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PREPARATION OF FLY ASH MONOLITHS CONSOLIDATED WITH A SODIUM SILICATE BINDER AT AMBIENT TEMPERATURE

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ABSTRACT

Sodium silicate binder prepared by diluting a commercially available sodium silicate having 2.1 SiO_2/Na_2O molar ratio with water has been applied for the consolidation of fly ash. Two kinds of fly ash, ordinary and ultrafine, were mixed to enrich fine particles of 1-2 μm in diameter. Granulated blast furnace slag was added as a hardener as much as 10 percent of the solid. The, fly ash monoliths were prepared by casting slurries having 0.50 binder-liquor to solid ratio. After demolding at 1 d samples were kept in air for 28 d with subsequent water soaking for 3 d and finally air-dried for 7 d. This successive process was all carried out at ambient temperature and humidity. Strength tests revealed that blending the ultrafine fly ash and the slag are effective to obtain high strength materials in addition to the soak-dry process. A monolith, for instance, having flexural and compressive strengths of 9.6 and 25.1 MPa, respectively, was obtained. © *1997 Elsevier Science Ltd*

Introduction

Alkali-silicate binders have been known for long time (1-3) and the mechanism of solidification has been gradually revealed in relevance to the sol-gel technique of materials preparation. This binder technique may have a promising future primarily because of energy saving of traditional ceramics production, secondly because of capability of solidifying industrial wastes and thirdly because of immobilization capability of hazardous elements of urban refuses. It should be noted that alkali-silicate binders solidify basically through the polycondensation process, i.e., dehydration. According to literatures (4), (5) preparation of monoliths by the alkali silicate binder technique may require following 3 basic sources:

Alkali-silicate binder liquor, active filler and hardener.

Generally, alkali-silicate solutions, metakaoline and fine grained amorphous silica, and granulated blast furnace slag (6) or malladrite, Na_2SiF_6 (5) are used, each corresponding to the

TABLE 1

Chemical Composition of Sodium Silicate Binder Liquor

Binder liquor (%)	SiO_2 18.6	Na_2O 9.0	H_2O 72.4
SiO_2/Na_2O molar ratio	[2.1]		

3 basic sources. Sometimes strong alkali solutions called activation liquors are introduced, when fillers are not active enough. Alkali-silicate binders are generally thermohardening around 80°C, but solidification at ambient temperature will be attempted in this paper in view of waste reuse and energy saving.

Experimental

Commercially available sodium silicate solution was used for the binder liquor by diluting with water. The chemical composition is represented in Table 1. Two kinds of fly ash, ordinary one, henceforth called F4, and ultrafine one, henceforth called FA2, collected by a bag filter were used for the active filler instead of metakaoline. Water quenched granulated blast furnace slag called "Esment" was used for the hardener. No activation liquor was used in this study because of sufficiently active nature of the fly ashes (7) applied. Physical characteristics and chemical compositions of these powders are represented in Table 2 and mixing proportions of the source materials in Table 3 at constant binder-liquor to solid ratio (P/S), 0.50, with variable filler modes. Two series were prepared with and without hardener and each designated as A-series and B-series. The filler and the hardener were bottle-mixed and transferred to a plastic beaker to well-mix with desired amount of the binder liquor. Then, the mixture was cast into a plastic mold having 60 × 95 × 20 mm dimension to keep at ambient temperature and humidity for 1 d without a cover. The hardened bodies demolded were further dept at ambient temperature and humidity for 28 d to dry spntaneously and cut into prismatic test-pieces with 60 × 10 × 10 mm dimension.

Then, the test-pieces were soakd in water for 3 d. After this treatment 3-point flexural strength with 25 mm span and compressive strength were measured using 3 test-pieces to obtain mean values. This is called wet body strength. After this soaking treatment some other

TABLE 2

Physical Characteristics and Chemical Compositions of Fly Ashes and Blast Furnace Slag

Source powder	Fineness, Blaine (cm^2/g)	Apparent density (g/cm^3)
Ordinary fly ash (F4)	3610	2.11
Ultrafine fly ash (FA2)	14200	2.32
Esment (Granulated slag)	4000	2.85

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	LOI	Total
F4	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
FA2	44.59	1.32	31.30	3.42	0.08	6.57	2.30	1.05	1.23	0.74	1.62	6.24	100.46
Slag	33.30	1.81	13.44	0.66	0.58	40.74	7.46	0.45	0.45	0.03	1.40	-	100.32

TABLE 3

Mixing Proportions of Source Materials

A-series				B-series			
Sample	Filler(F4:FA2)	Hardener	P/S	Sample	Filler(F4:FA2)	Hardener	P/S
A-0	90 (100: 0)	10	0.5	B-0	100 (100: 0)	0	0.5
A-10	90 (90:10)	10	0.5	B-10	100 (90:10)	0	0.5
A-20	90 (80:20)	10	0.5	B-20	100 (80:20)	0	0.5
A-30	90 (70:30)	10	0.5	B-30	100 (70:30)	0	0.5
A-40	90 (60:40)	10	0.5	B-40	100 (60:40)	0	0.5
A-50	90 (50:50)	10	0.5	B-50	100 (50:50)	0	0.5

P/S denotes binder-liquor/solid ratio. Filler and hardener are included to S. Granulated blast furnace slag was applied for the hardener.

test-pieces were dried at ambient temperature and humidity for 7 d to measure also the strength in the same way. This is called dry body strength. Fractured monoliths were examined by XRD and SEM, employing MAC Science MXP3 and Hitachi S-510 apparatus, respectively.

Grain size distributions of the fly ashes, F4 and FA2 measured by a laser beam particle mode analyzer, Horiba LA700 showed medians of 13.67 and 1.27 μm, respectively and especially the latter is characterized by a sharp distribution of ultrafine particles. Under SEM bth fly ashes exhibity glassy globuets in shapes. However, by XRD quartz and mullite were identified small in number other than a broadened rise peculiar to vitreous materials. The granulated slag was almost glassy associated with a slight gehlenite-like phase.

Results and Discussion

Materials Strength. Results of strength tests were summarized in Fig. 1. Generally dry body strength was higher than wet body strength for both A- and B-series showed higher strength than B-series.

For A-series a general trend of increasing compressive strength was noted with enrichment of the ultrafine fly ash, FA2 on both wet and dry bodies disregarding A-50 that behaved exceptionally, while maxima appeared in flexural strength at 30 percent enrichment in both wet and dry bodies. Conclusively A-30 showed superior characters in both flexural and compressive strengths.

For B-series increasing strength was also noted with enrichment of the ultrafine fly ash especially for wet bodies. However, clear maxima appeared for dry bodies at 30 percent blend of ultrafine fly ash for both flexural and compressive strengths.

As a consequence, dosages of ultrafine fly ash as well as hardener slag are quite effective to elevate the strength, leading to the remarkable results firstly from filling effect of intergranular voids with ultrafine particles like MDF materials (8) and secondly from cementitious effect of the hardener slag as mentioned later. The 30 percent dosage of ultrafine particles found to be optimal especially for dry bodies in B-series is considered to a simple case of balancing the overall volumes between voids and ultrafine fly ash added due to lacking the hardener slag. However, others are not simple cases and presence of the hardener slag and also wet conditions effecting to the binder stabilities should be taken into account for materials strength.

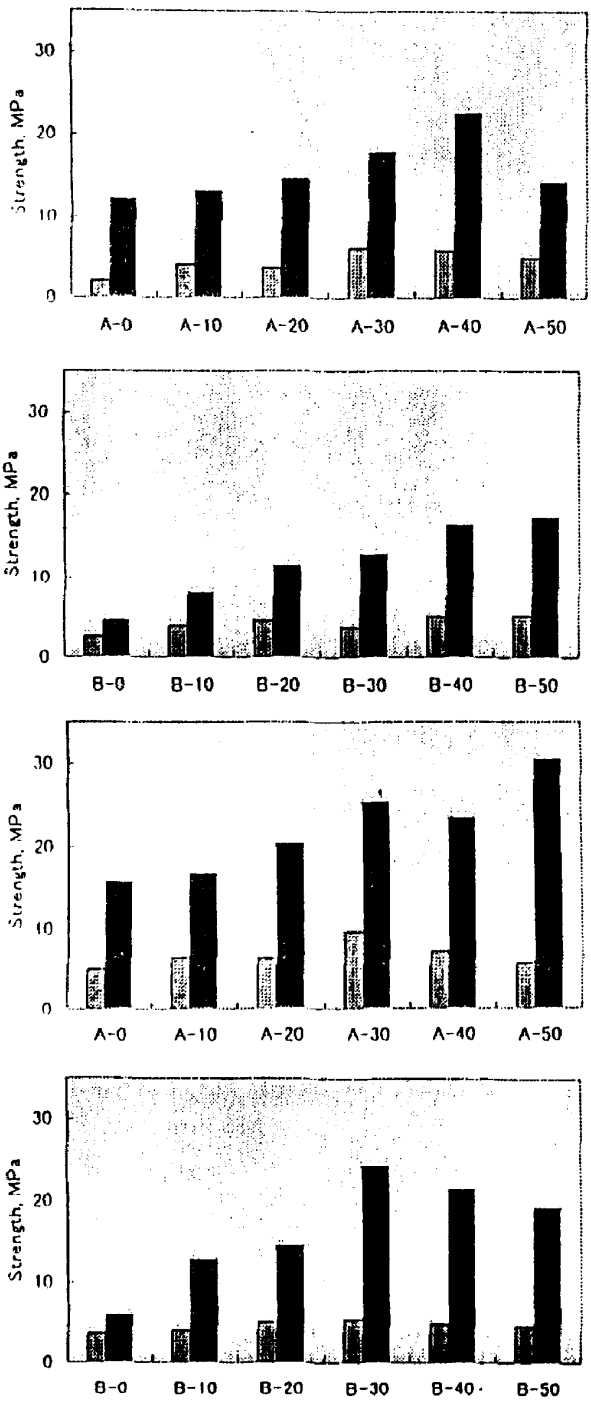


FIG. 1.

Results of strength test for fly ash monoliths. Gray and black columns showing flexural and compressive strengths, respectively. Top, after soaking. Bottom, after subsequent air-dry.

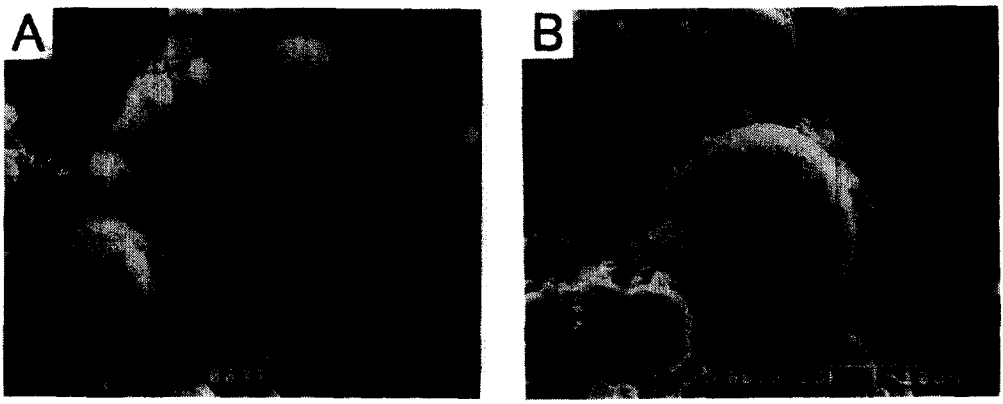
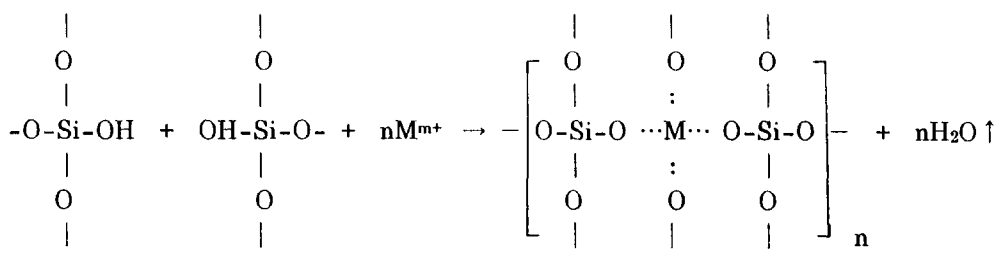


FIG. 2.
Exemplified SEM photomicrographs for fractured fly ash monoliths after the soak-dry treatments. (A) A-series, (B) B-series.

Sodium Silicate Binders. No crystalline products were detected in the monoliths by XRD as reported so far (4). However, completely different textures were observed between A-series and B-series specimens under SEM as seen in Fig. 2. Basically, solidification of the binder liquor may proceed in genuine polycondensation reaction generated by linking of metallic ions (1)(2)(3)(9) dissIved from fillers and hardeners accompanied by dehydration as follows:



Sodium ions and some adsorbed water molecules are disregarded in this scheme and the bridging arms of cations, M, dissolving from fillers and hardener depend on valences of the cation M.

The soak-dry treatments may promote the polycondensation due to leaching out some sodium ions from the reaction system and eventually may give rise to higher strength after dry due to occurring high degrees of polycondensation. This consideration would be right for B-series specimens added with no hardeners as shown in Fig. 2, where a very simple texture can be seen in matrices consisting of smaller particles of fly ash combined with amorphous-like binders. Although some traces of binders precipitated by the polycondensation process are noted on the fly ash particles irrespective of particle size, the fly ash particles exhibit rather smooth surfaces. To the contrary, a complicated texture completely different form that of B-series specimens is observed for A-series specimens, where no smaller particles of fly ash can be seen in matrices

any more, reacting with or covered with products occurring due to the reaction of the binder liquor with the hardener slag and the filler fly ashes. Some parts, especially on the surfaces of larger fly ash particles, show a mesh-like texture peculiar to II C-S-H, but the identification is unsuccessful at the moment. Sodalite composition, $Na_8(Al_6Si_6O_{24})(OH)_2$, stable at ambient temperature is most probably considered as a main frame of matrices for B-series (10) rather than natrolite composition of zeolite group, $Na_2(Al_2Si_3O_{10}).2H_2O$ stable at high temperature. On the contrary, calcium substitution of sodalite composition is considered for A-series due to the effect of lime component from the slag. According to Davidovits (11) his potassium-based binder solidified at 80°C showed X-ray diffraction, so that his binders were crystalline called polysialates comprising aluminum other than silicon and alkalies in addition to some combined water. This polysialate binder is characterized by high strength, 62 MPa maximal compressive strength, being basically rapid setting, crystalline and thermohardening. On the contrary, present sodium-based binder is characterized by moderately high strength, 30.3 MPa maximal compressive strength, being slow setting, nearly amorphous and ambient temperature hardening.

Conclusion

Following items have been reached as conclusions.

(1) Binders working at ambient temperature can be prepared from sodium silicate solutions mixing with fly ashes as fillers.
(2) Enrichment with ultrafine particle fly ash, 1.27 μm in median diameter, is very effective to preparing high strength fly ash monoliths.
(3) Granulated blast furnace slag acts as a hardener and 10 percent additio n of solid makes the materials strength markedly higher.
(4) Water soaking and subsequent air-dry treatments are useful to obtain stable and high strength monoliths.
(5) It is estimated that solidification of sodium silicate binder liquor proceeds in a simple polycondensation process, when hardener slag is absent, while a complicated process takes place caused by a reaction of the binder liquor with fly ash and blast furnace slag, when hardener slag is present.

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