THE EFFECT OF SULFATE-RICH SEWAGE SLUDGE ASH ON THE VOLUME DEFORMATION AND MICORSTRUCTURE OF CEMENT PASTE

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Abstract

Sewage sludge ash (SSA) is the combustion residue of the sewage sludge obtained from wastewater treatment plants. In China, SSA normally contains high content of SO_3, which may cause detrimental effect on the volume stability of cement-based materials. This study investigated the effect of sulfate-rich SSA (SR-SSA) on the volume deformation and the microstructure of cement paste. The autogenous shrinkage and drying shrinkage of cement pastes incorporating SR-SSA were tested. The microstructure of cement pastes incorporating SR-SSA was studied with mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM). The results show that the addition of SR-SSA reduced the autogenous shrinkage of cement paste, but increased the drying shrinkage of cement paste. Hence the addition of SSA may cause more serious cracking problem of cement-based materials under drying conditions, but could inhibit the cracking under sealed condition. The SEM and MIP investigations showed that, when SR-SSA was presented, more ettringite was generated in the cement paste and the porosity of the cement paste became higher.

Keywords: cement paste, sulfate, sewage sludge ash, shrinkage, microstructure

1. INTRODUCTION

Due to the increase in sludge production all over the world, the recycling use of SSA has attracted a lot of interest from the government and industry. One of the promising strategies of recycling SSA is to use it as cement replacement in cement-based materials [1,2]. Cement industry is well known for its ability to absorb and recycle different kinds of wastes. If the wastes have binding properties, they could reduce the use of Portland cement, which is indirectly beneficial for the environment because of the reduction of CO_2 emissions.

Many studies have attempted to explore the recycling use of sewage sludge ash (SSA) in cement-based materials. The addition of SSA would reduce the workability of cement-based materials [3,4]. According to the review of Lynn et al. [1], the average rates of decrease in workability of cement mortar and concrete slump were 6% and 12% respectively for every 10% cement replaced by SSA. Meanwhile, the addition of SSA would retard the initial and final setting of cement-based materials [5]. In addition, the improved content of SSA would cause the reduction of the mechanical properties of cement-based materials [6-8]. Hence, when recycling SSA in cement-based materials, its content should be controlled at a low level for safety reasons. Mix design adjustments, such as increasing cement content, using the water-reducing agent to reduce the water to binder ratio, adding the nano-materials and increasing the fineness of SSA, could be made to improve the mechanical properties the SSA-bleneded cement-based materials [1]. The addition of SSA would also increase the porosity of the cement-based materials [9,10], and thus reduce the carbonation resistance of cement-based materials [10]. Limited studies on the effect of SSA on the volume deformation of the cement-based materials showed that, the drying shrinkage could be reduced when the SSA content was higher than 20%, while the effect of SSA is negligible if the SSA content was lower (i.e. less than 20%) [9-11].

In China, high content of sulfate is normally present in the SSA. Some studies have shown that sulfates presented in SSA are not reactive in cement-based materials [9]. The effect of sulfate-rich SSA (SR-SSA) on the properties of the cement-based materials is not fully studied so far. The presence of high content of SO_3 may cause the formation of ettringite, which would lead to the expansion and cracking of the cement-based materials. Cement degradation caused by internal sulfate attack have been observed when sulfate-rich aggregates are used in concrete [12,13].

The aim of this study was to evaluate the recycling potential of SR-SSA in cement-based materials. The main concern of this paper is to study the effect of SR-SSA on the volume deformation of the cement paste. Moreover, the microstructure of the cement paste with SR-SSA was detected with mercury intrusion porosimetry (MIP), X-ray diffraction (XRD) and scanning electron microscope (SEM).

2. MATERIALS AND METHODS

2.1 Materials and mix proportions

The raw materials for this study included ordinary Portland cement (P·O 42.5) and SR-SSA. The particle size distribution of cement and SR-SSA measured with Mastersizer 3000 laser diffraction system are shown in Figure1. The size of SR-SSA was mainly in the ranges from 1 μm to 100 μm and was a little bigger than the cement particles. The average particle sizes for cement and SR-SSA were 16.3 μm and 24.1 μm respectively. The chemical compositions of cement and SSA are shown in Table 1. The mass content of SO_3 in SR-SSA was 23.2%.

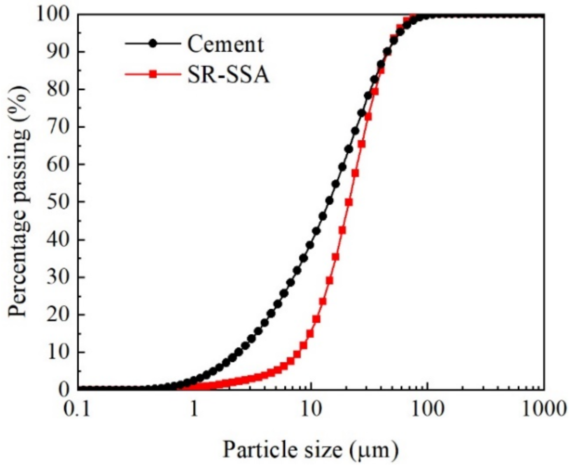


Figure 1: Particle size distributions of cement and SR-SSA

Table 1: Chemical compositions of OPC and SSA

	Cement (wt%)	SSA (wt%)
CaO	55.10	33.19
SiO_2	21.4	12.84
Al_2O_3	6.30	7.00
Fe_2O_3	4.30	15.89
SO_3	2.41	23.20
MgO	2.80	0.90
Na_2O	0.23	0.85
P_2O_5	3.61	---
ZnO	0.69	---
TiO_2	0.42	0.51
K_2O	0.46	0.45

In this study, cement pastes incorporating 0%, 5%, 10% and 15% SR-SSA were prepared, and the water to binder ratio (w/b) of the cement pastes was 0.4. Table 2 shows the mix proportions of the cement pastes.

Table 2: Mix proportions of the pastes

Sample	Cement (wt.%)	SR-SSA (wt.%)	w/b
Control	100	0	0.4
5%SSA	95	5	
10%SSA	90	10	
15%SSA	85	15	

2.2 Autogenous shrinkage and drying shrinkage

The autogenous shrinkage tests were performed according to ASTM C1698-09(2014)[14]. The cement pastes were cast in corrugated plastic tubes. The length change of the corrugated plastic tube was measured with digital dial gauges. The length measurements were started at the time of finial setting, and stopped at the age of 50d. The length data were recorded every 30 minutes with a data acquisition system.

The drying shrinkage tests were performed based on ASTM C596-09(2017) [15]. The size of the cement paste specimens was 25 mm × 25 mm× 285 mm. The specimens were demolded at 1d, and cured in water at 20±2℃ for 2 days. After that，the specimens were placed in a drying chamber with a temperature of 20±3℃ and a relative humidity of 50±4%. The length change of the specimens were monitored with displacement sensors, and the data were recorded with a data log till the age of 28d.

2.3 SEM and MIP

The crashed cement paste pieces were used as the samples for MIP and SEM tests. MIP was used to investigate the pore structure of cement pastes. The tests were carried out with Micromeritics AutoPore IV 9500. The contact angle was set to be 130° and the detected pore size was ranged from 7 nm to 200 nm. The samples at different ages were immersed in the acetone to stop the hydration, and dried in vacuum oven at 50℃ for 3 days before MIP tests. SEM was applied to detect the morphology of the fracture surface of the cement pastes. The samples were coated with gold before SEM observation, and secondary electron images were taken at the fractured surfaces.

3. RESULTS AND DISCUSSION

3.1 Autogenous and drying shrinkage

The autogenous shrinkage of cement pastes with different SR-SSA contents is shown in Figure 2. It can be seen that the addition of SR-SSA led to the expansion of the cement paste for some time depending on the contents of SR-SSA. The more SR-SSA resulted in the longer expensive duration and the higher expensive strain of the cement pastes. The cement paste with 5%, 10% and 15% SR-SSA expanded for 1.0 day, 3.0 days and 18.3 days respectively, and their highest expensive strains were 146.6 με, 505.2 με and 1264.4 με respectively. After the expansion, the cement pastes specimens shrank continuously until the end the test. The control cement paste did not show any expansion at early age and shrank all the time. At the age of 50d, the shrinkage strains of control, 5%SSA, 10%SSA and 15%SSA cement pastes were -1.387.4 με, -1159.7 με, -651.8 με and 452.8 με respectively. The ultimate shrinkage strain was lowered if more SR-SSA was added. 5% SR-SSA slightly reduced the autogenous shrinkage of cement paste, while 10% SR-SSA obviously reduced the autogenous shrinkage of cement paste. If 15% SR-SSA was added, the volume of the cement paste was always higher than the initial state during the tests. The addition of SR-SSA might be capable of reducing the cracking potential of the cement-based materials caused by the autogenous shrinkage, but if a high amount of SR-SSA was used, the cracking caused by the excessive expansion might be occur.

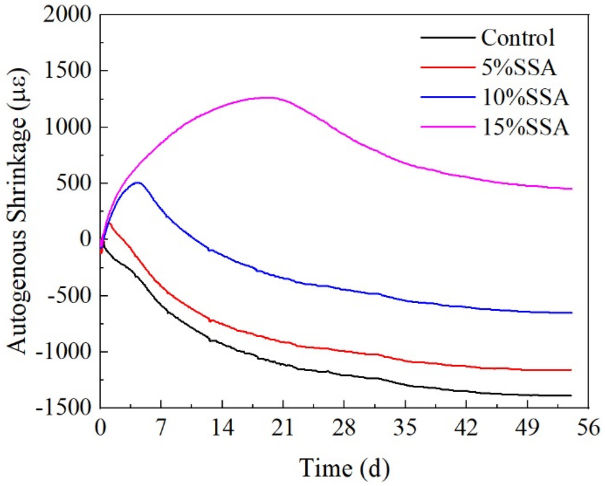


Figure 2: Autogenous shrinkage of cement pastes containing different amounts of SR-SSA (The positive value is for expansion and the negative value is for shrinkage)

The drying shrinkage of cement pastes with different SR-SSA contents is shown in Figure 3. The drying shrinkage increased very fast at the beginning of the tests, and became almost stable after the age of 24 days. When the amount of SR-SSA was 5%, the drying shrinkage of cement paste is similar to that of the control cement paste. When the amount of SR-SSA was 10% and 15%, the drying shrinkage of the cement pastes was lower than that of the control cement paste at early ages. Although the shrinkage caused by the drying was predominate at early ages, the expansion induced by the addition of SR-SSA was still effective. Hence at early age, the addition of SR-SSA reduced the drying shrinkage of cement paste, and the more SR-SSA was added, the lower drying shrinkage was. But afterwards, in spite of the expansion caused by the SR-SSA, the drying shrinkage of cement paste with 10% and 15% SR-SSA became higher than the control cement paste. This should be related to the difference in microstructure of cement pastes with and without SR-SSA. The early age expansion of 15%SSA was higher than 10%SSA, so the total drying shrinkage at 28d of 15%SSA was lower than 10%SSA.

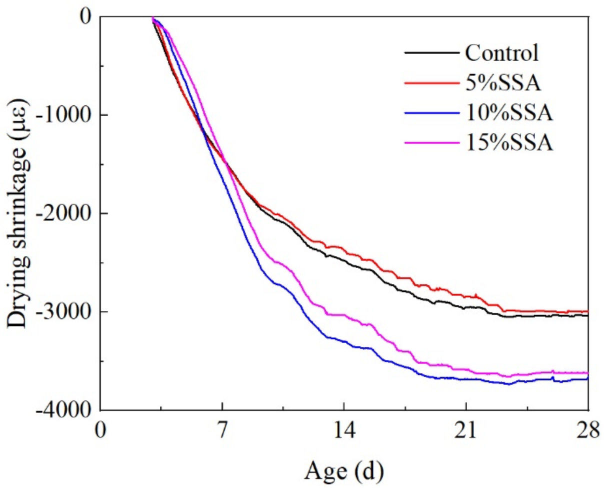
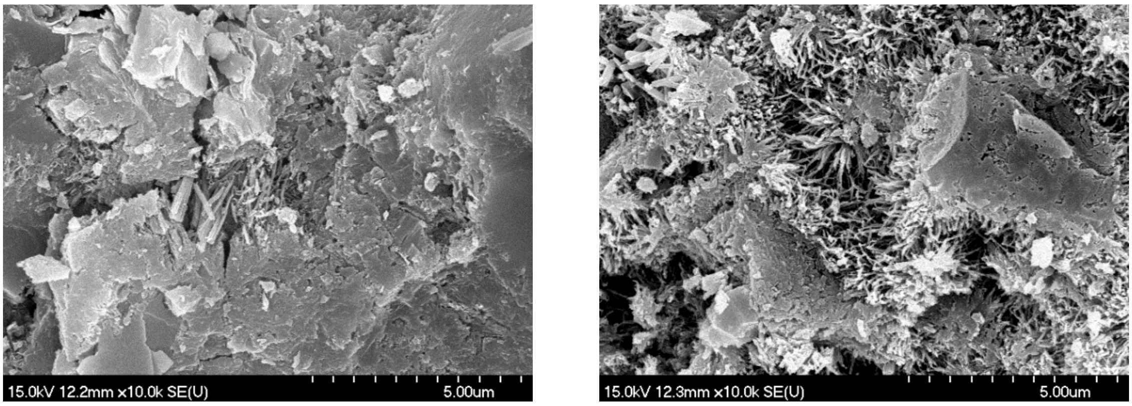


Figure 3: Drying shrinkage of cement pastes containing different amounts of SR-SSA

3.2 Microstructure

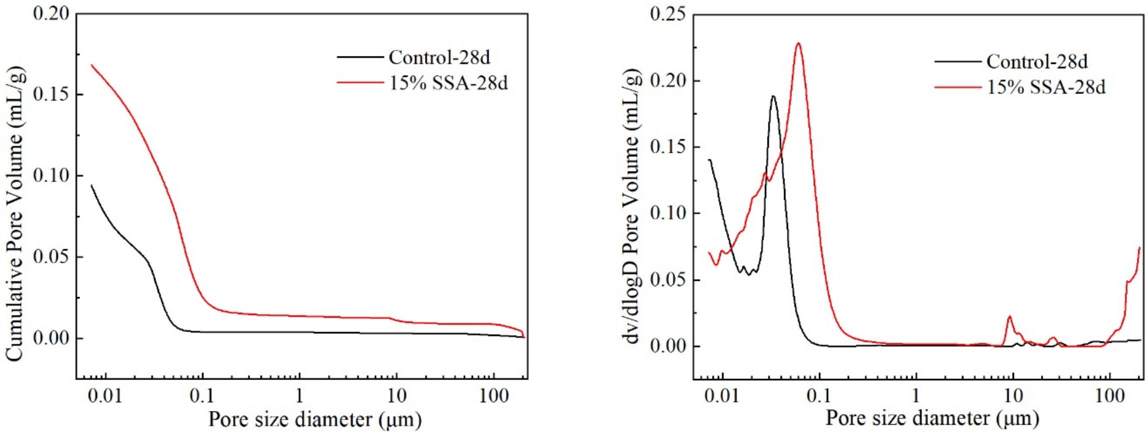
SEM was used to observe the morphology of cement pastes with and without SR-SSA. The AFt phase (ettringite) was the main concern of the observation. These images could help to explore the influence of SR-SSA on the microstructure of the cement paste. The SEM images of the Control cement paste and 15%SSA cement paste at the age of 7 days are shown in Figure 4. Needle-like AFt could be found in the control cement paste, but the amount of AFt was relative low. In the cement paste with 15% SR-SSA, more AFt could be fould. Moreover, the cement paste with 15% SR-SSA seemed more porous than the control cement paste.



(a) **(b)**

Figure 4: SEM images of (a) Control cement paste (b) cement paste with 15% SR-SSA

MIP was applied to detect the pore structure of cement pastes with and without SR-SSA. Figure 5 shows the cumulative intrusion curve and the pore size distribution of the control cement paste and the cement paste with 15% SR-SSA at 28 days. The total porosity of cement paste with 15% SR-SSA was higher than the control cement paste at 28 days. Moreover, the most probable pore size of cement paste with 15% SR-SSA was much bigger than the control cement paste. Due to the higher porosity of cement paste with 15% SR-SSA, the drying shrinkage was also increased, which may be detrimental to the cracking resistance of cement paste under drying conditions.



(a) the cumulative intrusion curve **(b) particle size distribution**

Figure 5: pore structures of the control cement paste and cement paste with 15% SR-SSA at 28d

4. CONCLUSIONS

- The addition of SR-SSA caused obvious expansion of the cement paste, hence the autogenous shrinkage was reduced with the increase of the content of SR-SSA in cement paste.
- The addition of 5% SR-SSA did not show much influence on the drying shrinkage of cement. The addition of 10% and 15% of SR-SSA reduced the drying shrinkage at the early age, but increased the drying shrinkage at the late age.
- The SEM and MIP investigations showed that, when SSA was presented, more ettringite was generated in the cement paste and the porosity of the cement paste became higher.
- To replace 5% cement with SR-SSA don't show much influence on the volume deformation of the cement, hence from the volume deformation point of view it is feasible to prepare cement-based materials with up to 5% SR-SSA.

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