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Comparative Study on Theory Model and Test Result for Dilute sulfuric Acid to Erode Concrete

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Abstract

In order to find the action mechanism for dilute sulfuric acid to erode concrete, immersion test has been carried out to concrete samples for a long time. Under the premise that PH value of immersion solution is kept constant basically, acid-consuming speed of concrete sample is determined according to titer, and according to assumption of reaction boundary layer and dynamic model of chemical reaction, the theory formula that acid-consuming speed changes with time is deduced, and the action rule for sulfuric acid to erode concrete is obtained finally: course of test sample that acid-consuming speed changes with time can be divided into two phases, respectively quick erosion and stable erosion. According to analysis of immersion test data, test result and theory model are of high degree of fitting, and theory model is correct.

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Keywords: dilute sulfuric acid; concrete; assumption of boundary layer; acid-consuming speed; uniform design

1. Introduction

With the rapid development of industrialization and urbanization, acid rain has become increasingly conspicuous, and the gradual aging of concrete structure due to sulfuric acid erosion has become a global problem. Scholars both in China and abroad have focused their attention on the sulfuric acid erosion to concrete due to various reasons since 1980s. Xie Shaodong and Zhou Ding [1] conducted test by two accelerated test methods, respectively period immersion and spray test. According to their test results, erosion of concrete and mortar under the action of acid rain is dissolution erosion caused by H⁺ and

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dilation erosion caused by SO_4^{2-} , materials are damaged due to combined action of H^+ and SO_4^{2-} . Zhou Fei peng [2] researched erosion of acid rain to mortar and concrete by dry-wet alternative method and thought that rigidity of the acid rain eroded mortar and concrete decreased at the beginning of erosion, increased in the middle of erosion and decreased again in the later stage. Israel [3] found obvious difference of two kinds of solution through immersing concrete of different densities in sulfuric acid, hydrochloric acid and nitric acid solution. Böhm [4] was the first to put forward the movable boundary layer diffusion model which could forecast the speed for sulfuric acid to erode concrete and specified the parameters affecting the speed. This movable boundary layer diffusion model is applied to study sulfuric acid eroded mortar and concrete and to forecast thickness of eroded layer (calcium sulfate), and it has been verified by test. On the whole, erosion rules of sulfuric acid to concrete materials are very complicated, and study results are different to some degree; comparing with carbonization, chloride penetration and other study field of concrete durability, its erosion mechanism and forecasting model are still immature, so it is a subject worthy of further study.

In order to find out common rules for sulfuric acid to erode concrete materials, the author has carried out 150 days' immersion test to study sulfuric acid erosion resistance of concrete. Uniform test method is applied for test design. Control factors are water cement ratio and PH value of immersion solution. Herein, scope of water cement ratio is 0.35~0.70; dilute sulfuric acid is used as immersion solution and its PH value is 2.00~4.00. Portable acidometer is used to measure PH value variation condition of immersion solution, and dilute sulfuric acid is titrated to ensure constant PH value of immersion solution and to determine acid-consuming speed of concrete sample according to titer. Besides, assumption of reaction boundary layer and dynamic model of chemical reaction are combined to deduce the theory formula that acid-consuming speed changes with time, and action rule for sulfuric acid to erode concrete is found finally.

2. Text

2.1. Assumption of reaction boundary layer

Michael Böhm and Fereidoun Jahani etc.[4-6] have studied sulfuric acid eroded concrete on the basis of movable boundary layer diffusion model. Its reaction mechanism: H^+ and SO_4^{2-} of the solution diffuse freely and reach the non-eroded concrete surface through eroded layer to react with it; then the reaction product diffuses to surface through the solution in holes.

However, reaction mechanism of the movable boundary layer diffusion model is totally inconsistent with actual conditions. On surface of the non-eroded test sample, $\text{Ca}(\text{OH})_2$ dissolves in water, forms saturated $\text{Ca}(\text{OH})_2$ solution and is ionized to OH^- and Ca^{2+} . Because of concentration gradient, OH^- and Ca^{2+} diffuse from inside to outside (non-eroded sample surface diffuses to immersion solution through eroded layer). In immersion solution, concentration of H^+ and SO_4^{2-} are the highest; because of concentration gradient, they diffuse from outside to inside (immersion solution diffuses to non-eroded sample surface through eroded layer). Thus, reaction boundary layer is formed. On the outer boundary of boundary layer (immersion solution), concentration of OH^- may be regarded as approximate to 0; concentration of H^+ is that of H^+ in immersion solution. On inner boundary of boundary layer (non-eroded sample surface), concentration of H^+ may be regarded as approximate to 0; concentration of OH^- is that of OH^- in saturated $\text{Ca}(\text{OH})_2$ solution; and the reaction from sulfuric acid to erode concrete happens in this boundary layer.

Thus, the real reaction mechanism should be: during immersion, $\text{Ca}(\text{OH})_2$ was produced in cement hydration of test sample dissolves in water, and OH^- layer is formed on the surface of test sample; under the action of concentration gradient, OH^- diffuses from inside of test sample to its outside and reacts with

H⁺ of immersion solution to form a reaction boundary layer. Fig.1 shows the reaction boundary layer when sulfuric acid erodes concrete sample.

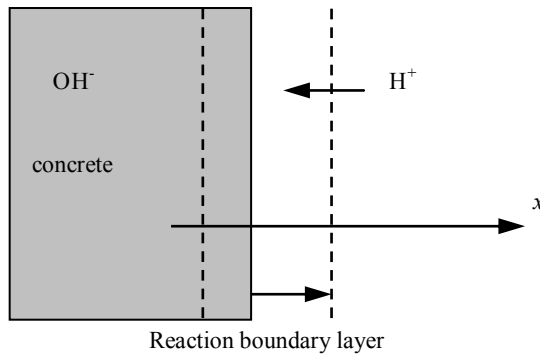
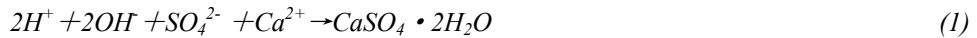


Fig. 1. The reaction boundary layer between sulfuric acid and concrete

2.2. Establishment of diffusion reaction formula

Erosion of concrete by sulfuric acid is a kind of strong acid erosion. Sulfuric acid reacts with Ca(OH)₂ of concrete and then hydrated calcium silicate etc. to form soluble calcium salt, so that chemical reaction continues repeatedly; alkalinity and strength of concrete decrease accordingly. Chemical reaction within the reaction boundary layer formed when sulfuric acid erodes concrete sample can be expressed by the following chemical formulas:



In formula (1), mole ratio of H⁺ and OH⁻ in this chemical reaction is 1:1, so apparent diffusion coefficient of concrete sample can be regarded as a constant. Through calculating change of OH⁻ concentration in the reaction boundary layer, it can be known that acid-consuming speed of concrete sample changes with time.

It is assumed that change of OH⁻ concentration in the reaction boundary layer conforms to diffusion procedure of chemical reaction [7] with second order homogeneous phase, and the whole diffusion procedure can be described as the following diffusion reaction formula:

$$\frac{\partial C_{OH}(x, t)}{\partial t} = D_{OH} \frac{\partial^2 C_{OH}(x, t)}{\partial x^2} - k C_{OH}(x, t) C_H(x, t) \tag{2}$$

- Herein: x — distance from certain point of the reaction boundary layer to non-eroded sample surface;
- t — immersion time;
- k — speed constant of the chemical reaction of H⁺ and OH⁻;
- $C_{OH}(x, t)$ — concentration of OH⁻ at position x in time t ;
- $C_H(x, t)$ — concentration of H⁺ at position x in time t ;
- D_{OH} — apparent diffusion coefficient of OH⁻ in the reaction boundary layer.

2.3. Solution of diffusion reaction formula

Obviously, at the position within the reaction boundary layer where $x=0$, concentration of OH⁻ is the

same as that of OH⁻ in saturated Ca(OH)₂ solution and is a constant, and the related concentration of H⁺ is approximate to 0; at the position within outer boundary of reaction boundary layer where x=δ, concentration of H⁺ is the same as that of H⁺ in immersion solution and is also a constant, and the related concentration of OH⁻ is also approximate to 0. Thus, the following reaction boundary condition can be specified according to the above analysis:

$$\begin{cases} C_{OH}(0, t) = C_{OH,s}; & C_{OH}(\delta, t) = 0 \\ C_H(\delta, t) = C_{H,s}; & C_H(0, t) = 0 \end{cases} \quad (3)$$

Herein: C_{OH,s}— concentration of OH⁻ in saturated Ca(OH)₂ solution;
 C_{H,s}— concentration of H⁺ in immersion solution;
 δ— thickness of the reaction boundary layer.

It is assumed that distribution of concentration of OH⁻ and H⁺ in the reaction boundary layer satisfies the following functional form:

$$\begin{cases} C_{OH}(x, t) = C_{OH,s}\varphi(\eta) \\ C_H(x, t) = C_{H,s}\psi(\eta) \end{cases} \quad (4)$$

Herein: φ(η)— shape function for the distribution of OH⁻ concentration in the reaction boundary layer, herein η=x/δ(t), δ(t) is the function relation in which thickness of the reaction boundary layer changes with time, and δ(0)=0;

ψ(η)—shape function for the distribution of H⁺ concentration in the reaction boundary layer.

It can be known from formula (3) and (4) that φ(η) and ψ(η) must meet the following conditions:

$$\begin{cases} \varphi(0) = 1; & \varphi(1) = 0 \\ \psi(0) = 0; & \psi(1) = 1 \\ \varphi'(1) = 0; & \psi'(0) = 0 \end{cases} \quad (5)$$

According to formula (2) and (4):

$$\varphi'(\eta)\left(-\frac{\eta}{\delta(t)}\right)\frac{d\delta(t)}{dt} = D_{OH}\varphi''(\eta)\frac{1}{\delta^2(t)} - kC_{H,s}\varphi(\eta)\psi(\eta) \quad (6)$$

Integrate at both sides of formula (6), then:

$$\int_0^1 [\varphi'(\eta)\left(-\frac{\eta}{\delta(t)}\right)\frac{d\delta(t)}{dt}]d\eta = \int_0^1 [D_{OH}\varphi''(\eta)\frac{1}{\delta^2(t)} - kC_{H,s}\varphi(\eta)\psi(\eta)]d\eta \quad (7)$$

To be simplified:

$$\frac{\int_0^1 [-\eta\varphi'(\eta)]d\eta}{\delta(t)} \frac{d\delta(t)}{dt} = D_{OH}\int_0^1 \varphi''(\eta)d\eta \frac{1}{\delta^2(t)} - kC_{H,s}\int_0^1 \varphi(\eta)\psi(\eta)d\eta \quad (8)$$

command,
$$\begin{cases} M = \int_0^1 [-\eta\varphi'(\eta)]d\eta \\ N = \int_0^1 \varphi''(\eta)d\eta = \varphi'(\eta) \Big|_0^1 = \varphi'(1) - \varphi'(0) = -\varphi'(0) \\ P = \int_0^1 \varphi(\eta)\psi(\eta)d\eta \end{cases} \quad (9)$$

Thus, formula (8) can be simplified as follows:

$$\frac{M}{\delta(t)} \frac{d\delta(t)}{dt} = D_{OH}N \frac{1}{\delta^2(t)} - kPC_{H,s} \quad (10)$$

According to the differential equation shown in formula (10) and the initial condition δ(0)=0, the

following function relation in which thickness of the reaction boundary layer changes with time can be concluded:

$$\delta^2(t) = \frac{D_{OH}^N}{kPC_{H.S}} \left(1 - \exp\left(-\frac{2kPC_{H.S}}{M} t\right) \right) \quad (11)$$

On the immersion surface (area is S), namely inner boundary of the reaction boundary layer, the following formula in which acid-consuming speed changes with time can be used:

$$V_h(t) = -SD_{OH} \left. \frac{\partial C_{OH}(x, t)}{\partial x} \right|_{x=0} = -SD_{OH} C_{OH.S} \phi'(0) \frac{1}{\delta(t)} \quad (12)$$

According to formula (9), (11) and (12):

$$V_h(t) = \frac{SC_{OH.S} \sqrt{D_{OH}^N kPC_{H.S}}}{\sqrt{1 - \exp\left(-\frac{2kPC_{H.S}}{M} t\right)}} \quad (13)$$

Thus, formula (13) can be simplified as follows:

$$V_h(t) = \frac{a}{\sqrt{1 - \exp(-bt)}} \quad (14)$$

Units of all parameters in the formula are international units. Herein, parameters, a and b, are called chemical reaction speed constant of acid-consuming speed, and it can be expressed as the following formula:

$$\begin{cases} a = SC_{OH.S} \sqrt{D_{OH}^N kPC_{H.S}} \\ b = \frac{2kPC_{H.S}}{M} \end{cases} \quad (15)$$

Integrate both sides of formula (14), then:

$$\int_0^t V_h(t) dt = \int_0^t \frac{a}{\sqrt{1 - \exp(-bt)}} dt \quad (16)$$

The total consumption $m(t)$ of H^+ within time t can be figured out:

$$m(t) = \frac{a}{b} \ln \left[\frac{1 + \sqrt{1 - \exp(-bt)}}{1 - \sqrt{1 - \exp(-bt)}} \right] \quad (17)$$

Total consumption of H^+ can also be regarded as total amount of eroded concrete. Through assumption of the reaction boundary layer, the theory formula in which acid-consuming speed changes with time is deduced. It can be known according to formula (14) that acid-consuming speed is high in the beginning, decreases rapidly with the increasing of reaction time and will tend to certain constant finally. Therefore, the whole reaction course can be divided into two phases, respectively quick decreasing phase and stable phase; total consumption of the related H^+ increases in a non-linear manner in the beginning and then increases in a line manner approximate to gradient = a when reaching certain time.

3. Test design

Generally, uniform design [8] conducts test design according to uniform design schedule. Certain code of every uniform design schedule is expressed as $U_n(q^5)$ or $U_n^*(q^5)$; herein, “U” is uniform design; “n” is

times of test; “q” means every factor has q levels; and “s” means this schedule has s lines. U with or without “*” at its top right corner represents two kinds of different uniform design schedule. In general, the uniform design schedule with “*” indicates more uniform and should be preferential.

There are many factors which may affect sulfuric acid erosion resistance of concrete, but this paper considers only two control factors, water cement ratio and pH value of immersion solution. Every factor has 8 levels, see Table 1. Two control factors are chosen for the test, and each factor has 8 levels. If it is designed according to orthogonal test [8], the test should be carried out for $8^2=64$ times, and test times are too much. Thus, it is designed according to uniform test, according to $U_8^*(8^5)$ and its use list [9], the 1st and the 3rd lists of $U_8^*(8^5)$ are chosen for test arrangement, see Table 2. See Table 3 for test design.

Table 1. Factors and Levels

Levels Factors	1	2	3	4	5	6	7	8
Water cement ratio	0.70	0.65	0.60	0.55	0.50	0.45	0.40	0.35
PH value of immersion solution	4.00	3.70	3.40	3.10	2.80	2.50	2.20	2.00

Table 2. Test Arrangement

NO.	1	2	3	4	5	6	7	8
Water cement ratio	0.70	0.65	0.60	0.55	0.50	0.45	0.40	0.35
PH value of immersion solution	3.10	2.00	3.40	2.20	3.70	2.50	4.00	2.80

Table 3. Test Design

Test group	Dimension of test sample	Mix proportion (mass ratio)				Slumps (mm)	Qty of test samples	PH value of immersion liquid	Titrated sulfuric acid concentration	Titrated PH value
		Water cement ratio	Cement	Sand	Stone					
1	100mm × 100mm × 100mm	0.40	1	0.98	1.99	50	3	4.00	0.125	5.00
2		0.50	1	1.47	2.62	35	3	3.70	0.125	4.00
3		0.60	1	1.93	3.15	45	3	3.40	0.125	3.60
4		0.70	1	2.55	3.52	45	3	3.10	0.125	3.30
5		0.35	1	1.11	2.36	40	3	2.80	0.125	3.00
6		0.45	1	1.26	2.33	35	3	2.50	0.500	2.70
7		0.55	1	1.74	2.84	40	3	2.20	0.500	2.30
8		0.65	1	2.29	3.29	50	3	2.00	0.500	2.10

Note: test samples in which water cement ratios are 0.35, 0.40 and 0.45 are added with water reducer because their slumps can't meet requirements (35~50mm).

4. Test course

After maintenance, test samples are naturally dried in room. Then, metal brush is used to remove the cement laitance on sample surface; melting olefin is used to seal 5 sides of test sample, and only a side is left for immersion test. Totally 8 plastic boxes (volume: 21L, dimension: 467mm × 323mm × 215mm) are used as immersion tanks. Every immersion tank will contain 3 test samples, and immersed sides of every

test sample are vertical to bottom of the related immersion tank. Volume of every group of immersion solution is 10L, and test samples are immersed for 150 days, see Fig. 3 for test layout. Self-made distilled water and 98.08% dense sulfuric acid are used to prepare two kinds of sulfuric acid with concentration of 0.125mol/l and 0.500mol/l respectively. 10ml and 50ml graduated cylinders are used to measure volume of titrated sulfuric acid every time; and portable acidometer is used to measure pH value of every group of immersion solution in real time, as shown in Fig. 2.



Fig. 2. Portable acidometer and combination electrode (left)

Fig. 3. Layout of concrete immersion test (right)

During immersion test, in order to ensure that pH value of every group immersion solution is kept approximate to the set initial pH value, a titrated pH value is set for every group of immersion solution, as shown in Fig. 3. When pH value of immersion solution increases to the set titrated pH value, sulfuric acid is titrated to the set titrated pH value; titration time and sulfuric acid titer are recorded. Through dividing the sulfuric acid titer of every time by interval of two succeeding titration time, average acid-consuming speed of concrete sample within the interval can be figured out.

5. Test result

5.1. Appearance characteristics of test samples

After concrete samples of different water cement ratios are immersed in immersion solution of different PH values for 150 days, test samples are dried naturally. Immersed sides of every group of test samples show different appearance characteristics. Their diversities are mainly shown in color and hardness of the immersed sides. Gray indicates that test samples are eroded lightly. Yellow indicates that test samples are eroded badly, and loose surface also indicates serious erosion. White indicates plenty of CaSO_4 deposits on sample surface; CaSO_4 will block holes of sample surface, so erosion will be slower and erosion degree will decrease gradually. Immersed sides of every group of concrete sample are shown in Fig. 4.

Average value of erosion thickness of the 3 test samples from every group is adopted as average erosion thickness of every group of test sample eroded by sulfuric acid, as shown in Table 4.

Table 4. Average thickness of eroded layer of every group of concrete sample

Test group	1	2	3	4	5	6	7	8
Water cement ratio	0.40	0.50	0.60	0.70	0.35	0.45	0.55	0.65
PH value of immersion solution	4.00	3.70	3.40	3.10	2.80	2.50	2.20	2.00
Average thickness of eroded layer (mm)	0.10	0.10	0.11	0.34	1.20	1.63	1.27	0.88

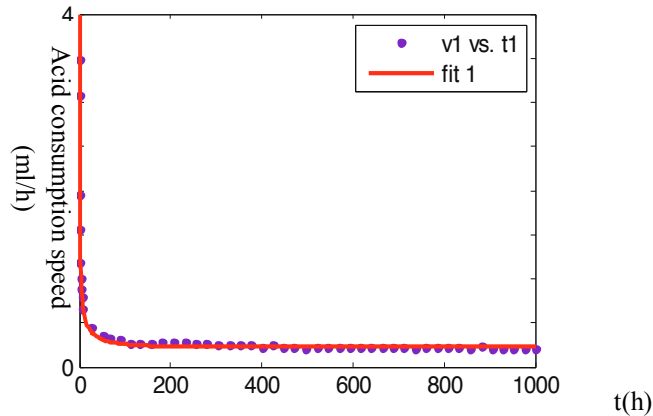
According to Table 4, erosion condition of the immersion solution (PH value= 2.50) to concrete sample is the worst. When PH value of immersion solution is within [2.50,4.00], with the decrease of PH value of immersion solution, erosion degree of test sample gets worse, and erosion reaction extends to inside of test sample constantly; when PH value of immersion solution is within [2.00,2.50], with the decrease of PH value of immersion solution, erosion degree of test sample becomes lighter; that is because plenty of CaSO_4 produced on sample surface deposits here and blocks holes of sample surface, so erosion becomes slower and erosion degree becomes lighter.



Fig. 4. Integral photo of a test sample selected randomly from 8 groups of test samples

5.2. Comparison between test data and theory model

According to the observed data, the relation between consumption speed $V(\text{ml/h})$ of sulfuric acid for different immersed test sample and immersion time $t(\text{h})$ of test blocks are obtained. Because test results of every group are common in characteristics, this paper describes only test results of the 1st group, as shown in Fig. 5. This figure gives the curve drawn according to formula (14). According to this figure, acid-consuming speed is fast in the beginning, decreases rapidly with the increase of immersion time and becomes stable gradually; that is, the speed for sulfuric acid to erode concrete indicates two phases, respectively quick erosion and stable erosion.



Parameters, a and b, and regression coefficient R according to MATLAB software are shown in Fig. 5.

Fig. 5. Test data results of Group 1

According to the above table, theory model reflects in general the rule that the measured acid-

consuming speed of concrete sample changes with time and verifies validity of the rule that the measured acid-consuming speed of concrete sample changes with time.

Table 5. Parameters and regression coefficient

Test group	$a(\times 10^{-8}\text{mol/s})$	$b(\times 10^{-5}\text{s}^{-1})$	Regression coefficient
1	2.1938	8.2583	0.9411
2	2.9611	8.6528	0.9520
3	5.1368	13.1528	0.8830
4	11.2014	13.7472	0.9157
5	20.6806	14.4028	0.8285
6	42.8333	15.2111	0.7160
7	74.4444	12.2472	0.5889
8	100.8056	8.9056	0.7013

6. Conclusion

Author of this paper has carried out 150 days' immersion test to study sulfuric acid erosion resistance of concrete. Through considering affecting factors, such as different water cement ratio and PH value of immersion solution etc. and combining theory model, erosion mechanism and action rule for sulfuric acid to erode concrete are found.

(1)When PH value of immersion solution is within [2.00, 4.00], with the decrease of PH value, immersed sides of concrete sample will turn gray, yellow and then white; the depth of concrete sample eroded by sulfuric acid doesn't increase with the decrease of PH value of immersion solution; when PH value of immersion solution is 2.50, the erosion depth is the maximum;

(2)Under the premise that PH value of immersion solution is kept constant basically, acid-consuming speed of concrete sample is determined according to titer, and according to assumption of reaction boundary layer and dynamic model of chemical reaction, the theory formula that acid-consuming speed changes with time is deduced, and the action rule for sulfuric acid to erode concrete is obtained finally: course of test sample that acid-consuming speed changes with time can be divided into two phases, respectively quick erosion and stable erosion. According to analysis of immersion test data, test result and theory model are of high degree of fitting, and theory model is correct.

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