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Investigation on Reaction Mechanism and Strength Properties of Fly Ash/Slag Based Geopolymer with Raman Spectroscopy

Kyoto University Student Member AN YAN
Kyoto University Regular Member SATOSHI TAKAYA
Kyoto University Regular Member TAKASHI YAMAMOTO

1. Introduction

Recently, geopolymer materials have attracted much attention as a promising alternative of ordinary Portland cement showing excellent mechanical properties and low CO_2 emission. Geopolymer is defined as a solidified framework body obtained from a mixture from amorphous alumino-silicate binders such with alkali activators. [1] Industrial wastes such as fly ash and slag are usually applied as solid binders, containing rich Si and Al. This research evaluates multiple synthesis parameters for fly ash/slag based geopolymer paste (FS-GP) activated by sodium hydroxide solution (SH) and sodium silicate solution (SS). The microstructure properties of FS-GP are investigated by Raman spectroscopy to understand the reaction mechanism and polymerization degree.

2. Materials

Table 1 describes the chemical composition and density of fly ash and slag. Fly ash is the main source of Si and Al which are the basic frame for geopolymer matrix. Slag provides additional Ca for better strength formation. Alkali activators with various concentrations are used to adjust the different alkalinity and the amount of soluble Si. The mix ratio of synthesis experiment is shown in **Table 2**.

Table 1 Chemical composition of fly ash and slag

%	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO
Fly ash	65.9	23.3	2.3	3.7	0.4
slag	33.2	12.0	43.1	0.8	6.0

Table 2 Mix ratio of geopolymer paste

No.	Fly ash	Slag	SS	Concentration	SH	Concentration	Water
1 (5)	839	210	337	55%	168	8mol/L	247
2 (6)	524	524	337	55%	168	8mol/L	247
3 (7)	878	220	337	55%	168	2mol/L	242
4 (8)	549	549	337	55%	168	2mol/L	242
9	942	235	485	38%	121	5mol/L	73
10	944	236	260	38%	260	5mol/L	103
11	944	236	91	38%	364	5mol/L	125
12	945	236	0	38%	420	5mol/L	137
13	486	730	501	38%	125	5mol/L	76
14	486	730	268	38%	268	5mol/L	106
15	488	732	94	38%	376	5mol/L	129
16	488	732	0	38%	434	5mol/L	141

3. Various influence factors on the properties of FS-GP

Experiment No. 1~8 study the effect of curing temperature (No. 1~4: 60°C and No. 5~8: 20°C), slag replacement ratio (0.2 and 0.5) and SH concentration (8mol/L and 2mol/L) on compressive strength of FS-GP. As shown **Figure 1**, it can be found that high temperature curing does not work for 0.5 slag replacement ratio. The rapid hydration of slag makes the polycondensation process an inhomogeneous reaction and cause drying shrinkage cracks. Also, slag replacement ratio has a positive influence on compressive strength because slag is easier to react with alkali activator and forms C-A-S-H gel. Finally, high alkali concentration has a negative effect on compressive strength under 0.5 slag replacement ratio. FS-GP with more slag in binder system usually does not require high alkali concentration to achieve better compressive strength, unlike those of fly ash based geopolymers.

Experiment No. 9~16 study the effect of soluble Si in alkali activators under the same alkali concentration and water amount. As shown in **Figure 2**, high amount of soluble Si contributes to better compressive strength of FS-GP under both 0.2 and 0.6 slag replacement ratio. Since Si-rich phase is the prerequisite for polymerization, soluble Si can promote the polymerization reaction with the dissolved Al from binders. In addition, the soluble Si also has positive influence on the hydration process of slag, in which the dissolved Ca^{2+} from slag can directly react with soluble Si to form C-S-H gel.

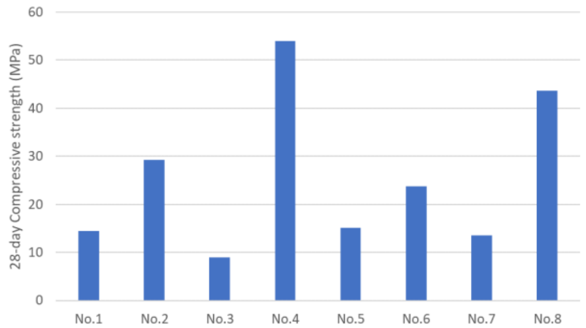

Figure 1 28-day compressive strength results

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Contact Address: Kyoto University Katsura, Nishikyo-ku, Kyoto, Japan, Tel: +81-075-383-3173

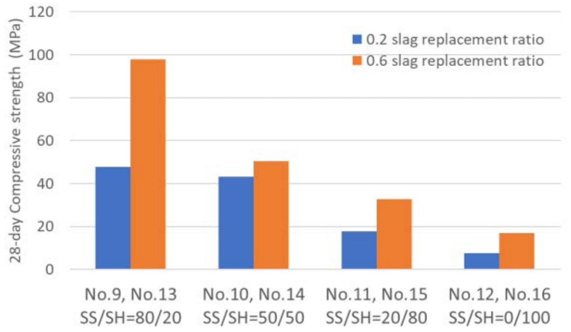

Figure 2 Relation of SS/SH and compressive strength

4. Raman Spectroscopy Analysis of FS-GP

Since the basic unit of geopolymer, mainly SiO_4 tetrahedral, has a well-defined vibration signature, Raman spectroscopy has great potential in investigating the polymerization process. Different types of Si network described as Q_n(mAl) are studied by Raman spectra curve fitting. **Figure 3** shows the Raman spectra curve fitting results for experiment sample No.9, No.13 and No.14. For 0.2 slag replacement ratio, Q_2 and Q_3 structures are dominant which shows large amount of unreacted fly ash. When slag replacement ratio is 0.6, the amount of Q_4(2Al) and Q_4(3Al) increases which comes from N-A-S-H gel, indicating the formation of more complicated geopolymer framework. Previous research [2] has found that C-A-S-H gel is favored under high alkaline environment. The hydration of slag consumes large amount of alkali which promote the formation of N-A-S-H gel. Also, lower amount soluble silica results in poor polymerization showing more Q_0 and Q_1 structure. The integrated area of each band can be used to classify the internal structure of geopolymer matrix. As shown in **Figure 4**, it can be concluded that the ratio of Q_4Si(nAl) structure increases with the addition of slag. With the decrease of soluble Si, the ratio of Q_0 and Q_1 structure increases which results in low compressive strength. The amount of Q_2+Q_3+Q_4 has a positive relationship with compressive strength for 0.6 slag replacement ratio.

5. Conclusions

The effect of various synthesis parameters for FS-GP is investigated by compressive strength test. The microstructure of geopolymer matrix is studied Raman spectroscopy. It can be concluded that slag replacement ratio and the amount of soluble Si are the most influential factors for FS-GP, showing higher amount of Q_2+Q_3+Q_4 structure from geopolymer gel formation.

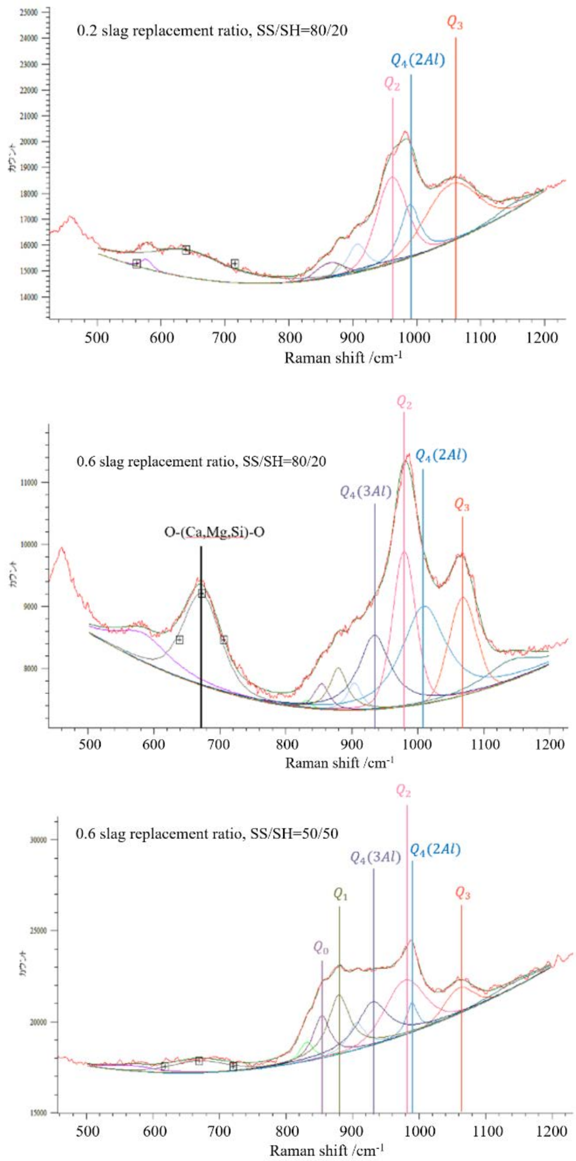

Figure 3 Curve fitting results of Raman spectra

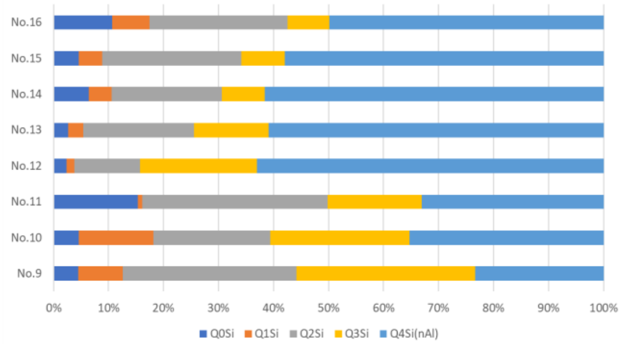

Figure 4 Integrated area ratio for Q_n structure

Reference

[1] Ichimiya, K. et al.: Committee Report: JCI-TC155A, 2020.
[2] Garcia-Lodeiro I. et al.: Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na_2O–CaO–Al_2O_3–SiO_2–H_2O, Cement and Concrete Research, Volume 41, Issue 9, Pages 923-93, 2011