

Consolidation of Silica Sand Slime with a Geopolymer Binder at Room Temperature and the Strength of the Monoliths*

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Consolidation of silica sand slime, a waste from silica sand mines, was attempted by the geopolymer technique. Fly ash and blast furnace slag were introduced as secondary raw materials. Sodium silicate having chemical composition of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ was used as a source of the geopolymer binder by diluting with water. The amount of the blast furnace slag acting as an accelerating agent of solidification was kept constant at the level of 10 % of the solid. Mixing the slime and the fly ash in variable ratio with the slag under the constant liquor—solid mass ratio, 0.60, geopolymer monoliths were prepared by slurry casting. All the process was performed at room temperature including the subsequent treatments. Demolded at 1 d age, solidified monoliths were kept drying in air for 28 d and then, cut into prisms having 1 cm × 1 cm cross-section and soaked in water for 3 d (wet bodies). Some test-pieces were further continued to dry in air for 7 d after the soaking (dry bodies). Strength tests showed maxima in 60 % blend of fly ash, indicating 4.6 MPa flexural and 13.4 MPa compressive strengths for the wet bodies and 8.3 MPa and 21.7 MPa for the dry bodies.

Cement chemistry notation: C – CaO, S – SiO_2 , H – H_2O .

Environmental issues are current problems of world concern, comprising air, water, and soil. Wastes produced from mines and processing factories are not exceptions and urgent reuse and safe disposal of wastes are requested especially in such countries where disposal yards are limited. The geopolymer technique now attracts a keen attention to be used for such a purpose due to capability of easy consolidation of slime that is a typical form of wastes from mines as well as processing factories.

Although water glass has long been known and used for repairing refractory parts of plants without clear understanding of polycondensation occurring in solidifying process of water glass, the concept of polycondensation of silicate monomer can be found in some literatures [1–5]. Under the concept of polycondensation some materials have been prepared so far at relatively low temperatures under 100 °C [6–8]. Especially that of *Davidovits* and *Sawyer* [8] using metakaolin is striking due to little shrinkage during solidification. According to references mentioned above, three essential raw materials are required for preparing geopolymer monoliths. Those are geopolymer liquor,

filler, and hardener. Sodium- or potassium-based water glasses are conveniently used for the liquor. Basically fillers should be inactive with the liquor and solidification of the liquor takes place by polycondensation of the liquor triggered by some dissolution of cations from the hardener. If the filler has some dissolution character, the hardener is not always necessary. Sometimes strong alkaline solutions are applied as activation agents for fillers. In this paper the geopolymer technique will be applied for consolidation of a slime discarded from a silica sand mine where silica sand consisting mainly of quartz is produced for a raw material of glass bottles.

EXPERIMENTAL

The geopolymer liquor used in this study was prepared by diluting a commercially available concentrated sodium silicate solution with water. The chemical composition of the liquor is presented in Table I. This silicate is most common and easily available and we found this concentration of the liquor can be easily handled in laboratories.

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Table 1. Chemical Composition of Sodium Silicate and Derivative Geopolymer Liquor Used in This Study

Commercially available sodium silicate			
w (Major components)/%		w (Minor components)/%	
SiO ₂	61.18	Al ₂ O ₃	0.04
Na ₂ O	29.63	CaO	0.22
LOI ^a	8.64	MgO	0.14
Total	99.45	Others	< 0.01
w_i (Geopolymer liquor)/%	SiO ₂ 18.6	Na ₂ O 9.0	H ₂ O 72.4
n (SiO ₂)/ n (Na ₂ O) mole ratio	2.1		

a) Loss of ignition.

The silica sand slime was air-dried before use and the constituent minerals were identified by XRD, X-ray diffraction, also for other raw materials. Since the slime showed inactive properties to the liquor, fly ash was mixed to the slime as an active filler [9] in variable ratio. Furthermore, water-quenched granulated blast furnace slag was applied in a constant ratio, 10 % of solid. Liquor—solid mass ratio was kept constant, 0.60 throughout this study.

Physical characteristics and chemical compositions of these raw materials in powdered state are presented

in Table 2 and mixing proportions of the raw materials in Table 3. The starting powders were well-mixed in a bottle by shaking and transferred to a plastic beaker. Then, the geopolymer liquor was introduced and the charge was well-mixed by stirring with a spoon and cast into a plastic mold having 45 mm × 70 mm × 14 mm dimension. After demolding at 1 d age, solidified monoliths were dried further up to 28 d age in 20 °C air to promote polycondensation. Then, the monoliths were cut into prisms having 10 mm × 10 mm cross-sectional size. After soaking in 20 °C water for 3 d, some monoliths were subjected to strength tests (the wet body strength). The other monoliths were air-dried for 7 d at 20 °C and also subjected to strength tests (the dry body strength). Average values were obtained as materials strength by using 3 test-pieces for the 3-point flexural test with 25 mm span and by using derived 6 test-pieces for compressive test. Cross-head speed was 0.016 mm s⁻¹ for both the tests and standard deviations of the strengths were also obtained. Fractured pieces were examined by XRD and SEM, scanning electron microscope, after storing in acetone.

RESULTS AND DISCUSSION

Strength of Monoliths

Results are summarized in Figs. 1 and 2 for the wet

Table 2. Physical Characteristics and Chemical Compositions of Silica Sand Slime, Fly Ash, and Blast Furnace Slag

Source powder		Fineness (Blaine) ^a cm ² g ⁻¹					Apparent density g cm ⁻³								
A	Silica sand slime	6700					2.57								
B	Fly ash	3610					2.11								
C	Blast furnace slag	4000					2.85								
i	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	w_i /%		CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	LOI	Total
A	72.43	0.17	14.99	1.89	0.03	0.57	0.26	1.21	5.72	0.06	–	3.23	100.56		
B	60.97	1.38	24.84	5.78	0.06	1.97	0.61	0.32	0.96	0.26	0.23	2.70	100.08		
C	33.30	1.81	13.44	0.66	0.58	40.74	7.46	0.45	0.45	0.03	1.40		100.32		

a) Conventional method used in cement research.

Table 3. Mixing Proportions of Raw Materials and Standard Deviations for Mechanical Strengths of Geopolymer Monoliths

Sample	w (Filler(w (X) w (Y)))		w (Z) ^a	w (L)/ w (S) ^b	σ_{wet}^c		σ_{dry}^d	
	flex.	comp.			flex.	comp.		
SF-0	90	(100 0)	10	0.5	0.10	1.03	0.07	1.98
SF-20	90	(80 20)	10	0.5	0.10	1.34	0.08	2.96
SF-40	90	(60 40)	10	0.5	0.09	1.12	0.20	2.54
SF-60	90	(40 60)	10	0.5	0.37	1.61	0.54	3.15
SF-80	90	(20 80)	10	0.5	0.28	1.90	0.05	1.92
SF-100	90	(0 100)	10	0.5	0.13	0.67	0.19	1.71

a) X, Y, and Z represent slime, fly ash, and slag, respectively; b) geopolymer liquor—solid mass ratio and w (S) is the sum of w (X), w (Y), and w (Z); c, d) standard deviations for wet and dry body strengths represented in Figs. 1 and 2, in MPa.

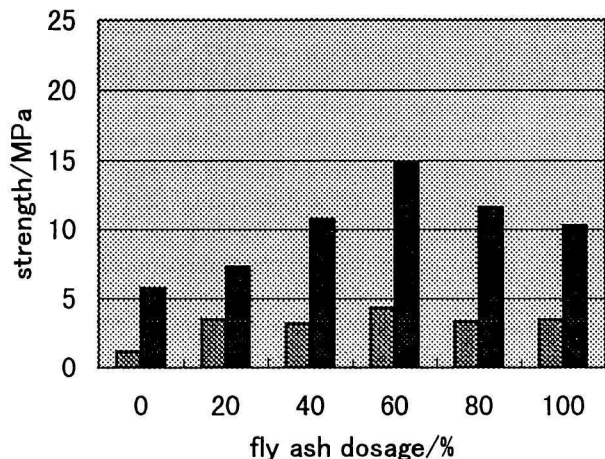


Fig. 1. Representative wet body strength of geopolymer monoliths. Flexural strength in gray, compressive strength in black.

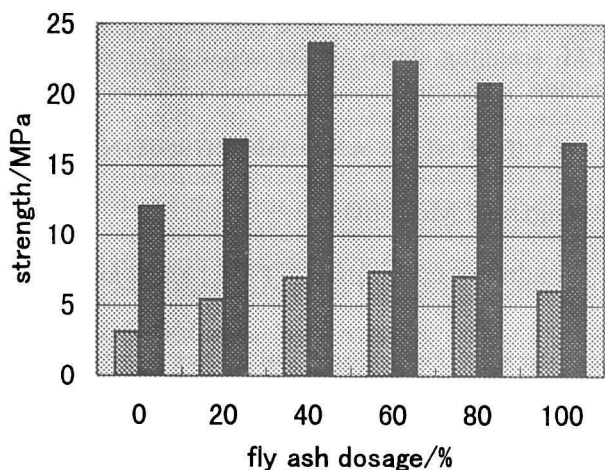


Fig. 2. Representative dry body strength of geopolymer monoliths. Flexural strength in gray, compressive strength in black.

body strength and the dry body strength, respectively. Standard deviations are given in Table 3. Increasing strength was observed with the increasing content of the fly ash and maxima appeared at 60 % blending of fly ash for both the flexural and compressive strengths. Then, the strength showed a gradual decrease with more content of fly ash, most clearly seen in the dry body strength. The strength trends show the filling effect of voids with the slime in the monoliths due to finer characteristics of the slime as indicated in Table 2 [10]. We consider that polycondensation reaction was promoted by the soak-dry treatments to realize higher strength due to leaching out sodium components.

XRD and SEM

For the slime a dominant presence of quartz was identified in association with orthoclase and albite due

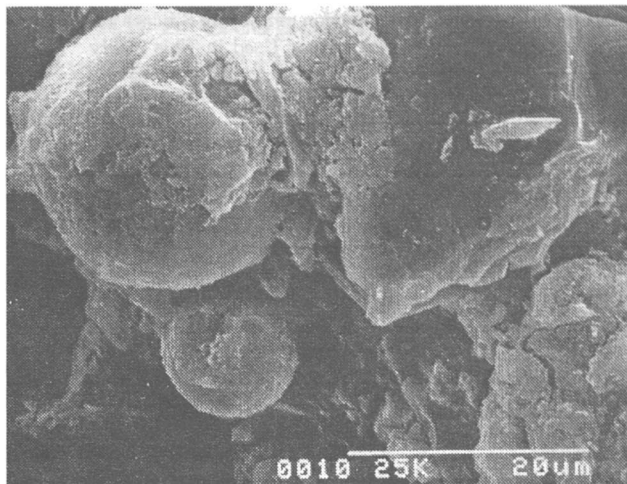


Fig. 3. An exemplified representation of SEM photomicrograph showing a geopolymer monolith for a wet body. Note the mesh-like texture of II C-S-H forming on spherical fly ash surfaces, geopolymer gels filling intergranular gaps and a rigid large quartz remaining intact on the upper right. II C-S-H forming from the blast furnace slag is also seen on lower right.

to granite origin of the slime. Presence of a very small amount of montmorillonite as a secondary mineral was also noted. For the fly ash a small presence of quartz associated with mullite was identified. However, the fly ash was fundamentally glassy. For the slag a very small presence of gehlenite-like phase was identified. However, the slag was also essentially glassy.

For the fractured monoliths, by the XRD no remarkable crystalline phases were identified other than a dominant presence of the constituent minerals of the slime and the fly ash. However, using SEM type II C-S-H, calcium silicate hydrate gel was noted as a poor crystalline phase appearing in small mesh-like texture in both wet and dry bodies as seen in Figs. 3 and 4. This phase could be a product from both the fly ash and the slag through hydration and this is most clearly seen on fly ash surfaces of wet bodies (Fig. 3). However, small crystals disseminated all over the matrices were encountered in dry bodies as seen in Fig. 4. It is clear that this phase formed during the dry treatment but the identification of this phase is very difficult at the moment due to its small occurrence and size. The quartz grains seemed to be inactive and remained intact. Gel-like phase filling among grains or being adherent on grains was also observed on some portions. This phase would be truly a geopolymer product precipitated by polycondensation but the chemical composition of this phase is unknown at present. Formation of a zeolite-like crystalline polysialate was found by *Davidovits* and *Sawyer* [8] in their geopolymer monoliths solidified at 80°C. Fly ashes are generally originating from clays contaminating coals. Accordingly, there is a possibility of forming polysialate even at 20°C due to dissolving Al- and Si-components

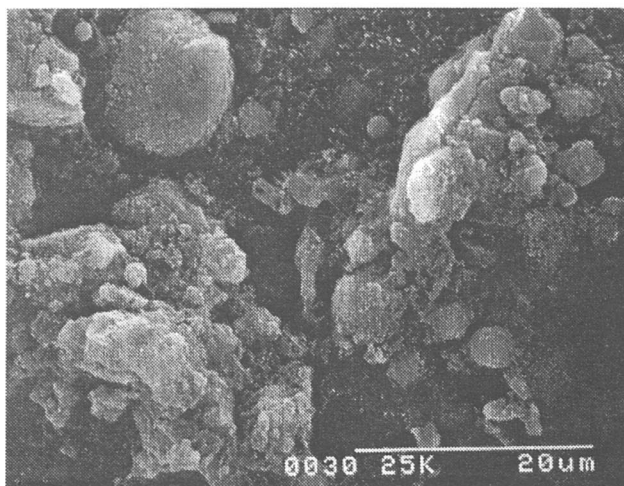


Fig. 4. An exemplified representation of SEM photomicrograph showing a geopolymer monolith for a dry body. Note the disseminated distribution of small crystals especially in central upper portion. II C-S-H is also observed as in Fig. 3.

from the fly ash. Effects of Ca-component dissolving from the added slag are also important and the role of calcium in the process of polycondensation other than forming II C-S-H should be taken into consideration.

CONCLUSION

Silica sand slime can be consolidated by the geopolymer technique into monoliths by blending fly ash and blast furnace slag at room temperature. The role of silica sand slime, fly ash, and blast furnace slag would be an inactive filler, an active filler, and a hardener, respectively, judging from the XRD and SEM results of fractured monoliths. Formation of II C-S-H was detected under SEM due to the results of hydration, both of the fly ash and the blast furnace slag. Besides, unidentified small crystals appearing disseminated in matrices were encountered in dry bodies. Gel-like intergranular phase was also observed due to the results of polycondensation of the geopoly-

mer liquor. Blending fly ash with slime is effectable, since the slime fills voids as it contains smaller particles than fly ash and nearly half amount of blending fly ash is recommended consequently. Blast furnace slag is conveniently used as a hardener and 10 % blending to solid is recommended. The soak-dry treatment is effectable for promoting the strength of geopolymer monoliths, probably due to resulting promotion of polycondensation occurring after some leaching out of sodium components from monolith matrices by soaking them in water.

Although the wet slime was pretreated by air-drying in this study, wet slime can be used without drying by adjusting the concentration of geopolymer liquor and this is a very important point for practical applications. Present monoliths have a high potential to be used widely as water-resistant materials in building and construction applications. After demolishing constructions debris can be safely discarded to environments due to immobilization of slime.

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