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Evaluation of elastic modulus of cement paste corroded in bring solution with advanced homogenization method

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HIGHLIGHTS

- The elastic moduli of the corroded cement paste was measured by nanoindentation technique.
- The XRD and SEM-EDS were combined to analyze compositions of the corroded cement paste.
- The combined MT with SC method was used to calculate the elastic moduli of nanoindentation points.
- The elastic moduli distribution of nanoindentation points were analyzed by BSE and contour maps.

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ABSTRACT

This paper presents an integrated investigation of elastic modulus of corroded cement paste by experiments and homogenization calculation. First of all, cured cement paste samples were immersed in brine solution with specific chemical compositions for 60 d. Then the elastic moduli of the samples were measured by the nanoindentation test. The test results demonstrated that the elastic moduli of the nanoindentation points decreased, compared with the original cement paste. In addition, X-ray Diffraction (XRD) and Scanning Electron Microscope-Energy Dispersive Spectroscope (SEM-EDS) were combined to analyze the compositions of the corroded cement paste quantitatively. As a result, volume fractions of nine compositions of the corroded cement paste in each nanoindentation point were calculated. Afterward, an advanced homogenization method combining Mori-Tanaka (MT) method with self-consistent (SC) method was proposed to calculate the elastic moduli of the nanoindentation points. The calculation results had good agreement with the experimental results due to small relative difference and standard deviation. The back-scattered electron (BSE) image was used to analyze the elastic moduli distribution of the nanoindentation points as well. The result indicated that the elastic moduli of the nanoindentation points were related to the elastic moduli of their main compositions.

1. Introduction

The elastic modulus of cement-based material on microscale is a key index in structural design, significantly affecting mechanical properties of cement mortar and concrete structure. As known, the elastic modulus of cement paste is determined by many factors, such as ratio of water to cement, pore structure, admixtures and mineral components [1]. Under normal circumstances, the calcium silicate hydrate (C-S-H) gel, calcium hydroxide (CH) crystal, and non-hydrated cement particles are regarded as the cement hydration products [2].

Concrete structures are often subjected to corrosion from complex water environments, for examples, salt lake, ocean, acid rain, causing the decrease of concrete strength. In particular, many researchers have studied the composition complexity, corrosion mechanism and macro mechanical properties of cementitious materials corroded in brine solution. Tumidajski et al. [3] studied the effect of different mineral admixtures on elastic modulus, erosion depth and pore size of concrete corroded by brine solution. Zhang et al. [4] proposed the corrosion mechanism of magnesium hydroxide-chloride magnesium oxide-calcium chloride-gypsum composites and used X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) to study the corrosion products and

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microstructure of concrete in salt lake area. Liu et al. [5] made a lot of research on concrete corroded in saline lake brine and suggested that sulfate cement, magnesium oxychloride cement and sulfoaluminate cement had better corrosion resistance, compared with ordinary Portland cement. However, there is no accurate study on the variation of elastic modulus and microstructure of cement paste corroded in complex brine solution yet.

So far, nanoindentation technique, as a popular approach, is introduced to measure elastic modulus of cement paste. Acker and Velez et al. [6,7] used nanoindentation tester to measure the elastic moduli of four phases of cement clinker, including C3S, C2S, C3A and C4AF, which were in the range of 125 to 160 GPa. Jennings et al. [8,9] measured the average elastic modulus of low density C-S-H gel and high density C-S-H gel by nanoindentation tester, which were 18 ± 3 GPa and 30 ± 3 GPa respectively. Li et al. [10] tested the mechanical properties of cement paste corroded in brine solution by nanoindentation combined with SEM, obtaining the hardnesses and elastic moduli of cement phases in different corrosion periods. Němeček et al. [11] measured the elastic moduli of cement phases and gypsum as the input parameters for homogenization of Mori-Tanaka model and it was found the numerical results had good agreement with experimental results. Ulm et al. [12] adopted Mori-Tanaka method and self-consistent method to establish multiscale meso mechanical model used to precisely predict the intrinsic elastic properties of cement-based materials. However, few research has been put on the compositions analysis and elastic modulus homogenization of the corroded cement paste material.

To sum up, this paper aimed to investigate the elastic modulus of cement paste corroded in brine solution with compositions analysis and homogenization method. First of all, the elastic moduli of 100 nanoindentation points of the corroded cement paste sample were measured. Subsequently, the XRD was combined creatively with SEM-EDS (Scanning Electron Microscope-Energy Dispersive Spectroscope) to investigate the chemical compositions of the nanoindentation points. Afterwards, the Mori-Tanaka method and self-consistent method were integrated to predict the elastic moduli of nanoindentation points. The roadmap of this paper is shown in Fig. 1.

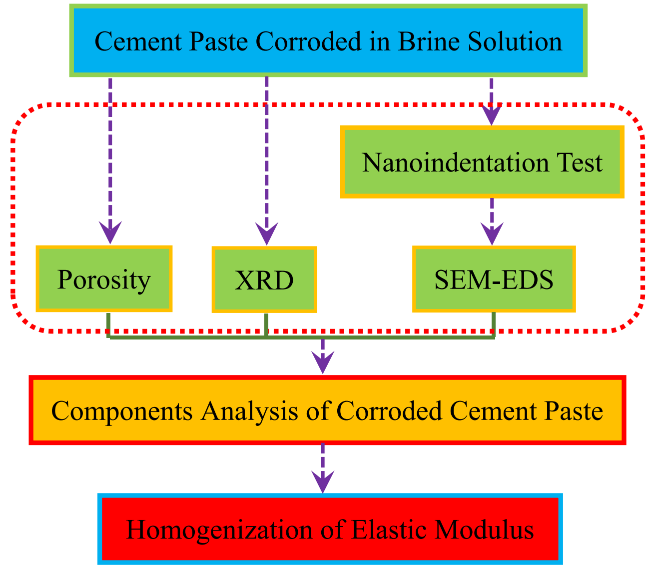

Fig. 1. Roadmap of this paper.

2. Materials and methods

2.1. Materials

In this study, the P·I 52.5 cement was used as cementitious material for experiments. The chemical compositions and mineral compositions are shown in Tables 1 and 2, respectively. The water-cement ratio (w/c) was selected as a high value of 0.53 because the authors preferred to enhance the corrosion effect of the cement paste samples. The brine solution was prepared on the basis of the compositions of Qarhan Salt Lake in Qinghai Province, China, displayed in Table 3. For researching convenience, four types of ions were chosen as the compositions of the brine solution, including Na^+, Mg^{2+}, SO_4^{2-} and Cl^-. After calculation, the brine solution was made with 1.80% of magnesium sulfate, 8.61% of magnesium chloride, 11.35% of sodium chloride by mass and deionized water.

2.2. Methods

2.2.1. Sample Preparation

The original cement paste sample used was cubic with a dimension of 20 mm × 20 mm × 20 mm. All the tested samples were cured in water with standard curing process (7 d, 20 ± 2 °C, relative humidity of 95%) before placed in the brine solution. After finishing curing in water tub, the samples were located in the brine solution for 60 d at room temperature. Subsequently, the salt crystals on surface of the samples surface were removed and the samples were dried.

In this study, three different experiments were conducted to investigate the chemical compositions and mechanical performance of the corroded cement paste, including XRD and nanoindentation and SEM-EDS. For XRD test, a cube of 5 mm^3 was cut off from the corroded original sample, grinded in an agate mortar for 10 min, shown in Fig. 2. For nanoindentation test, a 5 mm^3 cube was cut off from one corner of the corroded original cubic sample, pretreated due to the high requirement of flatness [13–15]. In the first place, the sample was soaked in alcohol phenolphthalein solution to prevent the further hydration of cement. Then the sample was trimmed to a cube of 3 mm^3, placed in a mold and sealed with epoxy resin. The surface of the resin-sealed sample was sanded by sandpapers (#400, #800, #1200 and #2500) of a grinding and polishing machine successively. After that, the sample was polished by canvas and silk with suspension of 0.25 μm diamond. Moreover, the roughness of the polished sample was analyzed by atomic force microscope (AFM) and the surface roughness was controlled to be less than 100 nm. Finally, the sample was washed by ultrasonic cleaner with absolute ethanol for 15 min to get rid of the adsorbed particles or powders. After dried, the sample was used to measure the elastic modulus. Fig. 3 shows the comparison of the corroded sample before and after pretreatment.

2.2.2. Measurement of porosity

An Auto Pore IV9500 mercury intrusion porosimeter (MIP) produced by MICROMERITICS Co., USA was used to measure the porosity of the corroded original cement paste. The pressure range of the MIP was 0.2–6000 lbs, which can be used to measure the pore sizes of the sample between 0.003 μm and 400 μm. In this research, the mercury injection test was conducted to measure the porosity of the cement paste corroded in brine solution for 60 d. As a result, 18.2% was assumed as the porosity of all the corroded original cement paste.

2.2.3. XRD analysis

A XRD-7000X diffractometer manufactured by Shimadzu Co., Japan was utilized to evaluate the compositions of the cement paste corroded in the brine solution. The angle of scanning ranged from −6 to +163° (2θ). The prepared powder from the original sample corroded in brine solution was placed on the special glass substrate, analyzed by the XRD. Then the compositions of the corroded cement paste were determined, discussed in Section 3.1.

2.2.4. Nanoindentation test

The nanoindentation test was conducted by a nanoindentation tester manufactured by NYSE: A. This machine adopted continuous stiffness method (CSM) to measure the elastic modulus of sample with nanoindentation depth. For cement-based material, it was necessary to select the appropriate depth of loading and distance of nanoindentation points due to the characteristics of heterogeneity. Based on some previous research [16–19], the depth of indenter in the sample ranged from 100 to 400 nm. The distance of nanoindentation points was normally approximate to the size of the nanoindentation mark [20].

Fig. 4 shows the elastic modulus measurement of cement paste by the nanoindentation tester. During the loading process, first of all, the elastic deformation of the sample occurred, followed by the plastic deformation with descending of the indenter. Then the loading was released when the depth of the indentater was 400 nm, reflecting the elastic recovery of the tested point. Fig. 5 displays the typical load-displacement curve of cement paste material which consists of two parts, the loading part and unloading part during the testing process. According to the principle of Oliver-Pharr [21], the elastic modulus of nanoindentation point can be calculated by Eq. (1) as long as the contact area was determined.

$$E = \frac{1 - \nu^2}{\frac{2\beta}{S}\sqrt{\frac{A}{\pi}} - \frac{1-\nu_i^2}{E_i}} \quad (1)$$