Pergamon

Cement and Concrete Research 29 (1999) 215–221

CEMENT AND CONCRETE RESEARCH

Mechanical strength enhancement of lower hydraulicity cementitious solid wastes using anhydrite and pozzolanic materials

Seong-Su Hong [a], Gye-Gyu Lim [a,*], Byoung-Ky Lee [b], Beom-Jae Lee [b], Jae-Seong Rho [b]

[a]*Department of Chemical Engineering, Hoseo University, Asan, Chungnam, Korea 337-795*

[b]*Department of Fine Chemical Engineering and Chemistry, Chungnam National University, Taejon, Korea 305-764*

Manuscript received 10 December 1997; accepted manuscript 29 June 1998

Abstract

Mechanical strength enhancement was investigated for recycling lower hydraulicity inorganic solid wastes (HISWs) from five different building material manufacturing processes. The source materials are cement-gypsum composite board, cement fiber-reinforced board, calcium silicate board, corrugated slate, and sludge from wastewater treatment plants. Mineral admixture of 80% anhydrite as an ettringite-forming agent and 20% slag/fly ash as pozzolanic materials was added by weight ratio of cement. The specimens were prepared by the press molding method or without pressure, and then cured with steam at 80°C. The flexural strength of specimens with added HISWs did not meet the target standards for special use, regardless of source processes, addition ratio, and preparation methods without mineral admixture. The long-term mechanical strengths of compacted specimens were enhanced under 50 kgf/cm^2 pressure with the addition of 10 wt% mineral admixture due to the stimulated pozzolanic reaction by slag/fly ash and the ettringite formation by anhydrite. The increased intensity of ettringite and CSH gel peaks was detected in X-ray diffraction patterns and confirmed by scanning electron microscopic analysis. The flexural strength was increased more than 30% and was not affected by the HISWs addition ratio. The water absorption ratio also was decreased with the addition of mineral admixture.

Keywords: Mechanical properties; Waste management; Pozzolan; Sulfate

Lower hydraulicity inorganic solid wastes (HISWs) are produced by the manufacturing processes for construction materials such as insulation, ceiling, and interior wall materials. When the HISWs are landfilled, the foundation can become soft and groundwater can be contaminated by alkaline leachates [1,2].

In Japan, study of the recycling of cement sludge as raw materials of cement, artificial lightweight aggregates, and fillers of concrete has been advanced since the early 1980s [3–5]. In Korea, the surface of HISWs was modified with an emulsion of stearic acid and sodium stearate so that they could be used as an additive for waterproofing cement mortar [6,7].

If treated properly, HISWs can be new sources of useful materials. Recycling and reuse of industrial, urban, and agricultural waste materials into new building materials may be a feasible alternative to waste disposal. Previous studies showed sludge had a chemical composition of CaO unsuitable for recycling because it had been exposed to excess water for a long period of time in a sedimentation tank [8–10].

In general, workability and bleeding can be improved pozzolanic materials and segregation of raw materials, and heat evolution of hydration also can be reduced. Products of pozzolanic reaction give enhanced effects on durability, watertightness, chemical resistance to brine water, and long-term mechanical strength. It also has been reported that tensile strength can be greatly increased. Ettringite is produced from the reaction of anhydrite (II-$CaSO_4$) with C_3A or C_4AF during steam curing. The initial hydration of C_3S also is stimulated by anhydrite at the beginning of steam curing [11–14].

In this study, the mechanical strength enhancement for recycling of HISWs from five different building material manufacturing processes was investigated. Mineral admixture of anhydrite and slag/fly ash was added to cement to improve mechanical strength. The effects on physical properties such as water absorption ratio, and compressive and flexural strengths of specimens were investigated.

* Corresponding author. Fax: 82-418-40-5501.

PII: S0008-8846(98)00187-2

1. Experiment

1.1. Experimental materials

The lower HISWs from five different building material manufacturing processes were used. The source materials are cement-gypsum composite board (CGC), cement fiber-reinforced board (CFR), calcium silicate board (CSB), corrugated slate (CGS), and sludge from a wastewater treatment plant (SLU). The chemical compositions of HISWs are given in Table 1. The average moisture content of sludge was adjusted to 50%. Because CSB and CGS had lower SO_3 content than SLU, CGC, and CFR, a smaller amount of gypsum was used in CSB and CGS.

A mineral admixture was prepared from anhydrite and slag/fly ash to improve strengths. Anhydrite was produced from manufacturing process of hydrofluoric acid with the reaction of CaF_2 and H_2SO_4 at 500°C. The mixing ratio of anhydrite, fly ash, and slag was 8:1:1, and mineral admixture was added to cement on the basis of weight ratio. The particle size in admixture was less than 10 μm.

Each mortar and specimen were made from ordinary Portland cement (OPC) and sand as specified by Korean Standard KS L 5100.

1.2. Experimental methods

According to KS L 5109, mortar were prepared with the mixing proportions given in Table 2. HISWs were added to sand for effective recycling as much as 30, 60, and 90 wt% of cement on the basis of weight ratio.

Mortar specimens were prepared with the cast or press molding method (50 kg_f/cm^2) in the mold, 40 × 40 × 160 mm, and then cured with steam at 80°C for 4 h. After steam curing, mortar specimens were dry cured. Compressive and flexural strengths of mortar specimens were investigated after curing periods of 1, 3, and 7 days.

CFR, CSB, and CGS in HISWs are recycled almost as raw materials in the field, but CGC and SLU are not reused nearly as much, so their amounts have accumulated gradually. Therefore, CGC and SLU were mixed as given in Table 3. The additional amount of mineral admixture for each mortar was 10 wt% by weight ratio of cement. The amount of mineral admixture was determined in previous experiments. Prepared specimens were cured by the same method as given earlier and tested for compressive and flexural strengths. After test of strengths (7 days), hydrates of mortar specimens were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Water absorption of mortar specimens was measured in accordance with KS F 2451. The specimens were dried to be constant weight at 80 ± 2°C, and then immersed in 20 ± 2°C water for 24 hours. The water absorption ratio was calculated using Eq. (1):

$$\text{Water absorption ratio (\%)} = (W_1 + W_0)/W_0 \times 100 \qquad (1)$$

where W_0 is the weight of the specimens before water immersion, and W_1 is the weight of the specimens after water immersion.

Table 1
Chemical compositions of sludge and solid wastes

Wastes	Components								
	SiO_2	CaO	MgO	Al_2O_3	SO_3	K_2O	Fe_2O_3	H_2O	Total
SLU	7.6	22.8	2.4	2.5	10.0	0.8	3.9	50	100
CGC	14.1	44.1	7.4	1.6	30.4	1.1	1.3	—	100
CFR	12.1	47.8	7.7	2.6	26.9	1.0	1.9	—	100
CSB	44.0	42.4	5.4	3.8	1.2	1.4	1.8	—	100
CGS	27.5	51.4	11.6	3.7	2.2	1.0	2.6	—	100

Values are given as wt%.
SLU: sludge waste from waste water treatment plant; CGC: powder waste from cement-gypsum fiber composite board; CFR: powder waste from cement fiber-reinforced board; CSB: powder waste from calcium silicate board; CGS: powder waste from corrugated slate.

Table 2
Mixing ratios of specimens using sludge and wastes

Sample name	Cement	Sand/ cement	SLU/ cement	Solid waste/ cement	Water/ cement
OPC	1	3.0	0	0	45
SLU-1	1	2.7	0.3	0	45
SLU-2	1	2.4	0.6	0	64
SLU-3	1	2.1	0.9	0	89
Solid waste-1	1	2.7	0	0.3	45
Solid waste-2	1	2.4	0	0.6	64
Solid waste-3	1	2.1	0	0.9	86

Values are given as wt%.
Note: Solid waste is a general name for CGC, CFR, CSB, and CGS.

2. Results and discussion

2.1. Compressive and flexural strength of specimens reusing HISWs

HISWs were added as much as 30 wt% (SLU-1 and powder waste-1), 60 wt% (SLU-2 and powder waste-2), and 90

Table 3
Mixing ratios of mixed wastes (sludge + cement-gypsum composite waste) substituted specimens

Sample name	Cement	Sand/ cement	(SLU + CGC)/ cement	Mineral admixture/ cement	Water/ cement
OPC	1	3.0	0	0	45
SC-1	1	2.70	0.30	0	45
SC-2	1	2.40	0.60	0	64
SC-3	1	2.10	0.90	0	85
SC-P-1	1	2.70	0.30	0.1	45
SC-P-2	1	2.40	0.60	0.1	64
SC-P-3	1	2.10	0.90	0.1	86

Values are given as wt%.
SLU + CG: in equal proportion; SC: SLU + CGC; SC-P: SLU + CGC + mineral admixture (10 wt%).

Table 4
Mechanical strengths of solid waste substituted specimens prepared by the cast molding method

Sample name	Added amount of solid waste (wt %)	Mechanical strength (kg_f/cm^2) Compressive strength 1 day	3 days	7 days	Flexural strength 1 day	3 days	7 days
OPC	—	210	262	318	35.0	40.0	48.0
	30	191	213	248	28.4	34.0	39.5
SLU	60	165	199	209	25.0	27.5	33.4
	90	147	176	190	20.0	25.0	28.8
	30	211	263	325	37.5	40.5	48.1
CGC	60	204	248	303	31.5	36.4	44.2
	90	200	235	272	29.4	34.0	35.9
	30	207	252	315	34.9	39.1	46.7
CFR	60	202	243	298	30.5	35.5	42.7
	90	197	231	269	28.4	33.1	41.0
	30	212	262	320	36.0	41.2	46.7
CSB	60	203	251	300	32.5	35.6	44.0
	90	200	239	268	28.2	32.8	39.0
	30	207	249	313	34.6	39.0	45.1
CGS	60	201	237	298	30.2	35.2	42.3
	90	196	232	260	27.5	32.0	37.5

wt% (SLU-3 and powder waste-3) as shown in Table 2, as parts of sand by weight ratio of cement to investigate the effect on cement mortar strength. Compressive and flexural strengths of specimens were tested after curing for 1, 3, and 7 days.

Except for SLU-1, specimens had similar values of compressive strengths compared to the OPC specimens for cast molding using 30 wt% HISWs as shown in Table 4. However, the strengths decreased with increasing replacement of HISWs. It is considered that the decreasing tendency of mortar strength was caused by the increasing water-to-cement ratios, which were increased more than those of OPC to maintain workability of mortars.

The compressive strengths of all specimens having more than 60 wt% HISWs were significantly decreased by 7 days. Lower hydraulicity of HISWs compared to OPC can cause structural defects and result in remarkable decrease in strength.

The moisture content of SLU was adjusted to 50% from 80% to 90%, which is the initial range of moisture content, by a drying process to obtain the effects of moisture in sludge on mortar properties. Moisture in SLU did not contribute to the workability improvement of cement, so water-to-cement ratios including moisture were much higher than those of other HISWs. For that reason, compressive strengths of cement mortar using SLU were remarkably decreased. Therefore, the optimum replacement amount of HISWs with sand was 30 wt% in the cast molding method. However, SLU was unsuitable when used as a part of the sand in cement mortar.

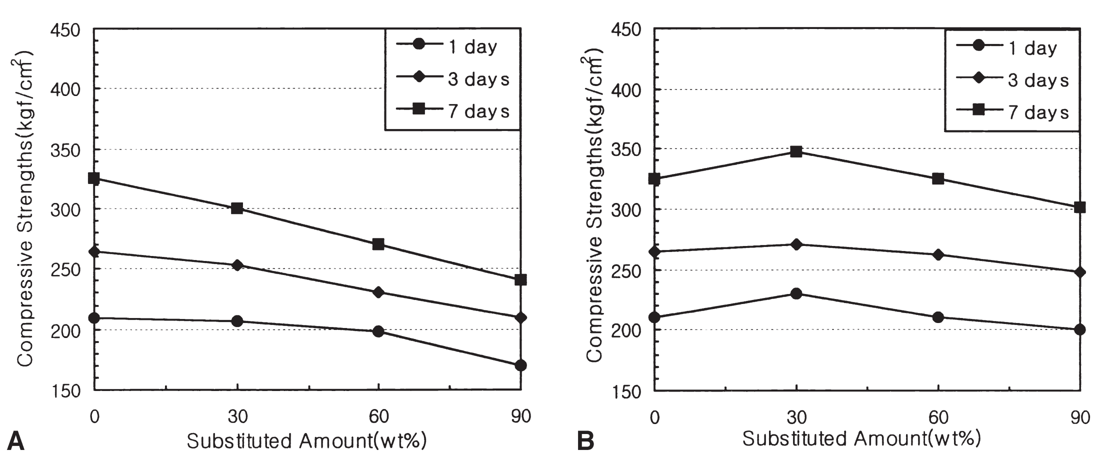

Fig. 1. Compressive strengths of SLU (*A*) and CGC (*B*) of recycled specimens prepared by the press molding method.

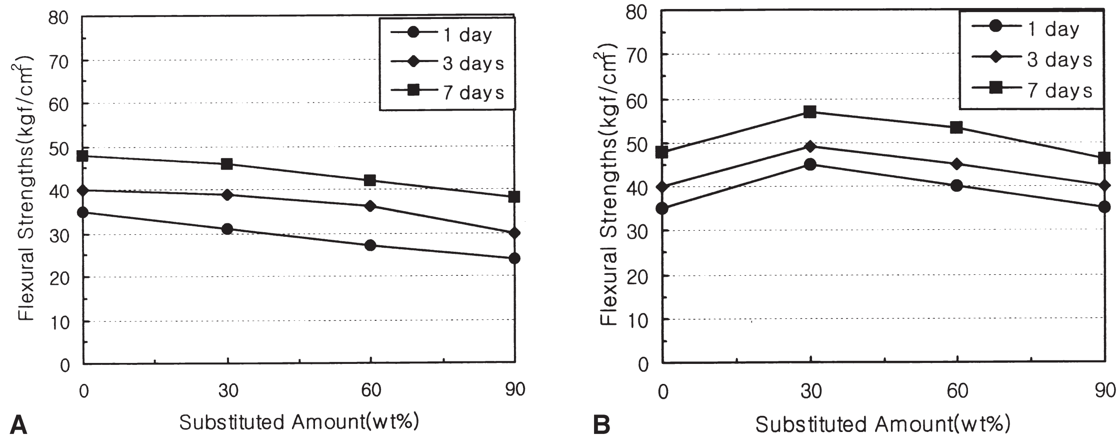

Fig. 2. Flexural strengths of SLU (*A*) and CGC (*B*) of recycled specimens prepared by the press molding method.

The flexural strengths with curing periods of specimens using HISWs are shown in Table 4. When HISWs were replaced with sand as much as 30 wt%, the flexural strength was nearly the same as that of OPC. The flexural strength of mortar using SLU was lowest. The compressive strengths of the mortar exceeded the requirements of KS F 4004, but flexural strength did not.

2.2. Compressive and flexural strength of compacted specimens

Press molded specimens using SLU were tested to determine how good the compressive and flexural strengths were. More SLU is produced than other HISWs, but the strengths of specimens using SLU seem to have the lowest values. Although CGC could be recycled as raw material, residual wastes have been accumulating.

Compressive strengths of compacted specimens using SLU and CGC were shown in Fig. 1. In Fig. 1A, the compressive strengths of specimens using SLU seemed lower than those of OPC but 20% higher than those of cast specimens. Fig. 1B shows that the strengths of specimens using CGC were much higher than those of OPC and 7% higher than those of cast specimens. But the compressive strengths showed decreasing tendency with an increasing amount of SLU and CGC, even in compacted specimens.

The reason for the increasing compressive strengths of compacted specimens can be explained as follows. When specimens were compacted, the pores of the specimens were filled with fine powder, so the structure became dense, and, as a result, compressive strength improved. As compared with Table 4, the compressive strength of specimens using SLU were improved to a greater extent than that of CGC.

Flexural strengths of the specimens using SLU and CGC are shown in Fig. 2. Flexural strengths of the specimens using SLU were lower than those of OPC, which is similar to the compressive strengths results, but the specimens using CGC 30 wt% have higher values than OPC. In particular,

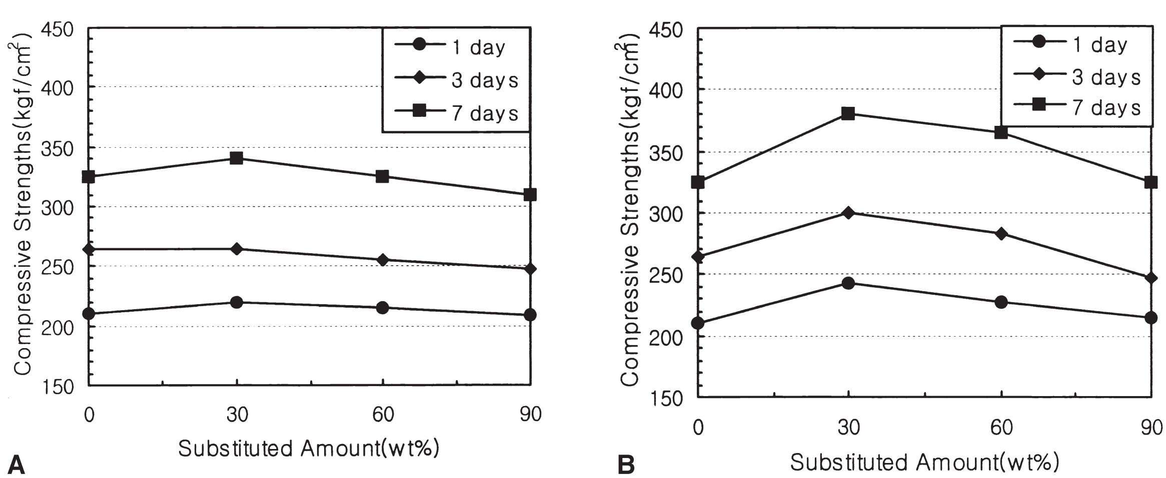

Fig. 3. Compressive strengths of SC recycled specimens prepared by the press molding method. (*A*) Without mineral admixture; (*B*) 10 wt%(C × %) mineral admixture.

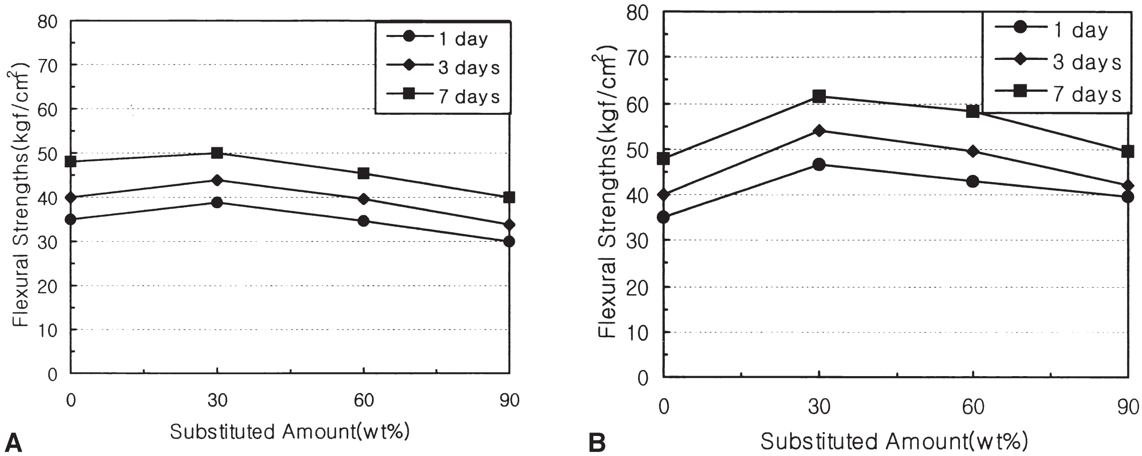

Fig. 4. Flexural strengths of SC recycled specimens prepared by the press molding method. (*A*) Without mineral admixture; (*B*) 10 wt%(C × %) mineral admixture.

the strength of the specimens using CGC 30 wt% appeared 30% higher than that of OPC at 7 days. This result was due to reinforcement by cellulose pulp, which was supplied during the CGC manufacturing processes as a reinforced fiber. The requirement of KS F 4004 for 7-day compressive strengths were met by specimens using both SLU and CGC, but only specimens using CGC met flexural strengths requirements.

2.3. Compressive and flexural strengths of specimens with added mineral admixture

Most SLU specimens did not meet the flexural strength requirement. Therefore, to use SLU in place of sand in cement mortar, it was mixed with CGC, as shown in Table 3. Compacted specimens were tested for compressive and flexural strengths for replacement amounts of 30% (SC-1 in Table 3), 60% (SC-2), and 90% (SC-3). At this time, the mineral admixture composed of anhydrite as an ettringite-forming agent and slag and fly ash as pozzolanic materials was added to improve the mechanical strength on the basis of weight ratio to cement. The mineral admixture had a composition of 80% anhydrite, 10% slag, and 10% fly ash. Generally 10 wt% mineral admixture was used.

Fig. 3A shows that the compressive strengths of the SC samples were remarkably improved and greater than those of specimens using SLU alone. Fig. 3B shows that the strengths of SC-P were more improved than those of specimens with added CGC alone. Therefore, mineral admixture improved of the compressive strengths of SC samples.

Fig. 4A shows that flexural strengths of SC samples were more improved than those of the specimens using SLU, but did not satisfy KS F 4004. In contrast, flexural strengths of SC-P-1 (Fig. 4B) were remarkably improved and satisfied the standard KS irrespective of the replacement amount of SC in 7 days. Therefore, SLU and CGC could be practically recycled as a part of sand in the production of cement block or in interlocking, if 10% mineral admixture of 10% is added on the basis of cement weight ratio.

2.4. Water absorption of specimens with added mineral admixture

Water absorption ratios of specimens using SC and SC-P after immersed for 24 h are shown in Table 5. The water absorption ratio of OPC was 12.5%. The ratio of SC was higher than that of OPC, and the ratio was more increased with an increasing replacement amount of SC. This tendency was considered to be that SC itself had high absorbing properties, and excess water was trapped in macropores in the mortar specimens.

The water absorption ratios of SC-P-1 were lower than those of OPC, and the ratio was slightly increased with an increase of replacement amount of SC-P. It is assumed that this tendency could result from adding mineral admixture of anhydrite as an ettringite-forming agent and slag/fly ash as pozzolanic materials.

The water absorption ratios of SC-P were slightly decreased due to the packing effect of hydrates. The water absorption ratios of SC and SC-P satisfied with 20% of KS F 2451.

Table 5
Water absorption ratios of SC and SC-P substituted specimens prepared by the press molding method

Added amount	Specimen		
(C × %)	OPC	SC	SC-P
0.0	12.5	—	—
0.30	—	14.5	12.0
0.60	—	16.7	13.4
0.90	—	19.4	16.5

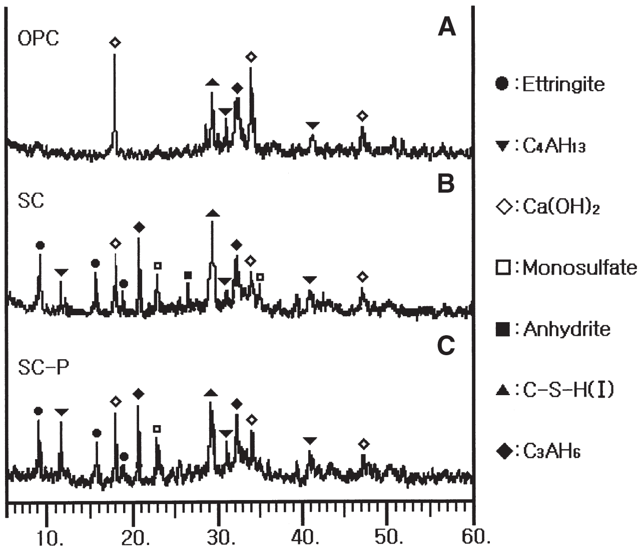

Fig. 5. XRD analysis of OPC hydrate (*A*) and hydrate with SC (*B*) and SC-P (*C*) after steam curing at 80°C for 4 h.

2.5. Analysis of hydrate by XRD and SEM

Figs. 5 and 6 show XRD analyses and SEM photographs of hydrates with added SC and SC-P, respectively. The major compounds of cement were not detected after steam curing at 80°C for 4 h (Fig. 5A), indicating complete hydration to $Ca(OH)_2$, CSH gel. Ettringite produced by the reaction of $CaSO_4 \cdot 1/2H_2O$ and C_3A changed into monosulfate. Calcium silicate hydrates and $Ca(OH)_2$ were observed in the SEM photograph in Fig. 6A.

In Fig. 5, various hydrates peaks were detected in XRD patterns of (B) and (C) added SC and SC-P, respectively. XRD patterns of (B) and (C) are nearly similar. The ettringite peak at 9.042 degree (2ϑ) strongly increased and did not change into monosulfate.

In Fig. 6, hydrate morphologies of (B) were different from those of (C). (B) shows long thin-plate hydrates considered to be hydrates already present in sludge. Ettringite and other hydrates grow into short needle-like crystalline; otherwise, ettringite and cement hydrates develop due to the reaction of anhydrite and $3CaOAl_2O_3$, pozzolanic materials and $Ca(OH)_2$, respectively, in (C).

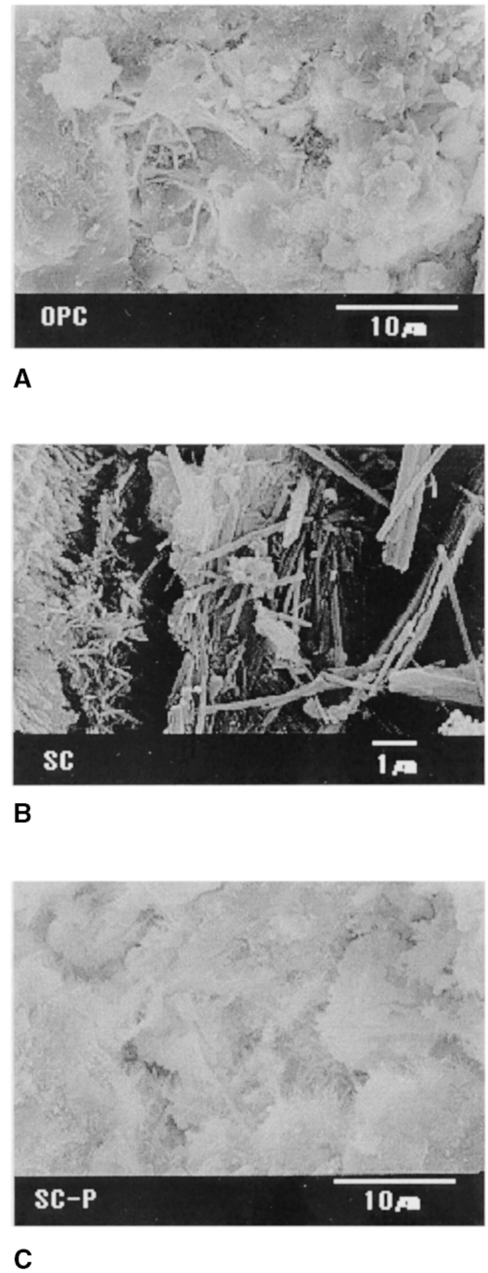

Fig. 6. SEM photographs of OPC (*A*), SC added (*B*), and SC-P added (*C*) hydrates after steam curing at 80°C for 4 h.

3. Conclusions

The conclusions are summarized as follows for physical properties and water absorption of cement mortars using mineral admixture and HISWs from five different building material manufacturing processes.

1. The highest compressive and flexural strengths were obtained from specimens using CGC from the cement-gypsum composite board producing process. The lowest strengths were seen in specimens using SLU with high moisture content.
2. Strengths of specimens prepared by press molding were higher than those of specimens prepared without pressure. Specifically, the compressive strength of press molded specimens using CGC were 7% higher than that of cast specimens; for specimens using SLU the increase was more than 20% that of cast specimens.
3. Compressive strength of specimens with mineral admixture added (SC-P 30 wt% on the basis of cement weight) was 7% higher than that of specimens without the admixture, and flexural strength of specimens using SC-P 30 wt% was improved by more than 30% compared to specimens using only SC.

4. Water absorption ratio of specimens using SC-P 30 wt% was 0.5% lower than that of OPC, but the water absorption ratios were slightly increased with increasing replacement of SC-P.
5. Ettringite and other hydrates were produced from the stimulated reaction by mineral admixture of anhydrite and slag/fly ash.

References

[1] H. Kikuchi, T. Nakamura, T. Ishikawa, Hokkaido ritukougyoshiken-jyoho-koku 278 (1979) 93.
[2] H. Kikuchi, T. Nakamura, T. Ishikawa, Hokkaido ritukougyoshiken-jyoho-koku 279 (1980) 89.
[3] K. Miyoshi, S. Tanabe, Kotuzaishigen 58 (1983) 126.
[4] K. Yukio, Jpn Concr Inst 26 (1988) 76.
[5] H. Uchikawa, Cem Concr Jpn 133 (1985) 227.
[6] J.S. Rho, H.Y. Cho, S.C. Yoon, J.J. Yoon, J Arch Inst Korea Soc 8 (1992) 173.
[7] J.S. Rho, H.Y. Cho, S.S. Hong, S.G. Oh, Trans Jpn Concr Inst 15 (1993) 63.
[8] D.C. Hughes, Mag Concr Res 37 (1985) 227.
[9] H. Uchikawa, Cem Concr Jpn 484 (1987) 81.
[10] P.B. Bamforth, In situ measurement of the effect portland cement replacement using either fly ash or ground granulated blast-furnace slag on the performance of mass concrete, Institute Civil Engineering (London), Part 2, 69, Proceedings, 1980, pp. 777–800.
[11] V. Riganti, A. Fiumara, G.B. Odobez, Waste Mgmt Res 4 (1986) 293.
[12] K.W. Nasser, H.M. Marzouk, Properties of mass concrete containing fly ash at high temperature, ACI J Proc 76 (1979) 537–550.
[13] C.J. Fordham, J.J. Smalley, Cem Concr Res 15 (1985) 73.
[14] J.-H. Tay, Properties of pulverized sludge ash blended cement, ACI Mater J September/October (1987) 358–364.