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THE INFLUENCE OF CALCIUM SOURCE ON THE PREPARATION OF GEOPOLYMER USING CIRCULATING FLUIDIZED BED FLY ASH

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ABSTRACT

Circulating fluidized bed（CFB）fly ash contains a high content of calcium and sulfur, which makes it difficult to be used as traditional construction and building materials. However, the chemical compositions and mineral compositions of CFB fly ash showed potential application in the synthesis of geopolymer. A mixture of metakaolin and $CaCO_3$, $CaSO_4$ and $Ca(OH)_2$ was used to investigate the influence of calcium source on the preparation of geopolymer in the SiO_2-Al_2O_3-CaO-Na_2O-H_2O system. The results showed that the presence of $CaCO_3$ played a catalytic role and accelerated the setting process. The $CaCO_3$-bearing sample showed the highest strength development at early curing age when the CaO/Al_2O_3 was 0.5, however, showed the highest after long-term curing when the CaO/Al_2O_3 was 0.1. New phases faujasite and zeolite formed in 90 day cured $CaCO_3$-bearing samples. When the CaO/Al_2O_3 was higher than 0.3 the $CaSO_4$-bearing sample quick set due to the formation of AFt. When the CaO/Al_2O_3 was 0.5 the 28 day cured $CaSO_4$-bearing sample showed a strength reduction due to continuous formation of AFt. New phases including thenardite and faujasite formed in $CaSO_4$-bearing sample. The pozzolanic reaction and the geopolymerization reaction were the main reactions in the $Ca(OH)_2$-bearing samples.

Keywords: Geopolymer, pozzolanic reaction, metakaolin, Circulating fluidized bed, fly ash

INTRODUCTION

Circulating fluidized bed（CFB）boilers showed advantages in the combustion of coal wastes and won their high acceptability for power plants in past twenty years in China. The quantities of combustion bottom and fly ash of CFB boiler were 2-3 times higher than those of pulverized coal fly ash. CFB ash contains a high content of calcium and sulfur due to desulphurization, which makes it difficult to be used as traditional construction and building materials. However, the chemical compositions and mineral compositions of CFB ash showed potential application in the synthesis of geopolymer.

Geopolymers are inorganic, typically ceramic, materials that form long-range, covalently bonded, three dimensional amorphous networks, similar to zeolites (Huang, Y. and Han, M., 2011). Metal cations such as Na^+, K^+ and Ca^{2+} in the networks balanced the charge associated with tetrahedral Al (Feng, D. et al., 2012). There were N-PS 、 N-PSS and N-PSDS geopolymers depending on the SiO_2/Al_2O_3 ratio (Pimraksaa, K. et al., 2011). The investigations on the preparation of geopolymers have lasted for more than half a century. Generally, the mechanism of geopolymerization can be divided into three main stages (Part W. K. et al., 2015): (1) Dissolution of oxide minerals from the source materials (usually silica and alumina) under highly alkaline condition; (2) transportation/orientation of dissolved oxide minerals, followed by coagulation /gelation; (3) polycondensation to form 3D network of silico-aluminates structures. The availability of dissolved Al and Si at a given moment highly influenced the kinetics of the alkaline activation of alumino-silicate materials (Fernández-Jiménez A. et al., 2006). The Na/Si ratio was positively related with the formation of aluminosilicate gel N-A-S-H (Criado M. et al., 2007) and the Na/Al ratio showed important effects on the formation of 3D network (Zhang Z. et al, 2012). The presence of $Ca(OH)_2$ showed influences on the formation of C-S-H, however, not on the formation of N-A-S-H (Alonso S. and Palomo A., 2001). However, many questions persist about the reactivity of alumino-silicate materials in strong alkaline environments and soluble silicates.

In this research a mixture of metakaolin and $CaCO_3$, $CaSO_4$ and $Ca(OH)_2$ instead of CFB fly ash was used to investigate the influence of Na_2O/Al_2O_3, SiO_2/Al_2O_3 and pozzolanic reaction on the setting time and compressive strength of geopolymer.

EXPERIMENTAL

Geopolymer Paste Formulation

The metakaolin material used in this research was prepared by heating a commercial kaolinite (D95 <0.08mm) at 860 ºC for 3 min. Chemical compositions of the metakaolin determined by X-ray fluorescence (XRF) spectroscopy (Thermo Fisher Scientific, ARL ADVANT 3600, America) were shown in Table 1. A sodium silicate solution with 27.3% SiO_2, 8.36% Na_2O and 64.34%H_2O and AR-grade NaOH, $CaCO_3$ $Ca(OH)_2$ and $Ca(SO)_4$ were used as additives. The mix formulation of geopolymer

paste was shown in Table 2. The sample with the addition of $CaCO_3$ was denoted as CC, CS for $CaSO_4$, CH for $Ca(OH)_2$.

Table.1 Chemical compositions of metakaolin (wt%)

SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	LOI
54.67	41.61	0.11	0.15	0.47	1.89

Table.2 Mix proportion of experimental material (wt%)

Sample	Designed composition	MK	$CaCO_3$	$Ca(OH)_2$	$CaSO_4$	NaOH	Na_2SiO_3	H_2O
CC-0.1	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.1CaO$	57.79	2.37	-	-	12.31	3.10	24.25
CC-0.2	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.2CaO$	56.63	4.62	-	-	12.03	3.03	23.69
CC-0.3	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.3CaO$	55.35	6.78	-	-	11.75	2.96	23.16
CC-0.5	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.5CaO$	52.96	10.81	-	-	11.25	2.83	22.16
CS-0.1	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.1CaO$	57.48	-	-	3.19	12.21	3.08	24.05
CS-0.2	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.2CaO$	55.70	-	-	6.19	11.83	2.98	23.30
CS-0.3	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.3CaO$	54.03	-	-	9.01	11.47	2.89	22.60
CS-0.5	$2.4SiO_2 \cdot Al_2O_3 \cdot 0.7Na_2O \cdot 0.5CaO$	50.97	-	-	14.16	10.82	2.73	21.32
CH-0.1	$2.5SiO_2 \cdot Al_2O_3 \cdot 0.3Na_2O \cdot 0.1CaO$	62.20	-	1.98	-	4.48	5.32	26.02
CH-0.2	$2.5SiO_2 \cdot Al_2O_3 \cdot 0.3Na_2O \cdot 0.2CaO$	60.99	-	3.88	-	4.40	5.21	25.52
CH-0.3	$2.5SiO_2 \cdot Al_2O_3 \cdot 0.3Na_2O \cdot 0.3CaO$	59.83	-	5.71	-	4.31	5.12	25.03
CH-0.5	$2.5SiO_2 \cdot Al_2O_3 \cdot 0.3Na_2O \cdot 0.5CaO$	57.63	-	9.17	-	4.15	4.93	24.11

Characterization of Geopolymers

The setting time for all mixes with w/silica of 2.10 was determined using a Vicat needle (1.13 ± 0.05mm) following the procedure outlined in GB/T1346. The initial setting time was the elapsed time after sample mixing when the distance between the needle and the base-plate supporting the sample is 4 ± 1mm. The final setting was the elapsed time when the needle only penetrates 0.5 mm into the specimen. Three specimens per mix were subject to compressive strength testing after curing for 1, 3, 7, 28 and 90 days. The strength results reported were the average of three specimens and varied by
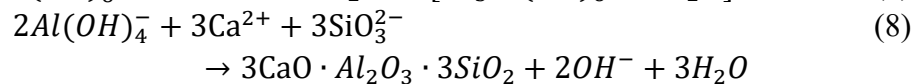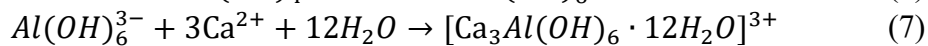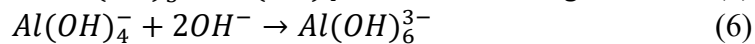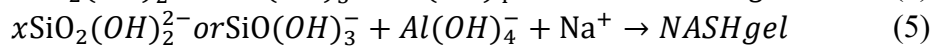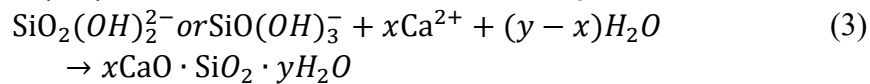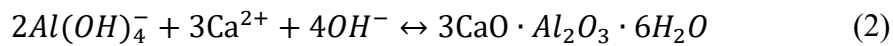
not more than 10%.

The hydration reactions were stopped after required curing days by immersing samples in ethanol for 7 days, with the ethanol replaced with fresh solution after the first 4 days. Samples were then dried at 45°C for 48h and ground to pass through a 76μm sieve. The ground samples were then used to determine the crystalline phases presented by X-ray diffraction (XRD, Rigaku D/MAX 2550 VB with a Cu target) and the structure variation by Raman spectrum measurement (Thermo Fisher, DXR, Laser wavelength 445 nm).

RESULTS AND DISCUSSION

Influence of CaCO₃ on the Geopolymerization

The results in Figure 1 showed that with the increase of CaO/Al_2O_3 molar ratio from 0.1 to 0.5 the initial setting time of sample CC varied from 271min to 15min， the finial setting time accelerated from 575min to 38min. The reactions occurred in the SiO_2-Al_2O_3-CaO-Na_2O-H_2O system of this research are shown in Equations 1-8 (Silva P. D. et al., 2014 and Suryavanshi A. K. et al. 1996). The geopolymerization began with the structure breakdown of metakaolin under the attack of alkaline activators, i.e. Equation 1. This reaction was dependent on the concentration of NaOH (Alonso S. and Palomo A., 2001). However, the presence of $CaCO_3$ accelerated Equations 1-8 (Rakhimova N. R. et al., 2016 and Gao X. et al., 2015). The presence of $CaCO_3$ also acted as fine aggregates to lower down the porosity of samples, which increased the compressive strength of early age cured samples with the increase of CaO/Al_2O_3 (Figure 2). However, the development of compressive strength varied with curing ages and CaO/Al_2O_3. The compressive strength of sample CC-0.5 was 9.1MPa after 1-day curing, increased to 14.3 and 17.2MPa after 3 and 7-day curing. After curing for 28 and 90 days the compressive strengths of sample CC-0.1 were 26.4 and 29.0MPa, respectively, which was the highest (Figure 2).
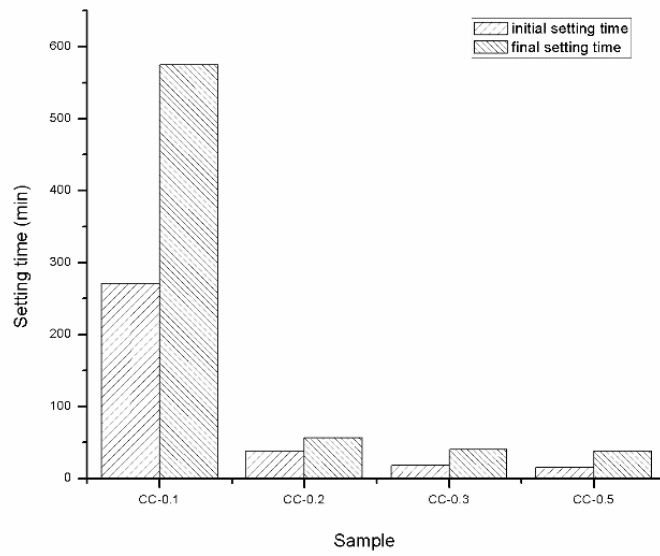
$$\text{Si}_2O_5 \cdot Al_2O_2 \xrightarrow{OH^-} \text{SiO}_2(OH)_2^{2-} \, or \, \text{SiO}(OH)_3^- + Al(OH)_4^- \tag{1}$$

$$2Al(OH)_4^- + 3Ca^{2+} + 4OH^- \leftrightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O \tag{2}$$

$$\text{SiO}_2(OH)_2^{2-} \, or \, \text{SiO}(OH)_3^- + xCa^{2+} + (y-x)H_2O \tag{3}$$
$$\rightarrow x\text{CaO} \cdot \text{Si}O_2 \cdot yH_2O$$

$$x\text{SiO}_2(OH)_2^{2-} \, or \, \text{SiO}(OH)_3^- + Al(OH)_4^- + Ca^{2+} \rightarrow CASH \; gel \tag{4}$$

$$x\text{SiO}_2(OH)_2^{2-} \, or \, \text{SiO}(OH)_3^- + Al(OH)_4^- + Na^+ \rightarrow NASH gel \tag{5}$$

$$Al(OH)_4^- + 2OH^- \rightarrow Al(OH)_6^{3-} \tag{6}$$

$$Al(OH)_6^{3-} + 3Ca^{2+} + 12H_2O \rightarrow [Ca_3Al(OH)_6 \cdot 12H_2O]^{3+} \tag{7}$$

$$2Al(OH)_4^- + 3Ca^{2+} + 3SiO_3^{2-} \tag{8}$$
$$\rightarrow 3\text{CaO} \cdot Al_2O_3 \cdot 3SiO_2 + 2OH^- + 3H_2O$$

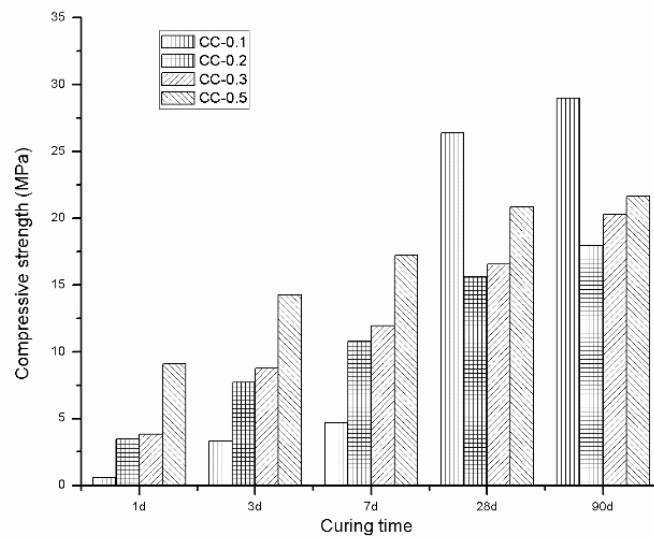Figure 1. Setting time of each $CaCO_3$-bearing sample.

Figure 2. Compressive strengths of $CaCO_3$-bearing samples.

The results in Figure 3 showed that calcite ($CaCO_3$) in sample decreased with curing ages. Quartz was detected in all samples, which suggested the presence of metakaolin in all curing age samples. A new phase faujasite formed after 90-day curing, which was the evidence of geopolymerization. It formed more in sample CC-0.1 than in

sample CC-0.5. Zeolite formed in 90-day cured sample CC-0.5, however, was not detected in sample CC-0.1. The influence of $CaCO_3$ on geopolymerization varied with CaO/Al_2O_3 and curing ages.
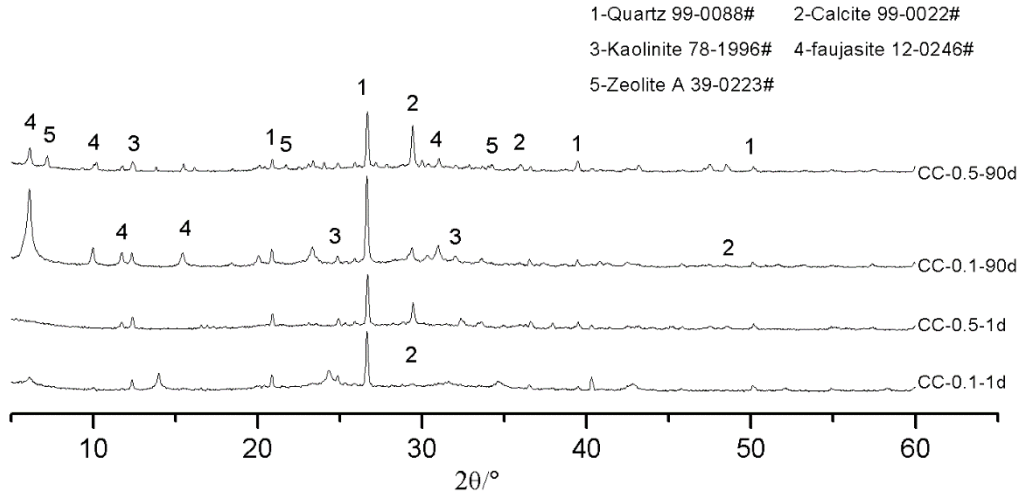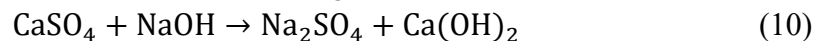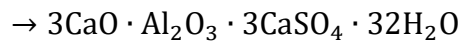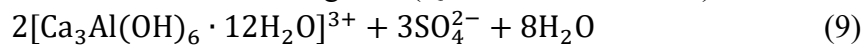

Figure 3. X-ray diffraction patterns of $CaCO_3$-bearing samples (normalized to the 100% intensity peak of quartz of sample CC-0.1-1d)

Influence of CaSO₄ on the Geopolymerization

The results in Figure 5 showed that setting time decreased with the increase of $CaSO_4$. When the CaO/Al_2O_3 was higher than 0.3, i.e. SO_3 in solid was 6.85%, the sample quick set. With the increase of the CaO/Al_2O_3 from 0.1 to 0.5 the initial setting time of sample CS accelerated from 1260min to 20min, the finial setting time was from 1380min to 80min. Comparing to the lower solubility of $CaCO_3$ ($Ksp=3.3\times10^{-9}$) higher solubility of $CaSO_4$ ($Ksp=3.14\times10^{-5}$) accelerated Equations 2-4 and 7-8 at the same CaO/Al_2O_3. The presence of $CaSO_4$ resulted in the formation of AFt (Equation 9). An appropriate amount of AFt showed the effect of retarding the initial setting time, however, too much formation of AFt accelerated the setting time due to fast reaction rate of Equation 9 and needle like morphology of AFt. The formed Na_2SO_4 due to Equation 10 also accelerated the setting time (Qiao X.C. et al., 2009).

$$2[Ca_3Al(OH)_6 \cdot 12H_2O]^{3+} + 3SO_4^{2-} + 8H_2O \qquad\qquad (9)$$
$$\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$
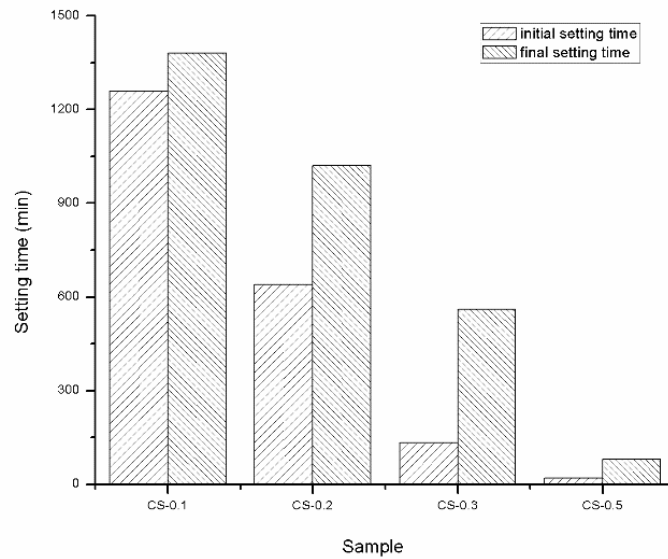$$CaSO_4 + NaOH \rightarrow Na_2SO_4 + Ca(OH)_2 \qquad\qquad (10)$$

Figure 4. Setting time of each CaSO₄-bearing sample.

The compressive strength of early age cured samples increased with the increase of CaSO$_4$ (Figure 5). The sample CS-0.5 showed a strength of 27.00MPa after 1-day curing and reached 35.9MPa after 7-day curing. After curing for 28 days the strength of sample CS-0.5 lowered down to 29.7MPa, although the other three samples' increased. After curing for 90 days the strength of samples CS-0.1, CS-0.2 and CS-0.3 largely increased and the sample CS-0.3 showed the highest strength of 44.3MPa. The 90 day cured sample CS-0.5 was only 34.6MPa. The strength reduction of sample CS-0.5 after 28 day curing was due to the formation of large amount of AFt vibrated at 995cm^{-1} (Figure 6), which was consistent with the setting time. The formation of AFt at long-term curing ages would lead to crack due to volume expansion.
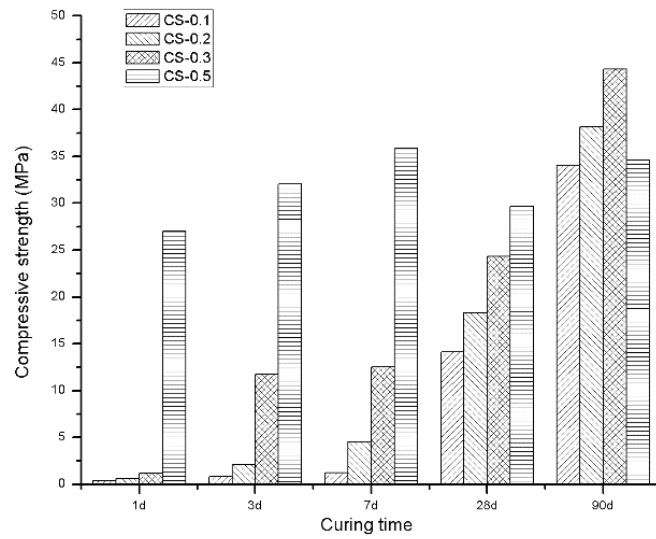
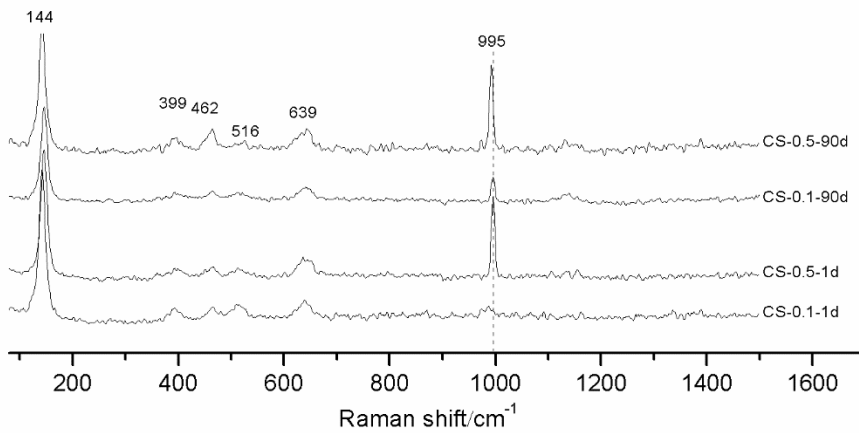Figure 5. Compressive strengths of CaSO₄-bearing samples.

Figure 6. Raman spectra of CaSO₄-bearing samples.

Although the Raman spectra showed the formation of AFt the XRD results in Figure 7 did not find obvious AFt peaks. Some new phases including thenardite and faujasite accounted for the geopolymerization. The characterization peaks of $CaSO_4$, Na_2SO_4 and $Ca(OH)_2$ were not detected in Figure 7, therefore, $CaSO_4$ in the paste was completely consumed due to Equations 2-4, 7-10.
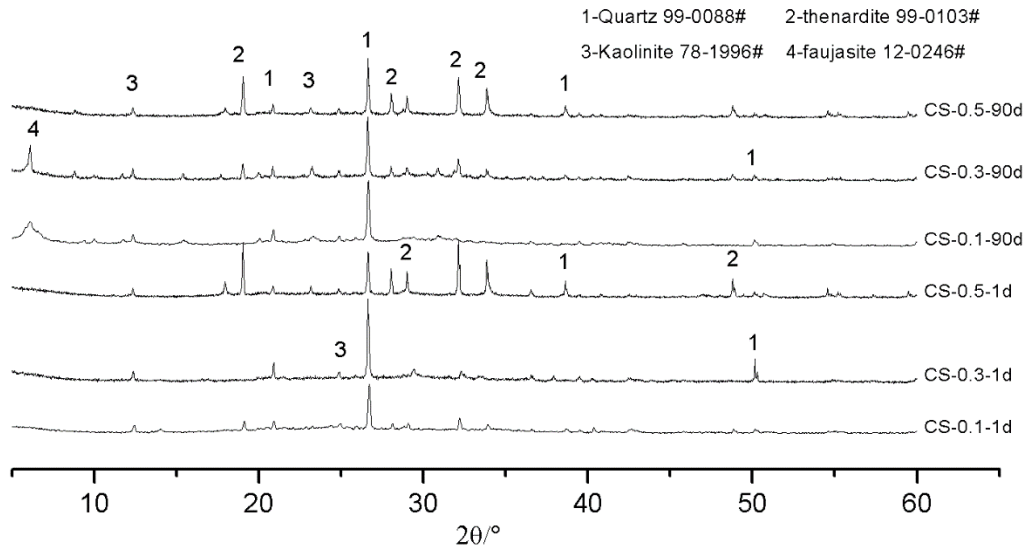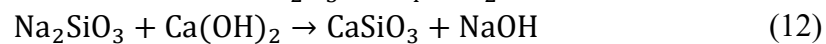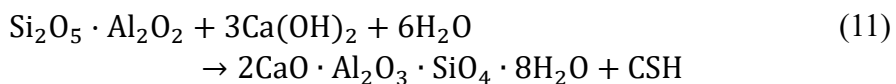
Figure 7. X-ray diffraction of CaCO₃-bearing samples (normalized to the 100% intensity peak of quartz of sample CC-0.1-1d)

Influence of Ca(OH)₂ on the Geopolymerization

Boonjaeng S. et al. reported that pozzolanic reactions and geopolymerization occurred simultaneously in SiO_2-Al_2O_3-CaO-Na_2O-H_2O system when Ca(OH)₂ was the Ca source (Boonjaeng S. et al., 2014). The reactions were dependent on the concentration of NaOH. When the concentration of NaOH was lower than 1M pozzolanic reaction (Equation 11) was dominant (Alonso S. and Palomo A., 2001 and Cabrera J. and Rojas M. F., 2001). When the concentration of NaOH was higher than 5M geopolymerization (Equations 1-8) was dominant. The concentration of NaOH in this research was lower but close to 5M. In this research Ca(OH)₂ also reacted with sodium silicate (Equation 12). When the CaO/Al_2O_3 increased from 0.1 to 0.2 the initial and finial setting times of samples contained Ca)OH)₂ accelerated from 330min to 43min, 520mim to 90min, respectively (Figure 8). However, the setting time varied little after further increase of CaO/Al_2O_3. Therefore, when the Ca(OH)₂ in solid was higher than 5.2% its effect on setting time can be neglected. However, the more Ca(OH)₂ the higher strength of sample (Figure 8). The results of XRD (not shown in this research) Ca(OH)₂ was not detected in all samples except sample CH-0.5, which suggested that the optimum of CA(OH)₂ per unit weight of metakaolin was between 9.6% and 15.9% in this research.

$$Si_2O_5 \cdot Al_2O_2 + 3Ca(OH)_2 + 6H_2O \qquad \qquad (11)$$
$$\rightarrow 2CaO \cdot Al_2O_3 \cdot SiO_4 \cdot 8H_2O + CSH$$
$$Na_2SiO_3 + Ca(OH)_2 \rightarrow CaSiO_3 + NaOH \qquad \qquad (12)$$
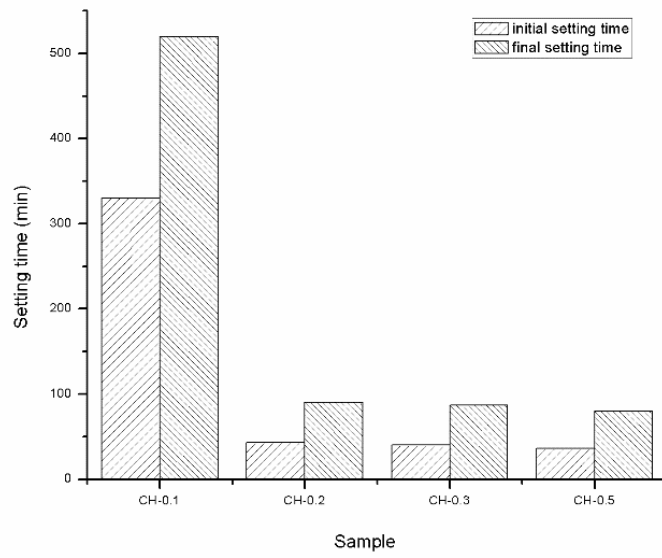
Figure 8. Setting time of each Ca(OH)$_2$-bearing sample.
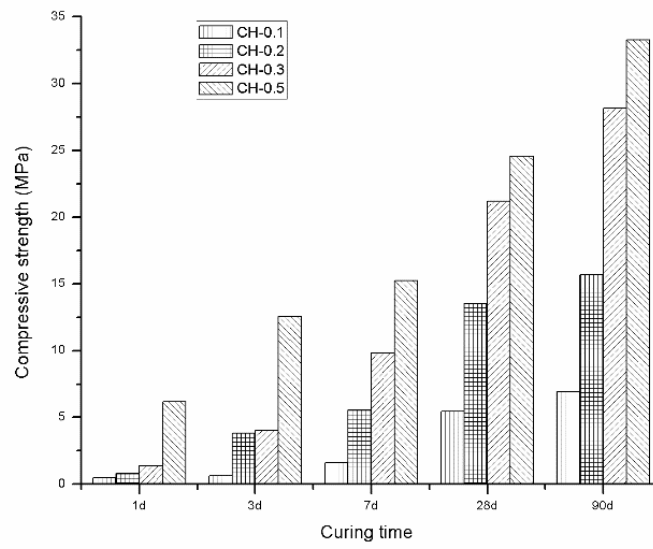

Figure 9. Compressive strengths of Ca(OH)$_2$-bearing samples.

CONCLUSION

The influence of $CaCO_3$ on the geopolymerization varied with CaO/Al_2O_3 and curing ages. $CaCO_3$ did not show negative effect, however, acted as the soluble calcium source and aggregates in the preparation of geopolymer. In contrast to zeolite the formation of faujasite in 90-day cured sample decreased with the addition of $CaCO_3$. Continuous formation of AFt in CaSO4-bearing sample resulted in strength reduction at long-term curing ages. The threshold of SO_3 for preparation of geopolymer using CFB fly ash was between 9.8 and 16.1 per unit weight of metakaolin in this research. $Ca(OH)_2$ reacted with sodium silicated to form calcium silicate and sodium hydroxide, which was helpful to the strength development. The optimum of $CA(OH)_2$ per unit weight of metakaolin was between 9.6% and 15.9% in this research.

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