Neutralization of Artificial Sand Concrete Caused by Acid Rain

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Abstract. With the effect of carbonation and coupled action of acid rain and carbonation, the carbonation depth of concrete with river sand and artificial sand was studied, respectively. The results show that the carbonation depth of concrete composed artificial sand is less than that with river sand in both cases, and the resisting carbonation ability of the former is better. Compared with accelerated carbonation, the neutralization of concrete is accelerated under the combined action of $[H^+]$ and $[SO_4^{2-}]$ in acid rain.

Introduction

With the population quickly increases, lots of chemicals produced from production and life lead to increasingly air pollution and the most is produced by burning. Large number of CO2 released in burning, the content of SO2 and NOx in air has also been enormously increased in sulfur coal and oil burning, which causes more acid rain and decrease the pH value of acid rain further. In fact, acid rain has become main environmental factor that causes neutralization of concrete structure and steel corrosion.

The official name of acid rain is acidic sedimentation, which refers to atmospheric rainfall with pH value less than 5.6, such as rain, freezing rain, snow, hail, and dew. As known, the pH value of atmospheric precipitation composed of carbonic acid is approximately 5.6–6.0. According to some data, acid rain has gradually become the international problem since the 1970s [1]. For the first time, acid rain appeared in large range of Europe, North America and other places. As for China, The scope affected by acid rain has also grown from mid of 1980s, which from north, southwest to south China gradually, and main in the east China coastal represented by Nanjing, Shanghai, Hangzhou, Fuzhou and Xiamen, meanwhile the acidity of acid rain is much higher.

With concrete consumption increased in recent years, as an important component of concrete, the river sand resources are increasingly scarce, especially in China, especially in GuiZhou, SiChuan and other Southwest provinces. The trend that river sand has been replaced by artificial sand used in concrete for transport infrastructure construction is irresistible. A large number of local concrete building/structures, including bridges, dams and other major projects are directly exposed in the atmospheric environment with high frequency of acid rain. The durability degradation of concrete is outstanding. However, the study on the neutralization of acid rain on concrete composed of artificial sand is rarely reported. By experiments, the neutralization mechanism of concrete with artificial sand and river sand under the effect of acid rain was studied in this paper, and the results will provides the theoretical basis for design and durability evaluation for the concrete structure.

Experimental

Materials and Composition

The material used in the experiment is following. P.O 52.5 cement is used and physical parameters are shown in Table 1. The class II fly ash is used. The fineness modulus of artificial sand of limestone is 3.07, stone powder content is 5.9%. The fineness modulus of river sand is 2.4, the silt content is 4.0%. Admixtures for retarded superplasticity of high performance water reducing agent. The compositions of concrete are shown in Table 2.
Table 1. The physical performance of cement.

<table>
<thead>
<tr>
<th>water requirement of normal consistency(%)</th>
<th>Setting time /h:min</th>
<th>Mechanical performance/ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial setting</td>
<td>Final setting</td>
</tr>
<tr>
<td>28</td>
<td>2:50</td>
<td>4:10</td>
</tr>
</tbody>
</table>

Table 2. The composition of concrete (kg/m³).

<table>
<thead>
<tr>
<th>Group</th>
<th>Cement</th>
<th>Fly ash</th>
<th>Sand</th>
<th>Gravel</th>
<th>Water</th>
<th>Superplastizer</th>
<th>W/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete with river sand</td>
<td>HC30</td>
<td>378</td>
<td>0</td>
<td>889</td>
<td>963</td>
<td>160</td>
<td>7.94</td>
</tr>
<tr>
<td></td>
<td>HC40</td>
<td>344</td>
<td>76</td>
<td>795</td>
<td>1010</td>
<td>150</td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>HC50</td>
<td>497</td>
<td>0</td>
<td>787</td>
<td>1000</td>
<td>154</td>
<td>13.42</td>
</tr>
<tr>
<td></td>
<td>HC60</td>
<td>492</td>
<td>54</td>
<td>841</td>
<td>950</td>
<td>143</td>
<td>18</td>
</tr>
<tr>
<td>Concrete with artificial sand</td>
<td>JC30</td>
<td>378</td>
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<td>950</td>
<td>147</td>
<td>18</td>
</tr>
</tbody>
</table>

Experiments

Accelerated Carbonation

With reference to the current specification of China, the specimen is cube with dimension of 100 mm×100 mm×100 mm, which will be dried in 60 h for 48h after 26d standard curing. Then, the specimen will be cut in half, one of which will be selected for further treatment. The surface except the cut surface and opposite shall be sealed by epoxy resin. Parallel line with 10 mm spacing is drawn along the length direction on the exposed side, as scheduled carbonation depth measurement point. The carbonation depth is measured after 7d, 14d, 28d and 60d of accelerated carbonation, respectively.

Combined Experiment of Accelerated Carbonation and Acid Rain

The specimen will be carried in wet-dry cycling after accelerated carbonation. The simulated acid rain is solution with 0.15 mol/l [SO₄²⁻] and pH value is 4.0. In testing, [SO₄²⁻] will be adjusted by ammonium sulfate, pH value by nitric acid. A whole wet-dry cycling is that, the carbonated specimen will be immersed in simulated acid rain for 36h and set in room for 1h, then removed for 1 h cool after 10h dried in 60 ℃ oven. The specimens will be carried accelerated carbonation after 10 cycles. Carbonization time is 7d, 14d, 28d and 60d.

Results and Discussion

The Outlook of Specimen

The outlook of specimen for two tests is compared in Fig. 1. After carbonization test, the specimen surface of concrete is relatively intact, carbonation depth grid lines clearly visible. The appearance of specimen after combined test is different, surface mortar layer looks loose and flaks.

(a)Accelerated carbonation   (b)Combined test

Figure 1. The outlook of specimen.
**The Carbonation Depth**

The carbonation depth of two group concrete specimen after different carbonation time is shown in Fig.2. The carbonation depth increases with carbonization time, and decrease with increasing of concrete grade, especially for C50 and C60 concrete. The carbonation depth of higher strength concrete is nearly zero in early. The carbonation depth of concrete with artificial sand is much smaller than that of river sand concrete.

![Graph](image1.png)

Figure 2. The carbonation depth of concrete with different time.

The reason for less carbonation depth of concrete composed of artificial sand may be explained as following, certain amount of stone powder will make interfacial transition zone (ITZ) more dense and enhance hydration effect, which improve the pore structure of hardened cement and enhance the carbonation resistance of concrete.

**The Effect of Acid Rain**

The effect of acid rain on the carbonated performance of two concrete is schematically shown in Fig.3.

![Graph](image2.png)

Figure 3. The carbonation depth of concrete exposed to acid rain with different time.

It can be concluded that the mechanism of combined carbonation and acid rain attack is much similar with that of accelerated carbonation, the carbonation depth increases with carbonization time, and decrease with increasing of concrete grade. And the carbonation depth of specimen exposed to the wet-dry cycling in acid rain solution is obviously deeper than that of only carbonation. Take C40 for example, the curve of carbonation depth of carbonation (T) and combined test (S+T) is compared in Fig.4. It is obviously that carbonation depth is much deeper for the concrete exposed in acid rain.

![Graph](image3.png)

Figure 4. The carbonation depth of C40 concrete.
The mechanism of acid rain can be explained with Eq.1.

\[
Ca(OH)_2 + 2H^+ + SO_4^{2-} \rightarrow CaSO_4 \cdot 2H_2O
\]  

(1)

The influence of acid rain on concrete looks like the carbonation caused by CO2, and the production are both soluble salts, which damage the durability of concrete once dissolving. Therefore, the acid rain process is also called similar carbonation of concrete[1]. Some research show that damage of acid rain on silicate cementitious material is the joint action of \([H^+]\)and\([SO_4^{2-}]\). \([H^+]\)

disintegrates the substances such as Ca (OH)2, CSH, CxAHx in the hardened cement. The other hand, being production of \([SO_4^{2-}]\) and hardened cement paste, CaSO4 \(2H_2O\) swells and results in corrosion expansion. In a word, the corrosive mechanism of acid rain is combined attack of decomposition and expansion[2].

In this experiment, the main component of simulative acid rain solution is H2SO4 and HNO3, which are strong acid electrolyte and fully ionized in aqueous solution. That is \(H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}\)

\(HNO_3 \rightarrow H^+ + NO_3^-\) With the effect of wet-drying cycle, the \([H^+]\) and \([SO_4^{2-}]\) in simulative acid rain solution penetrates into the concrete pore, and violent chemical reaction is caused by \([H^+]\) and cementitious hydration products. This process rapidly increase the \([H^+]\) concentration in pore liquid and weak dissociation of \(H_2CO_3\), which inhibit neutralization caused by CO2 also. However, with the increase of wet-drying cycles, the \([H^+]\) concentration increase obviously from strong electrolyte dissociation of \(H_2SO_4\) and HNO3, and enhance the pseudo carbonation of concrete, which result in much deeper carbonation depth than that of only carbonization. This is consistent with the literature[3-6]. In addition, \([SO_4^{2-}]\) in pore fluid reacts with cementitious hardened paste, generates swelling CaSO4 \(2H_2O\) crystals and non-viscous SiO2\(\cdot\)nH2O and Al2O3\(\cdot\)nH2O, which results in ingressive damage from outer to inner. The surface of concrete gradually soft, split, and crack, which pave the way for penetration of CO2 later. In the view of another reserachers, concrete neutralization will be abated by acid rain[7-10].

In order to compare the influence of carbonation and combined carbonation-acid rain on the steel corrosion, the Eq.2 is used to estimate the initial corrosion time for C40 concrete.

\[
t_i = \left(\frac{d-x_0}{k}\right)^2
\]  

(2)

In which, \(d\) is thickness of protective layer, assumed 30mm. \(k\) is impact factor, can be further explained as Eq.3 and parameter shown in Table.3. \(x_0\) is carbonation remains and can be calculated with Eq.3

\[
k = 3Kco_2 \cdot K_{i1} \cdot K_{u2} \cdot T \cdot RH^{1.5} \cdot (1 - RH)^{\frac{58}{f_{oc}} - 0.76}
\]  

(3)

\[
x_0 = \left(1.2 - 0.35k^{0.5}\right) \cdot D_e \cdot \frac{6.0}{m+1.6} \cdot (1.5 + 0.84k) \cdot \frac{m}{m+1.6}
\]  

(4)

\(m\) is local enviroemntal coefficient, 1.2 for carbonation and 4.2 for combined. For Eq.4, when \(d \leq 28mm, D_e=6d,\) when \(d > 28mm, D_e = d + 0.066(d - 28)^{0.15}\). \(k \geq 1.0\) if \(k \geq 3.3\).

The whole calculation is shown in Table.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{CO_2})</td>
<td>1.1</td>
</tr>
<tr>
<td>(K_{H_2}O)</td>
<td>1</td>
</tr>
<tr>
<td>(K_{H_2}S)</td>
<td>1.2</td>
</tr>
<tr>
<td>(T)</td>
<td>20</td>
</tr>
<tr>
<td>(RH_0)</td>
<td>60%</td>
</tr>
<tr>
<td>(f_{oc})</td>
<td>53.45MPa</td>
</tr>
</tbody>
</table>
Table 4. The calculation of initial corrosion time.

<table>
<thead>
<tr>
<th>Parameter Type</th>
<th>carbonation</th>
<th>Combined carbonation and acid rain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protective layer $d$(mm)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Carbonation factor(mm/year)</td>
<td>1.833</td>
<td>1.833</td>
</tr>
<tr>
<td>$D_C$</td>
<td>30.12</td>
<td>30.12</td>
</tr>
<tr>
<td>$m$</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>$x_0$</td>
<td>15.36</td>
<td>18.73</td>
</tr>
<tr>
<td>$t_1$(year)</td>
<td>63.81</td>
<td>37.82</td>
</tr>
</tbody>
</table>

It can be seen from calculation results the initial corrosion time is obvious different for carbonation and combined test, 63.81a and 37.82a respectively, and the conclusion can also be drawn that the combined carbonation-acid rain accelerate the neutralization, cause serious durability deterioration of concrete.

Conclusions

The accelerated carbonization and wet-dry cycle test has been carried out to study the influence of acid rain on the durability of concrete with river sand and artificial sand. The conclusion is drawn as following.

(1) For same strength grade, the carbonation depth of concrete composed of artificial sand is less than that of concrete with river sand. The reason may be explained as certain amount of stone powder will make interfacial transition zone (ITZ)more dense and enhance hydration effect, which improve the pore structure of hardened cement and enhance the carbonation resistance of concrete.

(2) Compared with accelerated carbonation, the combined action of $[H^+]$ and $[SO_4^{2-}]$ in acid rain accelerates carbonation front and weaks the carbonate resistance of concrete, both river sand and artificial sand. It is important that the durability deterioration caused by acid rain, some measures such as optimizing raw materials, improving the construction quality and surface protective measures is an effective way to resist pseudo carbonation of acid rain.

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References


