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Waste Management 28 (2008) 1081–1087
waste management
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Improvements of nano-SiO_2 on sludge/fly ash mortar

D.F. Lin [a], K.L. Lin [b], W.C. Chang [c], H.L. Luo [a,*], M.Q. Cai [a]

[a] Department of Civil and Ecological Engineering, I-Shou University, 1, Sec. 1, Syuecheng Rd., Dashu Township, Kaohsiung County, Taiwan, ROC
[b] Department of Environmental Engineering, National Ilan University, 1, Section 1, Shen Lung Road, I-Lan 260-41, Taiwan, ROC
[c] Department of Civil Engineering, Kao Yuan University, 1821, Jhongshan Rd., Lujhu Township, Kaohsiung County, Taiwan, ROC

Accepted 26 March 2007
Available online 18 May 2007

Abstract

Sewage sludge ash has been widely applied to cementitious materials. In this study, in order to determine effects of nano-SiO_2 additives on properties of sludge/fly ash mortar, different amounts of nano-SiO_2 were added to sludge/fly ash mortar specimens to investigate their physical properties and micro-structures. A water-binding ratio of 0.7 was assigned to the mix. Substitution amounts of 0%, 10%, 20%, and 30% of sludge/fly ash (1:1 ratio) were proposed. Moreover, 0%, 1%, 2%, and 3% of nano-SiO_2 was added to the mix. Tests, including SEM and compressive strength, were carried out on mortar specimens cured at 3, 7, and 28 days. Results showed that sludge/fly ash can make the crystals of cement hydration product finer. Moreover, crystals increased after nano-SiO_2 was added. Hence, nano-SiO_2 can improve the effects of sludge/fly ash on the hydration of mortar. Further, due to the low pozzolanic reaction active index of sludge ash, early compressive strengths of sludge/fly ash mortar were decreased. Yet, nano-SiO_2 could help produce hydration crystals, which implies that the addition of nano-SiO_2 to mortar can improve the influence of sludge/fly ash on the development of the early strength of the mortar.

1. Introduction

Reuse of sewage sludge has been widely promoted and applied in many engineering applications, especially in the development of construction materials such as eco-cement made by sludge ash, incinerated sewage sludge ash tiles, and backfill materials for the subgrade of pavements. However, parts of the original materials that were replaced by sludge ash could potentially influence the properties of construction materials, both positively and negatively. For example, when replacement of sewage sludge ash accounted for more than 50% of the original material used in making mortar, compressive strengths of the mortar specimens were reduced, due to a low pozzolanic reaction active index (Zeng et al., 2002). Hence, the pozzolanic reaction active index of sewage sludge ash should be considered in engineering applications. Yague et al. (2002) found that calcite and silica were observed and clay materials fell short in dry sewage sludge crystallization using DRX analysis. Hence, after the addition of sewage sludge ash to mortar, phenomena such as lower compressive strength and density of mortar, increase of porosity, and slower hydration processes of the cement were noticed. In recent years, and with the help of nano-technology breakthroughs, problems caused by the replacement of cement by sewage sludge ash were improved. Flores-Velez and Dominguez (2002) mixed zinc–iron oxide nano-particles with steel slag and Portland cement to make paste. They found that the strength of the paste at seven days was stronger than Portland cement paste, and hydrates generated at 28 days were the same as those in Portland cement paste. Further, the strength of the paste with 10% steel slag added reached 72 MPa after being cured for 42 days.

Fine particles, such as sludge ash, are easily attracted to each other to form floc structures, which would incur an insufficient water adsorption layer around the surface of

* Corresponding author. Tel.: +886 7 6577711x3318; fax: +886 7 6577461.
E-mail address: hlluo@isu.edu.tw (H.L. Luo).

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doi:10.1016/j.wasman.2007.03.023

the particles and result in a weak level of flowability for mortar with sludge ash added. Further, components of sludge ash, such as aluminum and silicon ions, can react with Ca^{2+} easily to produce a thin silicon/calcium film which coats the surface of ash particles. Accordingly, the nucleation of CH is delayed and pozzolanic reactions generated in the mortar become slow. Hence, these phenomena retard the development of the early compressive strength of the mortar when cement is replaced by sludge ash. In their study of the effects of nano-materials on the behaviors of sludge mortar specimens, Luo et al. (2004) found that the early strength of mortar specimens improved when 2% nano-composites were added. Li (2004) added nano-SiO_2 to study the effects on the properties of high-volume fly ash high-strength concrete. Fly ash has low initial activity; however, the addition of nano-SiO_2 can increase the pozzolanic activity of fly ash. He also concluded that nano-SiO_2 can enhance the short-term and long-term strength of high-volume, high-strength concrete. In order to increase the beneficial reclamation of sewage sludge ash and fly ash, part of the cement is replaced by incinerated sewage sludge/fly ash in mortar specimens in this study, and the effect of sludge ash/fly ash on the properties of mortar is investigated. Moreover, nano-SiO_2 is treated as an additive to help improve the properties of mortar caused by the replacement of sludge/fly ash in the specimens used.

2. Materials and research procedure

2.1. Materials

Dewatered sewage sludge sample cakes were obtained from a municipal wastewater treatment plant at Kaohsiung City in southern Taiwan. These samples were initially oven dried at 105 °C and then incinerated in an electronic furnace at 800 °C before being ground into fine particles and passed through a #200 sieve. Fly ash, which also passed through a #200 sieve, was collected from a thermal power plant near Kaohsiung City. Type I Portland cement was used and nano-SiO_2 containing 99.9% of SiO_{2-x} was applied as an additive in this study. In order to identify the fate of heavy metals in both incinerated sewage sludge ash and fly ash, and to observe the microstructures of the substituents, tests including toxic characteristic leaching tests (TCLP), inductively coupled plasma atomic emission spectrometry (ICP–AES), mercury intrusion porosimetry (MIP), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed. TCLP test results and regulatory limits are shown in Table 1. The leached metal concentrations of sewage sludge ash and fly ash met regulatory standards, NIEA R201.13C, set by the Environmental Protection Agency in the Republic of China. Fig. 1 displays pictures obtained from SEM for cement, sewage sludge ash, and fly ash. Sewage sludge ash is irregular in shape, fly ash appears in ball shapes, and cement comes in bulky irregular shapes. In general, these different particle shapes would affect the fineness of mixtures and hydrate reactions of mortar specimens.

2.2. Research procedures

Specimens were manufactured with a mix ratio of Type I Portland cement and fine aggregate, equaling 1:2.75, and a water-binding ratio (water/(cement + ash)) of 0.7 was assigned to the mix. Replacement of cement is assigned at the ratio of 1:1 for sludge ash and fly ash, respectively. Four different substitution amounts, according to weight percentages, of 0%, 10%, 20%, and 30% of sludge ash/fly ash were proposed. In addition, in order to improve the compressive strength of the specimens, 0%, 1%, 2%, and 3% of nano-SiO_2, defined as the percent weight of cement, sludge ash, and fly ash, was added to each proposed ash substitution in the mix. After the proposed materials were well mixed, mortar specimens were manufactured with the size of 5 cm × 5 cm × 5 cm. Note that those specimens with 0% sludge ash/fly ash replacement and 0% additives were assigned as the control group, while others belonged to the experimental group. Specimens in both groups were demolded 24 h after casting and left in a curing room where the humidity and temperature were kept at 100% and 25 °C, respectively, for 3, 7, and 28 days. A detailed procedure of this study is illustrated in the flowchart shown in Fig. 2. Furthermore, in order to proceed with the study of micro-structure analysis using SEM, samples of the specimens taken after compressive tests were left in methanol solution to stop the hydration of the mortar.

3. Results and discussion

3.1. ICP–AES analysis

Chemical components of sludge ash, fly ash, and cement obtained from ICP–AES are shown in Table 2. Both the fly ash and the cement contained components with closed quantities. The amount of SiO_2 in the sludge ash was about 65%, which was less than that in the fly ash (about 74%). Results obtained from ICP–AES disclosed that the sludge ash consisted of about 88% pozzolanic materials, presented mainly in two chemical compositions, Al_2O_3 and SiO_2. The sludge ash could undergo a Pozzolans reaction with cal-

Table 1
Results of TCLP for the sludge and the fly ash (mg/l)

Heavy metals	Cd	Cr	Cu	Ni	Pb	Zn
Sludge ash	0.03	0.01	11.9	0.06	0.02	2.07
Fly ash	0.01	0.11	0.12	0.10	0.02	0.50
Allowable leached concentration	1.0	0.5	15.0	–	5.0	25.0

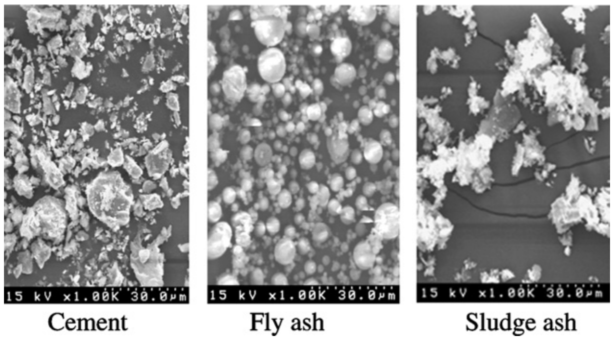

Fig. 1. SEM pictures for different materials.

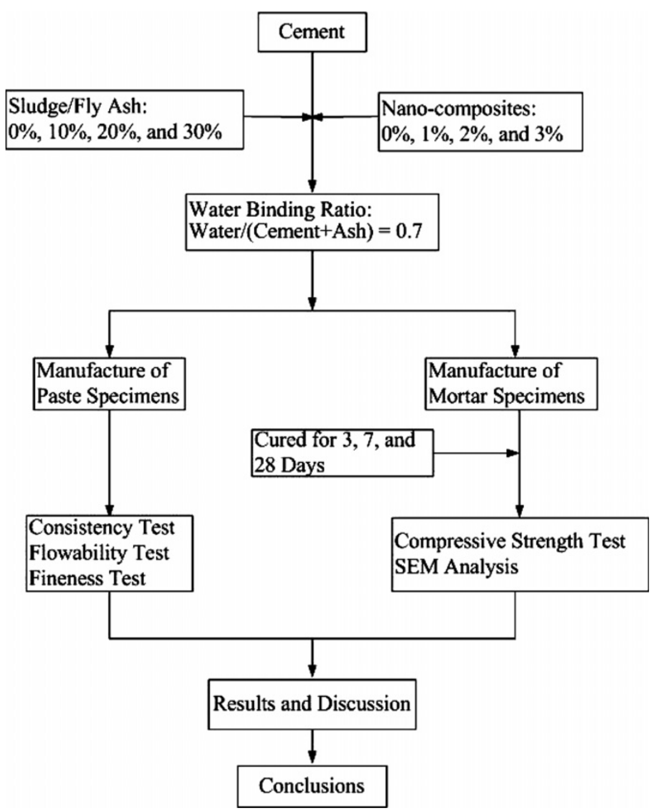

Fig. 2. Flowchart of the study.

Table 2
Chemical composition of the sludge ash, fly ash and Portland cement

Composition	Sludge ash	Fly ash	Portland cement
SiO_2 (%)	64.6	73.5	21.2
Al_2O_3 (%)	23.1	21.6	5.9
Fe_2O_3 (%)	1.31	0.12	3.7
MgO (%)	1.1	0.6	2.3
CaO (%)	8.6	2.9	63.7
Cu (mg/kg)	0.5	0.03	0.1
Ni (mg/kg)	0.7	0.66	0.1

cium hydroxide, $Ca(OH)_2$, through the hydration reaction of the cement, to produce C–S–H and C–A–H gel in the calcium silicate hydrates, and become solidified as well as develop strength. On the other hand, the fly ash contained about 95% pozzolanic materials and Al_2O_3 and SiO_2 were also the major components, but with higher characteristic peak values during analysis, which implies that fly ash is richer in these two minerals. The SiO_2, and Al_2O_3 in the fly ash could react with $Ca(OH)_2$ in the cement paste to produce crystalline C–A–H and low density C–S–H gel, which can fill up micro pores in mortar, increasing the bond strength between the interface of aggregates, and reducing the permeability as well as improving the durability of the mortar.

3.2. SEM analysis

In order to understand the influences of sewage sludge ash, fly ash, and nano-SiO_2 on the micro-structures of the mortar, samples obtained from the central part of mortar specimens were analyzed by SEM, particularly focusing on hydrates of the C–S–H gel (spiculate ball shapes) and monosulfoaluminate crystals (hexagonal sheet shapes). Fig. 3 shows SEM pictures for specimens with different amounts of sludge/fly ash and 0% nano-SiO_2 added when cured at seven days. When part of the cement was replaced by sludge/fly ash, the C–S–H gel became relatively fine and poor agglomeration was observed. Smaller monosulfoaluminate crystals were also seen. Moreover, incomplete hydration cakes were noticed (circled) in the SEM pictures. This implies that sludge/fly ash interfered with the growth of hydration and crystallization, which resulted in a lower early compressive strength of the mortar specimens. In Fig. 4, SEM pictures for specimens with 0% and 1% nano-SiO_2 added when cured for seven days are shown. It is noticed that hydrates of C–S–H gel and monosulfoaluminate crystals increased with the addition of nano-SiO_2, which indicates that nano-SiO_2 can improve the hydration of sludge/fly ash mortar specimens. Further, crystallizations produced by nano-SiO_2 and $Ca(OH)_2$ can fill up the pores shown in the shadowy areas of the pictures.

3.3. Fineness test

Fineness of the cement (3367 cm^2/g), sludge ash (3920 cm^2/g), fly ash (3727 cm^2/g), and their mixtures was measured with a Blaine gas permeation meter, and the effects of nano-SiO_2 on the mixtures were observed using the same equipment. As stated above, sludge ash particles are porous with irregular shapes. Hence, more pores cause a higher fineness when compared with the same volume of cement. Again, fly ash particles occur in ball shapes, which are relatively hard to compact with other particles when compared to the bulk irregular shapes of cement. Hence, the fineness of fly ash is higher than that of cement. Fig. 5 illustrates the fineness of mortar specimens with different amounts of sludge/fly ash and nano-SiO_2 added. When more sludge/fly ash with higher fineness was mixed in the mortar, more pores were created in the mixture. Therefore, the fineness of the mortar specimens increases when higher amounts of cement were replaced by sludge/fly ash. It is also noted in the figure that the addition of

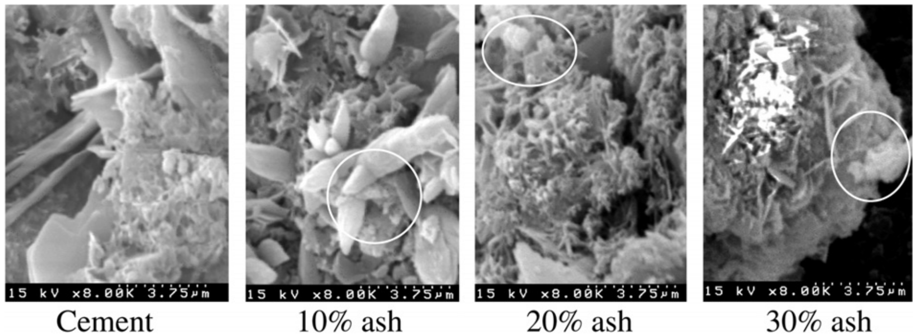

Fig. 3. SEM pictures for the specimens with different amount of sludge/fly ash and 0% nano-SiO_2 added when cured for seven days.

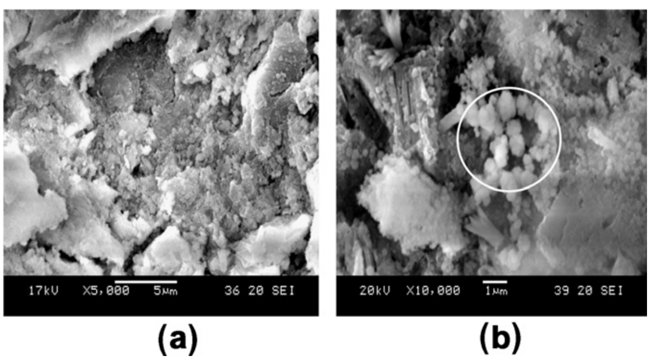

Fig. 4. Microstructures for the specimens with (a) 0% and (b) 1% of nano-SiO_2 added when cured for seven days.

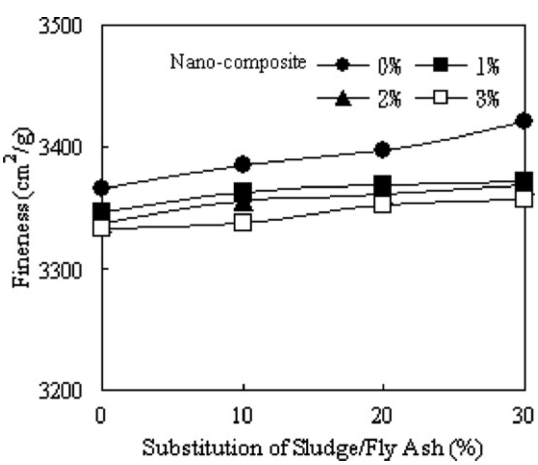

Fig. 5. Fineness for the specimens with different amounts of sludge/fly ash and nano-SiO_2 added.

nano-SiO_2 can reduce the fineness of mortar specimens. Amounts reduced ranging between 20 and 30 cm^2/g. The finer particles of nano-SiO_2 can lower the specific surface area of mortar specimens by filling up pores among sludge/fly ash particles, as well as gaps generated from rearranging particles of different materials in the mortar.

3.4. Consistency test

Fig. 6 shows the relationship between consistency, sludge/fly ash, and nano-SiO_2. Results indicate that consistencies of the mortar specimens increase when additional amounts of cement are replaced by sludge/fly ash and nano-SiO_2. Amounts increased range from 5 to 7% and 2 to 3% for the additions of sludge/fly ash and nano-SiO_2, respectively. The increase in consistency is due to the improvement of water adsorption by the paste, since a large amount of gaps in the paste were created by the porous irregular shapes of the sludge ash and rearrangement of sludge/fly ash particles. Moreover, because of high specific surface areas, nano-SiO_2 would tend to integrate with the water at the early stage of mixing, which also resulted in a higher consistency of the mortar.

3.5. Condensation time

In order to investigate the influences of sludge/fly ash and nano-SiO_2 on the hardened properties of mortar specimens, tests of initial-set time and final-set time were performed. As shown in Fig. 7, the initial setting and final setting time for pure cement paste are 140 and 230 min, respectively. However, 200 and 270 min of initial and final setting time are observed for cement paste with 10% sludge/fly ash added. This implies that the addition of sludge/fly ash can extend the initial and final setting time

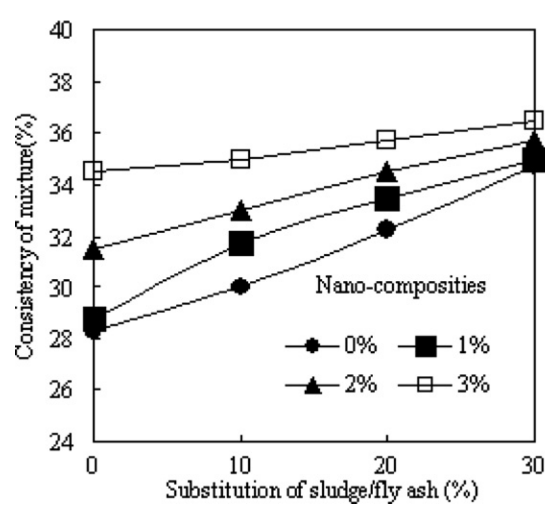

Fig. 6. Consistency of the specimens with different amounts of sludge/fly ash and nano-SiO_2 added.

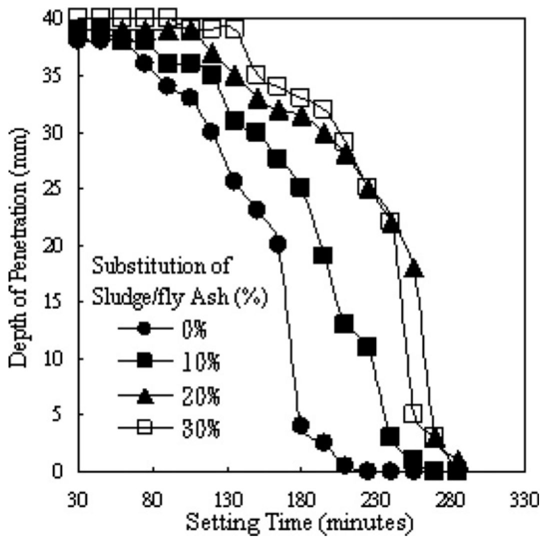

Fig. 7. Setting time for the specimens with different amounts of sludge/fly ash and 0% nano-SiO_2 added.

of the paste and the amount of time extended increases with increasing amounts of sludge/fly ash. The average increase in minutes ranges from 60 to 120 and 60 to 80 for initial and final settings, respectively. The component of alumina in the sludge/fly ash could block the production of C–S–H gel, which leads to the delay in the initial hydration of cement. As a result, initial and final setting times of the paste are delayed. Fig. 8 displays different settlement times for specimens with different amounts of sludge/fly ash and 1% nano-SiO_2 added. With the help of nano-SiO_2, the initial and final setting times for paste with 10% sludge/fly ash added are 140 and 170 min, respectively. Note that this is at least 60 to 100 min earlier than those with no nano-SiO_2 added. Although the nano-additives can affect the workability of the mortar, the initial-set time and final-set time for specimens with nano-SiO_2 added are close to those mortar samples made by type I Portland cement. Therefore, nano-SiO_2 as an additive has a slight effect on the workability of the mortar without the addition of sludge/fly ash in the practical engineering applications.

3.6. Compressive strength tests

Figs. 9 to 11 show the relationship between the compressive strength and different amounts of sludge/fly ash and nano-SiO_2 added for mortar specimens cured at different ages. In general, it is noticed that the compressive strength of the mortar specimens are reduced as increasing amounts of sludge/fly ash are added. As more cement is replaced by sludge/fly ash, less compressive strengths are observed. The average amount of strength reduction falls between 5 and 10 kg/cm^2. The reduction in early compressive strength is mainly due to the immature pozzolanic reaction in the mortar and the preventive growth of C–S–H gel caused by components in sludge/fly ash. Further, the addition of nano-SiO_2 is helpful to the improvement of compressive strength in the mortar specimens. Reductions in early compressive strength for specimens with nano-SiO_2 added were slower and the average increases in compressive strengths were between 3 and 5 kg/cm^2 when compared with those specimens with no nano-SiO_2 added. This indicates that nano-SiO_2 can improve the effects of sludge/fly ash on the development of the early strength of mortar specimens. The addition of nano-SiO_2 can enhance the nucleation of CH, as well as reduce the toxic influences of silicate and aluminate dissolved from the sludge/fly ash throughout the progression of hydrate nucleation and crystal growth in CH and C–S–H. Consequently, nano-SiO_2 can raise the hydrate reaction of cement and produce more hydration crystals, which can be observed from the SEM pictures.

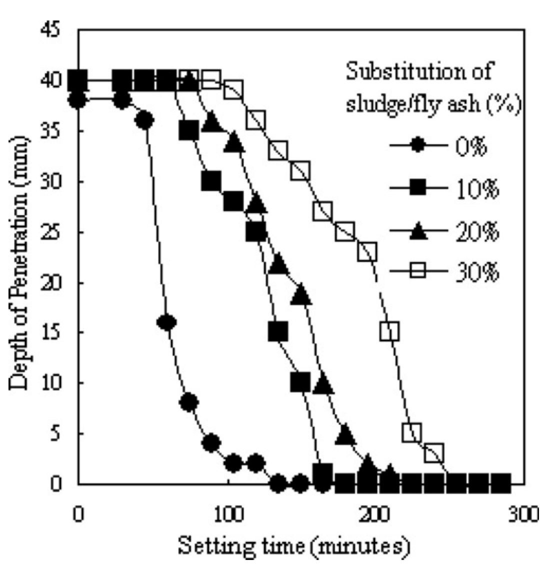

Fig. 8. Setting time for the specimens with different amounts of sludge/fly ash and 1% nano-SiO_2 added.

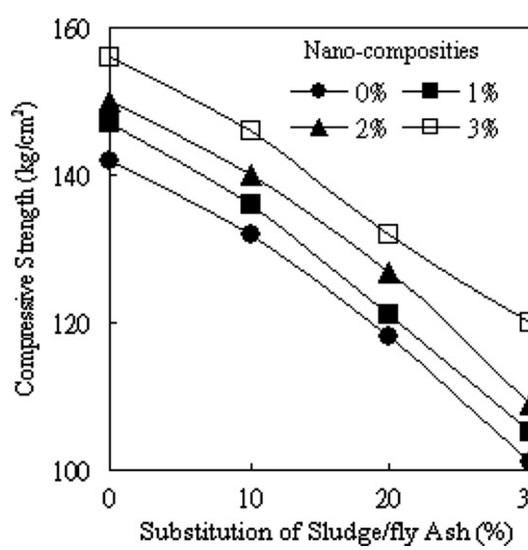

Fig. 9. Compressive strength for the specimens with different amounts of sludge/fly ash and nano-SiO_2 added and cured for three days.

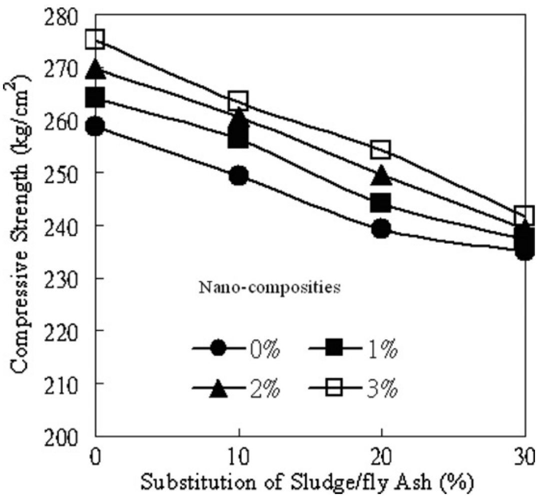

Fig. 10. Compressive strength for the specimens with different amounts of sludge/fly ash and nano-SiO_2 added and cured for seven days.

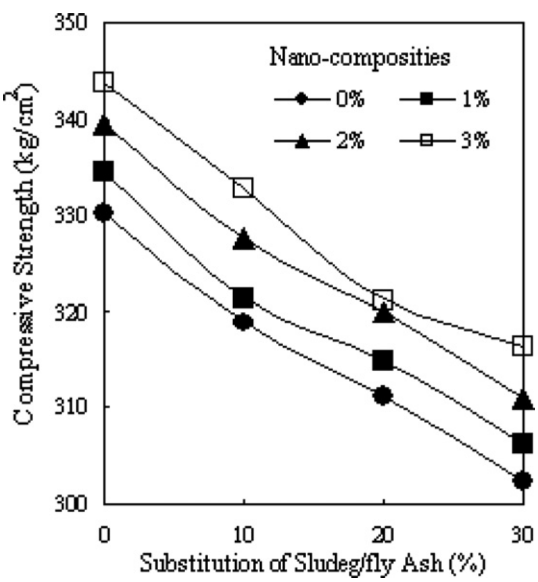

Fig. 11. Compressive strength for the specimens with different amounts of sludge/fly ash and nano-SiO_2 added and cured for 28 days.

3.7. MIP and TEM analysis

Table 3 shows the results obtained from MIP for specimens with 20% sludge/fly ash and different amounts of nano-SiO_2 added. When cured for three days, due to the fact that sludge/fly ash was not fully participating in the initial hydration of cement, the pore size observed in specimens increased from 63 to 136 nm. This indicates that, at early hydration times, the presence of sludge/fly ash can increase pore size. However, the pore size reduced to 129 nm at seven curing days, which implied that more mature hydration can improve pore size. Table 3 also shows that, with different substitutions of nano-SiO_2 additives, the pore size of sludge/fly ash mortar gradually decreased from 136.48 nm (0% nano-SiO_2) to 114.76 nm (3% nano-SiO_2) and from 129.18 nm (0% nano-SiO_2) to 110.90 nm (3% nano-SiO_2) for specimens cured at three and seven days, respectively. Hence, nano-SiO_2 additives can fill pores in sludge/fly ash mortar. Furthermore, in order to study the effects of nano-SiO_2 on sludge/fly ash mortar, TEM was carried out on 20% sludge/fly ash mortar with 0% and 2% nano-SiO_2 added. Fig. 12 shows that the micro-structure of specimens with 2% nano-SiO_2 was denser than that of specimens with no nano-SiO_2 added. Hence, the addition of nano-SiO_2 to sludge/fly ash mortar can accelerate the hydration reaction and improve properties of the specimens.

Table 3
Pore sizes for the specimens with 20% sludge/fly ash and different amounts of nano-SiO_2 added

	Pore sizes (nm)				
Nano-SiO_2	0%		1%	2%	3%
Sludge/fly ash:	0%	20%	20%	20%	20%
Curing time					
Three days	63.0	136.48	126.65	120.21	114.76
Seven days	55.4	129.18	121.30	115.40	110.90

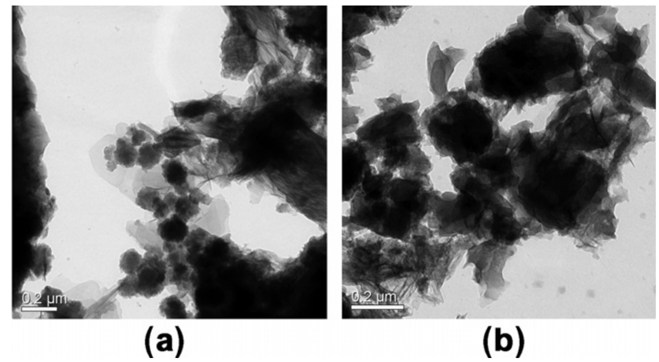

Fig. 12. TEM results for 20% sludge/fly ash mortar cured for seven days with (a) 0% and (b) 2% nano-SiO_2 added.

4. Conclusions

In this study, the influences of different amounts of nano-SiO_2 additives on the physical properties and micro-structures of incinerated sewage sludge/fly ash mortar were investigated. Results based on the experimental data are summarized as follows:

1. Sludge/fly ash can make the crystals of the cement hydration product finer. Further, after nano-SiO_2 was added, crystals increased and aluminate dissolved from the sludge/fly ash throughout the progression of hydrates nucleation and crystal growth in C–S–H gel. The addition of nano-SiO_2 to sludge/fly ash mortar can also accelerate the hydration reaction and improve the properties of specimens.
2. Sludge/fly ash can lengthen the initial and final setting time of paste; the amount of the time delay increases with the increase in sludge/fly ash. However, the addition of nano-SiO_2 can improve the initial and final setting times for paste with sludge/fly ash added. Further, the initial-

set time and final-set time for specimens with nano-SiO_2 added were close to those of mortar samples made by type I Portland cement. Results obtained from MIP and TEM indicate that the addition of nano-SiO_2 to the sludge/fly ash mortar can accelerate the hydration reaction and improve the properties of specimens.

3. Compressive strengths of sludge/fly ash mortar specimens are reduced. Yet, nano-SiO_2 can increase the compressive strength for sludge/fly ash mortar specimens. The addition of nano-SiO_2 to mortar can improve the negative effects caused by sludge/fly ash on the early strength of mortar.

Acknowledgement

This study was partly supported by the National Science Council of Republic of China (Grant No. NSC 94-2211-E-214-003).

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