Indo. J. Chem., 2011, 11 (1), 90 - 95

CRYSTALLINE PHASE REACTIVITY IN THE SYNTHESIS OF FLY ASH-BASED GEOPOLYMER

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Received October 17, 2010; Accepted November 19, 2011

ABSTRACT

Aluminosilicate, alkaline solution and fly ash from a power plant have been used to synthesize geopolymer at ambient temperature. SiO_2/Al_2O_3 mole ratio of the starting materials was varied by the addition of pure, insoluble corundum and quartz. The geopolymer exhibited some differences in the ratio of initial reaction mixtures and that of final products. The corundum gave no influence to the compressive strength while the quartz at SiO_2/Al_2O_3=4.0-6.0 produced significant change in the strength. The highest compressive strength achieved was 65 MPa. XRD using analysis Rietveld method proved that quartz has been found both in starting materials as well as in the geopolymer indicating the involvement of crystalline phases, to some extent, in geopolymerization process.

Keywords: *geopolymers, fly ash, alumina-silica, crystalline phase reactivity*

INTRODUCTION

Indonesian Government has announced their plan to build 35 new coal-fired power plants with 10,000 MW capacity in the next few years to supply electricity needed by both domestic and fast growing industries. According to the Government itself, fly ash as the by-product of this type of plant is classified to dangerous materials and should have specific waste treatment. In addition to the existing power plants, this Government's plan will increase dramatically fly ash which is already millions of tons generated each year in Indonesia. The disposal of fly ash is the environment issues and would cause serious problems as air pollutions, water contaminations and degradations of ecosystem quality [1].

One of the primary efforts to reduce the problem is fly ash conversion to geopolymer by polymerization of silica and alumina available in the fly ash [2]. Geopolymer is inorganic materials containing Si-O-Al chain built tetrahedrally with SiO_4^{4-} and AlO_4^{5-} by oxygen atom. Silica and alumina as major component of fly ash could have an important role in the formation of the chain [3] and the ratio of Si/Al in the mixture of the starting materials is one of the main factors. The less affecting factor is that some minerals contained in the fly ash to some extent would determine geopolymer properties because their activated form encourages polymerization reaction. Some crystalline phases of fly ash like mullite and quartz are among of the minerals which are difficult to be activated. The amorphous phases, however, are reactive and have reasonable role in geopolymerization.

Xu and van Deventer [4] showed the substantiality of amorphous phase in fly ash structure and some amount of crystalline phase from mullite and quartz. The mechanical strength of geopolymer containing more amorphous phase is higher than that of geopolymer with less amorphous phase as Si and Al from the phase is easier to dissolve in alkaline solution. Si and Al are important to form 3-D structure in geopolymerization. Other research reported [5] that the higher the reactivity of Si and Al, the higher their solubility to the solution, and the higher the strength of related geopolymer.

This work is objected to study the effect of silica and alumina crystalline phase to the geopolymer properties by examining the possibility of Si and Al from the crystalline phase to take a role in geopolymerization process.

EXPERIMENTAL SECTION

Materials

The materials used were class F fly ash (ASTM C-618) from Asam-Asam (South Kalimantan) coal-fired power plant. Analytical grade sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) as well as quartz (SiO_2, 99%), corundum (α-Al_2O_3, 99%) and rutile (TiO_2, 99%) were all obtained from Merck.

Instrumentation

X-ray diffractometry (Philips X'pert MPD) and Scanning Electron Microscopy coupled with EDS (JEOL

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Table 1 Chemical composition of fly ash in percent

SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SO_3	TiO_2	MnO	BaO	SrO	LOI
43.70	21.00	4.85	22.50	0.88	2.55	0.44	0.07	0.58	0.95	0.44	0.21	0.05	1.66

Table 2. SiO_2/Al_2O_3 ratio of starting materials and related reactants

Geopolymer	SiO_2/Al_2O_3 Ratio	Fly ash (g)	NaOH (g)	H_2O (g)	SiO_2 (crystalline) (mole)	α- Al_2O_3 (crystalline) (mole)
A	1.5	100	4	8	0	0.27
B	2.0	100	4	8	0	0.15
C	2.5	100	4	8	0	0.09
D	3.0	100	4	8	0	0.03
E	3.5	100	4	8	0	0
F	4.0	100	4	8	0.1	0
G	4.5	100	4	8	0.2	0
H	5.0	100	4	8	0.3	0
I	5.5	100	4	8	0.4	0
J	6.0	100	4	8	0.5	0

JSM-6360 LA) were conducted to the fly ash. The chemical composition of fly ash as determined by by X-ray Fluorescence (XRF) is given in Table 1. The reactivity of the starting material (fly ash, quartz and corundum) was examined by dissolving them to alkaline solution and mixed at room temperature for 5 h. The filtrate and the residue were analyzed using Inductively Coupled Plasma – Atomic Emission Spectrometer (Fison3410+) and X-ray Diffractometry, respectively. Distilled/deionized water was used throughout. Some standard tools, i.e plastic cylinder mould (15 x 30 mm), mixer, oven, analytical balance, stopwatch, and plastic equipments such as polypropylene beaker, bottle, and glasses were used during samples preparation.

Procedure

Geopolymer synthesis

Two types of geopolymer were synthesized. The first type represents geopolymer without quartz and corundum addition and its SiO_2/Al_2O_3 is 3.5 (Table 2). The second type of geopolymer contains quartz and corundum as much as described in Table 2 where the total SiO_2/Al_2O_3 ratio was between 1.5 and 6.0. For both of them, fly ash was dried at 105 °C for 4 h to remove unbounded water. Sodium hydroxide, sodium silicate and water were mixed to obtained alkaline silicate solution and regarded as activators. The solid to liquid ratio (S/L) was chosen to be as high as possible while obtaining reasonable sample workability. A simple consistency test was conducted to ensure that a change in S/L due to change in SiO_2/Al_2O_3 ratio still give geopolymers with same workability. Fly ash was combined with the solutions and mixed for 5 min. Specimens were then casted in plastics moulds and vibrated for 2 min. All samples were cured at 60 °C for 24 h, demoulded, and sealed in plastic bags for curing at room temperature until further tests were carried out at 7, 14, 21 and 28 days.

Sample analysis

Compressive strength was studied at the age of 7, 14, 21 and 28 days by Universal Testing Machine using three cylinders mould 30 mm height and 15 mm in size. Qualitative and quantitative analysis using Rietveld method of XRD was conducted with Cu Kα radiation generated at 30 mA and 40 kV. The step scan was 2θ at 0.02° and mounts from 5 to 70°. Microstructural images were obtained from randomly selected, fractured samples using SEM combined with EDX (10 kV) to determine SiO_2/Al_2O_3 ratio in geopolymer product. Both Inductively Coupled Plasma (ICP) and X-ray fluorescence (XRF) were used for chemical analysis when needed.

RESULT AND DISCUSSION

Compressive Strength Analysis

Compressive strength developments of geopolymer varied with SiO_2/Al_2O_3 ratios at different ages is presented in Fig. 1. As estimated, the compressive strength increased with the increasing of ages. For all samples, the greater the SiO_2/Al_2O_3 ratio, the greater compressive strength until it reached optimum strength at SiO_2/Al_2O_3 = 5.0. In the range represent corundum additions (geopolymer A to D) there is no significant increase at all ages and strength lies at around 34–35 MPa. The crystalline phase of corundum does not influence the strength of geopolymer and Phair [6] had also stated that the crystallinity is not the factors affected the strength. In quartz additions (geopolymer F to J), however, an impressive fact emerged. The compressive strength

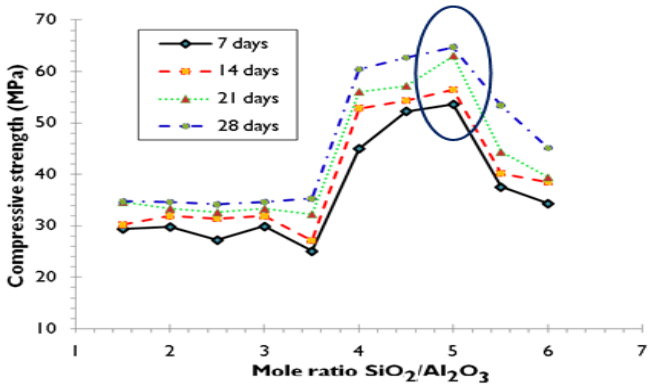


Fig 1. Compressive strength of geopolymer with various SiO_2/Al_2O_3 at different ages

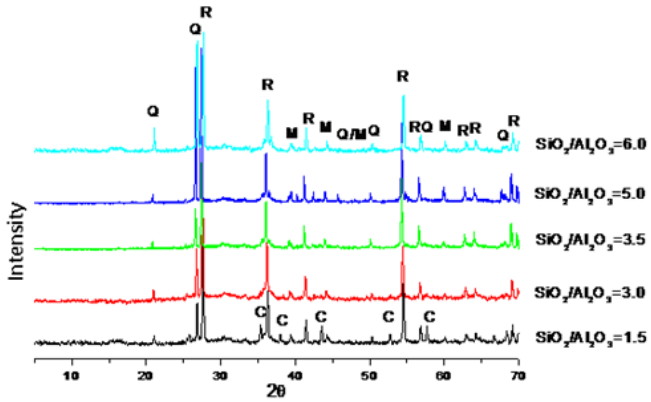


Fig 2. XRD diffraction patterns of geopolymer at various SiO_2/Al_2O_3. Q: quartz, R: rutile, M: mullite, C: corundum

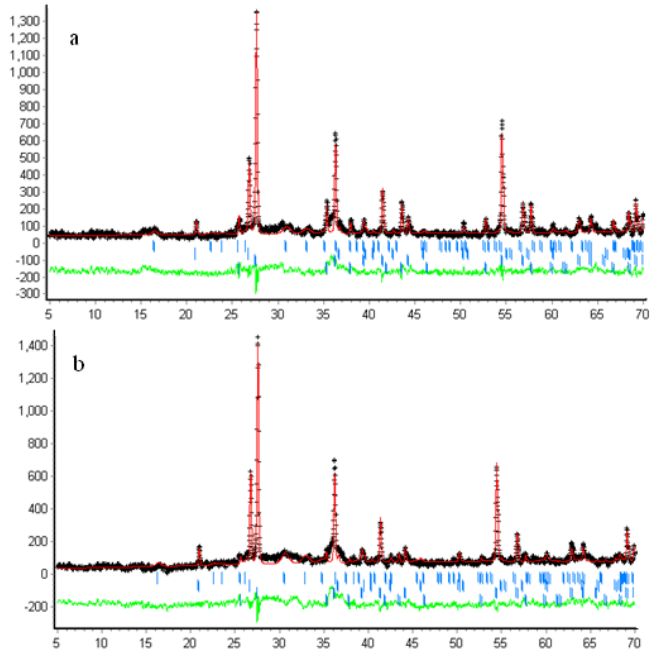


Fig 3. Rietveld refinement plot (a) SiO_2/Al_2O_3=1.5, (b) SiO_2/Al_2O_3=3.0; (+ = measured data, -- model)

increased dramatically and reached 65 MPa when the SiO_2/Al_2O_3 ratio of the samples is 5.0. The strength began to decrease at SiO_2/Al_2O_3 = 5.5. Duxson [7] reported that the greater SiO_2/Al_2O_3, the greater the compressive strength, but at a certain SiO_2/Al_2O_3 ratio the strength would decrease as a result of unreacted Si forms defects in the aluminosilicate structure.

The behavior of the strength due to SiO_2/Al_2O_3 changes seems related to the reactivity of the starting materials. In the elemental analysis using ICP-AES to the materials, the aluminium solubilities to alkaline solution from corundum and fly ash were 0.14% and 9.63%, respectively. The same trend was also obtained when the solubility of silicon from quartz and fly ash was analyzed, i.e. 1.94% and 10.59%, respectively. Other test, X-ray fluorescence analysis, has been applied to remaining aluminium in the corundum and remaining silicon in the quartz after the solubility tests and the results were 93.7% and 93.5%. Both elements were also analyzed in the fly ash after soaked with alkaline solution and the results were 16% for aluminium and 34% for silicon. From these data, it can be seen that aluminium and silicon have different reactivity to alkaline solution and the value is depend on the starting materials. The addition of corundum having the lowest reactivity gives no significant change in the compressive strength of geopolymer (Fig. 1). The addition of quartz, however, contribute reasonable amount of silicon to the forming of Si-O-Si bond in the geopolymer matrices lead to a higher compressive strength. Therefore, the contribution of the crystalline phase of quartz is evident.

Phase analysis by X-ray diffraction using Rietveld refinement method

Fig. 2 shows the XRD patterns of geopolymers at various SiO_2/Al_2O_3 using internal standard rutile (TiO_2) for quantitative analysis. The XRD patterns of geopolymers display peaks due to quartz, mullite, corundum and rutile, also other crystalline phases at trace levels. In addition to these crystalline components, a broad peak not clearly seen in the region around 30° 2θ arising from amorphous phase could be found. Detail analysis to the XRD pattern was conducted using Rietveld refinement as normal procedure was not able to overcome peak overlapping, preferred orientation, peak broading as a result of small crystal size, weak intensity and microabsorption [8]. The refinement process included some parameters: background coefficient, lattice parameter, peak form parameter, and phase fraction.

According to the quantitative mineralogical composition of geopolymer samples (Table 3), the contents of quartz after pure quartz addition to fly ash as

Table 3 Mineralogical composition (wt %) of geopolymer as determined by Rietveld refinement

Geopolymer with and without addition	(wt %)		
	Quartz	Mullite	Corundum
Corundum addition (SiO_2/Al_2O_3 = 1.5)	31	29	37
Corundum addition (SiO_2/Al_2O_3 = 3.0)	37	30	8
Without any addition (SiO_2/Al_2O_3 = 3.5)	50	33	-
Quartz addition (SiO_2/Al_2O_3 = 5.0)	56	16	-
Quartz addition (SiO_2/Al_2O_3 = 6.0)	82	9	-

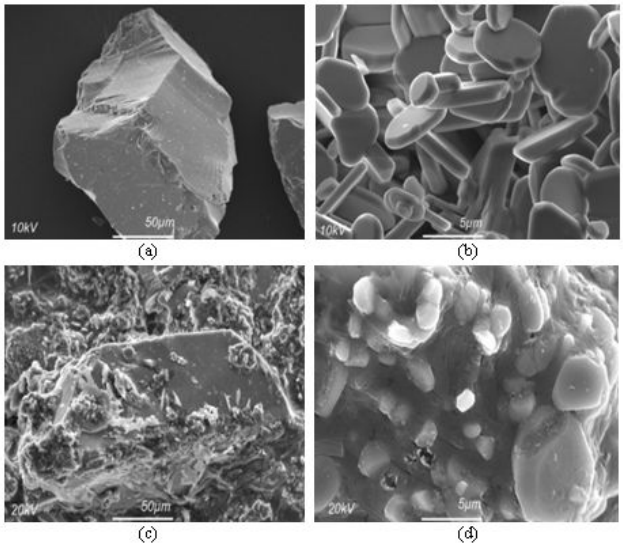


Fig 5. SEM images of additive material: (a) Quartz crystalline phase, (b) Corundum crystalline phase, (c) Quartz after alkaline treatment (d) Corundum after alkaline treatment

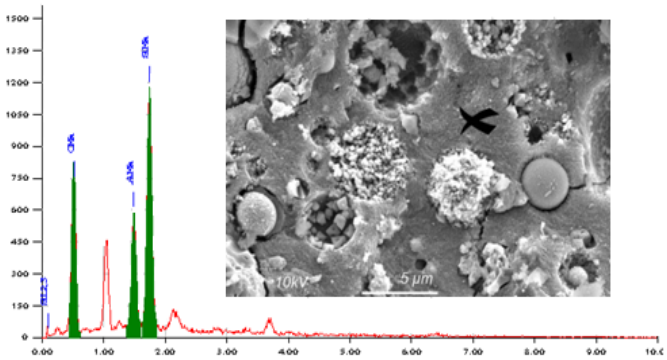


Fig 6. SEM-EDX micrograph of corundum-added geopolymer D presenting SiO_2/Al_2O_3 = 3.0. X: point at which EDX analyzer worked

starting materials in samples with SiO_2/Al_2O_3 ratio 5.0 and 6.0 are 56% and 82%, respectively, while for samples without any addition the corresponding quartz content is 50%. Such differences in the quartz content could explain the higher compressive strength values displayed by fly ashes after being treated by alkaline solution (Fig. 1). It is also clear that some parts of quartz involved in geopolymerization process. The addition of new quartz, however, reduces the mullite content which displays values in the range 9–16%. This is probably due to some parts of mullite crystalline phase transform to glassy and semicrystalline phases.

Using Rietveld refinement plot for samples with related SiO_2/Al_2O_3 presented in Fig. 3, the additions of corundum to the starting materials show an interesting result. In both SiO_2/Al_2O_3 = 1.5 and 3.0 type samples, new peaks of corundum are found in addition of quartz and mullite peaks. The peaks lay in 25, 35, 43 and 57° 2θ. The occurrence of such peaks suggests that the corundum was re-formed in the geopolymer system structurally and could mean that it did not react with alkaline solution and the starting materials. The existence of corundum which found as crystalline phase was also mean its reactivity is very low lead to high difficulty to involve during geopolymerisation process. The relatively high reactivity of a material will have more interaction with gel phase and enhance its capability to influence the process [9]. Comparing with the case of quartz which in some degree involves in the process, the crystalline phase of corundum is unlikely to have a role in the process.

Scanning Electron Microscopy Analysis (SEM) with EDX

Fig. 4 presents morphological features and EDX of geopolymer without any addition (geopolymer E, SiO_2/Al_2O_3 = 3.5). Some unreacted fly ash as residual matter was clearly observed. The EDX peaks exhibit the amount of Si and Al as 57.28 and 22.38%, respectively, meaning that the actual SiO_2/Al_2O_3 value was 3.0. The difference of the ratio was due to partially reacted or unreacted fly ash exist in all parts of the sample. Such observations suggest that Si and Al were dissolved by alkaline solution prior to form geopolymer matrices.

The reactivity of the crystalline materials could be examined by comparing SEM images of both quartz and corundum before and after 5-h alkaline solution treatments. Fig. 5 (a) and (b) show quartz and corundum at initial state and (c) and (d) exhibit their corresponding images after the treatment. Partly dissolved quartz and no-dissolved corundum crystalline particles were observed clearly. As both Si and Al in the crystalline form are available in every type of fly ash,

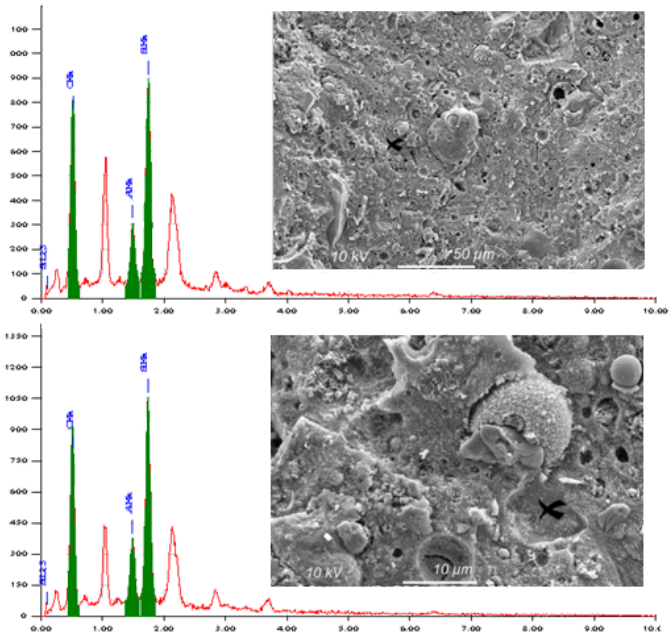
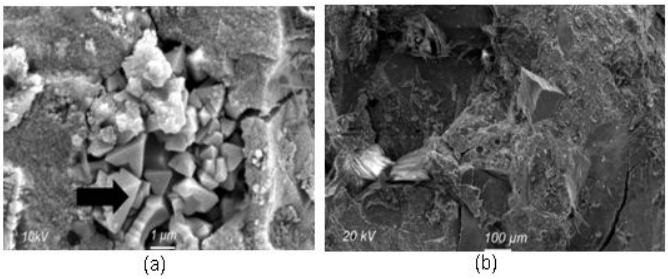


Fig 7. SEM-EDX micrograph of quartz-added geopolymer H (above) and J (below) presenting SiO_2/Al_2O_3 = 5.0 and 6.0, respectively. X: point at which EDX analyzer worked



(a) (b)

Fig 8. SEM images of (a) corundum-added geopolymer and (b) quartz-added geopolymer. →: unreacted corundum crystalline phase

the same low reactivity of them is also happen in related geopolymer.

Fig. 6 represents one of chemical analysis conducted by EDX to corundum-added geopolymer matrices (geopolymer D, SiO_2/Al_2O_3 = 3.0) showing the value 26.62% for Al element. This value leads to SiO_2/Al_2O_3 ratio close to the initial, starting material ratio 3.0. In general, it was more evident for previous statement that corundum crystalline phase has no contribution to the geopolymerisation process. The chemical analysis to quartz-added geopolymer matrices (geopolymer H, SiO_2/Al_2O_3 = 5.0 and geopolymer J, SiO_2/Al_2O_3 = 6.0) presented in Fig. 7, however, displays different behavior. The amount of Si obtained was 81.55 and 80.06%, respectively, lead to actual, after-alkaline-treatment SiO_2/Al_2O_3 ratio 4.5 and 4.0. The quartz crystalline phase which involved in geopolymerisation process at J was less than that of H. SiO_2/Al_2O_3 ratio changed during the process due to changed in the amount of Si but not in the amount of Al. From the light of the present results, it could be derived that some crystalline phases did influence the geopolymerisation.

Morphological images of the corundum-added and quartz-added geopolymers also show differences in compactness of the remaining crystalline phase. Whereas unreacted corundum crystalline phase (Fig. 8a) displayed incomplete fusion to geopolymer matrices, the quartz crystalline phase (Fig. 8b) was characterized by a much higher degree of compactness with its surrounding matrices, especially in their boundaries. This observation is in line with the reactivity of both corundum and quartz mentioned previously. As it is well known that in general high compactness enhances the mechanical performance of geopolymer, such observations agree well with the compressive strength depicted in Fig. 6: the higher was the SiO_2/Al_2O_3 caused by quartz addition, the higher were the compressive strength values.

CONCLUSION

Compressive strength development of geopolymer synthesized from fly ash with and without addition of crystalline phases was dependent on type of the additive materials. Quartz-added geopolymers displayed higher compressive strength values than that of corundum-added geopolymers due to a better reactivity shown by quartz crystalline phase. Values about 65 MPa were achieved by starting materials with SiO_2/Al_2O_3 more than 3.5 which obtained by quartz additions. In the case of lower reactivity shown by corundum crystalline phase, the related geopolymers achieved only half of them, about 33 MPa. It was found that in some degree crystalline phase did involve in the geopolymerisation process.

ACKNOWLEDGEMENT

The authors wish to thank Asam-Asam Power Plant, South Kalimantan, for supplying the fly ash. The present study was conducted as part of the project financially supported by Ministry of National Education through Post Graduate Grant 2009 contract number 10473/I2.7/PM/2009.

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