Investigation on effect of aggregate on three non-destructive testing properties of concrete subjected to sulfuric acid attack

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Abstract: In order to investigate the effect of aggregates on the concrete sulfuric acid resistance, accelerated corrosion experiments were conducted with four types of concretes composed of coarse and fine aggregates with two different chemical compositions. All the concretes with the same water/cement ratio of 0.45, and the pH value was kept in the range of 0.93 to 0.97. With continuous monitoring of each concrete specimen, corrosion depth, mass loss, and dynamic modulus elasticity loss

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were calculated. The results showed that the dynamic modulus of elasticity loss can be regard as an acceptable indicator for evaluating the resistance of concrete to sulfuric acid attack as well as corrosion depth and mass loss. A regression model proposed in this paper could provide good predictions. Concrete with marble aggregates rich in calcium carbonate have better performances in sulfuric acid solution than that with inert aggregates. Effect of fine aggregate on concrete sulfuric acid corrosion rate is more significant than coarse aggregate in the term of corrosion depth, mass loss, and dynamic modulus of elasticity loss.

Key words: Siliceous and calcareous aggregates, Sulfuric acid attack, Dynamic modulus of elasticity, Thermodynamics, Range analysis

1 Introduction

It is recognized that the hydration products of Portland cement concrete are alkaline and the pore solution in the concrete typically has a pH value ranging between 12 and 13.5. So it cannot be immune from acid attack. Owing to the spread of concrete structures damages in both urban and industrial areas, concrete acidic attack has attracted more and more attention in recent years. Sulfuric acid is the most widely distributed acid medium in the environment. Sulfuric acid can be generated from the oxidation of sulfide minerals (e.g. pyrite) [1]. Sulfuric acid is also a chief component of acid rain. It is reported that acid rain falls cover at least one third of Chinese territory[2]. Moreover, biogenic sulfuric acid corrosion is a common type of damage in sewage pipe systems [3, 4]. It is estimated that costs of maintenance and repair due to sulfuric acid

42 attack are several ten billion dollars in U.S. on sewer systems, which are even more
43 than the costs of constructing new wastewater structures[5, 6]. Hence there is an urgent
44 need to investigate the deterioration rules of sulfuric acid attack on concrete structures
45 in order to minimize its impact. Several researchers [6-9] have studied the effect of
46 cement type, cement content, water-to-cementitious materials ratio on improving the
47 resistance of mortar or concrete to sulfuric acid attack. It has also been reported that the
48 use of supplementary cementitious materials (SCM) such as silica fume, fly ash, blast
49 furnace slag, limestone filler, and natural pozzolana in concrete has improved the
50 resistance of concrete to sulfuric acid attack because of its finer pore structure and the
51 reduced presence of calcium hydroxide, which is most vulnerable to acid attack[10-13].
52 But, aggregate consists 65-80 percent of concrete proportion and has the main role in
53 concrete behavior such as durability, dimensional stability and workability [14, 15].
54 Therefore, it appears necessary to better understand the deterioration mechanisms
55 associated with aggregate when concrete subjected to sulfuric acid attack. According to
56 the mineralogical composition, aggregate can be divided into two types: one type is
57 calcareous aggregate which is rich in calcium carbonate and is more vulnerable to acid
58 attack. The other type is siliceous aggregate which is rich in silicon dioxide and is more
59 resistant to acid attack. Which type of aggregates should be chosen in the acid
60 environment remains controversial. Some researchers are convinced that aggregate is
61 the main component of the concrete, and the concrete corrosion process will be
62 accelerated if the aggregate is damaged by the acid first[16]. However, other

63 researchers have published results that concrete with coarse calcareous aggregate offers
64 better resistance to sulfuric acid attack. Hughes et al.[17] reported that the mass loss of
65 cubes with limestone coarse aggregate and siliceous sand was less than that with
66 limestone coarse and fine aggregates. In his study, only the mass loss and visual
67 inspection were researched and just three combinations of coarse and fine aggregates
68 were adopted in concrete without the cubes with siliceous coarse aggregate and
69 limestone fine aggregate. Belie et al.[18] found that the aggregate type had the largest
70 effect on concrete degradation after sulfuric acid corrosion. Concrete with limestone
71 aggregates showed a smaller degradation depth than that with inert aggregates. Chang
72 et al.[19] presented that concrete made with limestone aggregates and the ternary
73 cement containing 7% silica fume and 33% fly ash has an excellent acid resistance in
74 1% sulfuric acid solution. The fine aggregate used in his study was only silica river
75 sand. Bederina et al.[20] pointed out that the mass loss in the case of limestone sand is
76 lower than that of silica sand mortar when exposed to hydrochloric acid solution.
77 However, an extensive review of literature indicates that the significance of coarse and
78 fine aggregate on the concrete sulfuric acid corrosion is not clearly clarified. In order to
79 explore the question that which has greater influence on the concrete sulfuric acid
80 resistance, coarse aggregate or fine aggregate, concretes with four different
81 combinations of aggregates were adopted in the accelerated sulfuric acid corrosion test.
82 In previous studies, mass loss and corrosion depth were regarded as acceptable
83 indicators for evaluating the resistance of concrete to sulfuric acid attack. In this paper,

in addition to the above two indicators, dynamic modulus of concrete after sulfuric acid corrosion was also measured through impact resonance test, which is a non-destructive testing method.

2 Experimental investigation

2.1 Raw materials

Local Portland cement (P·Ⅱ52.5R) with a 28d compressive strength of 55.3 MPa was used, which complies with Chinese standard GB175-2007 and is similar to ASTM C150 type I cement[21]. The specific gravity of the cement was 3.1. River sand and gravel were used as fine and coarse siliceous aggregates, which come from a local pipe pile corporation at Suzhou in China. Crushed marble sand and stone were used as fine and coarse calcareous aggregates, which come from a whole rock block bought at a stone market in Shanghai, China. The phases for gravel and marble were tested with X-ray fluorescence (XRF), and the results are listed in Table 1. Because the main composition of the marble was calcium oxide (CaO) as shown in Table 1, marble stone and sand can be classified into calcareous aggregates category. Since the river sand is mainly composed of silicon dioxide (78.56% in Ning Y.'s paper[22] and 88.54% in Limbachiya M.'s paper[23]), the gravel and river sand can be classified into siliceous aggregates category.

<Table 1>

Gravels with a maximum nominal size of 25mm. and water absorption of 0.92% were obtained for concrete specimens. Table 2 shows the particle size gradation

of gravel (coarse aggregates) used in the trial mixture. Natural river sand (fine aggregates) with a fineness modulus of 2.61 and water absorption of 1.79% was used for concrete specimens. Table 3 shows the particle size gradation of river sand used in the trial mixture.

<Table 2>

<Table 3>

Marble stone and sand, cut from the same parent natural rocks, were made into crushed stones by a crusher and were subsequently divided into 9 kinds of particle sizes by a sieve shaker sized 0.15-0.3 mm, 0.3-0.6 mm, 0.6-1.18 mm, 1.18-2.36 mm, 2.36-4.75 mm, 4.75-9.5 mm, 9.5-16 mm, 16-19 mm, 19-26.5 mm. These crushed marble stones were used as coarse and fine calcareous aggregates. In order to accommodate marble stone and sand with the gravel and river sand in the aspect of aggregate gradation, the mass percentages of marble stone sized 2.36-4.75mm, 4.75-9.5mm, 9.5-16mm, 16-19mm, 19-26.5mm were 4%, 19%, 30%, 22%, 25% (Data from Table 2), respectively. The mass percentages of marble sand sized 0.15-0.3mm, 0.3-0.6mm, 0.6-1.18mm, 1.18-2.36mm, 2.36-4.75, 4.75-9.5mm were 9.2%, 44.4%, 17.8%, 10.2%, 10.8%, 5.6% (Data from Table 3), respectively.

2.2 Mixture design

In this paper, the specimens were divided into four groups denoted by C1F1, C1F2, C2F1, and C2F2. The coarse and fine aggregates of C1F1 were gravel and river sand, C1F2 were gravel and crushed marble sand, C2F1 were crushed marble stone and

river sand, and C2F2 were crushed marble stone and marble sand, respectively. The water/cement ratio were 0.45 (by weight), and the mass ratio of fine aggregate to total aggregate was 0.31 for all mixture proportions. Tap water with ambient temperature was used. The apparent density of gravel, river sand, marble stone, marble sand were 2644kg/m³, 2540kg/m³, 2575kg/m³, 2630kg/m³, respectively. Mix proportions for concrete specimens are given in Table 4. Naphthalene based superplasticizer was added to obtain sufficient workability. The mass ratio of superplasticizer to cement was 0.6%. The compressive strength at 28 days before corrosion is designed to be approximate 45Mpa.

<Table 4>

2.3 Experiment design

2.3.1 Twelve specimens preparation

Although both cylindrical specimen and prismatic specimen can be tested, the prism corners will suffer more severe damage than that of lateral plane in the corrosion environment. So the cylindrical specimen was chosen in this study. Concrete was mixed in the laboratory using an electric mixer. Freshly mixed concrete was casted into cylinder steel molds, which were 100mm in diameter by 200mm in height, and then compacted on a vibration table. After that, the concrete specimens were cured 24h in laboratory at 18±5 °C and relative humidity about 70%. Prior to the exposure to the sulfuric acid solutions, all specimens were stored under standard moist curing room at 20±2 °C and 95% relative humidity for 28 days.

2.3.2 Sulfuric acid immersion test

Specimens were fully immersed in an aggressive sulfuric acid solution. There are four types of concrete, and three specimens for each concrete were adopted. The specimens were arranged into two layers in a plastic vessel as shown in Fig.1. The cylinders were sealed by paraffin wax at both ends, and only the side surface of which were exposed to the sulfuric acid. In order to accelerate the corrosion process, the pH value around 0.95 was chosen in the paper referring to the previous studies[19]. A portable pH meter (0.01 precision) was used to measure pH of solutions during the testing period of 194 days. It was kept in the range of 0.93 to 0.97 by daily adjusting the pH value using concentrated sulfuric acid (98% by weight). The solution was thoroughly stirred after adding the concentrated sulfuric acid everyday in order to reduce differential concentrations of the acid within the solution vessel. It should be pointed out the protective layer formed around concrete specimens was more or less interrupted by stirring the solution once a day. Sulfuric acid solution was refreshed every month.

<Fig. 1>

2.4 Test procedures

Despite the fact that various physical and chemical tests on the resistance of concrete to acids have been developed, there are no standard procedures available to test the resistance of concrete to sulfuric acid attack [24-26]. Zivica et al.[27] pointed out that the used methods to evaluate the properties of cement based materials under acidic attack embraces the observation of the changes of the appearance, mechanical

properties, chemical composition, pore structure, and so on. In this paper, corrosion depth, mass loss and dynamic modulus of elasticity loss were used as acceptable indicators for evaluating the resistance of concrete to sulfuric acid attack. During the immersion period for 194 days, the cylinder specimens were periodically removed from the acid solution, rinsed with tap water, and brushed gently with a plastic soft brush to remove loose particles. And then the specimens were put into electric dry oven under 60 °C (preventing additional damage to the specimens) for 24 hours and cooled to room temperature. A series of tests, including dimension measuring, weighing, and impact resonance test, were conducted at regular intervals for 194 days (0 days, 6 days, 12 days, 21 days, 25 days, 37 days, 52 days, 66 days, 80 days, 108 days, 136 days, 164 days, 194 days) to determine corrosion depth, mass loss, and dynamic modulus of elasticity loss. The specimens were reimmersed in the sulfuric acid solution after periodical test.

2.4.1 Diameter, length, and corrosion depth

Diameters were measured using digital vernier caliper (0-300mm range and 0.01mm precision) at three different places along an axial plane of cylinder and the other three places at right angles. Four lengths were also measured with digital vernier caliper around each cylinder. The mean value of six diameters was calculated as the diameter of the specimen and the mean value of four lengths was calculated as the length of the specimen. The average of diameters and lengths of three specimens was taken as the representative diameter and length of each concrete, respectively. The

corrosion depth for each concrete was calculated as follow:

$$h_i = (d_0 - d_i) / 2 \quad (1)$$

Where, h_i is the corrosion depth at i day (mm), d_0 is the initial representative diameter before exposure to sulfuric acid (mm), d_i is the representative diameter after i day exposure to sulfuric acid (mm).

2.4.2 Mass loss

Masses were measured with digital balance (0-30kg range and 1g precision). The average of three specimens' masses was taken as the representative mass of each concrete.

2.4.3 Impact resonance tests

Most investigations have been used mass loss and corrosion depth as acceptable indicators for evaluating the resistance of concrete to sulfuric acid attack, but dynamic modulus of concrete after sulfuric acid corrosion was rarely studied. Dynamic elastic material constants of concrete may be used for quick assessment of material quality and uniformity [28-30]. Moreover, the dynamic test is a non-destructive testing (NDT) method, so the specimens used for this test can be used again for the following immersion test. In order to measure the dynamic modulus of elasticity, impact resonance test were performed according to ASTM C215-08[31], using the longitudinal mode. Fig.2 shows a schematic of the impact resonance test used in this study. A miniature piezoelectric accelerometer that has a flat response from 1 to 12,000 Hz with a sensitivity of 10 mV/g at 160 Hz (LC0159 manufactured by lance) was mounted at the

center of one end surface of the cylinder specimen. A steel ball with a diameter of 12 mm was used as the impact source and applied at the center of the opposite end surface.

According to this setup, the data were recorded from the data acquisition system and both the amplitude-time and amplitude-frequency graphs were obtained. From the amplitude- frequency graph, the peak value which shows the resonant frequency value of the concrete specimen was recorded in the computer. The average of three specimens' fundamental longitudinal frequency was taken as the representative fundamental longitudinal frequency of each concrete. The dynamic modulus of elasticity was obtained from the following equations according to ASTM C215-08:

$$E_d = 5.093M \times L \times d^2 \times f^2 \quad (2)$$

Where E_d is the dynamic modulus of elasticity. L, d, M, and f are the representative value of the specimen's length, diameter, mass, and fundamental longitudinal frequency, respectively.

<Fig. 2>

3 Results and discussion

3.1 Mechanism of concrete sulfuric acid corrosion

Portland cement consists of pulverized cement clinker and gypsum. Cement clinker consists of four major minerals: alite (mainly $3CaO \cdot SiO_2$), belite (mainly $2CaO \cdot SiO_2$), aluminate phase (mainly $3CaO \cdot Al_2O_3$) and ferrite phase (mainly $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$), as well as some impurities. Alite and belite, which are calcium silicates, comprise around 85% of cement clinker[32]. At the early stage of

concrete, $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ react with water to produce calcium silicate hydrate (abbreviated as C-S-H) and calcium hydroxide ($Ca(OH)_2$) [21]. The Ca/Si ratio of C-S-H in neat Portland cement pastes varies from 1.2 to 2.3 with a mean of 1.75 [33]. $3CaO \cdot 2SiO_2 \cdot 3H_2O$ and $2CaO \cdot SiO_2 \cdot 1.167H_2O$ are suppose to be two representative constituents of C-S-H. So corrosion of concrete due to sulfuric acid can be characterized by the following reactions:

It can be seen from the above chemical reaction equations, Sulfuric acid penetrates into concrete and reacts first with the calcium hydroxide ($Ca(OH)_2$), calcium silicates (not involved in hydration) and calcium silicate hydrate (C-S-H) in the concrete to form gypsum ($CaSO_4 \cdot 2H_2O$). This process could decrease the performance of concrete since gypsum has barely no strength. Then the gypsum would react with calcium aluminate hydrate to form ettringite ($CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). As the pH value decreases, calcium hydroxide (12.6), ettringite (10.7), C-S-H (≈ 10.5) and finally calcium aluminate and ferrite hydrates decompose successively until a silica gel residue is obtained at pH values below roughly 2 (the value in parentheses referring to pH

stability) [15]. So, ettringite is unstable in the sulfuric acid environment. After sulfuric acid corrosion, a soft and pulpy layer with an increased porosity is formed on the concrete eroded surface, which may dominantly compose of gypsum and silica gel residue.

3.2 Visual inspection

Photographs were taken of cylinder specimens after immersion in the sulfuric acid over regular time periods to record changes in surface appearance. Typical surface appearances of four types of concrete cylinders after 164 days immersion in sulfuric acid solution with a pH around 0.95 are shown in Fig.3. It is clearly shown in Fig.3 that cylinders of concrete C1F1, containing gravel and river sand has suffered the most severe damage with exposure of coarse aggregates and significant loss of cement mortar. The specimens' surface of concrete C1F1 and C2F1 became significantly rougher than C1F2 and C2F2 after immersion in sulfuric acid, which appeared to indicate that those concretes containing river sand as fine aggregate were more vulnerable to acid attack. Surface appearances of cylinders of concrete C1F1 during the period of 194 days immersion in $\text{pH} \approx 0.95$ sulfuric acid are shown in Fig.4. The corrosion process is clearly shown in the photograph: the uncorroded surface was flat and smooth casted by steel mold. At the initial stage of corrosion (0~37 days), the corroded surface became soft and white because of the formation of corrosion products (speculated to be mainly gypsum [11, 15, 25, 34]) deposit on the cylindrical surface. When the corrosion continued, the corroded concrete lost its fine aggregates (37~108

days) and coarse aggregates (108~194 days).

<Fig. 3>

<Fig. 4>

3.3 Corrosion depth and mass loss and dynamic modulus of elasticity loss

The corrosion depth of each concrete can be calculated by Eq. (1) as previously mentioned. The other indicators for evaluating the resistance of concrete to sulfuric acid attack, including mass loss and dynamic modulus of elasticity loss were calculated by the following Eq.(9) and Eq.(10), respectively.

$$K_m = (m_i - m_0) / m_0 \times 100\% \quad (9)$$

$$K_{Ed} = (E_{di} - E_{d0}) / E_{d0} \times 100\% \quad (10)$$

Where, K_m and K_{Ed} represent mass loss and dynamic modulus of elasticity loss, respectively. m_0 and E_{d0} represent mass and dynamic modulus of elasticity before exposure to sulfuric acid, respectively. m_i and E_{di} represent mass and dynamic modulus of elasticity after exposure to sulfuric acid i days.

It can be observed in Fig.5 that the trend of concrete specimens' corrosion depths versus corrosion time was similar. The corrosion depths of all the cylinders were negative values at the initial stage of corrosion (0~37 days), and then became positive values as the corrosion continues. A negative value represents an expansion of the cylinders compared to the initial dimensions, while a positive value means that due to loss of material, the radius of the cylinder decreased compares to the initial size. This could be attributed to the formation of gypsum, which was difficult to brush from the

surfaces at the initial corrosion stage. As the corrosion continued, corrosion depths became deeper because of the detachment of corrosion products, fine and coarse aggregates from the specimens. The corrosion depths for C1F1, C1F2, C2F1, and C2F2 concrete specimens after 194 days of immersion in sulfuric acid were 6.04mm, 2.64mm, 3.34mm, and 2.25mm, respectively.

<Fig.5>

The cylinders' mass changes of each concrete with the immersion time in the sulfuric acid solution is plotted in Fig.6. As shown in this figure, all the cylinders had mass gain over the first 21 days immersion in the acid solution. And then cylinders of concrete C1F1 started to lose mass with immersion time. The others began to lose mass after 52 days immersion. The mass gain during the early immersion period could be attributed to a number of factors, which include continued hydration of cement and formation of gypsum. Since locations of fine and coarse aggregates lost due to deep degradation in the cement paste of the specimen, the mass loss decreased. The mass loss for C1F1, C1F2, C2F1, and C2F2 concrete specimens after 194 days of immersion in sulfuric acid were 26.5%, 13.95%, 18.75%, 11.56%, respectively.

<Fig. 6>

The similar tendency of concrete specimens' changes in dynamic modulus of elasticity loss versus corrosion time under sulfuric acid actions was shown in Fig.7. At the initial stage, the dynamic modulus of elasticity of deteriorated specimens increased slightly, and then decreased gradually. The increase of dynamic modulus of elasticity

could be attributed to the formation of gypsum, which deposited within the pore of concrete so as to increase the compactness at the initial stage. And then, the volume expansion caused by gypsum will increase in internal pressure and subsequently cause internal cracking and pitting. These damages could lead to the reduction in dynamic modulus of elasticity in the following corrosion process. The dynamic modulus of elasticity loss for C1F1, C1F2, C2F1, and C2F2 concrete specimens after 194 days of immersion in sulfuric acid were 11.44%, 3.2%, 13.77%, 5.31%, respectively.

<Fig. 7>

As shown in Fig.5, Fig.6 and Fig.7, aggregates type had a pronounced effect on corrosion depth, mass loss and dynamic modulus of elasticity loss. These could attribute the reasons as follow. In concrete containing siliceous aggregates, only cement hydration products react with acid and the effect of neutralization during acid attack would be very limited. However, marble aggregates are composed mainly of calcium carbonate, which will react with acid and the concrete would then have much greater capacity to neutralize acid. The neutralization effect of sacrificial marble aggregates could significantly reduce the local acid concentration and the rate of acid attack on concrete [12, 19]. The chemical equation of calcium carbonate and sulfuric acid [35] is given as Eq. (11).

Advantageous effect of marble aggregate containing mainly of calcium carbonate in sulfuric acid resistance could also been found in the aspect of thermodynamics. The

Gibbs free energy is defined in terms of thermodynamic properties that are state functions. The Gibbs energy change $\Delta_r G_m^\ominus$ is a useful tool to describe in what manner the reaction is conducted. If $\Delta_r G_m^\ominus < 0$, the reaction is spontaneous in the forward direction, which means the reaction could proceed in the forward direction on its own without any outside assistance. Superscript “ $\ominus$ ” means standard state (298 Kelvin and 1atm pressure), subscript “m” means 1 molar, subscript “r” means reaction. The change in Gibbs free energy under standard-state is a function of the change in two terms: enthalpy and entropy, as expressed by the Gibbs-Helmholtz equation: $\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T\Delta_r S_m^\ominus$. For a chemical reaction $aA + bB \rightarrow dD + eE$ (the reactants A and B combine to form products D and E, and a, b, d, e are the stoichiometric coefficients for corresponding species), the enthalpy change $\Delta_r H_m^\ominus$ and the entropy change $\Delta_r S_m^\ominus$ for the reaction under standard-state can be expressed as:

$$\Delta_r H_m^\ominus = \sum \Delta_r H_m^\ominus (\text{products}) - \sum \Delta_r H_m^\ominus (\text{reactants}) = [d\Delta_f H_m^\ominus (D) + e\Delta_f H_m^\ominus (E)] - [a\Delta_f H_m^\ominus (A) + b\Delta_f H_m^\ominus (B)]$$

$$\Delta_r S_m^\ominus = \sum \Delta_r S_m^\ominus (\text{products}) - \sum \Delta_r S_m^\ominus (\text{reactants}) = [d\Delta_f S_m^\ominus (D) + e\Delta_f S_m^\ominus (E)] - [a\Delta_f S_m^\ominus (A) + b\Delta_f S_m^\ominus (B)]$$

where $\Delta_f H_m^\ominus$ and $\Delta_f S_m^\ominus$ (subscript “f” means formation) denote the molar enthalpy and entropy of formation of a compound from its constituent elements at standard state respectively. $\Delta_f H_m^\ominus$ and $\Delta_f S_m^\ominus$ values can be found in the handbook of minerals and the related compounds thermodynamic data[36], or be queried through HSC Chemistry® v. 5.0[37]. The standard molar enthalpies $\Delta_f H_m^\ominus$ and entropies $\Delta_f S_m^\ominus$ of formation of compounds needed to compute $\Delta_r H_m^\ominus$ and $\Delta_r S_m^\ominus$ (subscript “r”

means reaction) of chemical equation (3) ~ (7) & (11) are listed in Table 5.

<Table 5>

The equilibrium constant $K^\ominus$ is related to the standard Gibbs free energy change $\Delta_r G_m^\ominus$ by the following equation: $\Delta_r G_m^\ominus = -RT \ln K^\ominus = -2.303RT \log K^\ominus$, where T is the absolute temperature in Kelvin, and R is the gas constant with a value of $8.314 J \cdot (mol \cdot K)^{-1}$. This equation allows us to calculate the equilibrium constant for any reaction from the standard-state Gibbs free energy change of reaction. The larger the equilibrium constant $K^\ominus$, the farther the reaction has to go to reach equilibrium. Usually, if the logarithm of the equilibrium constant ($\log (K)$) is greater than 5, the reaction can go to completion. Results of thermodynamic calculation for Eq. (3) ~ (7) & (11) are given in Table 6. In order to be better understood the thermodynamic calculation results in Table 5, taking chemical reaction Eq. (6) as example, thermodynamic calculations are provided as follows:

$$\Delta_r H_m^\ominus = [-3 \times 2022.629 - 2 \times 1456.961] - [-4782.312 - 3 \times 813.989 - 4 \times 285.930] = -613.808 kJ \cdot mol^{-1}$$

$$\Delta_r S_m^\ominus = [3 \times 194.1 - 2 \times 500.503] - [312.126 + 3 \times 156.904 + 4 \times 69.95] = -1481.344 J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta_r G_m^\ominus = \Delta_r H_m^\ominus - T \Delta_r S_m^\ominus = -613.808 - 298 \times (-1481.344 \div 10^3) = -172.367 kJ \cdot mol^{-1}$$

$$\log K^\ominus = -\Delta_r G_m^\ominus / (2.303RT) = 172.367 \times 10^3 / (2.303 \times 8.314 \times 298) = 30.21$$

<Table 6>

As shown in Table 6, Gibbs free energy changes ($\Delta_r G_m^\ominus$) of the six reactions are negative, and the logarithm of the equilibrium constants ($\log (K^\ominus)$) are greater than 5. It indicates that all the reaction can go to completion. It can be seen from Eq. (3) ~ (7) in

Table 6, calcium silicates ($3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$), calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrates ($3CaO \cdot 2SiO_2 \cdot 3H_2O$ and $2CaO \cdot SiO_2 \cdot 1.167H_2O$) are vulnerable to sulfuric acid attack. It can explain why concrete cannot be immune from acid attack. Results of thermodynamic calculation for Eq. (11) indicate calcium carbonate which is the main component of marble aggregates, will react with sulfuric acid spontaneous. So the concrete containing marble aggregates would then have much greater capacity to sulfuric neutralize acid.

4 Corrosion regression model

Correctly calculation and prediction of corrosion depth is necessary to accurately estimate the minimum thickness of the concrete cover in reinforced concrete structures or to adequately design for sacrificial layers in concrete structures exposed to sulfuric acid solutions[38]. Many researchers developed models to predict the corrosion depth of the concrete in acid environment. It is generally believed that the degradation depth of concrete due to acid attack including sulfuric acid attack is proportional to the square root of the exposure time as follows[39]:

$$h = b\sqrt{t} \quad (12)$$

Where, h is the degradation depth, t is the exposure time in acid solution and b is constant. According to this equation, the rate of degradation is dominated by the diffusion rate of acid under the assumption that corrosion products remain on surface [40, 41]. But in actual structures, concrete is often exposed to flowing water that contains sulfuric acid such as sewage[42]. Because of almost no strength damaged zone,

the corrosion products would be removed by the shearing force of flowing solution. In these instances, it was predicted that concrete deterioration caused by sulfuric acid attack would proceed at a greater rate than that predicted from the square root relationship. Kawai et al.[42] found that the depth of erosion of concrete was nearly proportional to the exposure time when concrete was exposed to flowing acid solution. Pavlik [39] and Grube [43] also found when the corroded layer is stable due to the absence of any external mechanical, corrosion depth or mass loss with time would follow a parabolic function [44]. But a disturbance of the protective layer by external mechanical effects, even if it occurs at relatively long intervals, the parabolic function would turn to a linear one. In this experiment, in order to reduce differential concentrations of the acid within the solution vessel after adding 98% sulfuric acid, the solution was stirred once a day. Since stirring action generates the flow of solutions and the shearing force of the flow is applied to the surfaces of the specimens. Moreover, the protective layer was also largely interrupted when the specimens were periodically removed from the acid solution. So the protective layer formed around concrete specimens was largely interrupted in this study. So indicators (corrosion depth or mass loss et al.) with time would follow a linear relationship. In addition, Daczko[45] found that the mass of all the concrete specimens increased initially and after 50 days, the mass of all the specimens decreased when exposed to pH=1 sulfuric acid solution. Chang[19] found that all the concrete cylinders had mass gain over the first 21 days immersion in the acid solution and then started losing mass with immersion time when

exposed to 1% sulfuric acid solution (pH was kept in the range of 1.27 to 1.35). The cylinder specimens' crushing loads in his research were also recorded an increase before 56 days and then a decrease. It seems that hyperbolic function may be suitable for the relationship between indicators (corrosion depth or mass loss et al.) and time.

In order to make a reasonable choice of corrosion depth regression models, take concrete C2F1 as an example. 12 experimental corrosion depths of concrete C2F1 obtained during 194 days were divided into two parts. 10 depths obtained from 0~136 days were used to fit the empirical model, and the remaining 2 depths obtained from 136~194 days were used to verify the fitted model. Fig.8 shows two fitting curves including linear regression model recommended by previous studies[42, 43] and hyperbolic regression model proposed in this paper when protective layer are interrupted. Obviously the hyperbolic regression model is closer to the experimental data than linear regression model. So a hyperbolic regression model could provide better prediction to corrosion depths than linear relationship in this paper. The equation of the hyperbolic regression model is given as follow:

$$h = 1 / (A \times t^B + C) + D \times t + E \quad (13)$$

Where, h is the degradation depth, t is the exposure time in acid solution. A, B, C, D, and E are coefficients from regression. The curve fitting coefficients are listed in Table 7 for corrosion depth. Fig. 9 shows the result of Eq. (13) and experimental data of concrete corrosion depths.

<Fig. 8>

<Fig. 9>

After several attempts, Eq. (13) is also suitable for the regression of mass loss and dynamic modulus of elasticity loss experimental data. The coefficients from regression are also listed in Table 7. Fig. 10 and Fig. 11 show the result of Eq. (13) and experimental data of concrete mass loss and dynamic modulus of elasticity loss, respectively.

<Fig. 10>

<Fig. 11>

<Table 7>

Generally, the first derivative of the corrosion depth with respect to time represents the rate of the corrosion. When the corrosion time tends to infinity, the rate of deterioration tends to D (shown as Eq. (14)), which means that the coefficient D represents the ultimate rate of the concrete sulfuric acid.

$$\lim_{t \rightarrow \infty} \frac{dh}{dt} = \lim_{t \rightarrow \infty} \left(\frac{-A \times B t^{B-1}}{A \times t^B + C} + D \right) = D \quad (14)$$

After comparing parameter D in Table 7, the corrosion rate in the terms of corrosion depth and mass loss was sorted in the following sequence: C1F1 (gravel and river sand)>C2F1 (marble stone and river sand)>C1F2 (gravel and marble sand)>C2F2 (marble stone and marble sand). The corrosion rate in the aspect of dynamic modulus of elasticity loss was sorted in the following sequence: C1F1>C2F1>C2F2>C1F2. The cylinders of concrete C2F2, containing marble stone and sand had the best performance in the terms of corrosion depth and mass loss. This could attribute to the marble

aggregates, which locally creating a buffering environment and protecting the cement paste, showed a smaller degradation depth and mass loss than the concrete with inert aggregates. However, the cylinders of concrete C1F2, containing gravel and marble sand had the best performance in the terms of dynamic modulus of elasticity. It is speculated that the dynamic modulus of elasticity of the gravel exposed on cylindrical surface would be less damaged than the marble stone, which could react with the sulfuric acid.

The orthogonal design is a mathematical method used for planning multifactor tests. Because there were two factors at two different levels in this test as previous mentioned, the orthogonal table $L_4(2)^3$ was used to arrange the tests. In this case, two factors were coarse aggregate and fine aggregate. Two levels were gravel (C1) and marble stone (C2) for coarse aggregate, and river sand (F1) and marble sand (F2) for fine aggregate. The range analysis was adopted to clarify the significance of coarse and fine aggregate on the concrete sulfuric acid corrosion rate, which could be represented as regression coefficient D. The results of range analysis are given in [Table 8](#). The K value represents the average of the two values of each level for each factor. R is the absolute value of the difference between K1 and K2. A large R value indicates the significant effect of the influencing factor[46]. According to the results of range analysis showed in [Table 8](#), Effect of fine aggregate on concrete sulfuric acid corrosion rate is more significant than coarse aggregate in the terms of corrosion depth, mass loss, and dynamic modulus of elasticity loss. The reason could be attributed to the large

surface to volume ratios of the fine aggregate. Take a sphere with the radius of “ r ” for example, surface area equals to “ $4\pi r^2$ ” and volume equals to “ $4\pi r^3/3$ ”. Surface-area-to-volume ratio of the sphere equals to $3/a$, which means the greater the radius of a sphere, the lower the surface area to volume ratio. As shown in [Table 2](#) and [Table 3](#), coarse aggregate is predominantly greater than 9.5mm, while fine aggregate is predominantly less than 1.18mm. So the surface-area-to-volume ratio of the fine aggregates is bigger than that of coarse aggregates. In chemical reactions involving a solid material, the surface area to volume ratio is an important factor for the reactivity. Materials with high surface area to volume ratio react at much faster rates than monolithic materials, because larger surface is available to react for a unit volume. So the marble sand will react with sulfuric acid more complete and will neutralize more sulfuric acid than marble stone.

<[Table 8](#)>

5 Conclusion

- 1) The dynamic modulus of elasticity loss can be regarded as an acceptable indicator for evaluating concrete sulfuric acid resistance as well as corrosion depth and mass loss.
- 2) A hyperbolic regression model was proposed in this paper, which could provide better prediction to indicators than linear relationship when concrete sulfuric acid corrosion layer interrupted. The model parameter D in the model has easily understood physical meanings, which represents the ultimate rate of the concrete sulfuric acid.
- 3) The corrosion rate in the terms of corrosion depth and mass loss was sorted in the

following sequence: C1F1 >C2F1>C1F2>C2F2. The corrosion rate in the aspect of

dynamic modulus of elasticity loss was sorted in the following sequence:

C1F1>C2F1>C2F2>C1F2. (the value in parentheses referring to parameter D

representing the corrosion rate)

4) Concrete with marble aggregates showed a smaller degradation depth, mass loss,

and dynamic modulus of elasticity loss than concrete with inert aggregates. Effect of

fine aggregate on concrete sulfuric acid corrosion rate is more significant than coarse

aggregate in the terms of corrosion depth, mass loss, and dynamic modulus of elasticity

loss.

Acknowledgments

The authors would like to acknowledge the financial supports by the National science foundation

(51208373) and the Shanghai Pujiang Program (12PJ1409000) .Special thanks are extended to

Associate prof. Hesheng Tang at Tongji University, China.

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Tables**Table 1** Chemical composition of two types of aggregates (% by mass)

Constituent	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₃
Gravel	59.323	14.923	4.089	1.134	3.487	4.449	3.914	nd	7.831
Marble	nd	nd	0.028	nd	56.636	0.002	0.008	0.034	44.134
Sand[22]	78.56	7.02	2.58	0.78	3.66	1.51	1.39	nd	nd

*Note : nd means content is lower than the limit of detection.

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648 [Table 2](#) Results of sieving test for gravel

Sieve size (mm)	26.5	19	16	9.5	4.75	2.36
Grader retained (%)	0	25	22	30	19	4
Accumulated retained (%)	0	25	47	77	96	100

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666 [Table 3](#) Results of sieving test of river sand

Sieve size (mm)	9.5	4.75	2.36	1.18	0.6	0.3	0.15	Bottom
Grader retained (%)	0	5.6	10.8	10.2	17.8	44.4	9.2	2
Accumulated retained (%)	0	5.6	16.4	26.6	44.4	88.8	98	100

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Table 4 Mix proportions for concrete specimens (kg/m³)

Specimens	Water	Cement	Fine	Coarse
			aggregate	aggregate
C1F1	205	456	516	1149
C1F2	205	456	522	1162
C2F1	205	456	507	1129
C2F2	205	456	513	1141

Table 5 Compounds standard molar enthalpies and entropies of formation in Eq. (3) ~ (7) & (11)

Compound	$\Delta_f H_m^\ominus$ /kJ · mol ⁻¹	$\Delta_f S_m^\ominus$ /J · mol ⁻¹ · K ⁻¹	Compound	$\Delta_f H_m^\ominus$ /kJ · mol ⁻¹	$\Delta_f S_m^\ominus$ /J · mol ⁻¹ · K ⁻¹
<i>Ca(OH)</i> ₂	-985.9	83.4	<i>Si(OH)</i> ₄	-1456.961	-500.503
<i>CaSO</i> ₄ · 2 <i>H</i> ₂ <i>O</i>	-2022.629	194.1	3 <i>CaO</i> · <i>SiO</i> ₂	-2929.202	168.598
<i>H</i> ₂ <i>SO</i> ₄	-813.989	156.904	<i>H</i> ₂ <i>O</i>	-285.93	69.950
2 <i>CaO</i> · <i>SiO</i> ₂	-2315.216	120.792	<i>CaCO</i> ₃	-1206.6	91.710
2 <i>CaO</i> · <i>SiO</i> ₂ · 1.167 <i>H</i> ₂ <i>O</i>	-2665.208	160.666	3 <i>CaO</i> · 2 <i>SiO</i> ₂ · 3 <i>H</i> ₂ <i>O</i>	-4782.312	312.126
<i>CO</i> ₂	-393.505	213.769			

Table 6 Results of thermodynamic calculation for Eq. (3) ~ (7) & (11)

Chemical equation	Eq.	$\Delta_r G_m^\ominus$ /kJ · mol ⁻¹	log K [⊖]
$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$	(3)	-208.97	36.62
$(2CaO \cdot SiO_2) + 2H_2SO_4 + 4H_2O \rightarrow 2CaSO_4 \cdot 2H_2O + Si(OH)_4$	(4)	-168.95	29.61
$(3CaO \cdot SiO_2) + 3H_2SO_4 + 5H_2O \rightarrow 3CaSO_4 \cdot 2H_2O + Si(OH)_4$	(5)	-453.66	79.51
$(3CaO \cdot 2SiO_2 \cdot 3H_2O) + 3H_2SO_4 + 4H_2O \rightarrow$ $3(CaSO_4 \cdot 2H_2O) + 2Si(OH)_4$	(6)	-172.367	30.21
$(2CaO \cdot SiO_2 \cdot 1.167H_2O) + 2H_2SO_4 + 2.833H_2O \rightarrow$ $2(CaSO_4 \cdot 2H_2O) + Si(OH)_4$	(7)	-165.079	28.93
$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$	(11)	-136.23	23.88

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Table 7 Regression coefficients of Eq. (13)

Indicators	Specimens	A	B	C	D	E	Adj.R ²
Corrosion depth	C1F1	0.0075	1.3634	0.6480	0.0390	-1.5415	0.997
	C1F2	0.0311	1.6136	1.3580	0.0177	-0.7404	0.998
	C2F1	0.0076	3.1670	1.4812	0.0215	-0.6755	0.993
	C2F2	0.0215	2.3422	2.9692	0.0142	-0.3384	0.984
Mass loss	C1F1	-0.0029	1.7437	-0.1991	-0.1657	5.0827	0.998
	C1F2	-0.0082	1.5722	-0.2258	-0.0973	4.4581	0.992
	C2F1	-0.0069	2.5943	-0.2470	-0.1227	4.0510	0.992
	C2F2	-0.0625	1.2695	-0.2922	-0.0815	3.4263	0.985
Dynamic modulus of elasticity loss	C1F1	12.0395	-1.9100	0.1530	-0.0700	-4.7536	0.969
	C1F2	16.9162	-2.1097	0.13692	-0.0245	-5.4834	0.596
	C2F1	8.2627	-1.3283	0.1909	-0.0696	-5.3059	0.895
	C2F2	7.3259	-1.1099	0.1570	-0.0379	-3.3778	0.674

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Table 8 Range analysis for coefficient D

Indicators	Specimens	Coarse aggregate	Fine aggregate	Coefficient D in Eq.(10)
Corrosion depth	C1F1	1	1	0.0390
	C1F2	1	2	0.0177
	C2F1	2	1	0.0215
	C2F2	2	2	0.0142
	<i>K1</i>	0.028	0.030	
	<i>K2</i>	0.018	0.016	
	<i>R</i>	0.010	0.014	
Mass loss	C1F1	1	1	-0.1657
	C1F2	1	2	-0.0973
	C2F1	2	1	-0.1227
	C2F2	2	2	-0.0815
	<i>K1</i>	-0.132	-0.144	
	<i>K2</i>	-0.102	-0.089	
	<i>R</i>	0.030	0.055	
Dynamic modulus of elasticity loss	C1F1	1	1	-0.0700
	C1F2	1	2	-0.0245
	C2F1	2	1	-0.0696
	C2F2	2	2	-0.0379
	<i>K1</i>	-0.047	-0.070	
	<i>K2</i>	-0.054	-0.031	
	<i>R</i>	0.007	0.039	

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Figures

Fig.1 Specimens immersion arrangement

Fig.2 Experimental setup for the impact resonance test

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[Fig.3](#) Appearance of concrete cylinders after 164 days corrosion

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[Fig.4](#) Appearances of concrete cylinders (C1F1) during 194 days corrosion

Fig.5 Relationship between corrosion depth and time

Fig.6 Relationship between mass loss and time

Fig.7 Relationship between dynamic modulus of elasticity loss and time

Fig.8 Comparison of hyperbolic and linear models with test results of C2F1 corrosion depth

Fig.9 Comparison of hyperbolic model with test results of corrosion depth

Fig.10 Comparison of hyperbolic model with test results of mass changes

Fig.11 Comparison of hyperbolic model with test results of dynamic modulus of elasticity loss