Effect of cornstalk ash on the microstructure of cement-based material under sulfate attack

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Abstract. Cornstalk ash is one of the most abundant, renewable and green supplementary cementitious materials, which is an effective approach to decrease the amount of cement in concrete structures for reducing CO\textsubscript{2} emission. In this paper, the influence of mechanical properties and microstructure of the mortar with different proportion of corn stalk ash under sulfate attack are investigated, and it can provide necessary theoretical basis and practical guiding significance for practical engineering. A series of measurements are used to characterize the effect of the corn straw ash of cement hydration products, such as XRD, hydration heat and SEM. It is concluded that corn stalk ash can partly replace cement without reducing the compressive strength and enhance the compressive strength under sulfate attack, the data of TG shows that the content of the calcium dioxide is obviously decreased with corn straw ash.

1. Introduction

In agricultural-based countries such as China and India, emissions of gaseous and particulate pollutants from open burning of agricultural residues are one of the most important sources of air pollution[1]. The biomass power plant, among other alternatives, is widely used for the disposal of biomass wastes, in order to solve the environmental problems[2]. According to research, the cornstalk ash containing much active silica and alumina possesses good pozzolanic activity such that it can be potentially reused as supplementary cementitious material to partially replace cement, gradually[3-5].

Sulfate erosion is an important factor for the durability of cement-based materials. And it mainly comes from sodium, magnesium, calcium sulfate in soil or underground, which is a complex coupling of a chemical reaction and physical process[6]. The gypsum resulted from the reaction of sodium sulfate and calcium hydroxide reacts with calcium aluminate hydrate to produce ettringite, while the process causes expansion and destruction of cement-based materials[7]. On the other hand, the replacement of calcium ions by magnesium ions in C-S-H gel makes the gel become M-S-H gel with the weak performance[8].

Previous work has done for the sulfate attack resistance of cement-based materials. The expansion mechanism and expansion character of cement mortar with different water to cement ratio under
sulfate attack was studied[9]. It was reported that the addition of the traditional supplementary cementitious materials could improve the mechanical properties[10,11].

In the view of the sulfate erosion resistance of cement-based materials mixed with SCM, numerous researches have been done. However, the effect on the sulfate erosion resistance of cement-based materials is different for the differences in composition and structure. In this paper, the microstructure of cement pastes containing cornstalk ash was studied.

2. Materials and Methods

2.1 Raw materials

The cornstalks in this study were obtained from Heilongjiang Province, northeast of China. The chopped cornstalk was calcined at 600°C for 6h in a muffle, and the cornstalk ash was ground manually and sieved with 200 mesh. And the chemical composition determined by XRF was shown in Table 1. The specific surface area of cornstalk ash and fly ash were 331.99 m²/kg and 29079 m²/kg, respectively. The particle size distribution was measured by laser diffraction (Beckman Counter LS 13 320) shown in Fig. 1. The microstructures of sieved cornstalk ash and fly ash were shown in Fig. 2. It could be seen that cornstalk ash exhibited various shapes such as flocculent, flaky and fibroid while fly ash was almost globular. The chemical composition of cornstalk ash and fly ash was measured by XRF, as shown in Table 1.

![Fig 1. The particle size distribution of cornstalk ash and fly ash sample.](image)

| Composition | Cornstalk ash | Fly ash |
|-------------|---------------|---------|
| SiO₂        | 64.80         | 50.61   |
| Al₂O₃       | 9.42          | 35.77   |
| K₂O         | 6.50          | 0.45    |
| MgO         | 5.06          | 0.36    |
| CaO         | 4.95          | 3.43    |
| Fe₂O₃       | 2.88          | 4.52    |
| SO₃         | 0.65          | 1.13    |
| Cl          | 1.50          | 0.00    |
| ROX         | 4.24          | 3.73    |
| LOF         | 1.54          | 3.31    |
Fig 2. SEM micrograph of cornstalk ash and fly ash.

2.2 Sample Preparation
The mixture proportion of the cement-based mortar and paste with the water to binder ratio of 0.4 was shown in Table 2. The bars of the cement-based mortars with 40 mm × 40 mm× 160 mm were prepared, and the pastes were cast into the cylindrical molds (50 mL) and sealed with the lids and then cured under a temperature of 21℃ and relative humidity of more than 95% for 28 days. After demolding, the mortars and pastes were put into the solution of sodium sulfate with a mass fraction of 5 wt.% for 56 days.

2.3 Compressive strength
The compressive strength of cement mortars was tested by CMT5504 Electromechanical Universal Testing Machine and CDT 1305-2 Electromechanical Compression Testing Machine (MTS Systems (China) Corporation, China).

2.4 X-ray Diffraction
To determine the phase composition qualitatively, Rigaku Ultima IV with a 40 kV X-ray tube was used in this test. The 1.5g samples were flattened for testing. Cooper target was adopted with a wavelength of 0.154 nm. And the diffraction angle changed from 5-80° with 0.01° of step size.

2.5 Thermogravimetry (TG)
The cement pastes for thermogravimetric analysis were stopped hydration by 2-propanol and dried in vacuum for 1 day. Then the samples were ground manually and sieved with 200 mesh. The TA Instruments, SDT-Q600, was performed to study the changes in hydration products in the samples between 30 °C and 800 °C.

Table 2. Mixture proportions of mortars and paste.

| Samples | Cement (wt.%) | Fly ash (wt.%) | Cornstalk ash (wt.%) | Sand to binder ratio | Water reducing agent (wt.%) for mortar |
|---------|---------------|----------------|----------------------|---------------------|---------------------------------------|
| CSA0    | 85            | 15             | 0                    | 3                   | 0.3                                   |
| CSA2    | 83            | 15             | 2                    | 3                   | 0.3                                   |
| CSA4    | 81            | 15             | 4                    | 3                   | 0.3                                   |
| CSA6    | 79            | 15             | 6                    | 3                   | 0.3                                   |
| CSA8    | 77            | 15             | 8                    | 3                   | 0.3                                   |

3. Results and discussion

3.1 Compressive strength
The effects of cornstalk ash on the compressive strength of the cement-based mortars were shown in Fig 3. The compressive strengths of all samples were higher than 50 MPa. With the increase of cornstalk ash content, there was a slight increase in compressive strength for samples containing cornstalk ash. And the compressive strengths of samples mixed with cornstalk ash were lower by
5MPa than that of the control group, while that of sample CSA4 was higher than the control group under sulfate attack. It can be concluded that the addition of cornstalk ash can improve the mechanical property of cement-based material under sulfate attack.

![Fig 3. Effect of cornstalk ash on compressive strength under sulfate attack.](image1)

![Fig 4. Effect of cornstalk ash on chemical composition under sulfate attack.](image2)

### 3.2 XRD Patterns

To further investigate the interactive mechanism between cornstalk ash and compressive strength under sulfate attack, the chemical composition was studied. The XRD patterns of the crystalline phases of the cement paste with cornstalk ash were shown in Fig. 4.

It could be seen that the addition of cornstalk ash changed the phase composition of hardened pastes. The intensity of calcium hydroxide decreased for samples mixed cornstalk ash. The peak intensity of ettringite increased with the increase of cornstalk ash and aluminate product (gismondine, CaAl$_2$Si$_2$O$_8$·4H$_2$O) appeared in the samples mixed with cornstalk ash. It means the mixture of cornstalk ash could promote the consumption of calcium hydroxide reacting with sulfate ion to form more aluminate products under sulfate attack. And it can be found that there were peaks of quartz which came from the calcined cornstalk ash. And it could be deduced that more aluminate products caused expansion and cracking so that there was a decrease in compressive strength combined with the previous data. And more C-S-H gel formed from the pozzolanic reaction of cornstalk ash with calcium hydroxide could be the reason for the small difference in compressive strength.

### 3.3 Analysis of TG

The results of thermal analysis in relation to the addition of cornstalk ash under sulfate attack were shown in Fig. 5. The process of thermogravimetry can be divided into two stages according to the temperature. In the first stage from room temperature to 300 °C, C-S-H gel, calcium aluminate hydrate, AFm, and another hydration production were disintegrated. And the second stage concludes two parts, one from 350~550°C is the decomposition of calcium hydroxide, the other one higher than 600 °C is the decomposition of carbonate. The samples were not carbonized except control group. It can be seen from the figure that there was a significant difference between the control group and samples with cornstalk ash. The peak of the control group was much clearer than that of samples incorporating cornstalk ash. And with the increase of cornstalk ash content, the peak of calcium hydroxide got flat gradually due to the pozzolanic reaction or reaction with sulfate ions.
Fig 5. DTG curves of different samples under sulfate attack.

3.4 Morphology of samples
After soaking for 56 days, the morphology of different samples was captured in Fig. 6. There were much needle-like and short ettringite connected with each other, layered calcium hydroxide and globular fly ash for the control group (Fig. 6 (a)). Much monosulfate (AFm) was found in Fig. 6 (b) for the sample incorporation of 4 wt.% cornstalk ash, while the surface of the sample was much denser than that of the control group. It could be inferred that porosity might be increased and calcium hydroxide reacted with the sulfate ions to form more AFm. On the other hand, cornstalk ash could be filler particles and the gel from pozzolanic reaction could also cover the disadvantage of the increasing porosity. And with the increase of cornstalk ash, various hydration products were cemented together, which resulted in a more compacted structure. It can be concluded that the incorporation of cornstalk ash could compact the cement-based materials under sulfate attack.

Fig 6. Morphology of different samples under sulfate attack for 56 days.
4. Summary
Differential scanning calorimetry offers the possibility of studying the effect of cornstalk ash on the microstructure of cement-based material under sulfate attack.

1. Cornstalk ash possesses certain pozzolanic activity and the cooperation of cornstalk ash and fly ash can enhance the compressive strength of cement-based materials under sulfate attack.

2. The presence of cornstalk ash could improve the composition and compactness of cement-based materials under sulfate attack to some extent.

3. The pozzolanic reaction of cornstalk ash played a role to form gel for samples under sulfate attack.

Acknowledgments
Funding for this project was provided by the National Natural Science Foundation of China (No. 51802112 and No. 51761145023). Supports from the 111 Project of International Corporation on Advanced Cement-based Materials (No. D17001) is much appreciated. The funding is also supported by the Opening Project of State Key Laboratory of Green Building Materials and by the Taishan Scholars Program.

References
[1] ZHANG, H., HU, J., QI, Y., LI, C., CHEN, J., WANG, X., HE, J., WANG, S., HAO, J., ZHANG, L., ZHANG, L., ZHANG, Y., LI, R., WANG, S., CHAI, F. 2017. Emission characterization, environmental impact, and control measure of PM2.5 emitted from agricultural crop residue burning in China. Journal of Cleaner Production, 149: 629-635.
[2] EISENTRAUT A, B. A. 2012. Technology Roadmap Bioenergy for Heat and Power. International Energy Agency.
[3] AKSOĞAN, O., BINICI, H., ORTLEK, E. 2016. Durability of concrete made by partial replacement of fine aggregate by colemanite and barite and cement by ashes of corn stalk, wheat straw and sunflower stalk ashes. Construction and Building Materials, 106: 253-263.
[4] RAHEEM, A. A., ADEDOKUN, S. I., ADEYINKA, E. A., ADEWOLE, B. V. 2017. Application of Corn Stalk Ash as Partial Replacement for Cement in the Production of Interlocking Paving Stones. International Journal of Engineering Research in Africa, 30: 85-93.
[5] BINICI, H., Ortlek E. 2015. Engineering properties of concrete made with cholemanite, barite, corn stalk, wheat straw and sunflower stalk ash. European Journal of Engineering and Technology, 3.
[6] FENG, P., LIU, J., SHE, W., HONG, J. 2018. A model investigation of the mechanisms of external sulfate attack on portland cement binders. Construction and Building Materials, 175: 629-642.
[7] ADESANYA, D. A., RAHEEM, A. A. 2010. A study of the permeability and acid attack of corn cob ash blended cements. Construction and Building Materials, 24: 403-409.
[8] SANTHANAM, M., COHEN, M. D., OLEK, J. 2003. Mechanism of sulfate attack: a fresh look: Part 2. Proposed mechanisms. Cement and Concrete Research, 33: 341-346.
[9] ZHU, J., JIANG, M., CHEN, J. 2008. Equivalent model of expansion of cement mortar under sulphate erosion. Acta Mechanica Solida Sinica, 21: 327-332.
[10] LEE, S. T., MOON, H. Y., SWAMY, R. N. 2005. Sulfate attack and role of silica fume in resisting strength loss. Cement and Concrete Composites, 27: 65-76.
[11] GUO, Z., WANG, Y., HOU, P., SHAO, Y., ZUO, X., LI, Q., XIE, N., CHENG, X. 2019. Comparison study on the sulfate attack resistivity of cement-based materials modified with nanoSiO2 and conventional SCMs: Mechanical strength and volume stability. Construction and Building Materials, 211: 556-570.