Effects of reactivity of MgO expansive agent on its performance in cement-based materials and an improvement of the evaluating method of MEA reactivity

Fengze Cao [a], Miao Miao [b], Peiyu Yan [a,*]

[a] Department of Civil Engineering, Tsinghua University, Beijing 100084, China
[b] School of Material Science and Engineering, Chongqing University, Chongqing 400044, China

HIGHLIGHTS

- Study the reactivity of industrially produced MgO expansive agents.
- Propose a new evaluating method on the reactivity of MgO expansive agents.
- Generalize the influence of reacting speed on morphology, workability and expansion properties.

ARTICLE INFO

ABSTRACT

Determined by calcining temperature and duration, reactivity of MgO is a dominating role of the hydration and expansive properties of MgO expansive agent (MEA). In the present work, the characteristics of industrially produced MEA and the morphology of its hydration products were investigated with zeta potential analyzer (ZPA), Morphologi G3 optical microscope and scanning electron microscope (SEM). The influence of activity and dosage of MEA on fluidity and expansive properties of shrinkage-compensating binder was also investigated. Results indicated that the reactivity of industrially produced MEA is not a fixed value, but distributes in a range. The fluidity and expansive properties of binders containing MEA is affected by the reactivity and dosage of MEA. Besides, advantages and disadvantages of the standard evaluating method on reactivity of MEA were summarized. A new evaluating method of MEA reacting with ethylic acid buffer solution and weighing residue on the reactivity of MEA has been proposed.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Compensating the shrinkage of cementitious materials caused by hydration, temperature change and desiccation is an important subject in the research and application of cementitious material. Internal curing agent [1], organic shrinkage reducing admixture [2] and expansive agent [3] may be added into the mixture during the preparation of concrete to reduce or compensate its shrinkage.

Both sulfoaluminate-type and CaO-type expansive agents are the most widely used expansive agents to prepare shrinkage-compensating concrete [3–5]. Some disadvantages, such as poor thermal stability and uncontrollable hydration speed, limited their usage [6]. MgO expansive agent (MEA) is a newly-developed promising expansive agent, which is usually produced by calcining magnesite and the reactivity of MEA can be easily controlled by the calcining condition, e.g. kiln temperature and residence time [7,8]. MEA has been used to compensate shrinkage of concrete dams since 1970s in China [7]. The controllable reactivity of MEA makes the expansive speed of shrinkage-compensating concrete containing MEA a designable parameter, thus greatly facilitating the usage of MEA. Moreover, the hydration product of MgO, crystalline brucite, which has a perfect thermal and chemical stability and a relatively controllable forming speed, is the driving substance of the voluminal expansion of concrete containing MEA [9]. The retraction of long-term expansion of concrete containing MEA is prevented by the stable hydration product of MgO [10].

Chemical reactivity is the most important property of MEA. MEA produced under high calcining temperature and long residence time tends to have large grain size, little lattice distortion, small specific surface area and high density [8,11], and as a result, a low reactivity. The reactivity of MEA determines its expansive

* Corresponding author.
  E-mail address: yanpy@tsinghua.edu.cn (P. Yan).

property, especially the expansive speed and the ultimate expansion. Many researches [7,8,12–15] show that cement paste containing MEA with low reactivity expands moderately, but generates more ultimate expansion than that containing MEA with high reactivity.

Since the growth of brucite crystals is the reason for the expansion [9], it is helpful to understand the mechanism of expansion, especially the influence of MEA reactivity, by investigation of the morphology of crystalline brucite. Lv [16] et al. investigated the morphology of brucite crystal precipitated through solution, and classified the crystal into 3 types: needle-like, flake-like and rod-like. Deng [17] et al. indicated that brucite crystal is prone to grow with flake-like form in an alkali environment because of the high supersaturation of OH^-. Mo [8] et al. investigated the hydration product of MgO with different reactivity in water and found flake-like brucite on the surface of MgO particles. However, few investigations are focused on the growing process of brucite. Studying the morphology of hydration product of MEA with different reactivity contributes to a complete understanding of MEA.

Chemical reactivity of MEA also influences the workability of cement paste containing MEA [18]. The specific surface area of MEA powder is much larger than cement with similar particle size [8,18]. The workability of paste is determined by thickness of water film covering particles. Hydration of MEA consume much more water than cement to get a similar thickness of water film. Thus the workability of shrinkage-compensating concrete prepared with MEA is decreased severely.

Fluidity is a most important factor of workability of cementitious materials. The difference of fluidity of cement paste containing MEA with different reactivity is not only related to the thickness of water film, but also related to the agglomeration of particles. The calcining environment determines the reactivity of MEA by determining not only the specific surface area, but also the crystal grain size and the lattice distortion [8], both of which largely influence the surface property of MgO particles, thus influencing the agglomeration of particles and the fluidity of paste. Unfortunately, few researches dealt with this topic.

In an aqueous medium, the surface of cement and MEA particles bring surface charge. Ions in the liquid phase are attracted by the charged surfaces to obtain an electric balance, thus forming an electric double layer (EDL) [19]. The EDL controls the interactions between MEA and cement particles, hence affects the agglomeration of these particles. The zeta-potential is the electric potential in the interfacial EDL at the location of the slipping plane, where the bulk of particles can fluid away from the interface. It can reflect the electrokinetic behavior of EDL on the surface of particle [20]. The larger the absolute value of zeta-potential is, the larger the repulsive force among particles is, and the particles are prone to disperse from each other, thus increasing the fluidity of paste.

Reactivity of MEA dominates directly its expansive speed, the beginning and ending time of expansion and the ultimate expansive rate. Many researches focused on the relationship between reactivity and expansive behaviors of MEA [8,12–15]. However, most of researches concerning the reactivity of MEA were based on the MgO produced in laboratory. These MEAs were produced in a homogeneous calcining process, their grain size and reactivity is also homogeneous in a single specimen. The grain size and reactivity of industrially produced MEA waves grain by grain since the decomposition of magnesite particles is different in time and degree due to its nonuniform calcining condition in kiln.

In the Chinese standard, the evaluation method of reactivity of MgO is based on the neutralization reaction [21]:

$$3MgO + 2H_3CA \Rightarrow Mg_3(CA)_2 + 3H_2O \tag{1}$$
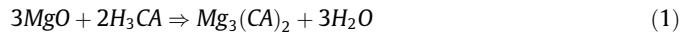
H_3CA represents citric acid. The molar ratio between MgO and citric acid is 1.5 from this equation.

The neutralization time of 1.7 g MEA and 200 mL of 0.07 mol/L citric acid solution at 30 ± 1 °C is used to evaluate the reactivity of MEA, e.g. "65 s MgO" means the neutralization time is 65 s. Long neutralization time means low reactivity. This evaluation method is incomplete to reflect the reactivity of industrially produced MEA since MgO in this process is highly excessive. The molar ratio between MgO and citric acid is 3.013 in the standard method while this ratio is only 1.5 for complete reaction. It means that at least half of MgO does not react when the reaction ends. Thus, the neutralization time can solely reflect the reactivity of the most activating part of MEA. If the calcination in kiln is heterogeneous or magnesite powder is thick (It is very likely to happen in an industrial process), a mixture of MEA with mutative reactivity may be produced. When this specimen is tested by the standard method, it may show a short neutralization time; but when it is really used to prepare concrete, it actually causes delayed expansion with the effect of lowly reactive MgO. Based on this background, a new evaluating method aiming to reflect the reactivity distribution of industrially produced MEA was proposed as a complement to the standard evaluating method.

2. Experimental

2.1. Raw materials

P.I. 42.5 Portland cement conforming to Chinese national standard GB 175 (CNS, 1999) was used in this study. Three types of MgO expansive agents with different reactivities of 65 s, 120 s and 220 s tested according to the standard neutralization method [21], produced by Wuhan Ujoin Building Material Technology CO. LTD., were used, designated as R(rapid)-MgO, M(medium)-MgO and S(slow)-MgO in the specimen name. The chemical compositions of raw materials are shown in Table 1 and the particle size distributions are shown in Fig. 1. The mean particle size of R-MgO, M-MgO and S-MgO are 14.615 μm, 15.468 μm and 19.794 μm respectively. ISO standard sand was used to prepare mortar prisms for the test of expansion properties. AR degree chemical reagent Critic acid, ethylic acid, sodium acetate and ethyl alcohol were used in test.

2.2. Test methods

2.2.1. Morphology investigation

MEAs with different reactivity were mixed with equivalent deionized water, then sealed in 10 mL plastic tubes and placed in a curing box with a constant temperature of 40 °C. The samples were removed at scheduled ages and were examined by SEM (SU-8000, Hitachi, Ltd., Japan) coated by carbon film. MEAs were also examined directly by SEM.

2.2.2. Fluidity of cementitious paste

Cement paste and pastes containing MEAs with different reactivities were prepared with a W/B ration of 0.40. The content of MEA is set to 6%, 10%, 15% and 20%. The fresh paste was filled into a truncated cone with an upper diameter of 36 mm, a lower diameter of 60 mm and height of 60 mm, then the cone is lifted up and paste

Table 1
Chemical compositions of raw materials (%).

	CaO	SiO₂	Al₂O₃	SO₃	Fe₂O₃	MgO	Na₂O	K₂O	Loss
Cement	62.51	19.77	4.86	3.87	3.04	2.9	0.14	0.78	1.59
R-MgO	2.17	3.19	0.39	0.09	0.62	91.27	0.00	0.03	2.00
M-MgO	2.43	2.17	0.24	0.29	0.5	94.01	0.00	0.00	0.4
S-MgO	2.15	3.99	0.48	0.07	0.55	89.4	0.00	0.03	3.13