Durability of concrete with nano-particles under combined action of carbonation and alkali silica reaction

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ABSTRACT
Subway concrete is easy to be attacked by carbonation in the relatively closed space, and alkali silica reaction (ASR) is a serious durability problem of concrete, which is difficult to find and repair. The damage caused by carbonation and ASR seriously affects the durability of subway concrete. Two kinds of nano-particles (nano-SiO$_2$ and nano-Fe$_2$O$_3$) are mixed into plain subway concrete in this paper, and their effects on the durability of concrete under the combined action of carbonation and ASR are studied experimentally. The test results show that, after mixing with nano-particles, the carbonation depth and expansion of subway concrete are decreased, as well as the sonic velocity of subway concrete is increased obviously, which demonstrate the durability of subway concrete with nano-particles is better than plain subway concrete. The enhancement of durability is due to the special physical and chemical properties of nanoparticles, which can improve the microstructure of concrete and the chemical composition of pore solution in concrete.

1. Introduction
The rapid development of urban economy makes the urban population concentrated in large numbers, and the pressure of public transportation becomes increasingly obvious. The urban subway has the advantages of environmental protection, high efficiency and high carrying capacity, which greatly relieves the traffic pressure.

However, the concentration of CO$_2$ and humidity in the subway is relatively higher due to the crowded population and relatively closed space, which will accelerate the carbonation of concrete (Rezagholilou, Papadakis, and Nikraz 2017). The carbonization of concrete is a complex physical and chemical process in which the hydration products of cement react with CO$_2$ in the air to change the composition, structure and properties of concrete. Carbonization reduces the alkalinity of concrete to destroy the passivation membrane of the steel surface and causes the steel to be rusted.

Alkali silica reaction (ASR) refers to the chemical reaction of alkali and active silica to generate expansive substances (or absorbent expansive substances), resulting in the formation of cracks in concrete due to swelling stress. Besides deteriorating the integrity of concrete, the cracks caused by ASR will also accelerate other corrosion. During the past decades, ASR has caused serious economic loss around the world (Dähn et al. 2016).

Nano-materials, as an appreciated admixture of concrete, have been verified to be more effective in improving the strength and durability of concrete than other traditional admixture (Zhang 2007). Therefore, the research on concrete with nano-particles has attracted wide attention in the academic fields.

At present, there are few reports on the durability of nano-concrete under the combined action of carbonization and ASR, and the durability of concrete under the action of carbonization or ASR cannot reflect the real condition of subway concrete sufficiently. Therefore, this paper selects nano-SiO$_2$ and nano-Fe$_2$O$_3$ as the admixture to study their effects on the durability of subway concrete under the combined action of carbonation and ASR, and the improvement mechanism is analyzed qualitatively.

2. Experimental program

2.1. Materials and mixture proportions
The Portland cement (P.O 42.5) is used as the binder, and additional NaOH solution is added into the cement to increase the total alkali content of cement to 1.25% corresponding to GB/T50,082-2009 (Standard for test methods of long-term performance and durability of ordinary concrete, China). The crushed andesite with a diameter of 5 ~ 31.5 mm is used as coarse aggregate, and the river-sand with a fineness modulus of 2.40 is used as fine aggregate. Nano-SiO$_2$ is one of the most widely used nano-additives which has attracted lots of attention due to the pozzolanic activity, nano-Fe$_2$O$_3$, another widely used nano-additive, can be mixed into concrete to fabricate pressure sensitive concrete to monitor the pressure.
internal stress. So, nano-SiO$_2$ and nano-Fe$_2$O$_3$ are selected as the additives in this paper and their technical indexes are shown in Table 1.

A certain proportion superplasticizer (0.25% by mass of binder) is adopted to, on the one hand, ensure the appropriate workability of fresh concrete; on the other hand, act as a better dispersant to prevent the agglomeration of nano-particles. Notably, the superplasticizer is dissolved in mixing water, then the nano-particles are dispersed in the solution. Besides, the defoamer is mixed with mass ratio of 4% to superplasticizer to eliminate air bubbles generated during the dispersion of nanoparticles.

The plain concrete is used as control specimens and marked as PC in this paper. The concrete mix is prepared with a W/C ratio of 0.45. The other two concrete types, the cement is equivalently replaced by different amounts of nano-particles (0.5%, 1.0%, 2.0% and 3.0% by mass), are respectively marked as NS and NF. Table 2 gives the detailed mixture proportions of concretes.

### 2.2. Test equipment and test methods

#### 2.2.1. Test equipment

According to the test methods of concrete carbonation and alkali-aggregation reaction described in GB/T 50,082–2009 (standard for test methods of long-term performance and durability of ordinary concrete, China), as well as the test methods for ASR from previous literature, the test box for concrete durability under the combined action of carbonation and ASR is independently developed and shown in Figure 1.

The work principle of test box for concrete durability is: (1) the thermostatic bath controls the U-type heating tube, trough the signal from temperature sensor, to adjust the water temperature in box A, so that the temperature in the test box B is stable at the required temperature. (2) Humidity switch controls the humidifier, through the signal from the humidity sensor, so that the humidity in the test box B is stable at the required humidity. (3) Extract some gas through extraction tube to determine the concentration of CO$_2$ in box B, and adjust the CO$_2$ tank to stabilize the concentration of CO$_2$.

#### 2.2.2. Test methods

According to GB/T50081-2002 (standard for test method of mechanical properties on ordinary concrete, China), the compressive test is conducted to verify the mix proportion of concrete after standard curing.

The durability tests are conducted after standard curing. The carbonation depth, expansion and sonic velocity are selected as the indexes to evaluate the durability of concrete under the combined action of carbonation and ASR. The test ages are 0, 3, 7, 14, 21, and 28 days. The durability tests in this paper contain two parts: (1) one test is under the combined action of carbonation and ASR and the test conditions are controlled at 70°C (70 ± 5%) humidity and (20 ± 3%) concentration of CO$_2$. Six prisms with the size of 100 × 100 × 400 mm for each mix no. are prepared, three prisms are used to measure length and sonic time to calculate expansion and sonic velocity. (2) another test is under the action of ASR alone and the test conditions are controlled at 70°C and (70 ± 5%) humidity. Three prisms with the size of 100 × 100 × 400 mm for each mix no. are prepared to measure length and sonic time to calculate expansion and sonic velocity.

The detailed test methods for these parameters reference the humidifier, through the signal from the humidity sensor, so that the humidity in the test box B is stable at the required humidity. (3) Extract some gas through extraction tube to determine the concentration of CO$_2$ in box B, and adjust the CO$_2$ tank to stabilize the concentration of CO$_2$.

| **Table 1.** Performance indices of nano-particles. |
|---|---|---|
| **Items** | Nano-SiO$_2$ | Nano-Fe$_2$O$_3$ |
| Purity/% | 99.5 | 99.9 |
| Particle size/nm | 20 | 50 |
| Specific surface area/m$^2$/g | $640 ± 60$ | 60 |
| Surface property | Hydrophilic | Hydrophilic |
| Bulk density/g/cm$^3$ | ≤0.1 | 0.38 |
| PH | 6–8 | 6–8 |
| Crystal phase | – | α phase |

| **Table 2.** The mixture proportion of concretes kg/m$^3$. |
|---|---|---|---|---|---|
| **Mixture no.** | **Water** | **Cement** | **Sand** | **Andesite** | **Nano-SiO$_2$** | **Nano-Fe$_2$O$_3$** | **Superplasticizer** | **Defoamer** | **NaOH** |
| PC | 184.5 | 410 | 614 | 1191.5 | – | – | 1.025 | – | 2.049 |
| NS05 | 184.5 | 407.95 | 614 | 1191.5 | 2.05 | – | 1.025 | 0.041 | 2.040 |
| NS10 | 184.5 | 405.9 | 614 | 1191.5 | 4.1 | – | 1.025 | 0.041 | 2.030 |
| NS20 | 184.5 | 401.8 | 614 | 1191.5 | 8.2 | – | 1.025 | 0.041 | 2.009 |
| NS30 | 184.5 | 397.7 | 614 | 1191.5 | 12.3 | – | 1.025 | 0.041 | 1.989 |
| NF05 | 184.5 | 407.95 | 614 | 1191.5 | – | 2.05 | 1.025 | 0.041 | 2.040 |
| NF10 | 184.5 | 405.9 | 614 | 1191.5 | – | 4.1 | 1.025 | 0.041 | 2.030 |
| NF20 | 184.5 | 401.8 | 614 | 1191.5 | – | 8.2 | 1.025 | 0.041 | 2.009 |
| NF30 | 184.5 | 397.7 | 614 | 1191.5 | – | 12.3 | 1.025 | 0.041 | 1.989 |

Mixing water contains the water from NaOH solution, “NaOH” shown in above table is the solute.
to GB/T 50082–2009 (standard for test methods of long-term performance and durability of ordinary concrete, China).

3. Test results and discussions

3.1. Compressive strength

Figure 2 shows the compressive strength of concrete with nano-particles at 28 days. After mixed with nano-particles, the compressive strength of concrete is increased obviously and the increased orders are NS30< NS05< NS10< NS20 and NF30< NF20< NF05< NF10. When the content of nano-SiO$_2$ and nano-Fe$_2$O$_3$ are, respectively 1.0% and 2.0%, the compressive strength of concrete (NS20 and NF10) increases most significantly. Compared with PC, the compressive strength of concrete with 2% nano-SiO$_2$ and 1% nano-Fe$_2$O$_3$ is increased by 14.65% and 12.06%, respectively. The above results can demonstrate that the mixture proportions of concrete are valid and the nano-particles can improve the compressive strength of subway concrete.

3.2. Test results of concrete durability

The results of durability contain two parts: “-2” presents the results for concrete under the combined action of carbonation and ASR; “-1” presents the results for concrete under the action of ASR to help supplementally analyze the interaction between carbonation and ASR.

3.2.1. Carbonation depth

The carbonization depth of concrete varying with the test ages and the content of nano-particles is shown in Figure 3.

From Figure 3 (a), it can be seen that the carbonization depth of concrete increases rapidly in the early test period. However, with the growth of test age, this increase trend becomes slower, and the difference of carbonization depth between plain concrete and nano-concrete increases gradually. When mixed with nano-particles, there is a significant decrease in the carbonization depth of concrete at all test ages, which indicates that both nano-SiO$_2$ and nano-Fe$_2$O$_3$ can mitigate the carbonation process of concrete under the combined action of carbonation and ASR. At each age, for the concrete with nano-SiO$_2$, the carbonation depth is minimum when the content of nano-SiO$_2$ is 2%; while for the concrete with nano-Fe$_2$O$_3$, the carbonation depth is minimum when the content of nano-Fe$_2$O$_3$ is 1%.

Figure 3 (b) shows that, at all test ages, the carbonation depth of concrete decreases gradually with the increasing content of nano-particles; when the contents of nano-SiO$_2$ and nano-Fe$_2$O$_3$ are, respectively, 2.0% and 1.0%, the carbonation depth of concrete is minimum; and then the carbonation depth of concrete increases with the increasing content of nano-particles. Moreover, at the age of 28d, compared with plain concrete, the carbonization depth of concrete with 2% nano-SiO$_2$ and 1% nano-Fe$_2$O$_3$ is, respectively, reduced by 58.65% and 45.86%.

Additionally, when the content of nano-particles is 1%, the carbonation depth of concrete with nano-Fe$_2$O$_3$ is less than that of concrete with nano-SiO$_2$; in turn, the carbonation depth of concrete with nano-Fe$_2$O$_3$ is larger than that of concrete with nano-SiO$_2$ in the case of other content. The effects of these two nano-particles on the carbonation performance of concrete under the action of ASR increase in the order: NS05< NS10< NS30< NS20 and NF30< NF05< NF20< NF10. Therefore, it can be concluded from the carbonation depth that the optimum contents of nano-SiO$_2$ and nano-Fe$_2$O$_3$ are 2% and 1%, respectively.

3.2.2. Expansion

The expansion of concrete varying with test ages is shown in Figure 4. It can be learned from Figure 4 that the expansions of all concretes increase with the

![Figure 2. Compressive Strength of concrete.](image)
growth of test age under the combined action of carbonation and ASR, or the action of ASR alone, and the expansion of concrete increases faster in early test ages. After mixed with nano-particles, the expansion of concrete is reduced by different degree, which means that the addition of nano-SiO$_2$ and nano-Fe$_2$O$_3$ can mitigate the expansion of concrete caused by ASR.

Whether affected by the combined action of carbonation and ASR or affected by the action of ASR alone, for the concrete with nano-SiO$_2$, the concrete shows minimum expansion when the content of nano-SiO$_2$ is 2%; for the concrete with nano-Fe$_2$O$_3$, the concrete shows minimum expansion when the content of nano-Fe$_2$O$_3$ is 1%.

Moreover, compared with the concrete under the action of ASR alone, the expansion of concrete under the combined action of carbonation and ASR increase faster, especially in later test ages, which illustrates that carbonation can accelerate the expansion of concrete caused by ASR.

**Figure 5** shows the relationship between the expansion of concrete and the contents of nano-particles. It can be learned that the expansion of concrete decreases gradually with the increasing content of nano-particles, when the contents of nano-SiO$_2$ and nano-Fe$_2$O$_3$ are, respectively, 2.0% and 1.0%, the expansion of concrete is minimum; and then the expansion of concrete increases with the increasing content of nano-particles.

When the content of nano-SiO$_2$ is 2%, the expansion of concrete is minimum; compared with plain concrete, the expansion of NS20 is reduced by 74.25% under the combined action of carbonation and ASR, meanwhile, the expansion of NS20 is reduced by 74.63% under the action of ASR alone. When the content of nano-Fe$_2$O$_3$ is 1%, the reduced degrees of

![Figure 3](#) Carbonation depth of concrete with nano-particles.

![Figure 4](#) Relationship between the expansion of concrete and the test ages.
expansion are, respectively, 61.33% and 61.22% for the above two experimental conditions.

Under the same experimental condition, when the content of nano-particles is 1%, the expansion of concrete with nano-Fe$_2$O$_3$ is less than that of concrete with nano-SiO$_2$, and in the case of other contents, the expansion of concrete with nano-Fe$_2$O$_3$ is larger than that of concrete with nano-SiO$_2$. The effects of these two nano-particles on mitigating expansion increase in the order: NS05< NS10< NS30< NS20 and NF05< NF30< NF20< NF10. The expansion results also imply that the optimum contents of nano-SiO$_2$ and nano-Fe$_2$O$_3$ are, respectively, 2% and 1%.

3.2.3. Sonic velocity

Figure 6 illustrates the sonic velocity of concrete varying with the test ages. It can be seen that the initial sonic velocity of concrete with nano-particles is significantly higher than that of plain concrete. This shows that after the nano-particles are incorporated, the microstructure of concrete is improved and becomes more compact. Once the test began, regardless of the combined action of carbonation and ASR or the action of ASR alone, the sonic velocity of concrete is decreased with the growth of test ages. In early test ages, the sonic velocity of concrete decreases faster, then this trend tends to be gentle. This implies that the internal damage caused by ASR is relatively faster in early test ages. At all test ages, the sonic velocity of concrete with nano-particles is higher than that of plain concrete, including the initial sonic velocity. This illustrates that the concrete with nano-particles still can maintain more compact microstructure to delay the decline of durability, even affected by the combined action of carbonation and ASR or the action of ASR alone.

Additionally, under the same test condition, the sonic velocity of concrete with 2% nano-SiO$_2$ is the largest in all test ages (including the initial sound velocity), followed by that of concrete with 1% nano-Fe$_2$O$_3$. When the content of nano-particles is 1%, the sonic velocity of concrete with nano-Fe$_2$O$_3$ is higher than that of concrete with nano-SiO$_2$, in turn, the sonic...
velocity is less than that of concrete with nano-SiO\(_2\) in the case of other content.

Figure 7 shows the relationship between the sonic velocity of concrete and the content of nano-particles. It can be seen that, regardless of the combined action of carbonation and ASR or the action of ASR alone, the sonic velocity of concretes at all test ages is firstly enhanced and then reduced with the increasing content of nano-particles. When the content of nano-SiO\(_2\) and nano-Fe\(_2\)O\(_3\) are 2% and 1%, respectively, the sonic velocity of concrete reaches the peak value.

At 28d test age, under the combined action of carbonation and ASR, the sonic velocity of plain concrete decreases from 5.31 km/s to 5.11 km/s, with a descent range of 3.69% for the concrete with 2% nano-SiO\(_2\) and 1% nano-Fe\(_2\)O\(_3\), the descent range of sonic velocity is, respectively, 2.36% and 2.31%, which decreased by 36.04% and 37.40% compared to plain concrete. Moreover, under the action of ASR alone, the descent range of sonic velocity for the concrete with 2% nano-SiO\(_2\) and 1% nano-Fe\(_2\)O\(_3\) is, respectively, decreased by 22.30% and 35.03% compared with plain concrete.

### 3.3 Discussions

#### 3.3.1 The mechanism of carbonation

Concrete carbonization can be explained that CO\(_2\) diffuses from surface to interior through the hardened cement paste and interface transition zone (ITZ), and reacts with hydration products of cement in a certain order (Liu 2005):

\[
\text{Ca(OH)}_2 + H_2O + CO_2 \rightarrow \text{CaCO}_3 + 2H_2O
\]

\(\Delta G^0_{298} = -74.75\text{kJ/mol}\) (1)

\[
3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{CO}_3
\rightarrow 3\text{CaCO}_3 + 2\text{SiO}_2 + 6\text{H}_2\text{O} \quad (\Delta G^0_{298} = -74.75\text{kJ/mol}) \] (2)

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 3\text{H}_2\text{O} \rightarrow 3\text{CaCO}_3 + 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 3\text{H}_2\text{O}
\]

\(\Delta G^0_{298} = -48.8\text{kJ/mol}\) (3)

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} \rightarrow 3\text{CaCO}_3 + 2\text{Al(OH)}_3 + \text{CaSO}_4 + 12\text{H}_2\text{O}
\]

\(\Delta G^0_{298} = -63.4\text{kJ/mol}\) (4)

Formula (3) represents the carbonization of Ca(OH)\(_2\), formula (4) represents the carbonization of C-S-H gel, formula (5) and formula (6) represents the carbonization of monosulfate and ettringite. \(\Delta G^0_{298}\) is the free enthalpy at 25°C, and the greater its absolute value, the easier the chemical reaction.

It can be concluded from free enthalpy that Ca(OH)\(_2\) and C-S-H gel are most susceptible and almost simultaneous to be carbonized among these hydration products (Castellote 2009). Some literatures also have shown that C-S-H gels are more prone to be carbonized (Slegers 1976), and C-S-H gel will continue to be carbonized even Ca(OH)\(_2\) has been completely carbonized (Parrott and Killoh 1989; Parrott 1992).

The carbonation process of Ca(OH)\(_2\) can be concluded as following: (1)CO\(_2\) is dissolved in water to form H\(_2\)CO\(_3\), then H\(_2\)CO\(_3\) is ionized to generate CO\(_2^2-\), which can combine with Na\(^+\), K\(^+\) and Ca\(^{2+}\) in the pore solution of concrete to form Na\(_2\)CO\(_3\), K\(_2\)CO\(_3\) and CaCO\(_3\). (2) CaCO\(_3\) is almost insoluble in pore solution, and deposited on the pore wall, which decomposes Ca(OH)\(_2\) crystals to maintain the concentration of Ca\(^{2+}\) in pore solution. In this process, the pH is basically stable, for Na\(^+\) and K\(^+\) exist as ions in pore solution all the time. (3) With the deposition of CaCO\(_3\) crystals, the Ca(OH)\(_2\) crystals are eventually exhausted.

Because the solubility of CaCO\(_3\) decreases with the increase of pH and the solubility product of Ca(OH)\(_2\) – K\(_{sp}\)Ca(OH)\(_2\) is constant at a certain temperature, the concentration of Ca\(^{2+}\) will reduce when the initial pH in pore...
solution is relatively high, which accelerates the decompose of Ca(OH)$_2$. Therefore, above explanations mean that high PH is in favor of carbonation (Liu 2005).

3.3.2 The mechanism of ASR

The mechanism of ASR has been discussed in another paper (Zhang, Zhang, and Xie 2019), from that paper, we can conclude that enough OH$^-$, Ca$^{2+}$ and water is essential for the process of ASR.

3.3.3 The interaction between carbonation and ASR

The factors that affect the durability of concrete under the combined action of carbonation and ASR can be analyzed from the microstructure of concrete and the chemical composition of pore solution. (1) The microstructure of concrete affects the migration of water, and also affects the diffusion of CO$_2$. (2) Both OH$^-$ and Ca$^{2+}$ in pore solution affect the carbonation and ASR process: on the one hand, OH$^-$ and Ca$^{2+}$ is the prerequisites for ASR; on the other hand, the concentration of OH$^-$ affects the PH of pore solution, and then affects the concentration of Ca$^{2+}$ in pore solution, and ultimately affects the carbonation process.

3.3.3.1 In terms of the microstructure of concrete

Under the combined action of carbonation and ASR, carbonization will cause the deposition of CaCO$_3$, resulting in the reduction of pore volume and aperture in carbonization area, even affected by carbonation process, and the pore volume and aperture in non-carbonized area will also reduce (Liu, Lv, and Li 2005), which will limit the migration of water in concrete. However, with the carbonation of concrete, some water will be released from hydration products (as shown in the formula (3) to (6)), which will provide some water for ASR. That is also the reason why the sonic velocity under the combined action of carbonation and ASR is relatively higher.

Generally, lower expansion and higher sonic velocity show better durability for concrete. While, under different test conditions, the test results show converse regularity: the expansion is larger when the durability of concrete is affected by combined action of carbonation and ASR, and the sonic velocity is higher. The results of expansion have testified that carbonation can accelerate the ASR process; however, the results of sonic velocity cannot testify that carbonation can accelerate the ASR process. It may be because that with the constant deposition of CaCO$_3$ and the release of water from hydration products, the microstructure of concrete will be increasingly compact and the saturation will be increased (Branch, Epps, and Kosson 2018; Branch et al. 2016), which leads to the concrete under the combined action of carbonation and ASR shows higher sonic velocity than that under the action of ASR alone. Conversely, ASR causes the concrete to expand and generate plenty of micro cracks to accelerate the diffusion of CO$_2$ and the migration of water.

3.3.3.2 In terms of chemical composition of the pore solution

Alkali ions in pore solution, such as Na$^+$ and K$^+$, participated in ASR process to form ASR gel. Although some Ca(OH)$_2$ crystals can be decomposed into the pore solution, it cannot make up for the loss of alkali ions due to the relatively lower solubility. Therefore, the pH of pore solution will be reduced to a certain extent in the process of ASR. As described above, the lower initial pH of pore solution can slowdown the speed of carbonation. Alternatively, from the point of the chemical composition of pore solution, ASR can mitigate the process of carbonation.

The Ca$^{2+}$ in non-carbonized area will migrate to the carbonized region in the process of carbonization, while this migration cannot cause ASR in carbonized region due to the low alkalinity. Meanwhile, the Na$^+$ and K$^+$ in carbonized region will migrate to non-carbonized region, which lead to the increase of PH of pore solution and the concentration of alkali ions in non-carbonized region (Liu et al. 2015). Additionally, some sol Si generated by the decomposition of C-S-H gel due to carbonation will also migrate to non-carbonized region (Branch et al. 2016) and maybe participate in ASR process.

3.4 Mechanism of nano-particles improving the durability of concrete

Under the combined action of carbonation and ASR, the durability of concrete with nano-particles is improved, which is mainly reflected in the influence on the microstructure of concrete and the chemical composition of pore solution. Nano-SiO$_2$ and nano-Fe$_2$O$_3$ have common mechanism on improving the microstructure of concrete and have different impact on the chemical composition of pore solution.

3.4.1 Common mechanism

In terms of the microstructure of concrete, due to the nano-scale size, nano-particles have higher activity and better filling effect than other additives, such as silica fume. So the microstructure of concrete is refined to different extent (Senff et al. 2010; Ye 2007), and the effect is more obvious in the ITZ (Najigivi et al. 2013). Meanwhile, the orientation of Ca(OH)$_2$ crystals is also improved. So, the concretes with nano-particles become more compact, which can limit the moisture transfer and the migration of Na$^+$, K$^+$ and soluble Si caused by carbonization (Branch et al. 2016; Liu et al. 2019)
The detailed common mechanism can be seen in other paper (Zhang, Zhang, and Xie 2019).

### 3.4.2 Different mechanism

In terms of the chemical composition of pore solution: (1) nano-SiO$_2$ has pozzolanic activity, which can consume Ca(OH)$_2$ crystals and convert Ca(OH)$_2$ to C-S-H gel, so that more Ca$^{2+}$ exist in the stable hydration products. Thus, the Ca$^{2+}$ which can participate in ASR will be decreased. Additionally, with the addition of nano-SiO$_2$, the C-S-H gel tends to have low Ca/Si, and the C-S-H gel with low Ca/Si can bind more alkali ions (Najgiri et al. 2013) to reduce the content of OH$^-$ in pore solution which is essential for ASR. Although the pozzolanic activity of nano-SiO$_2$ can help Ca(OH)$_2$ crystals to form C-S-H gel, as same as Ca(OH)$_2$, C-S-H gel is still prone to be carbonized. However, as mentioned above, the C-S-H gel with low Ca/Si can reduce the content of OH$^-$ to decrease the PH of pore solution and then the carbonation process of concrete with nano-SiO$_2$ will slowdown. (2) Different from the pozzolanic activity of nano-SiO$_2$, nano-Fe$_2$O$_3$ has intense absorbability which helps to form many Ca-rich spherical hydration products (Wang 2009; Zhu 2015). Then, the amount of Ca$^{2+}$ which can participate in ASR and CH which is prone to be carbonized is reduced. Also, through substitution effect (Taylor 1997), nano-Fe$_2$O$_3$ maybe contributes CH to form AFm or Aft phase hydration products, which is hard to be carbonized. Thus, the content of Ca$^{2+}$ essential for ASR and the hydration products prone to be carbonized will be reduced, which slows down the process of carbonation.

Inductively, the high pozzolanic activity of nano-SiO$_2$, the intense absorbability and substitution effect of nano-Fe$_2$O$_3$ can reduce the concentration of Ca$^{2+}$ and the PH of pore solution, as well as make CH to form C-S-H gel with low Ca/Si, AFm and Aft phase hydration products to enhance the durability of concrete under the combined action of carbonation and ASR.

### 4 Conclusions

(1) The addition of nano-SiO$_2$ and nano-Fe$_2$O$_3$ can, to different extent, improve the durability of concrete under the combined action of carbonation and ASR, as well as the optimum contents of nano-SiO$_2$ and nano-Fe$_2$O$_3$ for concrete durability are 2% and 1%, respectively.

(2) With the growth of test ages, the carbonation depth and expansion of concretes increase gradually and the sonic velocity of concretes decreases gradually. With the increasing content of nano-particles, the carbonation depth and expansion of concretes are firstly enhanced and then reduced, and the sonic velocity of concretes shows opposite tendency.

(3) The micro-cracks caused by ASR can accelerate the diffusion of CO$_2$, and the deposition of CaCO$_3$ caused by carbonation can limit the migration of water and CO$_2$, while carbonation process is accompanied with the release of water for ASR. ASR process will consume alkali ions to decrease the PH of pore solution which slows down the process of carbonation, while the migration of alkali ions caused by ASR will promote the carbonation in non-carbonized area.

(4) After mixing with nano-SiO$_2$ and nano-Fe$_2$O$_3$, due to the nano-scale size, high activity and filling effect, the concrete matrix becomes more compact to limit the migration of water and diffusion of CO$_2$.

(5) The secondary hydration caused by nano-SiO$_2$ consumes a part of Ca(OH)$_2$ and generates C-S-H gel with low Ca/Si which can bind more alkali ions. Then, the PH of pore solution and concentration of Ca$^{2+}$ is decreased, and the process of carbonation and ASR will slowdown.

(6) While, through absorbability and replacement with Ca$^{2+}$ in Ca(OH)$_2$ crystals, nano-Fe$_2$O$_3$ can make more Ca$^{2+}$ to form spherical hydration products and AFm or Aft phase hydration products. Furthermore, the content of Ca(OH)$_2$, which is essential for ASR and prone be carbonized, is decreased, and the content of AFm or Aft phase hydration products, which is hard to be carbonized, is increased. Moreover, more Ca$^{2+}$ exists in stable hydration products. Then, the durability of concrete with nano-particles is improved.

Through this paper, the impacts of nano-particles on the durability of concrete under the combined action of carbonation and ASR are discussed theoretically, further studies can be focused on the quantitative analysis of the concrete microstructure, ions in pore solution and the mineral composition of cement paste.

### Disclosure statement

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