The application of waterworks sludge ash to stabilize the volume of cement paste

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ABSTRACT

In order to extend the recycling of waterworks sludge to engineering applications, this paper addresses the influence of nano-SiO₂ on incinerated waterworks sludge ash (IWSA) cement paste attacked by sulfate. Tests were performed such as length measurement for volume change, compressive strength, weight loss, and micro-structural testing using scanning electron microscopy (SEM). The results indicate that when a portion of the cement in the paste was replaced by IWSA, the IWSA diluted the cementitious material C₃A, and filled the capillary pores in the hardened paste. Moreover, since IWSA has potential pozzolanic activity, it can chemically react with Ca(OH)₂ crystals in the paste and can consequently improve the resistance of the paste to sulfate attack. Test results also show that due to the fully developed pozzolanic effect of IWSA, the major reaction products of sulfate attack, gypsum and ettringite, were clearly reduced. Hence, the expansion rate in length decreased with the increase of IWSA replacement. Furthermore, the addition of nano-SiO₂ to IWSA cement paste can also reduce the length expansion rate.

Key words | cement, nano-material, paste, sulfate attack, waterworks sludge

INTRODUCTION

Waterworks sludge is the by-product of water treatment plants. After incineration, it contains a certain amount of aluminium and silicon minerals which provides it with potential activity. During the hydration process, the pozzolanic activity of waterworks sludge ash develops slowly, and the early strength of cementitious material supplemented with waterworks sludge ash also progresses slowly. However, the long term strength is higher than that of pozzolanic cementitious material. If the early strength and durability of waterworks sludge concrete could be improved, this material would be beneficial for engineering applications. Kuo et al. (2006) suggested that the early strength of waterworks sludge ash cement paste was improved by adding small amount of nano-SiO₂.

Mortar or concrete damage by sulfate is a complicated chemical process and is also accompanied by a physical process in some severe environmental conditions. Furthermore, since both mortar and concrete are porous materials, they would be saturated by a high concentration of sulfate solution when attacked by sulfate. This implies that the sulfate ion can infiltrate inside the cementitious material and react with hydrate products which lead to an expansion, splitting and peeling of mortar or concrete, resulting in a decrease in strength over time. The chemical and physical corrasions can be seen in the attack of sulfate on cementitious materials (Lea 1980; Mindess & Young 1981; Mehta & Monteiro 1993; Irassar et al. 2000; Irassar et al. 2003). The physical erosion is mainly caused by crystallized salts. For example, NaSO₄ and MgSO₄ absorb water to form NaSO₄·10H₂O and MgSO₄·7H₂O. As a result, the amount of crystallization water increased and the volume expands by 4 to 5 times the original volume. This leads to an increase of the crystallization pressure and the formation of micro-cracks in cementitious materials.
followed by deterioration. On the other hand, gypsum and ettringite are the products of chemical corrosion. Figures (1-3) are the chemical equations for gypsum and ettringite, respectively.

\[
\begin{align*}
\text{Ca(OH)}_2 + \text{NaSO}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O} + \text{NaOH} \quad (1) \\
\text{Ca(OH)}_2 + \text{MgSO}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O} \\
& + \text{Mg(OH)}_2 \\
3\text{CaSO}_4\cdot 2\text{H}_2\text{O} + 3\text{CaO}\cdot\text{Al}_2\text{O}_3 + 26\text{H}_2\text{O} & \rightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O} \quad (3)
\end{align*}
\]

Gypsum would expand the volume of the cementitious material, and the expansion pressure would lead to a decrease in the strength and rigidity of the cementitious material and decreased durability. Moreover, ettringite would also cause a volume expansion which would cause expansion pressure and damage by splitting. After the split of the concrete, sulfate ions could easily infiltrate inside the concrete, which would severely deteriorate the concrete.

The C-S-H gel occupies 50% to 70% of the solid volume of the cement paste and is the main source of the strength of the paste. As the cement paste is attacked by sulfate, the amount of Ca(OH)$_2$ reduces and the pH value becomes lower. In order to maintain the alkalinity inside the material, the decalcified decomposition of the C-S-H gel would occur. Hence, the paste, mortar, or concrete would lose its adherence and its strength would be reduced. This suggests that the durability of cementitious materials are reduced when attacked by sulfate. This article studies the
influences of different amounts of incinerated waterworks sludge ash (IWSA) and nano-SiO2 additives on the durability of cement paste when the paste specimens are left in sulfate solution for various curing times.

MATERIALS AND METHODS

Materials

The three main components used in this study are listed below.

1. Portland cement: Locally made type I Portland cement was used in this study. The specific gravity and Blaine specific surface area were 3.15 and 500 m²/kg, respectively.

2. Waterworks sludge: Dewatered waterworks sludge samples were obtained from a local waterworks treatment plant near Kaohsiung City in Taiwan. The samples were first oven-dried at 105 °C and incinerated at 800 °C before being ground into ash to pass through a #200 sieve. The physical properties are shown in Table 1.

3. Nano-SiO2: The nano-SiO2 was bought from a local materials company in Kaohsiung City, and its chemical components and physical properties are shown in Table 1.

Test parameters

The following parameters were used in this study.

1. Water/binder ratio: 0.45.

2. Amounts of incinerated waterworks sludge ash (IWSA) replacement by weight: 0%, 10%, 20%, and 30%.

3. Amounts of nano-SiO2 replacement: 0%, 1%, 2%, and 3%. Note that the total amount of replacement is fixed. For example, for the replacement of IWSA at 10%, 9% IWSA was mixed with 1% nano-SiO2, 8% IWSA was mixed with 2% nano-SiO2, etc.

4. Specimen size: 5 cm × 5 cm × 5 cm and 2.54 cm × 2.54 cm.

5. Curing conditions: Specimens were de-molded 24 hours after casting and were then cured in saturated lime water for 27 days. After 27 days, part of the specimens were taken out and placed in 4.2% magnesium sulfate (MgSO4) solutions until testing.

6. Curing time: 28, 60, 90, 120, and 210 days.

Methods

Tests performed in this study are described below.


2. Variation in length: Specimen length was measured by a comparator at each designated curing age as regulated by ASTM C187 standards.

3. Variation in weight: The specimens’ weight was obtained at each designated curing age.

4. Micro-analysis: After compressive strength tests were carried out at each designated curing age, a portion of the specimens were randomly selected and kept in a methanol solution to terminate the hydration in paste. Then, the study of micro-structural development was proceeded.

5. Effects of sulfate attack

(a) Coefficient of corrosion resistance

The coefficient of corrosion resistance is defined in Figure (4), where R is the coefficient of corrosion resistance, \( \sigma_s \) is the compressive strength of IWSA cement paste cured in 4.2% magnesium sulfate solutions, and \( \sigma_w \) is the compressive strength of IWSA cement paste cured in water. Note that both strengths were obtained at the same curing age.

\[
R = \frac{\sigma_s}{\sigma_w} \tag{4}
\]

(b) Weight change

The weight change is defined in Figure (5), where \( M \) is the weight change, \( W_0 \) is the mass of the specimens.
cured for 28 days, and $W_t$ is the mass of specimens cured for $t$ days in magnesium sulfate solutions.

\[
M = \frac{W_t - W_0}{W_0} \times 100\% \quad (5)
\]

(c) Change in length

The change in length is defined in Figure (6), where $L$ is the length change, $L_0$ is the length of the specimens cured for 28 days, and $L_t$ is the length of specimens cured for $t$ days in magnesium sulfate solutions.

\[
L = \frac{L_t - L_0}{L_0} \times 100\% \quad (6)
\]

RESULTS AND DISCUSSION

Influences of nano-SiO$_2$ and IWSA on compressive strength of sulfate attacked cement paste

Figure 1 shows the variations in compressive strength for paste specimens with IWSA replacement cured in saturated lime water. In general, since the pozzolanic effect of IWSA was not fully developed, the compressive strength of specimens decreased with the increasing amount of IWSA replacement. However, as the curing age was extended, the pozzolanic reaction gradually progressed and led to an increase in compressive strength. The compressive strengths of specimens with different amounts of IWSA replaced were about 89% to 95% of the control group when cured for 60 days. This implies that there was a filling effect and there was no cementitious reaction of IWSA in the mixtures at early stages of curing. When cured at 210 days, the pozzolanic effect was well developed and the compressive strengths of the 10% and 20% IWSA specimens were higher than that of the control group. Furthermore, there was a smaller difference in strength between the 30% IWSA specimens and the control group.

The compressive strength of specimens attacked by 4.2% magnesium sulfate solution at different curing ages is shown in Figure 2. After incubation in magnesium sulfate

Figure 4 | The influence of IWSA content on the coefficient of corrosion resistance of paste stored in 4.2% MgSO$_4$ solution at different attack times.

Figure 5 | The influence of nano-SiO$_2$ on the coefficient of corrosion resistance of 10% IWSA paste placed in 4.2% MgSO$_4$ solution for different attack times.

Figure 6 | The variations of weight change for paste specimens with IWSA replacement cured in 4.2% magnesium sulfate solution.
solution for more than one month, the physical etching produced by crystallization pressure and the chemical etching produced by gypsum and ettringite led to an expansion inside the paste specimens of the control group, and the compressive strength decreased with increasing of curing age. Hence, the durability of specimens was decreased by sulfate. However, when part of the cement was replaced by IWSA, the amount of cementitious material, C\textsubscript{3}A, was diluted, which resulted in a reduction of the expansion materials such as ettringite generated. Moreover, the addition of IWSA could consume a large amount of Ca(OH)\textsubscript{2} in the pozzolanic reaction. This would lower the amount of Ca(OH)\textsubscript{2}, which would indirectly reduce the amount of alkaline cementitious material in the paste. Therefore, the generation and stability of ettringite became more difficult. Furthermore, the IWAS particles can fill pores in cementitious paste. Through the pozzolanic reaction in IWSA, the C-S-H gel can also fill capillary pores, leading a finer pore structure of cementitious hydrates. Hence, the permeability resistance in paste was improved. As a result, the resistance to sulfate attack became stronger when more IWSA was added (between 0% and 30%) and the pozzolanic reaction was also better developed, especially for the IWSA cement paste specimens cured for longer periods of time.

The addition of nano-SiO\textsubscript{2} can also improve the resistance to sulfate attack of IWSA cement paste, as shown in Figure 3. More Ca(OH)\textsubscript{2} bonded to the surface of nano-SiO\textsubscript{2}, which led to the production of a C-S-H gel. Consequently, the amount of Ca(OH)\textsubscript{2} was reduced and the Ca(OH)\textsubscript{2} crystals became finer (Kuo et al. 2006). As a result, the resistance to sulfate attack was enhanced by the addition of nano-SiO\textsubscript{2}, especially for specimens with 2% nano-SiO\textsubscript{2} added.

Figure 4 shows the influence of IWSA content on the coefficient of corrosion resistance of paste stored in 4.2% MgSO\textsubscript{4} solution for different attack times. The coefficient of the control group began to decrease after it was attacked by 4.2% MgSO\textsubscript{4} solution for one month. The coefficient can only reach 80% of its original value after attack for six months. However, when 10% of the cement was replaced by IWSA, the coefficient was 103% of the original value after attack for one month, 110% after four months, and 101% after six months. Furthermore, the coefficient was 108% of the original value for specimens with 30% IWSA replacement after attack for one month, 122% after three months, and 116% after six months. Hence, the coefficients increased with an increasing amount of IWSA replacement, and a decrease in the coefficient for each IWSA replacement was observed after attack for four months. Figure 5 shows the influence of IWSA and nano-SiO\textsubscript{2} content on the coefficient of corrosion resistance of paste placed in 4.2% MgSO\textsubscript{4} solution for different attack times (IWSA content: 10%). As stated above, the coefficient of corrosion resistance for specimens with IWSA replacement was higher than that of the control group. The addition of nano-SiO\textsubscript{2} had a slight influence on the coefficient for 10% IWSA cement paste, especially for the replacements of 1% and 2%. However, the coefficient was 108% of the original value for specimens with 5% nano-SiO\textsubscript{2} added after attack for one month, 117% after two months, and 102% after six months. This suggests that when a sufficient amount of nano-SiO\textsubscript{2} was uniformly mixed and spread on the surface of cement particles, the pore size of the cementitious material was reduced and the structure of the paste became denser. Hence, with the help of the coupled actions of the IWSA and nano-SiO\textsubscript{2}, the coefficient of corrosion resistance of paste stored in 4.2% MgSO\textsubscript{4} solution can be effectively improved.

**Influences of nano-SiO\textsubscript{2} and IWSA on the weight variation of sulfate-attacked cement paste**

As sulfate attacked the cement paste, the sulfate reacted with aluminate mineral in the cement paste to produce expansive products such as ettringite and Aft. Moreover, the MgSO\textsubscript{4} would react with Aft in the presence of Ca(OH)\textsubscript{2} to produce gypsum. The gypsum filled in the pores inside the paste which led to an increase of weight for the paste. The weight increased with increasing curing times (from 1.76% for one month to 3.08% for six months), as shown in Figure 6.

After part of the cement was replaced by IWSA in paste specimens, the IWSA consumed a large amount of Ca(OH)\textsubscript{2} to proceed with the pozzolanic reaction, which led to a decrease in Ca(OH)\textsubscript{2}. The IWSA also caused a reduction in C\textsubscript{3}A, which resulted in a decrease of the hydrate product, ettringite. Hence, when sulfate attacked the
IWSA cement paste, the number of response factors in the paste reduced, and the related products of gypsum and Mg(OH)\(_2\) were also decreased. For example, the weight of the 10% IWSA paste increased from 1.28% to 2.39% for curing times of one and six months, and from 1.03% to 2.11% for the 30% IWSA paste. This implies that the weight increase for pastes with different amounts of IWSA replacement was less than that of the control group. The weight also decreased with increasing amounts of IWSA replacement, as shown in Figure 6.

The influence of nano-SiO\(_2\) on the weight change of 10% IWSA cement paste is displayed in Figure 7. As stated above, Ca(OH)\(_2\) bonded to the surface of nano-SiO\(_2\). Consequently, the amount of Ca(OH)\(_2\) was reduced and the Ca(OH)\(_2\) crystal was refined. Therefore, it became harder to produce and stabilize the ettringite. Moreover, the particle filling effect of nano-SiO\(_2\) made it difficult for the sulfate ion to attack the paste. Test results indicate that the weight of paste with 1% nano-SiO\(_2\) added increased from 1.02% to 1.98% for curing times of one and six months; from 0.83% to 1.71% for paste with 3% nano-SiO\(_2\) added. This suggests that with the help of the coupled actions of IWSA and nano-SiO\(_2\), the increase of the weight of the paste was clearly reduced.

Influences of nano-SiO\(_2\) and IWSA on the length variation of sulfate-attacked cement paste

Since pure cement paste contained a higher amount of Al\(_2\)O\(_3\) and produced more aluminate mineral, a large amount of aluminate hydrates were observed under sulfate attack. The expansion rate of pure paste specimens increased with increasing attack time, e.g. 0.194% for specimens cured for one month and 0.395% for six months. A sudden increase was noticed after curing for three months, as shown in Figure 8.

With the help of the pozzolanic reaction in IWSA, the amount of CH reduced and the restraint on the length variation for IWSA cement paste became evident as shown in Figure 8. The increased expansion rate of 10% IWSA paste was 0.146% for one month curing and 0.337% for six months, and for paste with 30% IWSA replacement, the rate was 0.141% for one month curing and 0.215% for six months. The expansion rates obtained for IWSA paste were less than the control group, and the restraint on the length variation was better for higher amounts of ISWA replacement, e.g. 20% and 30%. As shown in Figure 8, the increases in length for both 20% and 30% IWSA replacement pastes were less than that of the control group and than 10% IWSA paste cured for four months.

The influence of nano-SiO\(_2\) on the length variation of 10% IWSA cement paste is displayed in Figure 9. Since nano-SiO\(_2\) can produce a physical filling effect and reduce the amount of Ca(OH)\(_2\) in the paste, the specimens were resistant to attack by sulfate ions. Hence, with the help of the coupled actions of IWSA and nano-SiO\(_2\), a greater reduction was seen in the expansion rate. As shown in

![Figure 7](https://iwaponline.com/wst/article-pdf/57/2/243/438492/243.pdf) The influence of nano-SiO\(_2\) on the weight change of 10% IWSA cement paste placed in 4.2% MgSO\(_4\) solution for different attack times.

![Figure 8](https://iwaponline.com/wst/article-pdf/57/2/243/438492/243.pdf) The variations of the rate of length expansion for paste specimens with IWSA replacement cured in 4.2% magnesium sulfate solution.
Figure 9, the expansion rate in the length of the paste with 1% nano-SiO$_2$ added increased from 0.143% to 0.313% between curing times of one and six months, and it increased from 0.139% to 0.255% for paste with 3% nano-SiO$_2$ added. These results were less than that of the control group and than the paste with 10% IWSA replacement. Note that the expansion rate in the length of paste with 3% nano-SiO$_2$ added after curing for six months was 65% of the control group and 75% of the paste with 10% IWSA replacement. Although the expansion rate of the length of the paste increased when part of the cement was replaced by IWSA and nano-SiO$_2$, the increases were less than that of pure cement paste. This suggests that IWSA and nano-SiO$_2$ replacement can improve the resistance of the paste to sulfate attack, which is especially beneficial for those paste specimens cured for longer periods of time.

Figure 9 | The influence of nano-SiO$_2$ on the length expansion rate for 10% IWSA cement paste placed in 4.2% MgSO$_4$ solution for different attack times.

Figure 10 | SEM pictures of paste specimens with (a) 0%, (b) 10%, (c) 20%, and (d) 30% IWSA replacement after curing for one month (4500 x).
Influences of IWSA on the micro-structure of sulfate-attacked cement paste

Figure 10(a) to (d) show the SEM pictures for paste specimens with 0%, 10%, 20%, and 30% IWSA replacement after curing for one month. Large amounts of ettringite and gypsum columnar crystals were observed in the paste as shown in Figure 10(a), and the ettringite crystal was the main product. As the time of paste soaking in 4.2% MgSO₄ increased and the paste was further attacked by sulfate, the expansive products such as ettringite filled pores inside the paste. Hence, expansive stress was produced at the interface of the pores and ettringite, which resulted in micro-structural damage inside the paste. Eventually, this would lead to micro-structural damage of the paste specimens. However, the IWSA replacement in the paste reduced the amount of ettringite crystal produced, as shown in Figure 10(b) to (d).

CONCLUSIONS

This study investigates the influences of different amounts of IWSA and nano-SiO₂ replacements on the physical properties and micro-structures of sulfate-attacked cement paste. Results based on the experimental data can be summarized as follows.

1. When a portion of the cement was replaced by IWSA in paste, the IWSA had a physical effects on the paste by diluting the cementitious material, C₃A, and filling the capillary pores in hardened paste. Moreover, since IWSA has potential pozzolanic activity, it can have a chemical reaction with Ca(OH)₂ crystal in the paste, which improves the resistance of the paste attack by 4.2% MgSO₄.

2. Nano-SiO₂ can uniformly mix and spread on the surface of cement particles, and with the help of the particle’s filling effect, the pore size of the cementitious material was reduced and the structure of the paste became more dense. Furthermore, more Ca(OH)₂ was bonded to the surface of nano-SiO₂, which led to the production of a C-S-H gel. Consequently, the amount of Ca(OH)₂ was reduced and the Ca(OH)₂ crystal was refined. This implies that the coupled actions of IWSA and nano-SiO₂ improved the resistance of the paste to sulfate attack.

3. The expansive product ettringite was observed in the SEM pictures of paste attacked by sulfate.

REFERENCES


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