Research Article

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Evaluating Corrosion Damage Evolution of Cement Mortar in Acid Environment via Relative Elasticity Modulus Method

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Abstract

In order to study the damage variation along thickness from surface, a relative method combined with impulse excitation test was studied in this work to evaluate the elastic modulus of cement mortar corrosion damage layer, by simulating the damage layer as a coating. The damage layer with different damage degree is treated as multilayer coatings in which each layer has different properties. The elastic modulus of each layer is determined by using the relative method step by step. Single face of Portland cement mortar specimens was exposed in an aggressive environment, with 0%, 5%, 7.5% and 10% HCl content, respectively. The corrosion damage degree and evolution law of the mortar were investigated by measuring the elastic modulus of surface damage layer. With the increase of HCl concentration, thickness of corrosion damage layer increased and the modulus of the damage layer decreased greatly. The elastic modulus of each corrosion layer was obtained at different depths. By this way, damage depth and damage evolution were evaluated effectively.

Keywords: Corrosion damage layers, Cement mortar surface, Relative method, Impulse excitation test, Elastic modulus

Introduction

The performance degradation of the cement structures in complex environment is mostly caused by the mutual actions of physics, chemistry, stress and many other factors [1-4]. Corrosion and carbonization of the cemented materials resulted from acid rain, salt solution and CO2 has attracted increasing attentions of engineers [5-7]. The damage usually displays a gradient distribution along the direction normal to the surface plane, and the corrosion degree is closely related to the mechanical properties of corrosion damage layer. The structure of cement surface is considered as the first barrier against external erosion, which plays an important role in protecting the internal steel. Thus, determining the mechanical properties of surface damage layer may provide an approach for evaluating the reliability and lifetime of corroded cement components.

Some researchers have done a lot of work on the influence of acid corrosion on the mechanical properties of cement mortar [8-13]. However, the damage mechanism and damage evolution law of cement surface are seldom reported. And the damage degree of cement mortar corrosion layer is hardly evaluated with the present test technology. The relative method, a specialized method to measure the properties of coatings, is proposed to estimate the mechanical properties of cement mortar surface in this work [11]. Elastic modulus is an important parameter of mechanical properties. Jie Xiao et al studied that the dynamic modulus of elasticity loss could be regarded as an acceptable indicator for evaluating the resistance of cement to sulfuric acid attack as well as corrosion depth [14]. According to national standards, a cement component has been destroyed when its elastic modulus degrade to 60% of the initial value [15]. Since the elastic modulus loss can be regarded as a damage index of cement, impulse excitation tests for modulus measurement combined with the relative method are used to evaluate damage mechanism and evolution law of cement mortar in this work. The cement mortar corrosion layer with different properties, induced by the concentration variations reached in the diffusion process, is regarded as multilayer coating, and the variation of the properties of each layer displays the evolution law from surface to inner structure. It is supposed that the modulus of the cement is material constant for a given sample, regardless of the inhomogeneous composite. The aim of this work is to explore an approach for evaluating corrosion damage and evolution law of damage layer.

Experimental

Specimen preparation and test procedure

The cement mortar samples with sizes of 20×40×160 mm^3 were prepared according to GB/T 17671-1999, using 42.5 Portland cement and ISO standard sand with a fixed cement-sand ratio of 1/3 and water-cement ratio of 1/2 [16]. All the cement mortar samples were cured for 90 days in water with the temperature of 20±1 to get a complete maturation.

The cured samples were divided into five groups. Three groups were corroded respectively in 5%, 7.5%, 10% HCl contents for 10 h to prepare samples with different corrosion damage degree. Two groups of samples were corroded in 0%, 10% HCl contents for 24 h to study the damage variation along the thickness. Each group has three samples at least. The arithmetic mean of three samples was used as the experimental data of the group.

The schematic of surface corrosion of the sample is shown in Fig. 1. One side of sample with 40×160 mm2 was dipped into corrosive medium (HCl solution) in 0.2 mm depth and the other sides were exposed to the air. After 10 h and 24 h corrosion, clean the sample and dry it in drying oven at 45 with 24 hours. The dimensions (length, width), corrosion depth, mass and fundamental resonant frequency of the beam in flexure were measured by the vernier calipe, the optical microscope, the balance, and the apparatus of dynamic modulus of elasticity, respectively, after corrosion. The elastic modulus of the etched mortar (seen as composite, Eq) were measured by impulse excitation technique. According to national industrial standards of construction materials of JC/T 2172-2013[17], the elastic modulus can be calculated by

$$E = 0.9465\frac{mf^2}{b}\left(\frac{L}{t}\right)^3\left[1+6.585\left(\frac{t}{L}\right)^2\right] \quad (1)$$

Where m is the mass (g), f is the bending vibration response frequency, (Hz); b is the width, (mm), L is the length, (mm), t is the thickness, (mm).

To remove the corrosion layer, surface grinder was used. The elastic modulus of the rest part (seen as substrate, Es) of etched sample were also obtained using impulse excitation technique. Therefore, the elastic modulus of corrosion layer (seen as coating, Ec) can be calculated by the relative method [12] i.e. Ec can be obtained by Eq and Es using the analytical expression, *Ec=f(Eq, Es)*. Specific test methods and principles are shown as follows.

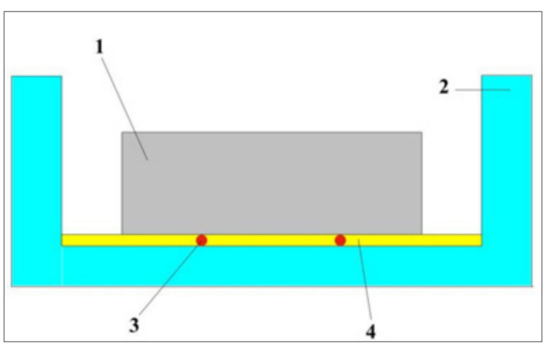

Figure 1: Schematic of surface corrosion of the sample 1-specimen; 2-specimen chamber; 3-support rod; 4-hydrochloric acid solution

Determining the elastic modulus of damaged layer

1. Considering a cement mortar sample with a corrosion damage layer like a coating on substrate, the properties of the coating reflect the properties of the damage layer and the properties of the substrate denote that of the cement. Impulse excitation technique based on the relative method was used to determine the elastic modulus of damage layer of cement mortar in this work. The key of this method is to establish the relationship among the elastic modulus of coating, substrate and composite sample. The validity of this method depends on a precondition that there exist a unique relationship among the three parameters, i.e. [12].

$$Ec = f(Eq,Es)$$

2. Where Ec is the elastic modulus of damaged layer (coating), Es the elastic modulus of substrate and Eq the elastic modulus of sample with damage layer. The specimen for the test is usually a rectangular block, schematically is shown in Fig. 2, the thickness of the damage layer is h and the thickness of the substrate is H.

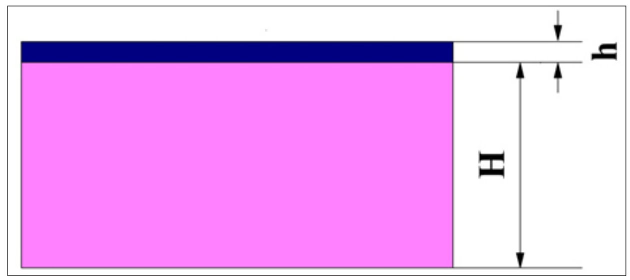

Figure 2: Schematic illustration of cross-section of cement specimen with a damaged layer

The thickness ratio is expressed as R.

$$R = h / H$$

3. The stiffness ratio of substrate sample to the damaged specimen, F, is related to the thickness ratio and the modulus of the specimen.

$$F = (1+R)^3 \cdot (Eq / Es)$$

4. The value of R can be measured by micrometer or microscope, and then the value of F could be obtained by excitation tests to substrate and composite sample, respectively. The modulus of the damage layer is then determined by Eq. (4)[18, 19].

$$Ec = \frac{-U+\sqrt{U^2+V}}{2(h/H)^3}\cdot Es$$

5. Where $V = 4(h/H)^2 \cdot \left[(1+(h/H))^3 \cdot Eq - Es\right] / Es$

6. $U = 4(h/H)^2 + 6(h/H) + 4 - (1+(h/H))^3 \cdot (Eq/Es)$

7. The test schedule is described as below: first prepare a block cement specimen with a damaged layer, the size of the specimen should be suitable for excitation test; and then measure the thickness ratio. The tests are carried out by three-step method: 1) Measure the modulus of the corrosion sample, Eq; 2) Grind off the corrosion layer of the sample and then measure the modulus of the rest (the substrate sample), Es; 3) Calculating the values of R and F by Eqs (3) and (4), and then determining the U and V values from Eqs (6) and (7); 4) Finally, the elastic modulus of the damaged layer is obtained through Eq. (5).

Damage variation along the depth

Gradual damage zone of cement is treated as multilayer coatings in which each layer has different properties and the variation is gradually from surface to subsurface. Dynamic modulus was determined by using the relative method step by step. To obtain the elastic modulus of each layer, the modulus of the original damaged specimen should be measured firstly and then wear off the first layer. The elastic modulus of the rest part was measured and treated as the substrate's modulus. Thus, the modulus of the first layer was obtained according the method for single layer coating. Repeat this step to determine the elastic modulus of each layer of the damage zone. The process can be described as below:

1) As shown in Fig.3, the damage zone consists of 3 layers with different properties. The width, thickness and length of original specimen should be measured firstly. And then get the elastic modulus of specimen, Eq1, using impulse excitation method.
2) Grind off the first layer (thickness is denoted as h1). Measure the residual thickness of the specimen, H1, and calculate the thickness ratio. Test the elastic modulus of remainder, Es1, using impulse excitation method.
3) Calculate the elastic modulus of the first layer, Ec1. Obviously, Eq2=Es1.
4) Grind off the second layer and test the elastic modulus of remainder, Es2. Calculate the elastic modulus of the second layer, Ec2. Similarly, Eq3=Es2, get the value of Ec3.
5) Step by step, get the elastic modulus of each layer in the damage zone.

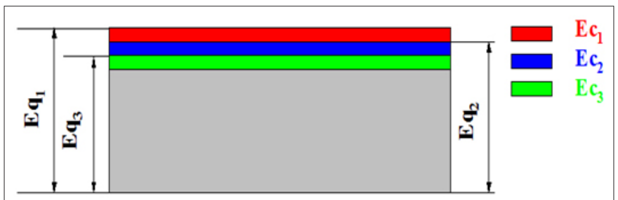

Figure 3: Schematic illustration of cross-sections of the simulated multilayer coatings for cement specimen

Results and discussion

The effect of HCl content on the modulus of cement mortar surface

To characterize the damage degree of the cement mortar surface layer corroded by HCl solution, relative elastic modulus loss variation is defined as

$$D = \left(1 - \frac{E_C}{E_S}\right) \times 100\%$$

8. Es is the elastic modulus of samples before corrosion, Ec is the elastic modulus of damage layer after corrosion.

Table 1: Thickness of the surface damage layer and the measured elastic modulus under different HCl contents.

HCl content	Thickness(mm)	Es(GPa)	Ec(GPa)	D
5%	0.23	40.50	22.27	45%
7.5%	0.34	40.10	18.20	55%
10%	0.81	40.14	6.75	83%

According to the test method mentioned above, the corroded thickness and the elastic modulus of the cement mortar surface corroded in different HCl contents for 10h were measured and the results are shown in Table1. It is obvious that the elastic modulus loss increased with increasing HCl content from 5% to 10% in this study. For the specimens under 5%, 7.5%, 10% acid solution, the elastic modulus of the corrosion layer after the 10 h exposure decreased 45, 55, 83 percent of that of the original specimen. Therefore, elastic modulus loss of cement mortar surface is very sensitive to acidity of corrosion environment.

The samples subjected to HCl corrosion for 10 h were examined by optical microscope, and the surface damage is shown in Fig 4. It was noticed that the aggregate on the surface of the cement mortar corroded in 10% HCl content has fallen off partly. A deteriorating effect of HCl corrosion is highest at the surface of the samples. Due to the strong acidity of HCl, a large number of calcium hydroxide are neutralized and produce calcium chloride. It reduces the basicity of the lime of internal pore water and results in the decomposition of hydrated calcium silicate and calcium aluminate hydrate [20]. Meanwhile, HCl also directly reacts with hydrated calcium silicate and calcium aluminate hydrate. The gel of cement pore structure is greatly destroyed and it leads to the degradation of the measured elastic modulus. The result shows that per unit time, the higher the HCl content, the more violent reaction, the deeper the corrosion depth.

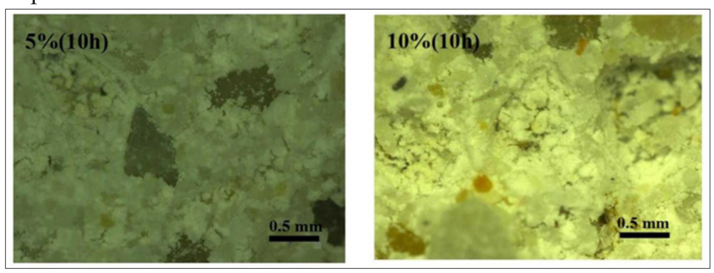

Figure 4: The surface of cement mortar after corrosion

Variation of the elastic modulus along depth for corroded sample

The variation of the elastic modulus of mortar samples from surface to inner structure is shown in Fig 5. The elastic modulus of each damage layer increased with the increasing depth from surface to inner structure and remained unchanged when the depth is over 2 mm. According to national standards mentioned above, from Fig.5, it was seen that the structure of the mortar corrosion layer was destroyed below the depth of 1.5 mm. The elastic modulus variation of the corrosion layers showed a greater tendency for increasing once the corrosion depth reached 1.5 to 2 mm and it remained constant when the depth exceeded 2 mm. Elements in the cement, with the exception of the alkaline salts, generally remain in the form of sparingly soluble hydroxides. These hydroxides, in some cases together with non-soluble Ca salts remain on top of the uncorroded cement mortar in the form of a corroded layer. The aggressive acid must first diffuse through this layer before it can reach and attack the undamaged cement. Thus, the differences of cement mortar corrosion layers in the chemical composition and mechanical properties at various depths are expected [21]. The elastic modulus of mortar corrosion layers at various depths which is not solved with modern measure technique was obtained via relative method accurately.

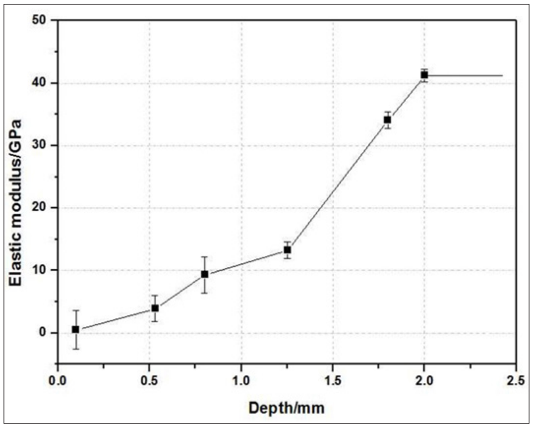

Figure 5: Measured elastic modulus of cement mortar corroded in 10% HCl content for 24 h and its variation along the depth direction

Variation of the elastic modulus along depth for mortar sample with 90d cured in water

It was said that the surface properties of a concrete component is usually higher than that of internal part. In order to seek the truth, cement mortar samples with 90 d cured in water was used to examine the change of the elastic modulus at different zones from surface to interior. The measured area was divided into four layers and each layer was 2 mm thick. The modulus of each layer was measured by relative method and the results are shown in Fig 6. It was found that the measured elastic modulus of the first layer was the highest, and it degraded slightly with the increasing depth from the surface layer (first layer) to the fourth layer and then remained basically steady. This phenomenon indicates that, under sufficient hydration condition, the elastic modulus of cement mortar surface layer has higher modulus than that of internal structure and the elastic modulus of the internal structure of mortar samples remained nearly constant. Thus, it was supposed that the modulus of the surface is about 10-15% higher than that of internal cement mortar.

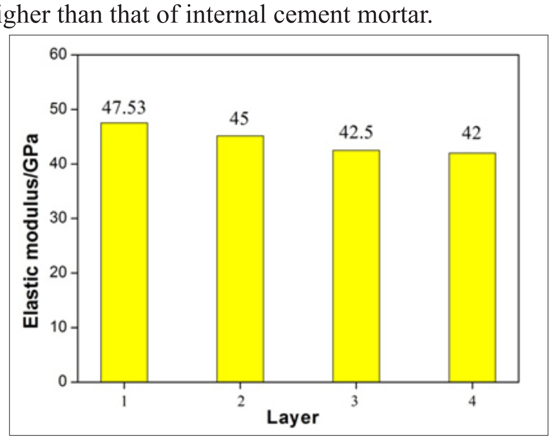

Figure 6: Measured elastic modulus varying along the thickness, simulated with 4 layers from the surface to substrate, and each layer has 2mm thickness.

Conclusion

1. It is a feasible approach to investigate the surface properties and surface damage evolution of cement mortar by simulating the surface layer as a coating for which the properties could be determined by the relative method. The elastic modulus of corrosion layer and its variation along to depth direction from the surface to substrate was conveniently and quantitatively determined via the relative impulse excitation technique.
2. By relative method combined with pulse excitation technique, under 90 days hydration condition, the measured elastic modulus of mortar surface layer was about 10-15% higher than that of internal structure.
3. The corrosion zone of cement mortar corroded in 10% HCl for 24 hours was divided into two damage layers (depth 0~1.5mm as the first layer, 1.5~2mm the second layer) according to gradient change law of the measured elastic modulus. The structure of the first damage layer (0~1.5mm) was destroyed completely. And the measured modulus of the second layer (1.5~2 mm) was between the first layer and the substrate (original material).
4. The elastic modulus loss of cement mortar surface layer showed an approximately linear relationship with HCl contents. After being immersed in acid solution with 5%, 7.5%, 10% contents for 10 h, the elastic modulus of corrosion layer decreased 45%, 55%, 83% of that of the original specimen, respectively.

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