Resistivity Measurements to Study the Early Chemical and Autogenous Shrinkage of a Binary Alkali-activated Slag-metakaolin System

Chunyan Zhu¹², Yu Zhou¹², Yaoxiang Guo¹², Zhiwen Wen¹², Liangwei Zhang¹², Zhihan Wang¹², Yuan Fang¹²* and Wujian Long¹²

¹ College of Civil and Transportation Engineering, Shenzhen University, Shenzhen, 518060, China
² Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, College of Civil and Transportation Engineering, Shenzhen University, Shenzhen 518060, China

*Corresponding author’s e-mail: yuanfang@szu.edu.cn

Abstract. Alkali-activated slag-metakaolin (AASM) has a lower shrinkage than alkali-activated slag, but its complex shrinkage behaviour remains elusive. In this paper, resistivity measurements were used to monitor the early chemical shrinkage and autogenous shrinkage evolution of AASM (containing 10%, 30%, 50%, or 70% metakaolin). The MK content greatly affected the development of autogenous shrinkage of AASM, and the specimens with 50% MK showed the lowest autogenous shrinkage of 49%. The presence of MK delayed the formation of calcium aluminosilicate hydrate (C-A-S-H) gels (the activation products of slag), thus mitigating autogenous shrinkage. A functional relationship between early autogenous shrinkage and resistivity was established, which showed that resistivity can be used to evaluate and predict the early autogenous shrinkage of AASM.

1. Introduction
The shrinkage of cementitious materials causes concrete to crack, allowing water and harmful ions to enter its interior, thereby affecting the durability of the concrete[1, 2]. As Alkali-activated materials, especially alkali-activate slag, have notably higher shrinkages than Ordinary Portland Cement (OPC), the alleviation of such phenomena is of crucial importance. The Alkali-activated slag-metakaolin binary system (AASM), on the other hand, has lower shrinkage than that of alkali-activated slag, whereas the shrinkage of the latter is 3 to 6 times of that of the OPC[3-5]. Due to the potential complementary advantages of metakaolin and slag behaving under alkaline conditions, AASM gains early mechanical strength mainly from slag, and exhibits reduced shrinkages due to the addition of metakaolin[6]. Hence, metakaolin can be perceived as an effective shrinkage reducing agent without compromising too much of the mechanical strengths for this more commercially viable binary system.

The microstructure of AASM is also much more complicated and evolves over time, which makes it difficult to study its autogenous shrinkage and its mechanism. The electrodeless resistivity meter invented by Li et al. can sensitively monitor the early microstructure development of cement-based materials[7]. Based on the principle of transformer, the electrodeless resistivity meter eliminates the electrode used in traditional methods and avoids the gas release problem induced by water electrolysis around the electrode caused by contact problems[8]. This method will be used to study the early...
autogenous shrinkage of AASM in this research, which provides a new perspective for the monitoring of autogenous shrinkage evolution.

2. Raw materials and experimental procedures

2.1. Raw materials and mixing proportions

The main compositions of blast furnace slag in this study are CaO (41.5%) and SiO$_2$ (32.6%), and metakaolin (MK) are Al$_2$O$_3$ (42.54%) and SiO$_2$ (49.67%). The activator used was sodium water glass with a modulus of 2.0 and a density of 1.44 g/cm$^3$.

The water-solid ratio (w/s) divided by binder quality (g)) of AASM prepared in this study was fixed at 0.4, and the alkali content was 5%. The specific mixing ratio design is seen in Table 1.

| Sample | MK  | slag | w/s | [m(Na$_2$O)/m(solid)] % |
|--------|-----|------|-----|-------------------------|
| MK10   | 10  | 90   | 0.4 | 5                       |
| MK30   | 30  | 70   | 0.4 | 5                       |
| MK50   | 50  | 50   | 0.4 | 5                       |
| MK70   | 70  | 30   | 0.4 | 5                       |

2.2. Testing methods

Chemical shrinkage test was conducted based on ASTM C1608 2012 standard[9]. Autogenous shrinkage was measured by the improved absolute volume method proposed by Lura et al.[10]. The test devices were placed in a water bath at constant temperature (20±3°C).

The resistivity of AASM paste was measured with a Electrodeless CCR-III resistivity measuring instrument. The temperature was 20±2°C and the relative humidity was 95%. The experiment was carried out with a seal to prevent moisture loss. The change in resistivity within 24 hours of the AASM slurry in the hardening process was continuously recorded, and the data recording system was enabled with a data reading time at an interval of 10 seconds.

3. Results and discussion

3.1. Autogenous shrinkage within 24 hours

The evolution of chemical shrinkage and autogenous shrinkage of the AASM over 24 hours is plotted in Figure 1 and Figure 2. The chemical shrinkage of all samples exhibits a consistent trend, in which it increases upon extending the reaction time. The addition of MK significantly decreased the chemical shrinkage of the AASM, and a higher MK content led to a greater reduction in chemical shrinkage. At 24 hours, compared with MK10, the chemical shrinkage of MK30, MK50 and MK70 decreased by 28.5%, 40.7% and 49.9%, respectively.

The overall evolution trend of autogenous shrinkage in Figure 2 is consistent with chemical shrinkage, that is, the autogenous shrinkage of all samples increased upon increasing the hardening time. The addition of MK could reduce the autogenous shrinkage of the paste. Compared with MK10, the shrinkage of MK30, MK50 and MK70 was 25.6%, 33.0% and 30.9% lower, respectively.
Figure 1. Chemical shrinkage of AASM within 24 hours.

Figure 2. Autogenous shrinkage of AASM within 24 hours.

3.2. Electrical resistivity evolution in 24 hours

Figure 3 shows the resistivity curves of cementitious materials with different MK content within 24 hours. All samples show a similar resistivity variation trend as a whole, that is, resistivity declined first and then rose.

In the earliest dissolution stage, the resistivity dropped. After the contact between the liquid phase and the solid phase, the hydroxide ions in water glass began to attack the Ca-O, Si-O and Al-O bonds in the slag particles, breaking them and releasing (H_2SiO_4)^-, (H_3SiO_4)^-, (H_4AlO_4)^- and Ca^{2+}[11]. MK particles also gradually decomposed into Si(OH)_3^- and Al(OH)_4^- under the condition of high pH[12]. Due to the increase of ion concentration in the solution, the current formed by charged ions increased accordingly, and the resistivity decreased rapidly.

After the resistivity decreased to the minimum value and began to rise, which was attributed to the fact that the cluster reaction products gradually formed a closed pore network, which blocked the migration path of ions and increased the resistivity. With the passage of time, the growth rate of resistivity changes.
3.3. Correlation between resistivity and autogenous shrinkage

Resistivity monitors the physical and chemical changes inside the paste, and these microscopic changes are accompanied by the development of macroscopic autogenous shrinkage. Based on this understanding, resistivity can be used as an indirect index of autogenous shrinkage. According to the above analysis, the qualitative correlation between autogenous shrinkage and resistivity can be determined, that is, the resistivity is positively correlated with autogenous shrinkage. Therefore, it is feasible to further establish the mathematical relationship between resistivity and autogenous shrinkage.

4. Conclusions

The work of this study was to analyze the autogenous shrinkage properties of alkali-activated metakaolin-slag binary system by resistivity. The following conclusions were drawn:

1. From 10% to 50%, the more MK was added, the more autogenous shrinkage was decreased. Until the MK content increased to 70%, the autogenous shrinkage was no longer reduced, but was slightly larger than the sample with MK content of 50%.

2. There is a correlation between resistivity and autogenous shrinkage of AASM. Autogenous shrinkage causes the change of pore structure, and pore structure is the main influence factor of resistivity, so resistivity can reflect the evolution of autogenous shrinkage.
Acknowledgments

This work was supported by the Chinese National Natural Science Foundation [Project No.52078300], [Project No.51508337], [Project No.51538007]; Natural Science Foundation of Guangdong Province [Project No.2019A1515012014]; Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering (SZU) [Project No.2020B1212060074]; Natural Science Foundation of SZU [Project No.8270000091].

References

[1] Al-Kamyani Z, Guadagnini M, Pilakoutas K. (2019) Impact of shrinkage on crack width and deflections of reinforced concrete beams with and without steel fibres. Eng Struct., 181:387-96.
[2] Li KF, Li L. (2019) Crack-altered durability properties and performance of structural concretes. Cement Concrete Res., 124.
[3] Neto AAM, Cincotto MA, Repette W. (2008) Drying and autogenous shrinkage of pastes and mortars with activated slag cement. Cement Concrete Res., 38(4):565-74.
[4] Cartwright C, Rajabipour F, Radlinska A. (2015) Shrinkage Characteristics of Alkali-Activated Slag Cements. J Mater Civil Eng., 27(7).
[5] Matalkah F, Salem T, Shaafaey M, Soroushian P. (2019) Drying shrinkage of alkali activated binders cured at room temperature. Constr Build Mater., 201:563-70.
[6] Burciaga-Diaz O, Escalante-Garcia JL, Arellano-Aguilar R, Gorokhovsky A. (2010) Statistical Analysis of Strength Development as a Function of Various Parameters on Activated Metakaolin/Slag Cements. J Am Ceram Soc., 93(2):541-7.
[7] Li ZCWB, HK), Li, Wenlai (Clear Water Bay, HK). (2003) Contactless, transformer-based measurement of the resistivity of materials. United States: The Hong Kong University of Science and Technology (Hong Kong, HK).
[8] Li ZJ, Wei XS, Li WL. (2003) Preliminary interpretation of Portland cement hydration process using resistivity measurements. Aci Mater J., 100(3):253-7.
[9] C1608-17 A. (2017) Standard Test Method for Chemical Shrinkage of Hydraulic Cement Paste.
[10] Lura P, Jensen OM. (2007) Measuring techniques for autogenous strain of cement paste. Mater Struct., 40(4):431-40.
[11] Heikal M, Nassar MY, El-Sayed G, Ibrahim SM. (2014) Physico-chemical, mechanical, microstructure and durability characteristics of alkali activated Egyptian slag. Constr Build Mater., 69:60-72.
[12] Weng L, Sagoe-Crentsil K. (2007) Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part I - Low Si/Al ratio systems. Journal of Materials Science., 42(9):2997-3006.