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Permeability and Prediction of Free Chloride Ion in Recycled Aggregate Concrete with Fly Ash

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Experimental work was carried out to investigate the free chloride ion penetration in recycled aggregate concrete with fly ash. By using the natural diffusion method, specimens with different fly ash content of 0%,10%,20% and 30% were tested after corroding in fully saturation or wet-dry circulation for 30days,60days, 90days and 120days respectively. And then specimen was drilled with diameter of 6mm to get the powder at the depth of 1~5mm, 6~10mm, 11~15mm and 16~20mm respectively, and then the powder was put in a bottle with distilled water. After 24 hours, this solution was filtered and neutralized by the diluted sulphuric acid; after ten drops of potassium chromate indicator was put into this solution, the silver nitrate solution was added to make it brick red, and the free chloride ion concentration was obtained by a formula. Then the impact of fly ash content and corroding time on free chloride ion (FCI) concentration (by mass) was discussed respectively; and the distributions of free chloride ion with the depth were also presented. And the mechanism of free chloride ion penetration was also put forward after comparison study between fully saturation and wet-dry circulation. Finally the improved grey model was applied to predict the FCI concentration in recycled aggregate concrete with different fly ash content after validation; and it is found that the model is feasible to predict with higher accuracy; and the prediction reveals that the effect of wet-dry circulation would decline with time and 20% was the best fly ash content for the durability of recycled aggregate concrete.

Keywords: fly ash; recycled concrete; free chloride ion; permeability; improved grey model;

1. INTRODUCTION

Nowadays recycling of demolition concrete is beneficial and necessary from the viewpoint of environmental preservation and effective utilization of resources. Although it has proved that some properties of recycled aggregate concrete may be generally lower than those of normal concrete, they are still sufficient for practical application in some constructions and buildings [1, 2].To make this technology feasible, a significant amount of experimental works has been conducted on mechanical properties of recycled concrete with the focusing on the compressive strength, the tensile and the flexural strengths, the bond strength, and elastic modulus of recycled concrete[3-10].

As the research of recycled concrete proceeds, some have paid attention to its durability and found that one of the key factors determining the durability of recycled concrete is the free chloride ion, for it lowers the compressive strength and accelerates the corrosion of rebar in recycled aggregate concrete [11-13]. And when free chloride ion, oxygen and water all exist at the surface of rebar, the chemical reaction occurs as

$$Fe + 2Cl^{-} \rightarrow FeCl_2 + 2e \rightarrow Fe^{2+} + 2Cl^{-} + 2e, \qquad (1)$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^{-}, \qquad (2)$$

And the Fe^{2+} could combine with OH^{-} the in the water to produce the $Fe(OH)_2$ which would expand and destroy the concrete. A few scholars and experts have dedicated to the research of free chloride ion. Xiao and Evangelista et al.has found that diffusion coefficient of chloride ion in recycled concrete increases with the increase of recycled fine aggregate content after conducting a research [14,15].Ann et al. used the same method to study the impact of fly ash and blast furnace slag on the recycled aggregate concrete's resistance to chloride ion penetration , and the results showed that the mixing and granulating of fly ash blast furnace slag can improve the recycled concrete resistance to chloride ion penetration[16].Chen et al. conducted the chloride ion test and found that chloride ion diffusion coefficient increases obviously after freeze-thaw cycle in recycled concrete[17].Zhang et.al studied the influence of water cement ratio, regeneration thickness aggregate content and mineral admixtures on the permeability of chloride ion in recycled concrete, and the results showed that chloride ion penetration resistance in high quality recycled fine aggregate concrete is better than that of natural aggregate concrete, and the high quality of the chloride ion penetration resistance in recycled coarse aggregate concrete is close to natural coarse aggregate concrete[18]. Lei et al. conducted the research and found that using the admixture aggregate can greatly improve the performance of recycled concrete resistance to chloride ion penetration but with a minor amplitude [19].Yue et al discovered that the concentration of combined chloride ion in recycled concrete increased with corroding time and fly ash content but decreased with the penetration depth, and the arid and humid circulating promotes the chloride ion’s combining ability [20]. Guneyisi et al discovered that sintered aggregate containing lightweight concretes had relatively better performance than those with cold bonded aggregates. Moreover, the incorporation of silica fum provided further enhancement in permeability and corrosion resistance of the concretes[21].Lima et al. carried out a wide experimental campaign on concretes using recycled concrete aggregates and fly ash in partial substitution of natural aggregates and cement, and found that the addition of fly ash in the mixture improves the workability of recycled concrete, and both compressive and tensile strengths increase in concrete mixes with the higher fly ash content and adding fly ash in the concrete mix produces a significant improvement in the resistance to chloride penetration[22]. All these has make people gain more acquaintance with characteristics of FCI concentration in recycled aggregate concrete, however, many problems still need to be solve before the recycled aggregate concrete is applied in large scale in actual engineering constructions. Thus it is of great necessity to conduct more experiments to investigate the mechanism of free chloride ion penetration in recycled aggregate concrete with fly ash.

In this paper, natural diffusion method was adopted in this research to simulate the natural condition [20]. And the specimens of recycled aggregate concrete with different fly ash content of 0%, 10%, 20% and 30% were tested after corroding in fully saturation or wet and dry circulation for 30days, 60 days, 90days and 120 days respectively. And the FCI concentration (by mass) in the specimen's depth of 1~5mm, 6~10mm, 11~15mm and 16~20mm were measured respectively. Then the impact of fly ash content and corroding time on the FCI concentration was discussed respectively; and the distributions of free chloride ion with the depth were presented to reveal the penetration process. Then the mechanism of free chloride ion penetration was proposed after comparison study between the fully saturation and dry-wet circulation; finally the improved grey model was employed to predict long term effect of fly ash on the FCI concentration after the model was validated; and the results were discussed to reveal the impact of fly ash content on the durability of recycled aggregate concrete.

2. EXPERIMENTAL DESCRIPTIONS

2.1. Materials and mixture ratio

Ordinary Portland cement with 28d compressive strength of 42.5MPa was adopted in this research, and the fly ash was from the Shanghai Waigaoqiao Electric Power Plant with its fineness 14.8% and ignition loss 5.79%. The recycled aggregate was obtained from the building demolition in a project in Shanghai, China, and its grain diameter was 5-20mm. And the fine aggregate used was river sand with a fineness modulus of 2.8. And the water was the ordinary drinking water in Shanghai. The ratio of water to cement was kept constant as 0.55 as Wang et al. suggest [10]. And the mixture was divided into four series, and their difference is the fly ash content, which is 0%, 10%, 20%, and 30% respectively. The mix proportions of concretes are shown in Table.1.

Table 1. Mix proportions of concretes

Sample	Replacement(by mass)%		Cement	Fly ash	Mix proportion/(kg/m^3)		
	recycled aggregate	fly ash			water	sand	recycled aggregate
Series 1	100	0	293	0	170	624	1107
Series 2	100	10	264	29	170	624	1107
Series 3	100	20	235	58	170	624	1107
Series 4	100	30	205	89	170	624	1107

2.2. Preparation of specimens

The preparations of specimens were conducted strictly according to the laboratory regulations.

As Figure.1 indicated, the mixture in each group was casted in 100 × 100 × 100mm cubes in steel moulds and then compacted on vibration table. They were removed of the mould a day after casting and were cured in a fog room (20 ± 2 °C, relative humidity of 95%) for 28 days. And the chlorination solution was made up of industrial salt and drinking water, and the density of this solution was 5% by mass to accelerate the corrosion. There were two kinds of corroding conditions including fully saturation and wet-dry circulation; In fully saturation, the specimens were immersing in the chlorination solution directly until the corroding time was met; and in wet-dry circulation, the specimens were immersing in the chlorination solution for 16 hours and then taking out for 8 hours every day until the test day had come. The immersing of concrete specimens was shown in Figure.2.

Figure 1. Concrete casting

Figure 2. Concrete curing

Before testing, the specimens were taken out and open-air drying for a day. Then the specimen was drilled with diameter of 6mm to get the powder. And the depth of four layers were 1~5mm, 6~10mm, 11~15mm and 16~20mm respectively. And the powder was collected by a sieve of 0.63mm and put into a container with temperature of 105 °C± 5 °C, and then placed into the desiccators to cool off and store until the test began. The powder was shown in Figure.3.

Figure 3. Concrete powder

2.3. Testing methods

The powder of a specimen was divided as two equally, and each was tested by the water soluble chloride ion titration method recommended by the China's national standard of Testing Specification for Concrete in Water Transport Engineering. The test procedures were as follows; the powder of 20 gram in weight was put in a bottle, then 200 milliliter distilled water was added; and the bottle was sealed and shaken for about two minutes.

After 24 hours, the solution was filtered to get rid of the impurities; and then 20 milliliter solution was put in a triangle breakers with the help of pipette; then phenolphthalein was added to make the solution become thin red, and diluted sulphuric acid was added to make it neutralization; then ten drops of potassium chromate indicator was put into the solution, and the silver nitrate solution was added to make the solution become brick red; and the consuming of silver nitrate solution was recorded. Thus the free chloride ion concentration was calculated by

$$P = \frac{C_{AgNO_3} V_3 \times 0.03545}{G \times \frac{V_2}{V_1}} \times 100\% \qquad (3)$$

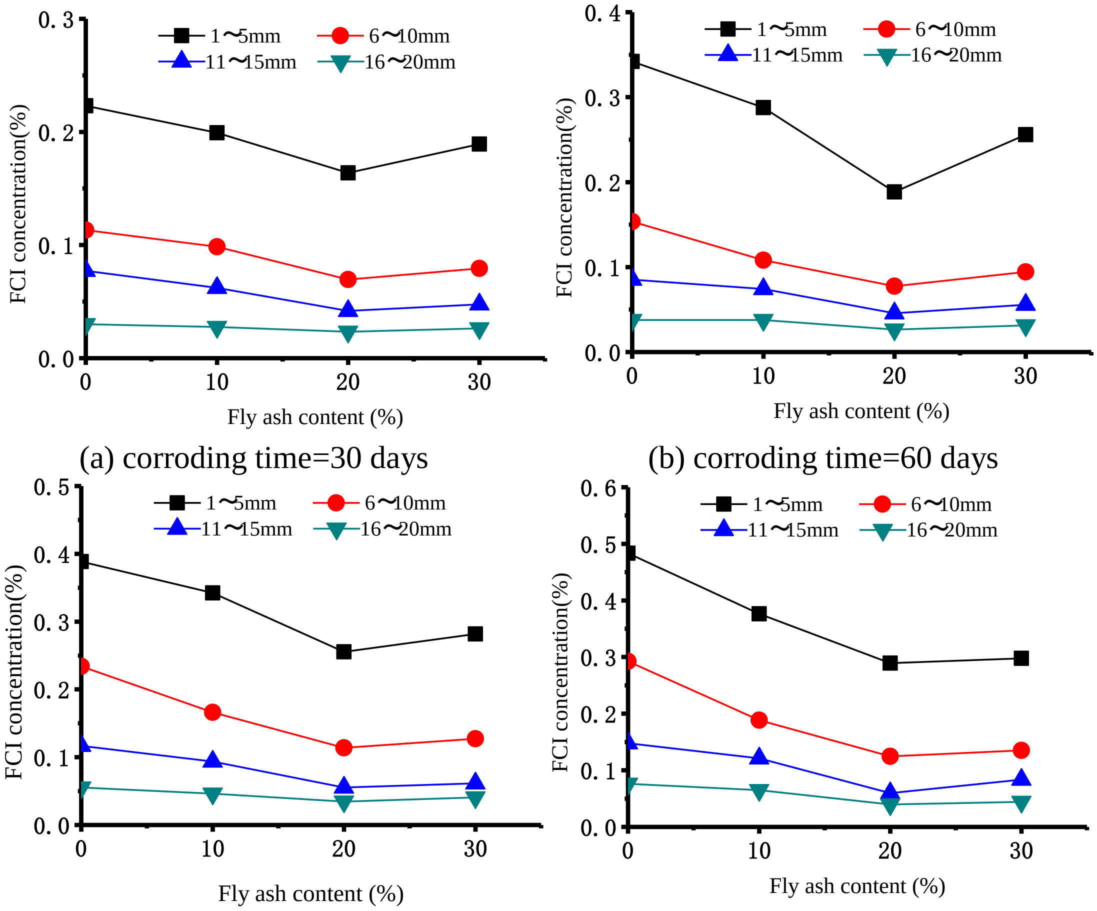
where P was the free chloride ion concentration (%); C_{AgNO_3} was the standard silver nitrate solution concentration (mol/L); G was the weight of the sample (g); V_1 was the water for immersing the sample (ml); V_2 was sample solution for testing (ml); V_3 was the consuming amount of silver nitrate solution (ml);

And the mean value of the every two test was considered as the final value of FCI concentration in a specific depth of specimen.

3. RESULTS AND DISCUSSION

3.1. Effect of fly ash content on free chloride ion penetration

The curves between fly ash content and FCI concentration in fully saturation were drawn in Figure.4. The test results in wet-dry circulation were attached in Appendix (A.1) to shorten the passage length.



(a) corroding time=30 days

(b) corroding time=60 days

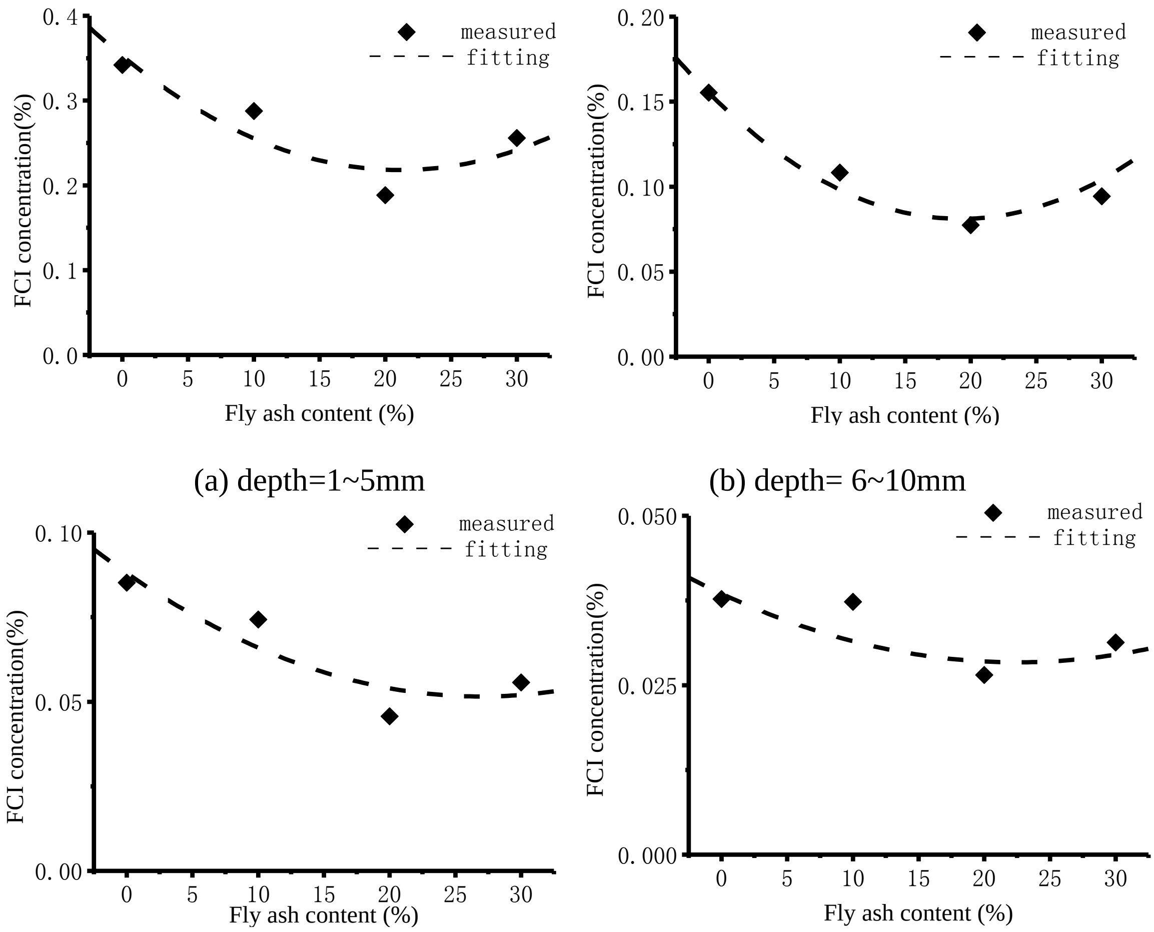
(c) corroding time=90 days

(d) corroding time=120 days

Figure 4. Curves between fly ash content and FCI concentration in fully saturation

As indicated, the free chloride ion penetration in recycled aggregate concrete was restrained after fly ash was added. And the ability of recycled aggregate concrete to resist free chloride ion penetration increased when the fly ash content increased from 0% to 20% but decreased when the fly ash content increased from 20% to 30%. And the anti- free chloride ion ability of recycled aggregate concrete was the best when the fly ash content was 20%. The main reason for this was that fly ash can improve the binding ability of chloride ion, reduce the total porosity in recycled aggregate concrete, and fill the pores in recycled aggregate concrete. The fly ash would generate secondary hydration reaction when triggered by the cement hydration product of $Ca(OH)_2$, and the hydration products can not only fill and refine the pore of recycled aggregate concrete, but also consume some of the $Ca(OH)_2$, thus improving the interfacial structure between the recycled aggregate and cement mortar; meanwhile the fly ash could also fill the pore in the crack of recycled aggregate and decrease the total porosity of recycled aggregate concrete [24]. However, the total porosity of recycled aggregate concrete remained nearly the same when the fly ash content was more than 20%. And the proportion of large pores in the specimens gradually increased as fly ash content was exceeding 20%; this may be caused by the low activity of fly ash. The low activity of fly ash would slow down the secondary hydration speed, loosen the structure of recycled aggregate concrete and decrease the ability to resist free chloride ion in recycled aggregate concrete.

In order to learn more about relationship between fly ash content and FCI concentration, the test results (corroding time=60 days) in fully saturation were used to conduct the fitting as shown in Figure.5.



(a) depth=1~5mm (b) depth= 6~10mm

(c) depth= 11~15mm (d) depth=16~20mm

Figure 5. Correlation between fly ash content and FCI concentration (60 days)

From the fitting, it was found that the relationship of fly ash content and FCI concentration confirms to a polynomial function and the function was

$$c_f = ax^2 + bx + c \qquad (4)$$

where c_f was the FCI concentration (%); x was the fly ash content (%); a, b, c were the three constant in the polynomial function; And the fitting parameters were listed in Table.2

Table 2. Fitting parameters (corroding time=60 days, condition= fully saturation)

Depth(mm）	*a*	*b*	*c*	**Correlation coefficient(CR)**
1~5mm	0.0003	-0.0127	0.3525	0.9848

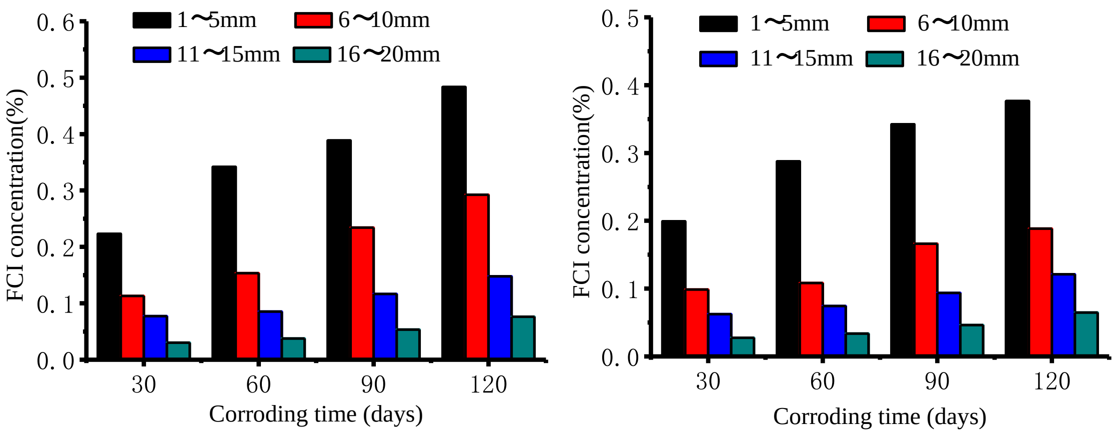
6~10mm	0.0002	-0.0077	0.1552	0.9913
11~15mm	5E-05	-0.0027	0.088	0.9831
16~20mm	2E-05	-0.0009	0.0385	0.9879

It was shown in Table.2 that the polynomial function was feasible to express the relationship between the fly ash content and FCI concentration when the corroding time was 60 days. The correlation coefficients were from 0.9831 to 0.9913, which shown the good conformity between the fly ash content and FCI concentration. Similarly, the fitting parameters of the tests with corroding time 30 days, 90 days, and 120 days in fully saturation respectively were listed in Table.3.

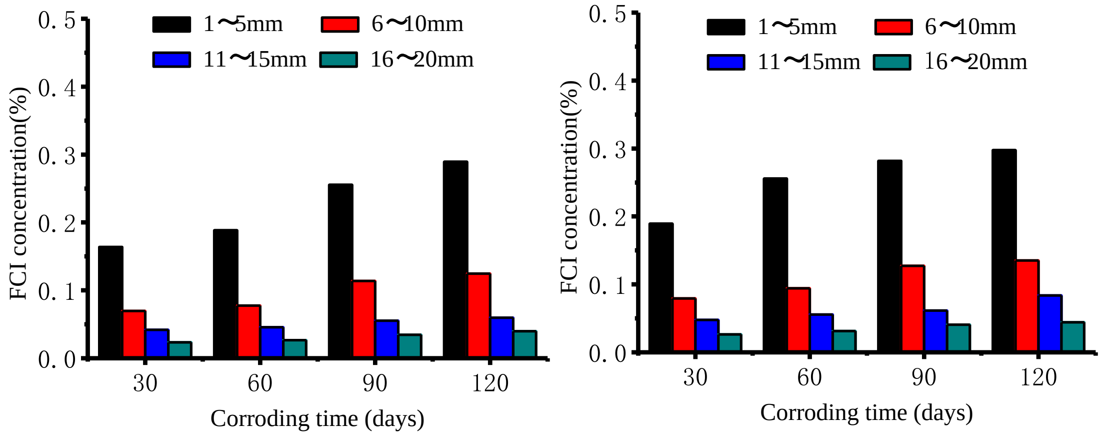
Table 3. Fitting parameters (corroding time=30, 90and 120 days, condition=fully saturation)

Time	Depth(mm)	*a*	*b*	*c*	Correlation
30 days	1~5mm	0.0001	-0.0051	0.2268	0.9842
	6~10mm	6E-05	-0.0031	0.1159	0.9861
	11~15mm	5E-05	-0.0027	0.0789	0.9667
	16~20mm	1E-05	-0.0006	0.0305	0.9888
90 days	1~5mm	0.0002	-0.0095	0.3962	0.9832
	6~10mm	0.0002	-0.0098	0.2367	0.9927
	11~15mm	7E-05	-0.0042	0.1197	0.9839
	16~20mm	3E-05	-0.0015	0.0544	0.9892
120 days	1~5mm	0.0003	-0.0151	0.4871	0.9942
	6~10mm	0.0003	-0.014	0.2943	0.9983
	11~15mm	0.0001	-0.0063	0.1538	0.9978
	16~20mm	4E-05	-0.0024	0.0784	0.9875

3.2. Impact of corroding time on free chloride ion penetration



(a) fly ash=0% (b) fly ash =10%



(c) fly ash =20% (d) fly ash =30%

Figure 6. Curves between corroding time content and FCI concentration in fully saturation

Table 4. Fitting parameters (fly ash =0%, 10%, 20%and 30%, condition=fully saturation)

Fly ash	**Depth(mm)**	*a*	*b*	**Correlation coefficient(CR)**
0%	1~5mm	0.0363	0.5373	0.9929
	6~10mm	0.0101	0.6938	0.9814
	11~15mm	0.0015	0.4602	0.9920
	16~20mm	0.0031	0.6462	0.9857
10%	1~5mm	0.0417	0.4646	0.9960
	6~10mm	0.0171	0.4922	0.9911
	11~15mm	0.0123	0.4618	0.9806
	16~20mm	0.0034	0.5949	0.9934
20%	1~5mm	0.0371	0.4225	0.9833
	6~10mm	0.0144	0.4462	0.9906
	11~15mm	0.0164	0.2661	0.9637
	16~20mm	0.0060	0.3858	0.9614
30%	1~5mm	0.0631	0.3303	0.9840
	6~10mm	0.0193	0.4066	0.9726
	11~15mm	0.0131	0.3652	0.9827
	16~20mm	0.0068	0.3915	0.9796

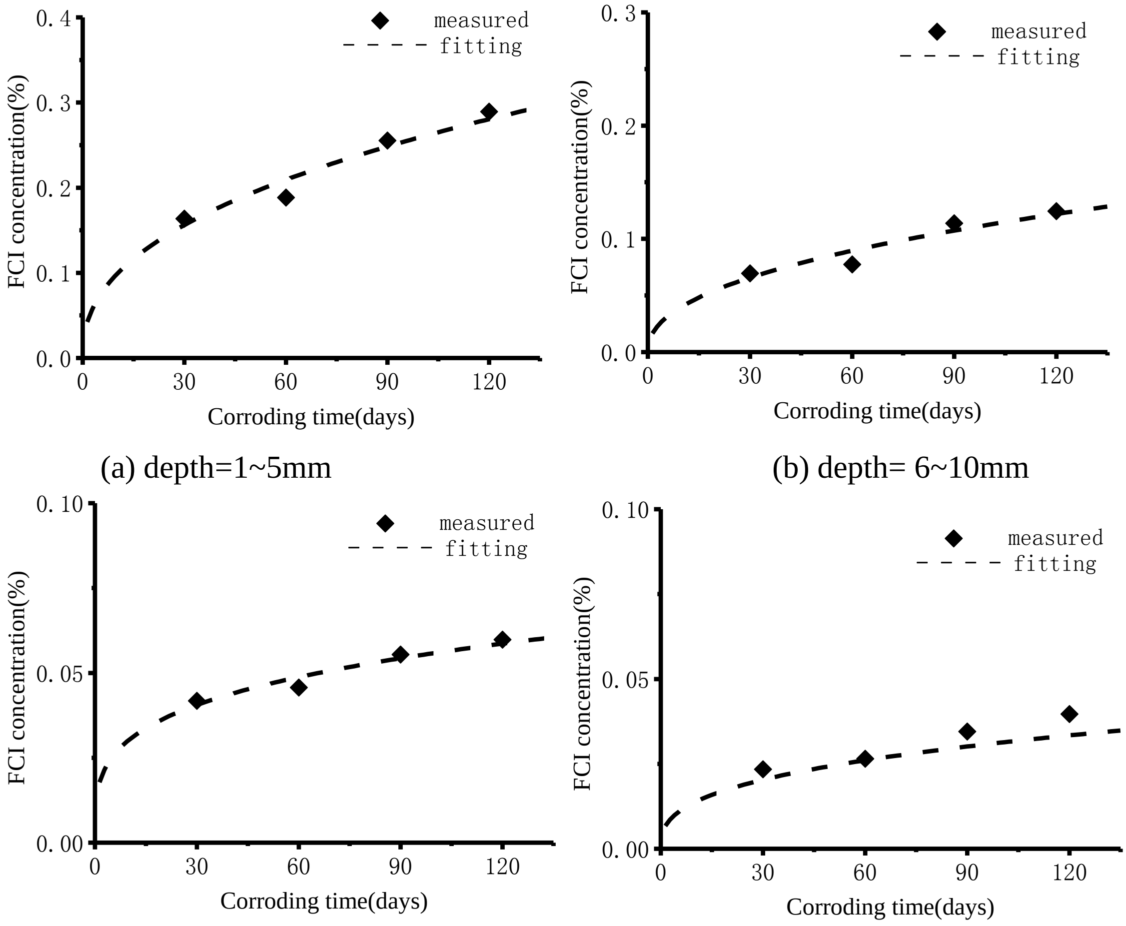
The curves between corroding time and FCI concentration in fully saturation were shown in Figure.6. And the test results in wet-dry circulation were also attached in Appendix (A.2) to shorten the length.

It was found that the FCI concentration decreased with the penetration depth when the corroding time was fixed; and the magnitude of decreasing was declined with the depth of free chloride ion penetration. This may be caused by that the resistance free chloride ion encountered when penetrated from the concrete surface to the depth. And the FCI concentration increased with time regardless of adding the fly ash or not, which may be caused by the accumulated free chloride ion sedimentation during penetration. The more time of immersing means more accumulated sedimentation of free chloride ion thus the FCI concentration increased with the corroding time obviously in Figure.6.With the help of fitting software, it was found that the curves of corroding time and FCI concentration were in power correlation and the function was

$$c_f = ax^b \qquad (5)$$

where c_f was the FCI concentration(%); x was the corroding time; a and b were the two constant in the power function; And all the fitting parameters were listed in Table.4.

The test with fly ash content 20% was chosen to conduct fitting in Figure.7 , and it was found the conformity was quite good.



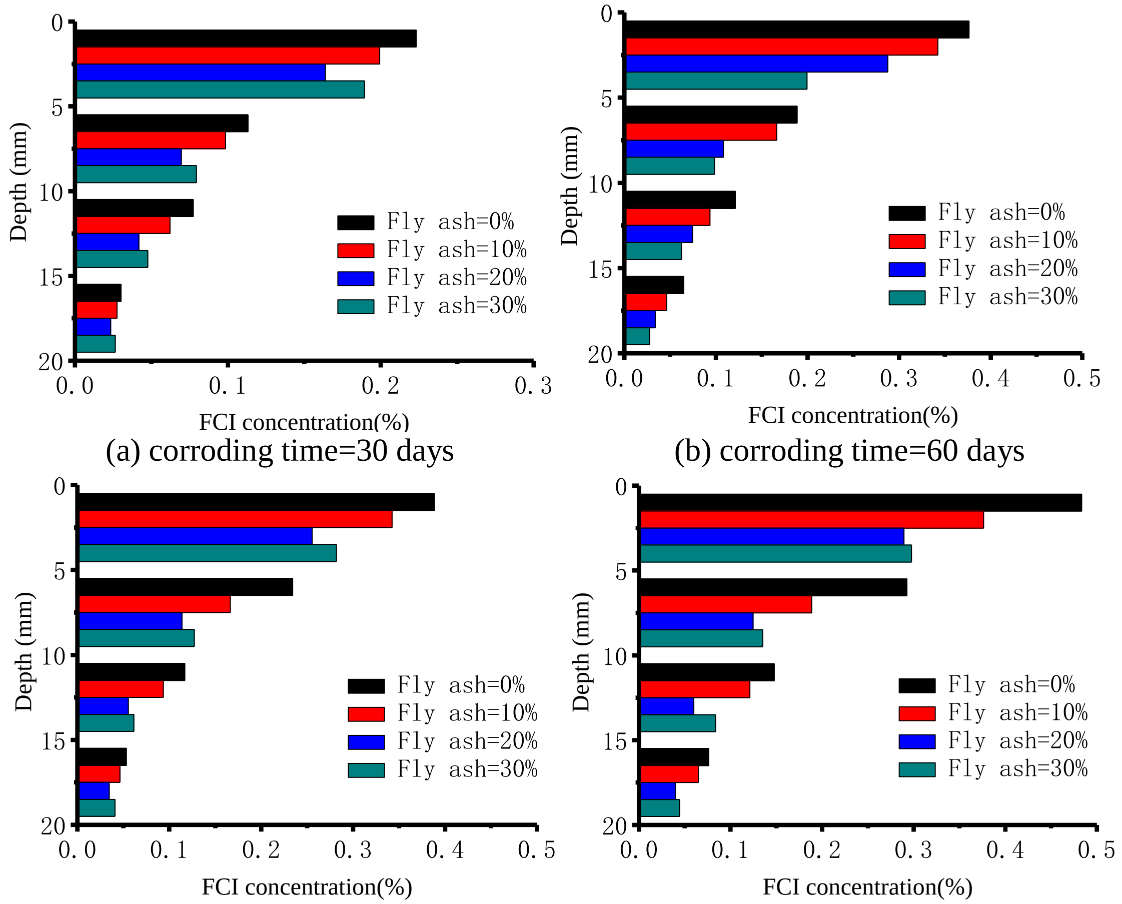
(a) depth=1~5mm (b) depth= 6~10mm

(a) depth=11~15mm (b) depth=16~20mm

Figure 7. Correlation between corroding time and FCI concentration (fly ash =20%)

3.3. Distributions of free chloride ion concentration with depths

The distributions of FCI concentration with depths in fully saturation were drawn in Figure.8, and the similar curves in wet-dry circulation could be found in Appendix (A.3).



(a) corroding time=30 days (b) corroding time=60 days

(c) corroding time=90 days (d) corroding time=120 days

Figure 8. Distribution of FCI concentration with depths

As shown in Figure.8, the FCI concentration changed obviously with the depths from recycled aggregate concrete surface. The FCI concentration was the biggest at the surface. As the penetration depth increased, the FCI concentration decline dramatically and came down to a smaller value. Comparing among the four series of test with different corroding time, It was also found that the FCI concentration demonstrated a bigger difference at the surface layer of 0 to 5mm; and this difference decline as the penetration depth increased; and the convergence of the FCI concentration in four series of different corroding time tests was about 0.05. Thus it was found that the penetration process of free chloride ion was very fast at the beginning, then it came to decline and converged after being immersing in the solution for a certain time.

With the help of fitting tool, it was found that the curves of penetration depth and FCI concentration was in natural logarithm like this:

$$c_f = ae^{bx} \qquad (6)$$

where c_f was the FCI concentration(%); x was the depth form the recycled aggregate concrete surface; a and b were the two constant in the natural logarithm function; And the fitting parameters were listed in Table.5.

Table 5. Fitting parameters of penetration depth in fully saturation

Time	Fly ash (%)	*a*	*b*	Correlation coefficient(CR)
30 days	0	0.314	-0.12	0.9869
	10	0.237	-0.12	0.9945
	20	0.205	-0.12	0.9929
	30	0.238	-0.12	0.9929
60 days	0	0.482	-0.11	0.9965
	10	0.466	-0.13	0.9990
	20	0.366	-0.13	0.9945
	30	0.273	-0.12	0.9869
90 days	0	0.583	-0.13	0.9955
	10	0.466	-0.13	0.9990
	20	0.331	-0.13	0.9935
	30	0.359	-0.13	0.9905
120 days	0	0.693	-0.12	0.9975
	10	0.482	-0.11	0.9965
	20	0.366	-0.13	0.9889
	30	0.381	-0.12	0.9955

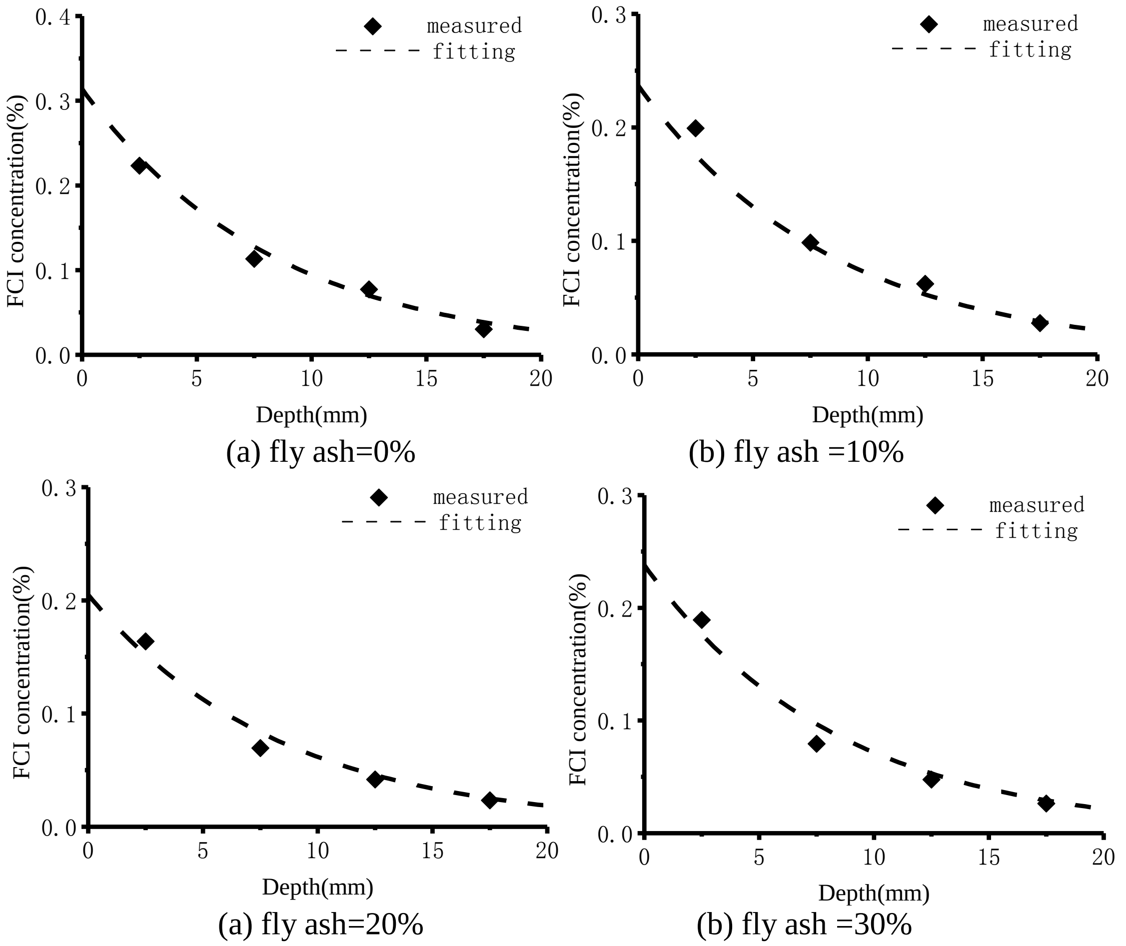


Figure 9. Correlation between depth and FCI concentration (corroding time =30 days)

The fitting of tests with corroding time 30 days were drawn in Figure.9, and it was found the conformity was quite good too.

3.4. Mechanisms of free chloride ion penetration

To shorten the length, only the test results (corroding time =90 days) were used to demonstrate the difference between fully saturation and wet-dry circulation condition. And the correlation of fly ash content and FCI concentration under the two conditions were drawn in Figure.10.

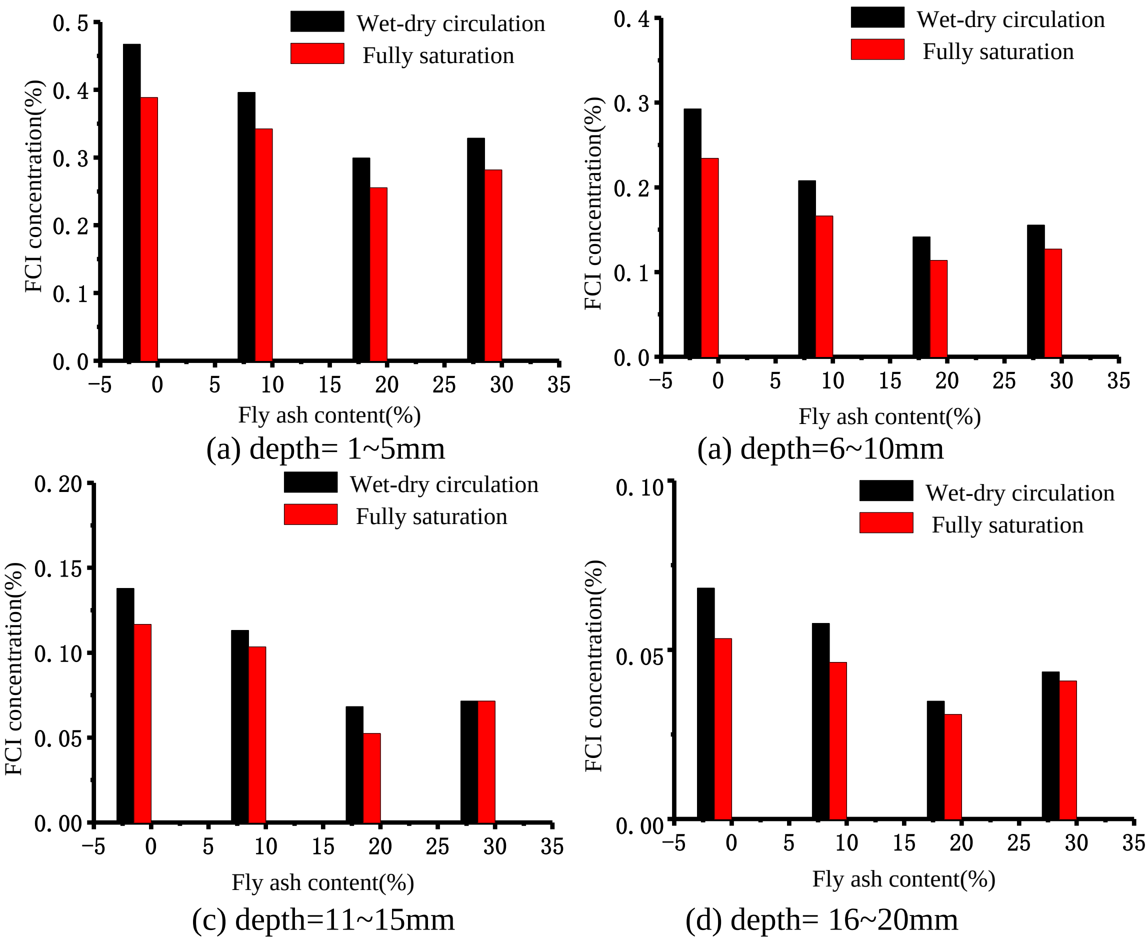
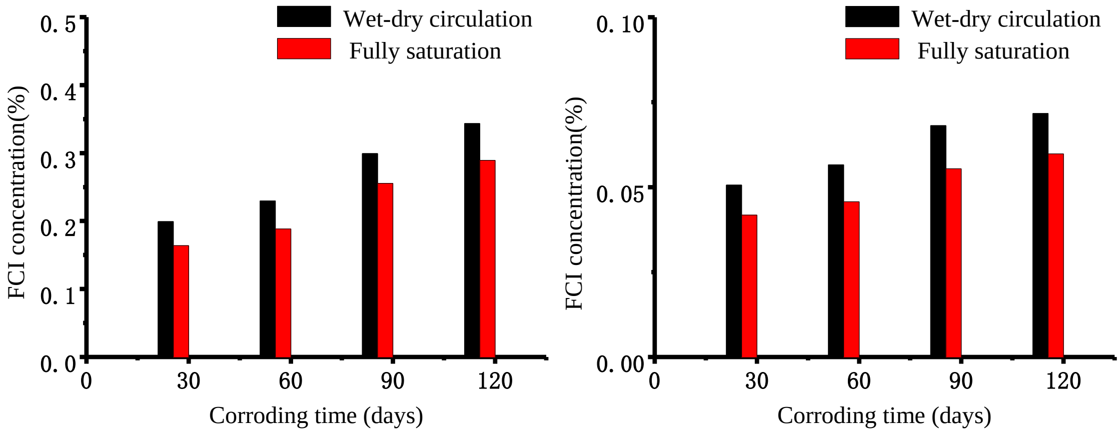


Figure 10. Comparison curves with different fly ash content

As indicated, the FCI concentration increased and then decreased with fly ash content in both conditions. And the turning point was at 20%. And the FCI concentration in wet-dry circulation condition was larger than in fully saturation for the wet and dry circulation accelerated the movement of free chloride ion; however the difference of FCI concentration was decreasing when the fly ash content increased. Thus the effect of wet-dry circulation on the FCI concentration was obvious on in the concrete surface but minor in the internal.

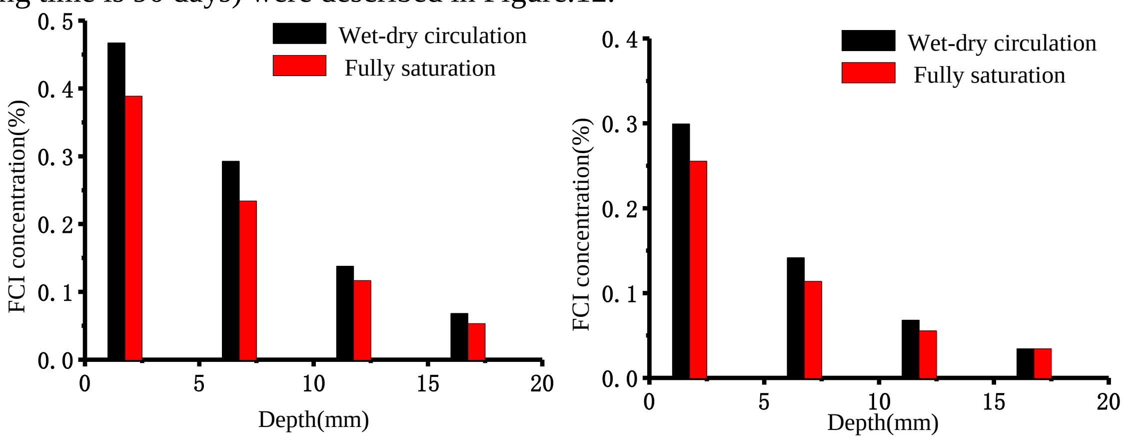
The tests with fly ash content 20% were also utilized to draw the comparison curves between corroding time and FCI concentration. And the curves in penetration depth of 1~5mm and 11~15mm were shown in Figure.11.



(a) depth=1~5mm (b) depth=11~15mm

Figure 11. Comparison curves with different corroding time

From Figure.11, it was found that the FCI concentration was increasing with the corroding time in the two conditions. And the increasing magnitude of FCI concentration became smaller as the time prolonged. The free chloride ion moved faster in wet-dry circulation than in fully saturation. The distributions of FCI concentration with depths of the tests (whose fly ash content is 0% and 20 % and corroding time is 90 days) were described in Figure.12.



(a) fly ash =0% (b) fly ash =20%

Figure 12. Comparison curves with different penetration depth

As was shown in Figure.12, the FCI concentration decreased with the depth in fully saturation and wet-dry circulation. Then FCI concentration in wet-dry circulation was larger than in fully saturation when fly ash content and corroding time were kept constant. And the difference was declined when the depth increased, thus the impact of wet-dry circulation was largely on the surface of recycled aggregate concrete but not internal.

The analysis above shows that the mechanism of free chloride ion penetration in fully saturation was different with that in wet-dry circulation. The wet-dry circulation can accelerate the penetration speed of free chloride ion in the surface. The mechanism of two conditions showed a bigger difference at the surface but had a convergence trend with the increasing of depth.

For the specimens in fully saturation of chloride solution, there existed a difference of FCI concentration between the solution and the concrete surface, the surface and the internal. And this difference drives the free chloride ion move into the internal of recycled aggregate concrete, which was confirming to the Fick's second law [20]. The process was demonstrated in Figure.13.

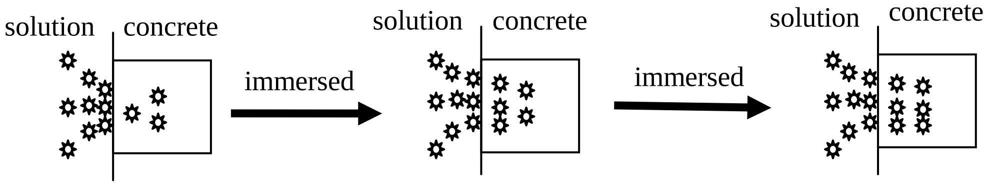


Figure 13. Penetration process of free chloride ion in fully saturation

And for those in wet-dry circulation, the pore water of the recycled aggregate concrete evaporated because the outer environment was dryer when the saturated specimen was naturally dried. This leads to the increase of salt content in the surface pore water of recycled aggregate concrete, and resulted in free chloride ion difference between the surface and the recycled aggregate concrete internal and makes the salt move from the surface to internal. And the pore water decreased as the time of air drying prolonged, which would also accelerate the free chloride ion penetration at the surface. The free chloride ion solution penetrated into the pore of the recycled aggregate concrete specimen when immersed again. Thus the salt of chloride solution penetrated into the internal of recycled aggregate concrete under the wet and dry circulation. And this process was described in Figure.14.

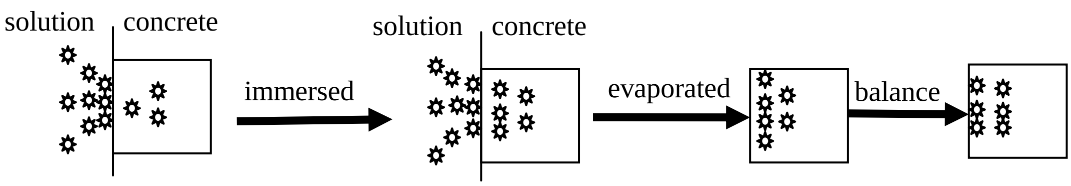


Figure 14. Penetration process of free chloride ion in wet-dry circulation

4. IMPROVED GREY MODEL AND ITS APPLICATION

4.1. Grey model and its improvement

In 1982, grey model, developed originally by Chinese famous professor Deng, is a truly multi disciplinary and generic theory that deals with systems that are characterized by poor information and for which information is lacking [25]. The grey theory does not require a large amount of data and the typical distributing order, but it has high prediction precision, thus it is widely used for prediction in agriculture, geology and civil engineering etc [26-32]. And the steps for building the grey model are given as below:

An original data sequence is constructed as this:

$$x^{(0)} = \{x^{(0)}(t_1), x^{(0)}(t_2), \ldots, x^{(0)}(t_n)\} \quad (7)$$

with time step $t_{i+1} - t_i = k = \text{constant}, i = 1, \ldots, n-1.$

One-step accumulated generation sequence of $x^{(1)}$ is built like this:

$$x^{(1)} = \{x^{(1)}(1), x^{(1)}(2), \ldots, x^{(1)}(n)\} \quad (8)$$

where $x^{(1)}(k) = \sum_{i=1}^{k} x^{[0]}(i), (k = 1, 2, \cdots, n)$.

The mean sequence of $x^{[1]}$ is defined as:

$$z^{(1)} = \{z^{(1)}(2), z^{(1)}(3), \ldots, z^{(1)}(n)\} \quad (9)$$

where $z^{(1)}(k) = (x^{(1)}(k) + x^{(1)}(k-1))/2, (k = 2, 3, \cdots, n)$.

The equation $x^{(0)} + az^{(1)} = b$ is called the basic form of grey model, its corresponding whitening differential equation is

$$\frac{dx^{(1)}}{dt} + ax^{(1)} = c \quad (10)$$

where the parameter values of a and b can be recognized by least square method,

$$\hat{a} = [ab]^T = \left(B^T B\right)^{-1} B^T Y \quad (11)$$

where

$$B = \begin{pmatrix} -z^{(1)}(2) & 1 \\ -z^{(1)}(3) & 1 \\ \vdots & \vdots \\ -z^{(1)}(n) & 1 \end{pmatrix}, \ \mathrm{Y} = \begin{pmatrix} x^{(0)}(2) \\ x^{(0)}(3) \\ \vdots \\ x^{(0)}(n) \end{pmatrix}$$

The equation

$$\hat{x}^{(1)}(k+1) = \left(x^{(0)}(1) - \frac{b}{a}\right)e^{(-ak)} + \frac{b}{a}, (k = 0, 1, 2, \cdots, n), \quad (12)$$

is called the time response equation. Prediction values are generated by

$$\hat{x}^{(0)}(k+1) = \hat{x}^{(1)}(k+1) - \hat{x}^{(1)}(k) \quad (13)$$

that is

$$\hat{x}^{(0)}(k+1) = \left[1 - e^{a}\right]\left(x^{(0)}(1) - \frac{b}{a}\right)e^{-ak} \quad (14)$$

Some professors has pointed out that the equation $\hat{x}^{(1)}(1) = x^{(1)}(1) = x^{(0)}(1)$ in equation 8 and 12 was not adequate [31, 32], and Li et al employed the exponential smoothing method and swarm optimization algorithm to enhance the prediction power of grey model [33], and Niu et al. extend the traditional grey model by introducing linear time-varying terms to optimized its capability to prediction [34]. However, the methods adopted have never involved the optimization of Model itself. Thus a fresh new theoretical method was put forward to perfect the Grey model based on the research of Liu [35], and the optimized form of equation 12 was

$$\hat{x}^{(1)}(k+1)=c_m^* e^{(-ak)}+\frac{b}{a},(k=0,1,2,\cdots,n), \tag{15}$$

where c_m is the undetermined coefficient.

A new function was got based on equation 4.7

$$\hat{x}^{(0)}(k+1)=\hat{x}^{(1)}(k+1)-\hat{x}^{(1)}(k)=c_m^*(1-e^a)^* e^{-ak},(k=1,2,\cdots,n), \tag{16}$$

we put $c=c_m^*(1-e^a)$ into equation 4.9 and 4.10, Then got

$$\hat{x}^{(1)}(k+1)=c^*(1-e^a)^{-1}e^{-ak}+\frac{b}{a},(k=0,1,2,\cdots,n),$$

(17) $\hat{x}^{(0)}(k+1)=\hat{x}^{(1)}(k+1)-\hat{x}^{(1)}(k)=c^* e^{-ak}+\frac{b}{a},(k=1,2,\cdots,n),$ (18)

where c is defined as

$$c=\frac{\dfrac{\left[x^{(0)}(1)-b/a\right]\left[1-e^a\right]^{-1}}{x^{(0)}(1)^2}+\sum_{i=2}^{n}\dfrac{e^{\left[-a(i-1)\right]^2}}{x^{(0)}(i)}}{\left[\dfrac{\left[1-e^{-a}\right]}{x^{(0)}(1)}\right]^2+\sum_{i=2}^{n}\left[\dfrac{e^{\left[-a(i-1)\right]}}{x^{(0)}(i)}\right]}, \tag{19}$$

4.2. Application of improved grey model in free chloride ion penetration

According to Kai[36], and the smallest thickness of concrete protective layer was between 10-30mm in ordinary environment in table.6, thus the test results with the depth of 20mm(mean value of 10 and 30 mm)could be used to make the prediction of free chloride ion penetration in recycled aggregate concrete with fly ash.

Table 6. The smallest concrete protective layer thickness for design base period of 50 years [36]

Structure thickness(mm)	Smallest protective layer thickness(mm)	
	Ordinary environment	Corrosive environment
<150	10	15
150~300	30	35

With the help of software and programming, improved grey model was applied to predict FCI concentration in recycled aggregate concrete with fly ash. And taking the RC-20 as example, the predict values of improved grey model were also compared with the grey model and measured values in Figure.15, and the absolute mean percentage error were drawn in Figure.16.

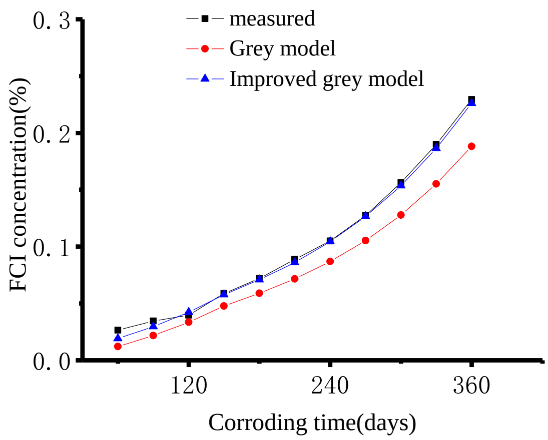


Figure 15. Comparison of grey model and its improved form

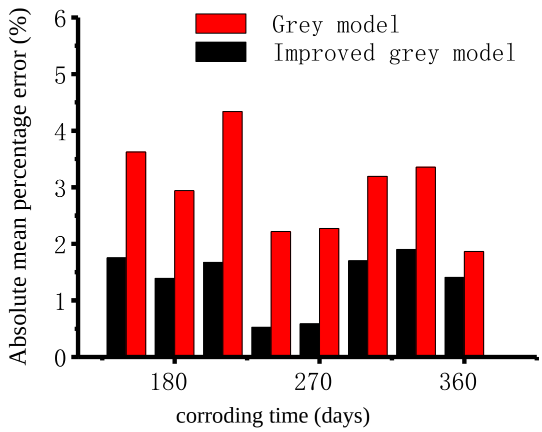


Figure 16. Absolute mean percentage error distribution

It was found in Figure.15 that the improved grey model was feasible to predict the value of FCI concentration in recycled aggregate concrete with higher precise value when compared to grey model. The values of improved grey model were closer to the results measured. From the absolute mean percentage error distribution, it was also found that the improved grey model has improved the accuracy of the predict from a great extent, the percentage error distribution has been cut from nearly 4% to only 1.5% as Figure.16 shows, which means the predicted values of the improved grey model were more close to the truth values. So the improved model was a good model with high accuracy and could be further used to conduct the long term prediction of the FCI concentration in recycled aggregate concrete with fly ash.

4.3. Long term effect of fly ash content on free chloride ion concentration

According to Glass [37], the maximum limit of FCI concentration in concrete was 2.5%. In this research, 2.5% was presumed as the limit of FCI concentration under long term corroding , which was analyze the effect of fly ash content on FCI concentration in recycled aggregate concrete. By using the improved grey model, the predictions of free chloride ion penetration in recycled aggregate concrete were shown in Figure.17 and18 for fully saturation and wet-dry circulation respectively.

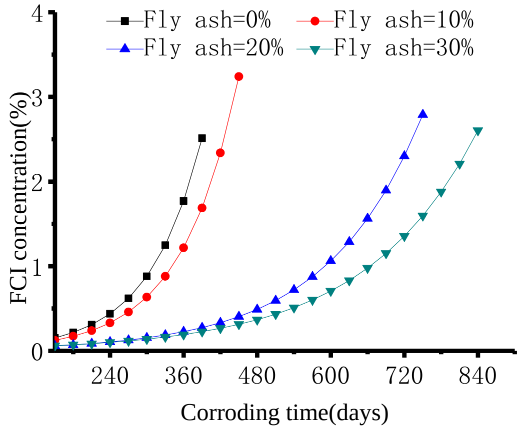


Figure 17. Predictions of FCI concentration in fully saturation

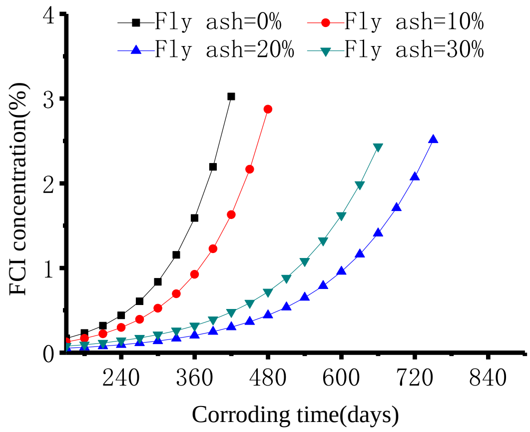


Figure 18. Predictions of FCI concentration in wet-dry circulation

From the two figures, it was found that the free chloride ion penetration was slow down by the fly ash adding in recycled aggregate concrete at the beginning, which was confirming to the discussion in section 3.1. Additionally, it was also found that the long term free chloride ion penetration was faster in wet-dry circulation than in fully saturation when the fly ash content was below 20%, but the penetration speed was accelerated in fully saturation when the fly ash content was 30%, which shows that the effect of wet-dry circulation would decline in the long run for it was largely on the surface of recycled aggregate concrete but not in internal as section 3.4 discussed. And the penetration speed was nearly the same when the fly ash content was 20%. Therefore 20% was the best content of fly ash in recycled aggregate concrete for its durability. In casting the concrete, chemical reaction was induced between fly ash and calcium hydroxide of cement, which resulted in the production of calcium silicate hydrate to improve the resistance of free chloride ion [38]. When fly ash was adding too much and immersed in fully saturation, it would lead to the decrease of calcium hydroxide in primary hydration products and hinder the forming of calcium silicate hydrate, which would decrease the forming of binding chloride and promote the forming of free chloride ion. Therefore the fly ash content should be monitored when the recycled aggregate concrete with fly ash was applied to engineering structure.

5. CONCLUSION

In this paper, natural diffusion method was adopted to conduct the research of free chloride ion penetration in recycled aggregate concrete with fly ash, the main conclusions were

(1)The free chloride ion penetration reduced as the fly ash content increased from 0% to 20%but accelerated when the content increased from 20% to 30%; and the fly ash content and free chloride ion concentration confirms to a polynomial function.

(2) When the corroding time was fixed, the free chloride ion concentration decreased with the penetration depth; and the magnitude of decreasing was declined with the penetration depth; and the curves of corroding time and free chloride ion concentration was in power correlation.

(3) The free chloride ion concentration was the biggest at the surface and declined dramatically as the penetration proceeded; and the penetration depth and free chloride ion concentration fitted to natural logarithm well.

(4) The difference of free chloride ion concentration between solution and concrete surface drive the free chloride ion move into the internal of recycled aggregate concrete in fully saturation; and the free chloride ion difference between the surface and internal of recycled aggregate concrete make the salt move from the surface to internal of recycled aggregate concrete in wet-dry circulation. And the effect of wet-dry circulation was largely on the surface of recycled aggregate concrete.

(5)The improved grey model was feasible to conduct the prediction of free chloride ion concentration in recycled aggregate concrete with higher accuracy; and the long term prediction also reveals that the effect of wet-dry circulation would decline with time and 20% was the best fly ash content for the durability of recycled aggregate concrete.

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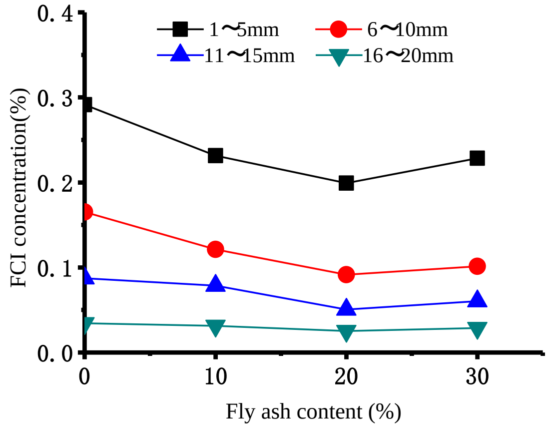
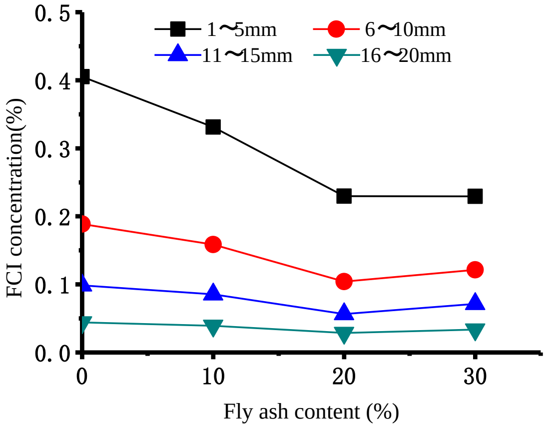
APPENDIX:

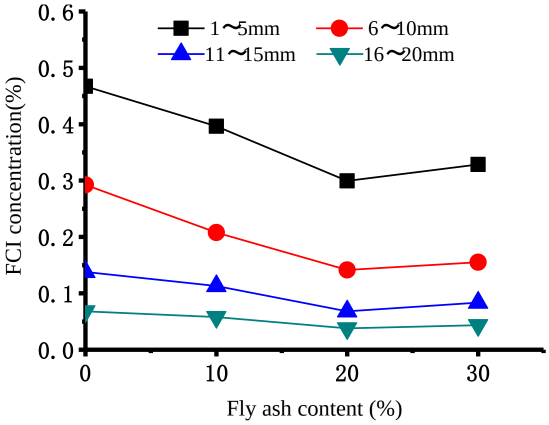
(A.1)Curves between fly ash content and FCI concentration in wet-dry circulation were drawn as below:



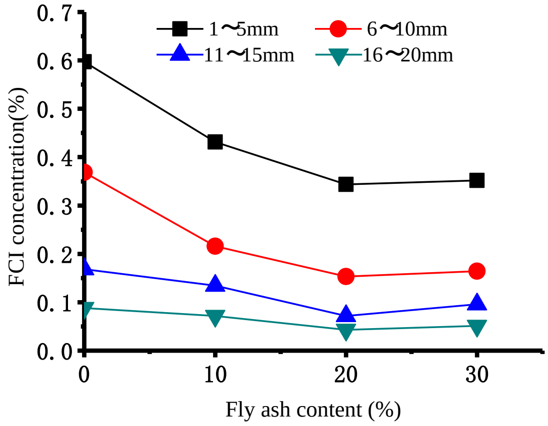
(a) corroding time=30 days



(b) corroding time=60 days

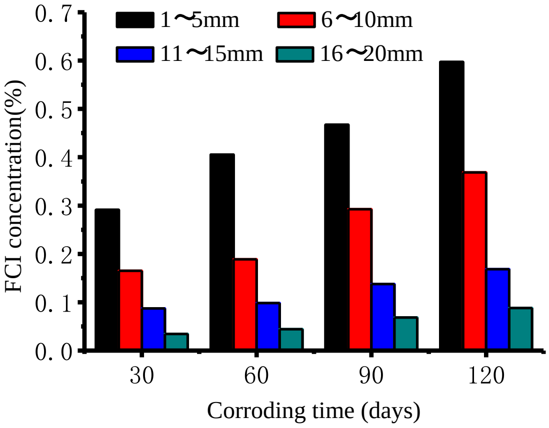


(c) corroding time=90 days

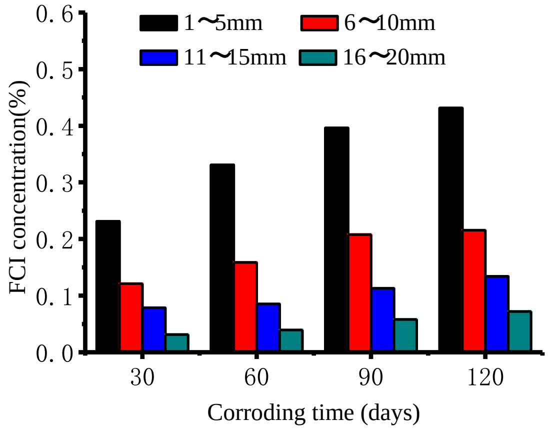


(d) corroding time=120 days

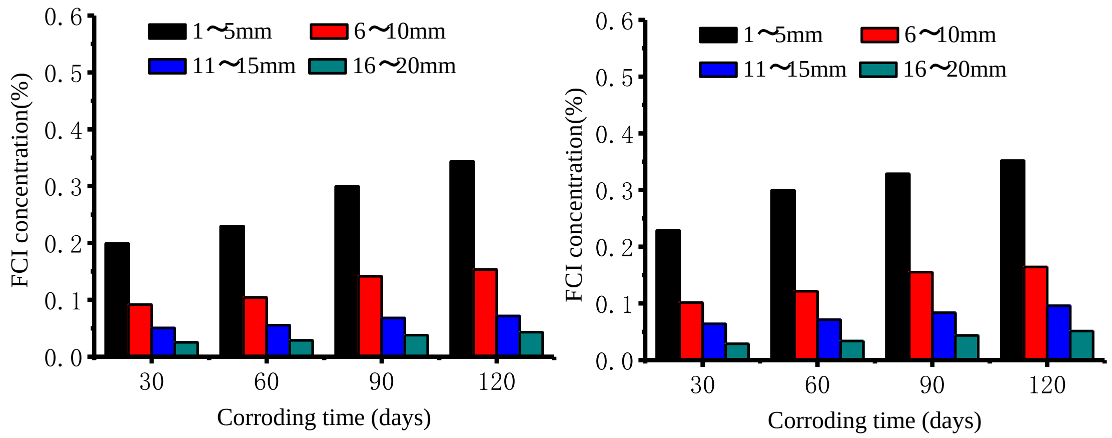
(A.2) Curves between corroding time and FCI concentration in wet-dry circulation were:



(a) fly ash =0%

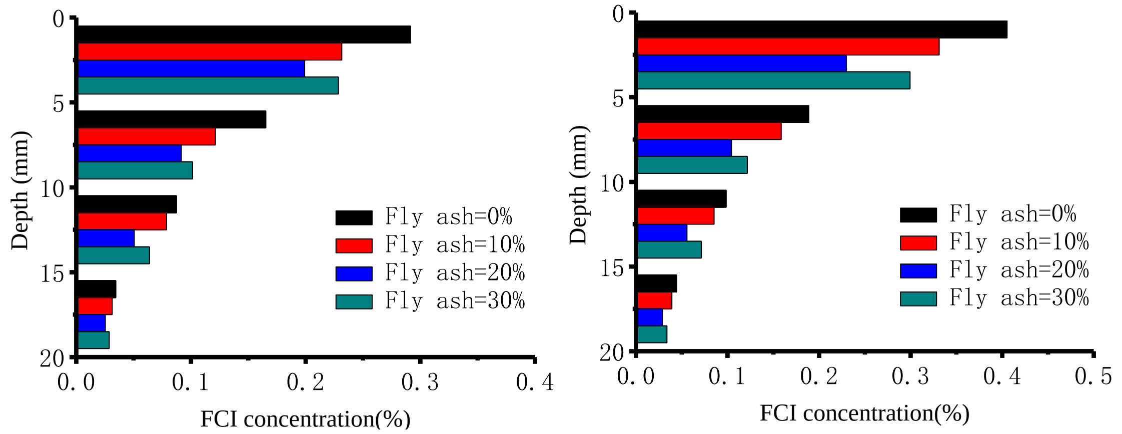


(b) fly ash =10%

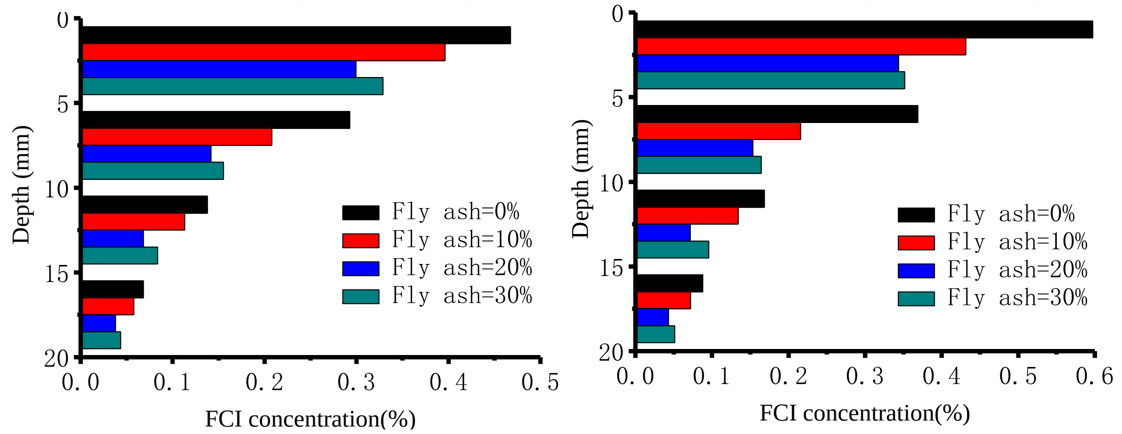


(a) fly ash =20% (b) fly ash =30%

(A.3) Curves between corroding depth and FCI concentration in wet-dry circulation were drawn as below:



(a) corroding time=30 days (b) corroding time=60 days



(a) corroding time=90 days (b) corroding time=120 days

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