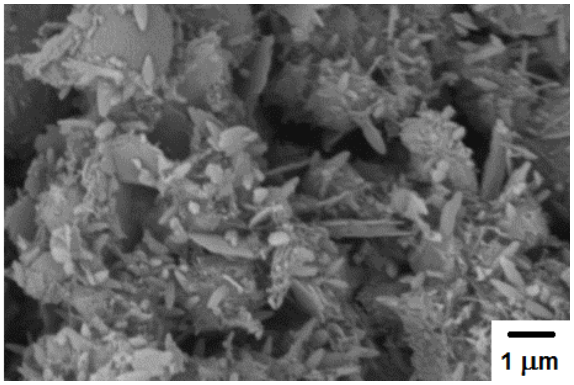
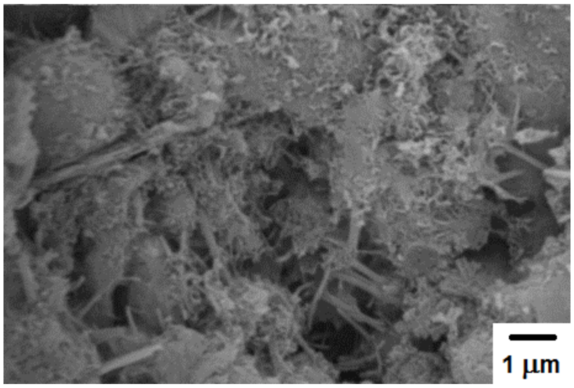


Fig. 5 XRD pattern of P-A pastes



(a) 7 days



(b) 28 days

Fig. 6 SEM micrographs of P-A pastes

C. Hybrid Alkali-Activated Lime-Pozzolan Cement

The strength development results of P-H pastes in the presence of 4% Na_2SO_4 and 30% OPC are shown in Fig. 7. The rate of strength gain of P-H pastes increases significantly between 7 to 28 days. The outcome of XRD pattern analysis of P-H pastes at 7 and 28 days is as illustrated in Fig. 8. The XRD pattern at 7 days shows the presence of CH (Portlandite), Q (SiO_2), AFt and minor CSH phases. It shows that CH phases could be a result of the hydration products of OPC, not just from the manufactured hydrated lime. At 28 days, CSH phases increase while CH phases decrease. SEM images in Fig. 9 indicate the growth of hydration products as fabric structures when curing proceeds.

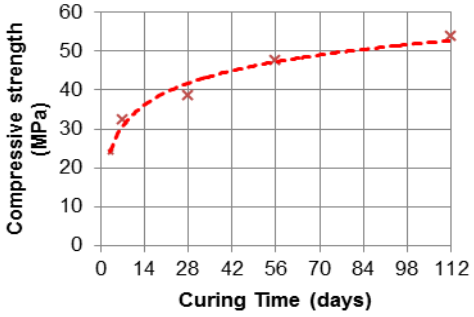


Fig. 7 Compressive strength development of P-H pastes

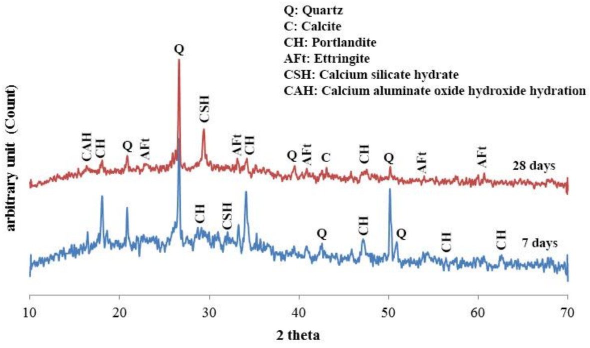
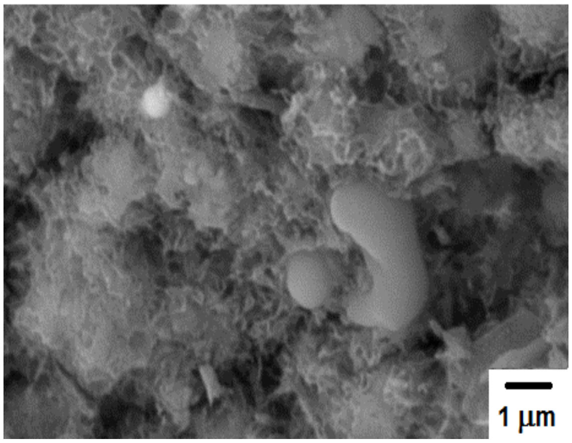
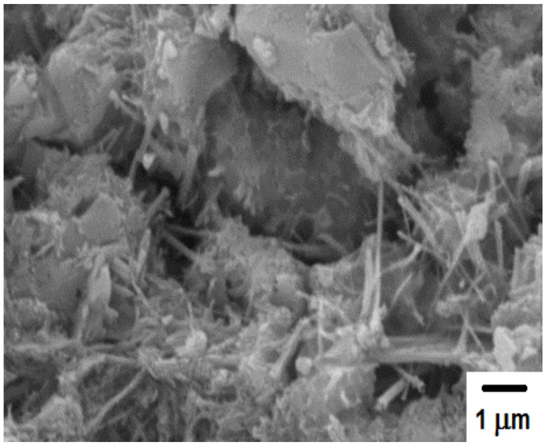


Fig. 8 XRD pattern of P-H pastes



(a) 7 days



(b) 28 days

Fig. 9 SEM micrographs of P-H paste

D. Comparison of Lime-pozzolan Based Cement Pastes

Fig. 10 indicates the compressive strength development of LPC based pastes in the different mixtures. The results show that P-H pastes have greater strength development than that of P-L and P-A pastes. This is as expected as additional OPC in alkali-activated LPC would enhance the early strength. The enhancement of the compressive strength development in LPC with Na_2SO_4 and OPC can be explained by two mechanisms. The first mechanism is due to the influence of adding 30% OPC in alkali-activated LPC pastes. The hydration products of OPC enhance the early strength development due to dissolution of $Ca(OH)_2$ in the mixture. The second mechanism is the pozzolan effect on OPC that can interact with free $Ca(OH)_2$ which is one of hydration products of OPC. The freshly produced $Ca(OH)_2$ is more soluble than manufactured hydrated lime [21]. Thus free $Ca(OH)_2$ can react with pozzolan quicker than the manufactured hydrated lime.

E. High Temperature Exposure

Fig. 11 presents the residual strength and relative strength percentage of original strength values of LPC based pastes after exposure to high temperature. The test results show that each temperature range has a distinct pattern of strength gain or loss.

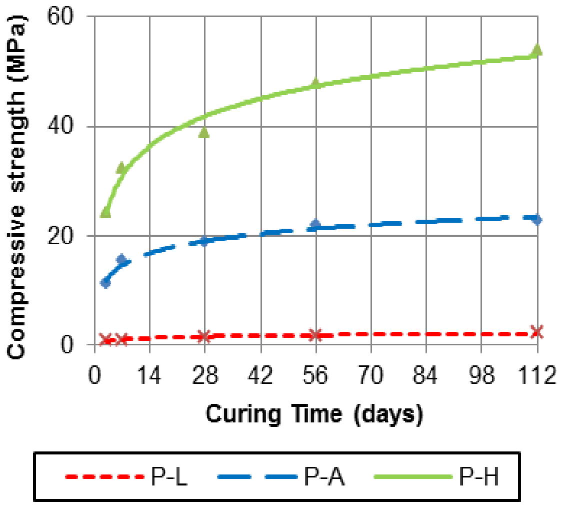


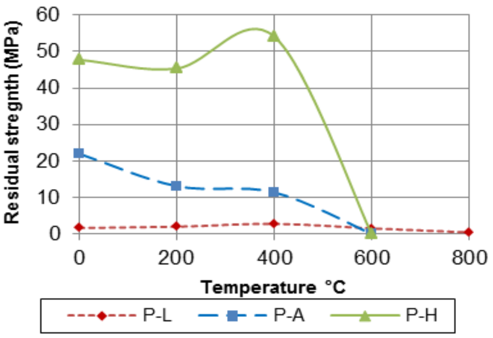
Fig. 10 Compressive strength development of LPC based pastes

The residual strength results of P-L pastes are at the low value of around 2 MPa. Due to the extremely low strength in P-L pastes, the effect of exposure to high temperature could not be indicated. The SEM micrographs of LPC based pastes at 25°C and after exposing to 600°C are shown in Fig. 12. The SEM micrograph of P-L pastes at 25°C is not different from that of the specimen exposed to 800°C. The image shows that unreacted fly ash particles of P-L paste exist at 800°C.

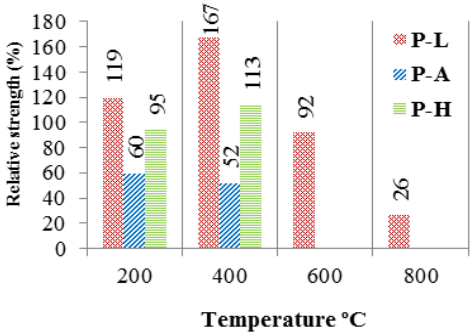
With P-A pastes, a significant decrease in the strength is observed when exposed to 200°C. The relative residual strength is 60% of the original ambient strength. At the same temperature level of 200°C, the P-H pastes performed better with 95% relative residual strength from the original ambient strength.

The residual strengths of P-A and P-H pastes after 400°C temperature exposure are, respectively, 52% and 113% of the original ambient strength. The increase in the strength of P-H pastes can be partially attributed to the evaporation of water which leads a strong resistance between the failure planes.

More significant loss in strength is observed when exposed to 600°C. Further evaporation of water could cause the decomposition of the hydration products resulting the deterioration of P-A and P-H pastes. The SEM image of P-A and P-H pastes after exposed to 600°C shows that there has been limited amount of fabric structures compared to the image of the pastes after exposed to 25°C. This indicates that the internal structure has disintegrated which could be a reason for the decomposition of hydration products that lead to a decrease in the residual strength of P-A pastes.

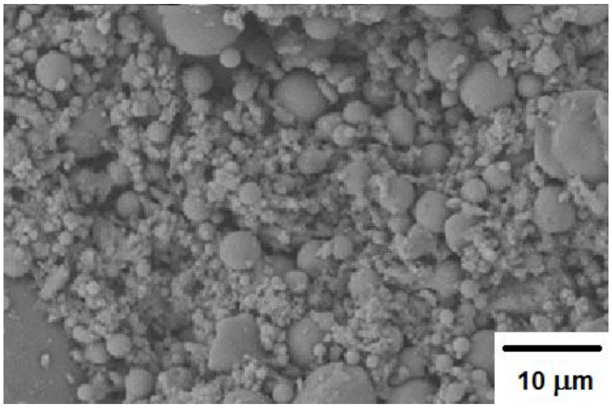


(a) Residual strength

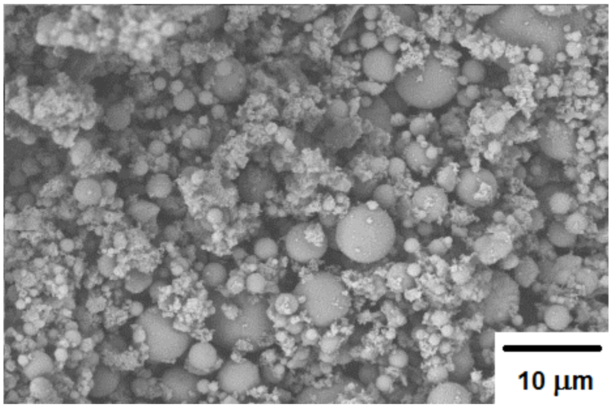


(b) Relative strength

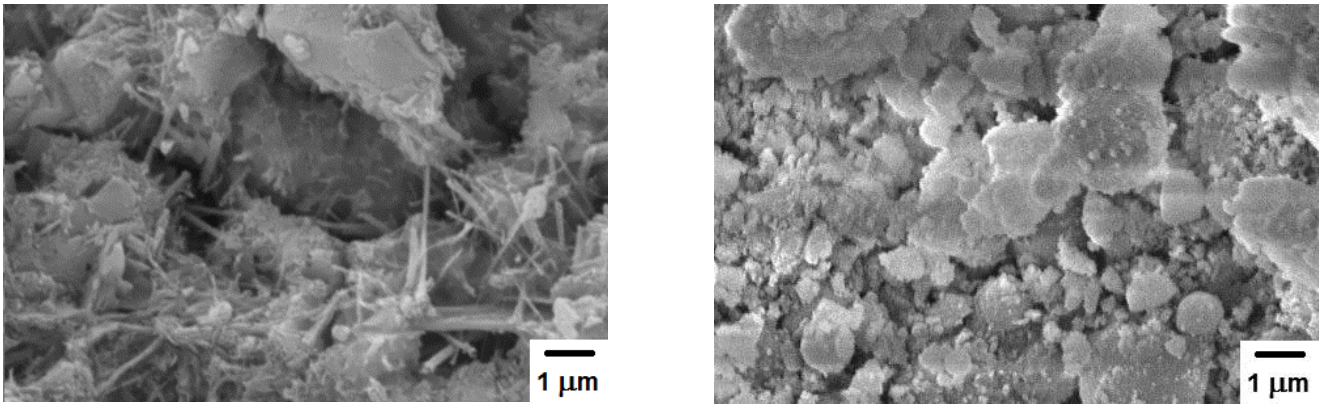
Fig. 11 Residual and Relative strength of LPC based pastes



a) 25°C P-L

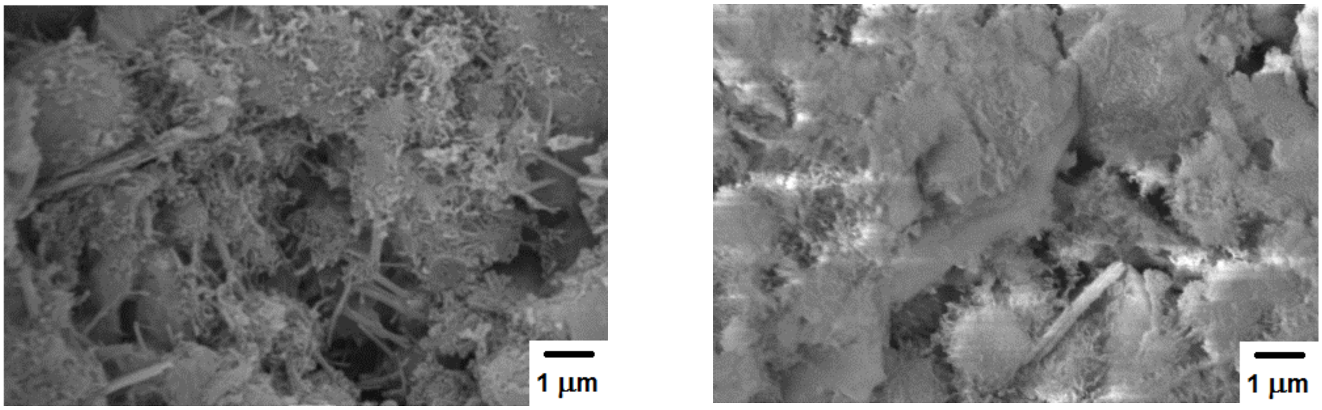


b) 800°C P-L



c) 25°C P-A

d) 600°C P-A



e) 25°C P-H

f) 600°C P-H

Fig. 12 SEM micrographs of LPC based paste

IV. CONCLUSION

The results obtained from this investigation provide a preliminary study on the possibility of using lime-pozzolan cement based pastes to resist high temperatures. The following conclusions are drawn:

1. $Ca(OH)_2$ from hydration reaction of OPC and Na_2SO_4 could enhance the strength development due to CSH formation in hybrid alkali-activated lime-pozzolan cement.

   The hydration products of OPC enhance the early strength development due to the dissolution of fresh $Ca(OH)_2$ in hybrid alkali-activated lime-pozzolan cement pastes. The pozzolanic effect of OPC, which can interact with the free $Ca(OH)_2$, improves hydration products.
2. The residual strength of alkali-activated lime-pozzolan cement pastes and hybrid alkali-activated lime-pozzolan cement pastes were deteriorated after exposed to 600°C whereas the hybrid alkali-activated lime-pozzolan cement pastes were increased the residual strength at the temperature range of 200°C to 400°C
3. The limited fabric structures of the specimens after exposed to high temperature as illustrated in the SEM micrographs indicate the decomposition of hydration products resulting a decrease in the residual strength.

This research can be extended to investigate the properties of mortars, concretes and durability of lime-pozzolan based cements at elevated temperatures.

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