

Influence of axial loads on CO₂ and Cl⁻ transport in concrete phases: paste, mortar and ITZ

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Abstract: In most studies concerning the influence of external loads on transport properties of concrete, concrete is assumed to be homogeneous and hence, differences in the transport properties of its components, which have various physicochemical properties, are not examined. The differences would be further changed, when there is load on the concrete. Therefore, the results obtained can seldom explain changes in the transport properties due to the applied loads and neither can they further enhance existing transport knowledge. An experimental study on carbonation and Cl⁻ ingress in concrete components, *viz.*, paste, mortar and the interface transition zone (ITZ), subjected to different levels of non-destructive axial tensile and compressive loads, was carried out. The results obtained indicate that there was an approximately linear relationship between the non-destructive load and the depth of carbonation. The external load had a significant effect on the CO₂ and chloride transport process in the ITZ, where a large amount of calcium hydroxide crystals can be found; for the mortar and ITZ samples, the influence of load on the depth of Cl⁻ ingress was more significant than on the carbonation, whereas the influence of the load on the ingress of CO₂ and Cl⁻ was similar in the interface-free paste sample. It is also found that comparing to tensile loads, compressive loads inhibited the transport of CO₂ and Cl⁻ at the later stage of exposure.

Key words: axial load; concrete components; transport process; carbonation; chloride ingress

1. Introduction

Corrosion is one of the key factors affecting the service life of reinforced concrete structures. The initiation of corrosion is generally triggered by CO₂ and/or Cl⁻, which cause neutralisation of concrete pH or an increase in Cl⁻ concentration near the reinforcement. Understanding the transport process of CO₂ and Cl⁻ is important in assessing the service life of concrete structures^[1,2]. For the transport of CO₂ and Cl⁻ in cover concrete, the reaction mechanisms and research methodology have been established comprehensively. With regard to the different research aims, most experiments were carried out on concrete specimens in a load-free status without considering the effect of loads. In actual structures, however, the external loads can never be avoided and will change the size and connectivity of pores in concrete, consequently affecting the ingress of CO₂ and Cl⁻. For this reason, the research on the effect of loads on the transport of CO₂ and Cl⁻ in concrete is of great practical significance.

Samaha *et al.*^[3] studied the influences of loads on the transport properties of concrete by applying different compressive loads to concrete specimens and testing the chloride diffusion coefficient. Saito *et al.*^[4] also investigated the influences of cyclic loading on the chloride permeability of concretes. Fu *et al.*^[5] reported the influences of uniaxial tensile fatigue loads on chloride ingress. Yildirim^[6] and Sahmaran *et al.*^[7] proved that tensile loading induced cracks significantly increased the gas permeability and Cl⁻ diffusivity. Sahmaran *et al.*^[8] also reported that applying external loads can generate damage (micro cracks) within the concretes and the ingress of Cl⁻ becomes faster. All of these studies detected transports of Cl⁻ in concretes after the applied loads were released from the specimens, which means that the results actually reveal damage

49 accumulated in the concrete during the loading stage that naturally affect the transport properties. As some of
50 the generated cracks might be healed once the loads were removed, these results cannot reflect the actual
51 transport process of chloride in continuously loaded concrete.

52 Fang *et al.*^[9] worked on the carbonation of hardened cement paste and mortar under bending loads, and
53 Ma *et al.*^[10] reported transport regulation of Cl⁻ in composite fibre cement experiencing bending loads. In this
54 type of study, tensile stresses were applied to the sample by means of a three- or four-point bending method
55 in which the stress in the cross-section was unevenly distributed, and the detected depth-related results either
56 for the carbonation or chloride ingress processes were usually with obvious discreteness which were difficult
57 to analyse. For this reason, Jin *et al.*^[11] pointed out that the influence of bending loads on the transport
58 properties in concrete is sufficient for obtaining qualitative conclusions and future studies should be carried
59 out on the influence of axial tensile and compressive loads on the concrete transport properties.

60 Regarding the effects of axial loads on the transport properties of cement-based materials, Wang *et al.*^[12]
61 reported the influence of different levels of load and the formation of micro-cracks on the transport of Cl⁻.
62 Wang *et al.*^[13] also explored the ingress of Cl⁻ into concretes with different mechanical properties subjected
63 to cyclic wet-dry environments and axial compressive loads. Sun *et al.*^[14] studied the ingress mechanism of
64 Cl⁻ in concretes which were influenced by the coupled effects of distributed axial loads and carbonation. Gu
65 *et al.*^[15] investigated the generation of cracks in hydrated cement paste during an increase in tensile stress and
66 its effects on the ingress of CO₂. Du *et al.*^[16] simulated the change in concrete pores under compressive stress
67 and explored its influence on the Cl⁻ diffusion coefficient at the microscopic scale. Most of the above-
68 mentioned literatures addressed the effect of single stress (either compressive or tensile) on concrete transport
69 properties, which is difficult to reveal the influence of both compressive and tensile loads.

70 Fu *et al.*^[17] summarised the existing works and analysed the effect of different loading manners, *viz.*,
71 axial tension, axial compression and bending loads, on chloride transport in concrete. Chen *et al.*^[18]
72 investigated the distribution of Cl⁻ in concretes under tensile and compressive stresses and studied the
73 deterioration process of concrete under short-term and long-term loads. In these studies, the concrete was
74 assumed to be a homogeneous material in order to simplify the discussion of the effects of external loads on
75 the transport properties. Since the microstructure of concrete is significantly influenced by numerous factors
76 (e.g. raw materials, mix proportions, manufacturing process), the results obtained by different authors
77 generally do not agree with each other.

78 From the viewpoint of transport, concrete could be regarded as a multi-phase material, composed of
79 hardened cement paste, aggregate and an interface transition zone (ITZ). For a given concrete, chemical
80 compositions, mechanical properties and transport properties of the three components differ significantly.
81 Once concrete is loaded and the stress formed at a certain location exceeds its strength, micro-cracks will be
82 generated at this location. Even though the concrete retains its visual integrity, the transport of CO₂ and Cl⁻
83 has been affected^[19]. Therefore, investigation of the transport properties of concrete subjected to external
84 loads requires a detailed division of concrete based on its mechanical, chemical and transport properties, which
85 may provide a sound basis for establishing a mass transfer model for loaded concretes^[20].

86 Some researchers have attempted to incorporate the transport properties of different concrete components
87 in transport models. Li *et al.*^[21] found that the Cl⁻ diffusion coefficient of concrete can be accurately predicted
88 once it is considered as a three-phase material, *viz.*, mortar, aggregate and ITZ. By means of numerical
89 simulation, Zheng *et al.*^[22] assessed the influence of the ITZ on the steady-state chloride diffusivity of concrete.
90 Considering the effect of ionic exchange between pores of different sizes, ionic binding between liquid and
91 solid phases and the boundary-layer effect of the exposed surface on chloride transport, Li *et al.*^[23] presented
92 a new transport model to evaluate the penetration of Cl⁻ into concrete. Liu *et al.*^[24] proposed a three-phase
93 transport model to simulate chloride penetration in concrete in which they also considered the effect of multi-
94 component ionic. The above mentioned simulation models have been established or improved based on
95 experimental data obtained from Cl⁻ transport tests, while few of them has considered the influence of external
96 loads on the detailed transport process of Cl⁻ within the concrete. Therefore, the suitability of these models for

assessing the transport performance of different components under loads should be proved so as to reach a more accurate prediction of the ingress of substances into structural concretes. To address this problem, a series of experiments were carried out to explore the regulation of carbonation and Cl⁻ ingress into cement paste, mortar and ITZ samples which were subjected to axial tensile and compressive loads.

2. Experimental Procedures

2.1 Raw materials and mix proportion

Three types of samples, viz., cement paste, mortar and mortar with an artificial platy aggregate, were manufactured. The materials used include: Yuexiu brand P-II 42.5R Portland cement; commercial available standard sand conforms with GB/T 17671-1999 with a maximum particle size of 2.0 mm; tap water; basalt aggregate with the water absorption of 0.32%. It was coarsely polished into a dimension of 3 × 30 × 40 mm. The water–cement ratio of all the specimens was 0.5, and the sand ratio of the mortar and ITZ samples was 1:3. Detailed mix proportions of the samples are shown in **Error! Reference source not found.**

Table 1 Mix proportion of the samples (g)

	Cement	Water	Sand	Platy aggregate
Paste	100	50	0	0
Mortar	100	50	300	0
ITZ	100	50	300	~30*

* The mass of the platy aggregate was about 30 g and its dimensions were 3 × 30 × 40 mm.

2.2 Preparation, curing and pretreatment of the samples

To investigate the influence of loading on the ingress of CO₂ and chloride in conventional carbonation chamber and chloride immersion tank, prismatic cement paste and mortar samples with dimensions of 40 × 40 × 160 mm were cast. The middle part of the specimens under relatively uniform stress was used to analyse the ingress of CO₂ and chloride to minimise the influence of the regional stress concentration due to the external clamping at both ends^[25].

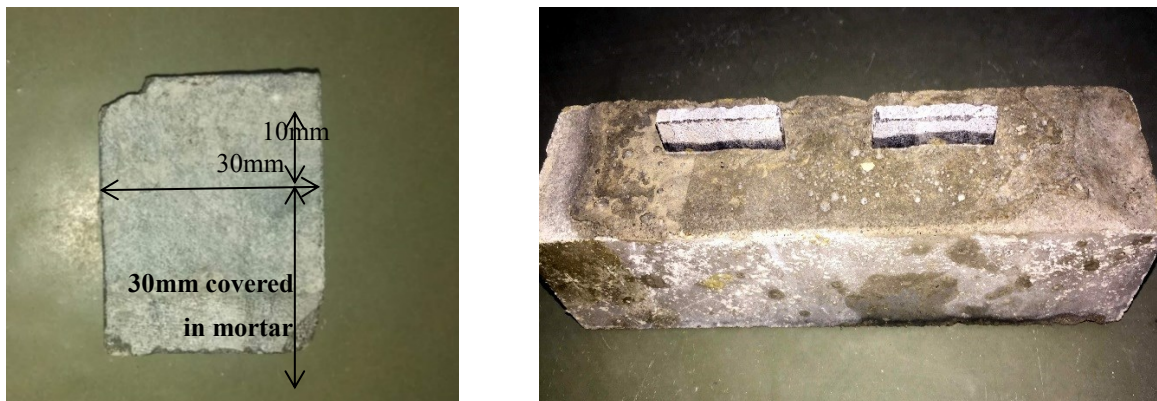


Fig 1 Platy basalt aggregate (left) and the prepared ITZ sample (right)

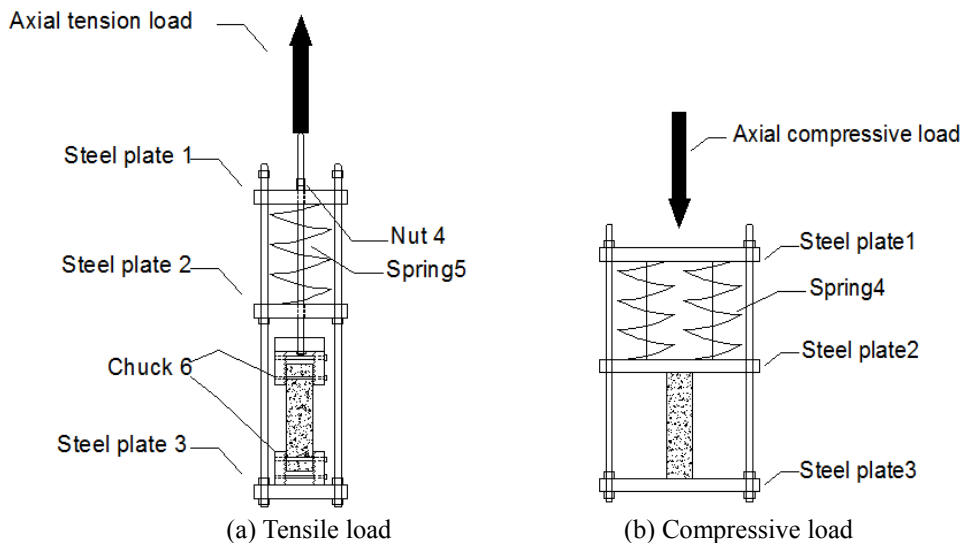
The three different types of specimens were manufactured following the Chinese national standard, GB/T 17671-1999. It needs to be mentioned that the “ITZ” samples, containing artificially prepared ITZs, were manufactured with freshly prepared mortar and polished platy basalt aggregate. During the casting of the ITZ samples, 40 × 40 × 160 mm fresh mortar samples were first prepared in steel moulds following the steps

131 prescribed in the standard. Subsequently, two pieces of platy aggregate (as shown in Fig 1) were vertically
 132 inserted into the axial of a fresh specimen with the help of a vibrating table. The insertion depth of each
 133 aggregate piece was about 30 mm (that is, a 10-mm-wide part remained uncovered at the mortar surface). All
 134 of the manufactured samples were demoulded after 24 hours from the cast and were placed in a 20°C water
 135 chamber for 28 days.

136 Moisture significantly influences the transport of Cl^- and CO_2 in hydrated cement paste. As such, the
 137 water-cured samples were directly immersed in a NaCl solution to study chloride ingress. Those for
 138 carbonation studies were preconditioned to a relative humidity (RH) of 65%, following the steps as described
 139 in section 2.4, after which five surfaces of each specimen were sealed with epoxy resin leaving only one $40 \times$
 140 160 mm surface exposed to the air (for the ITZ specimens, the aggregate surface was exposed) so as to form
 141 a one-dimensional ingress into the specimen during the carbonation and chloride ingress processes.
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143 2.3 Application of load

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 145 During the test, the samples were subjected to continuous loads using a self-made loading frame as shown in
 146 Fig 2. A ZY-3 digital anchor bolt produced by Shangyu Expand Equipment Co. Ltd (China) with an accuracy
 147 of 0.01 kN was used to apply the axial tensile loads to the specimens. A CNC hydraulic servo pressure testing
 148 machine produced by the MTS with an accuracy of 0.01 kN was used to apply axial compressive loads to the
 149 specimens. When the load reached the predetermined value, the heavy industrial springs shown in the figure
 150 were compressed, and subsequently, the bolts were tightened with a wrench, which allowed the specimens to
 151 be continuously loaded. The springs used had an elastic constant of 2.50 MPa, and the results showed that it
 152 did not display an obvious weakening after three months of continuous loading.
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 155
 156 Fig 2 Set-up for applying axial loads to the specimen
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158 As reported by Fu *et al.*, during a study of the influence of loads on the transport properties of concrete,
 159 the loads applied should be designed based on the tensile/compressive strength of the specimens [17].
 160 According to the literature [26], once concrete is subjected to a compressive load higher than 40% of its
 161 compressive strength (f_c), micro-cracks will be generated leading to fundamental changes in the transport
 162 mechanism. In comparison, cracks will also be generated when a concrete is subjected to a tensile load
 163 higher than 60% of its tensile strength (f_t) [27-28]. Meanwhile, existing results have proved that compressive loads have
 164 a relatively limited influence on transport performance compared to tensile loads [29-31]. Therefore, to explore
 165 the influence of non-destructive loads on the transport of substances in concrete components, the authors

planned two levels of compressive loads ($40\%f_c$, $20\%f_c$) and three levels of tension loads ($60\%f_t$, $40\%f_t$ and $20\%f_t$). For the cement paste samples, two compressive levels ($20\%f_c$, $10\%f_c$) and one tensile level ($60\%f_t$) were selected. This is because the paste samples have a higher compressive and lower tensile strength than the mortar and the available industrial spring cannot reach 40% of the compressive strength of the paste sample even it is fully compressed. Meanwhile, the low tensile strength makes it difficult to accurately apply a 0.05 MPa tensile load to the sample. For the samples with an artificial ITZ, the platy aggregate only takes up about 5.6% of the total cross-sectional area, so it is assumed that its influence on the compressive and tensile strengths was not significant in this configuration. Once the ITZ sample was subjected to a tensile force at the two ends, elongation of the mortar part and the volumetrically stable platy aggregate would result in a tensile force in the ITZ part. Therefore, the forces applied to the ITZ sample were the same as those for the mortar samples. The loads and stress levels formed in this study are summarised in Table 2.

Table 2 Stress generated within specimens under loading (MPa)

	Ultimate Stress		Applied Stress						
	100% f_c	100% f_t	40% f_c	20% f_c	10% f_c	0	20% f_t	40% f_t	60% f_t
Paste	-65	0.25	/	-13	-6.5	0	/	/	0.15
Mortar, ITZ	-40	1.6	-16	-8	/	0	0.32	0.64	0.94

2.4 Carbonation test

To minimise the influence of interior moisture on the progress of carbonation, all samples used for the carbonation study were conditioned to remove free moisture. The specimens were dried in a 60 °C oven for 48 h, followed with placement in a constant temperature and humidity chamber for 14 days, which was controlled at 20 (± 3) °C and an RH of 65 (± 3)%, respectively. Subsequently, the conditioned samples were loaded following the steps ascribed in section 2.3 and placed in a carbonation chamber (as shown in Fig 3-a), which had a set temperature of 20 (± 3)°C, RH of 65 (± 3)% and CO₂ concentration of 5 (± 0.3)%^[32-34]. After carbonation for 2, 4 and 8 weeks, two specimens were removed to determine the depth of carbonation using a 1% phenolphthalein solution according to GB/T 50082-2009. For the ITZ specimens, the platy aggregate was removed after splitting of the sample, and the interface between the aggregate and mortar matrix was tested for the depth of carbonation.

2.5 Chloride ingress test

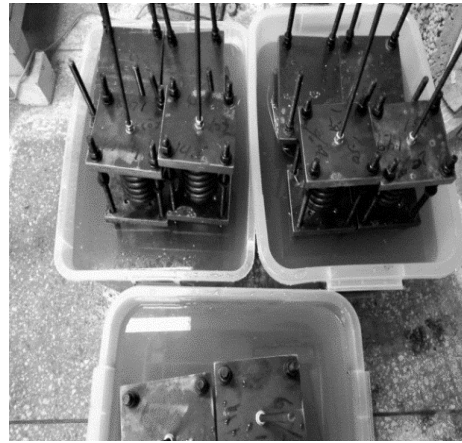
The loaded samples were placed in 165 g/L NaCl solution together with the loading device for the chloride ingress tests (Fig 3-b). The containers were sealed with plastic film to minimise any change in the chloride concentration due to the evaporation of water. After 2, 4 and 8 weeks of immersion, two specimens were removed each time to test the depth of chloride ingress by spraying a 0.1 mol/L AgNO₃ solution on the newly fractured cross-section.

3. Results and Discussion

In this part, the development of carbonation and chloride ingress into the mortar specimens is introduced first to explain the influence of axial loads on the transport properties. Then, the influence of axial loads on the transport performance of each component will be revealed by comparing the depths of the carbonation and chloride ingress into the hydrated cement paste, mortar and ITZ samples.



(a) Carbonation chamber



(b) Chloride ingress setup

Fig 3 Carbonation and chloride ingress

3.1 Effect of axial loads on the transport properties of mortar

3.1.1 Progress of carbonation in loaded mortar

The development of carbonation in the loaded mortar is presented in Fig 4. The bar chart indicates the carbonation depth in the samples, while the connecting dotted line represents the relationship between the average values for the 2-, 4- and 8-week durations and the applied loads. It should be pointed out that these average depths calculated from three test durations do not deliver any theoretical meaning; however, the curve can indicate the effect of different levels of stress on the carbonation depth. It can further reduce the influence of testing error on the obtained relationship in a statistical manner. The following features can be observed from the results. The dotted line shows a clear increase in the carbonation depth following the stress changing from a compressive load of -16 MPa to the unloaded state and then to a tensile load of 0.96 MPa. This is consistent with the conclusions of Tian *et al.*^[30] who reported that carbonation in concrete will be accelerated under the effect of tensile loads and slowed down under compressive loads. Xiao *et al.*^[35] explained this trend as being due to the expansion of the pore structure under tensile stress or even the formation of micro-cracks, which offer wider paths for the transport of CO₂; on the contrary, a compressive load may narrow the effective transport pores and disconnect proportions of the transport paths, inhibiting the diffusion of CO₂.

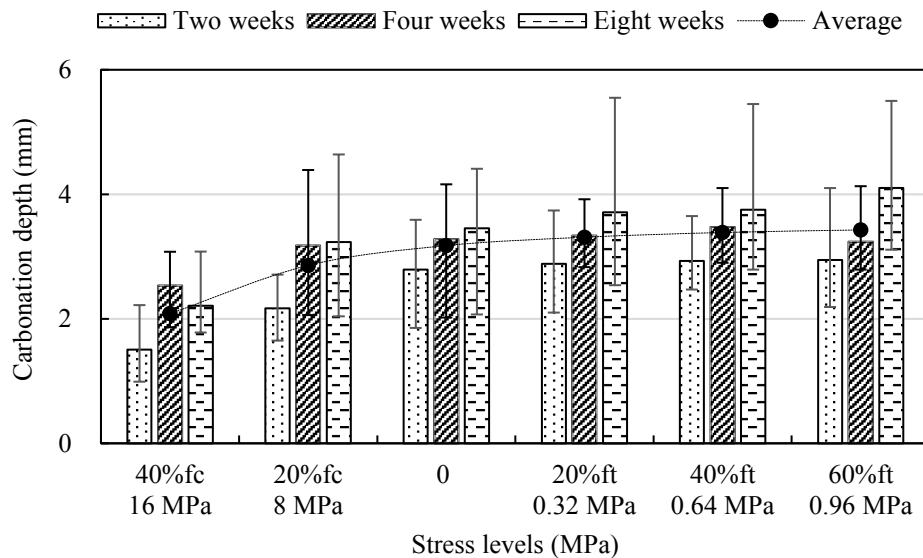


Fig 4 Relationship between carbonation depth and stress

Overall, there is an increase in the carbonation depth with the exposure duration except for 40% f_c , and the ingress of CO_2 is much faster at the early stage of exposure (0–4 weeks) than at the latter stage (4–8 weeks). This might be because calcium carbonates (CaCO_3) produced during the carbonation filled in pores of the samples and densified the matrix, which turns to be more obvious along with the carbonation duration and slowed down the increase in carbonation depth. Moreover, for the sample compressed with a high stress, this decrease in the carbonation speed was particularly prominent. In contrast, for the samples subjected to tensile stress, the carbonation depth still had an obvious increase in the later stage and this increase followed the increase in the tensile stress level. These results indicate that different types of loads lead to significant differences in carbonation performance, especially in the latter stage. For a compressed sample, the densification of its structure is caused by the external loads and the formation of CaCO_3 , both of which slow down the ingress of CO_2 during the latter stage of carbonation, whereas in a tensile sample, the increase in the pore diameter due to the external load results in an obvious increase in carbonation depth even in the latter stage.

Once subjected to compressive loads, the depth of carbonation obviously decreased with an increase in the stress level. When the samples were under the tensile stress, the depth increased along with the stress magnitude but to a limited extent. This difference should be due to the good compressive properties but relatively weak tensile properties of mortar specimens. The maximum compressive stress applied was about 16 times that of the maximum tensile stress and hence, the influence of the compressive loads on the pore structure must be relatively more significant, which leads to a more prominent change in the carbonation depth in the compressive state.

3.1.2 Chloride ingress into loaded mortar

Fig 5 shows the ingress of Cl^- into loaded mortar samples. It can be seen that the Cl^- ingress depth had an ascending trend as the stress changing from 40% f_c to the unstressed stage to 60% f_t . In order to minimise the influence of any differences in the tested samples and testing errors, the average Cl^- ingress depth (the dotted line) of the three test durations is plotted to reveal the effect of the type and stress magnitude on Cl^- ingress. Results indicate that tensile stress promoted Cl^- ingress, whereas compressive loads inhibited this process, similar to that observed for the carbonation process. Tu *et al.* [36] reported similar conclusions from a study of Cl^- equivalent diffusivity in loaded concretes. Therefore, it can be assumed that under the action of an axial tensile load, damage is formed at the internal part of the loaded specimen, which can be considered as a change in porosity and pore structure on the micro scale. When the loads increased, the microstructure of the samples changed gradually, including the accumulation and expansion of micro-cracks, increase in porosity and pore connectivity and finally leading to a higher Cl^- transport property. When the samples are compressed, pre-existing micro-cracks are closed and the size and the pore connectivity would be reduced, which significantly blocks Cl^- transport. A similar point of view is consistent with that reported by Fu *et al.* [29] for the progress of Cl^- transport in loaded concretes.

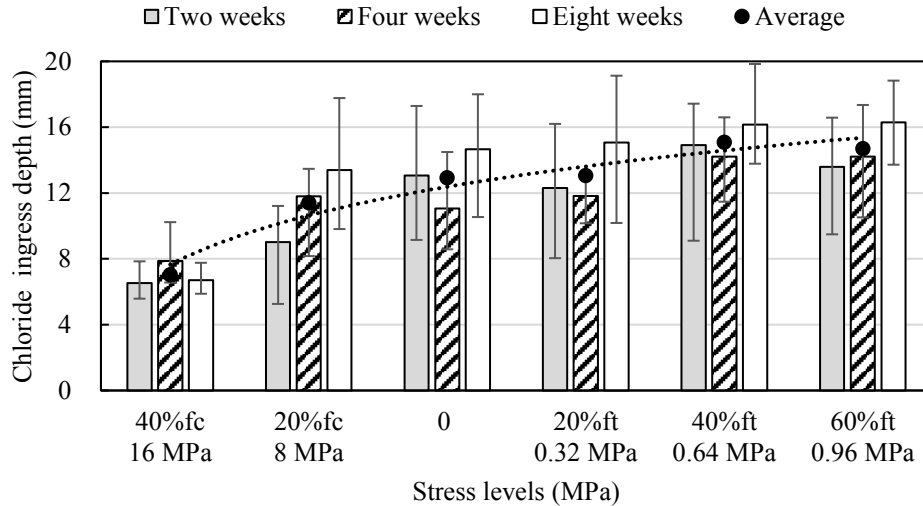


Fig 6 Relationship between chloride ingress depth and stress

3.1.3 Differences in carbonation and chloride ingress into mortar samples

Fig 7 compares the results of the depths of carbonation and chloride ingress (average of the three exposure durations) into the samples subjected to various loads. The variations for the ingress depths of CO_2 and Cl^- , calculated by comparing the depths for the loaded and unloaded samples, are also presented. The results show that the depth of carbonation was obviously lower than that of Cl^- ingress into the tested mortar samples. This difference is definitely related to the different permeation properties of CO_2 and Cl^- in the sample and would be due to the carbonation and chloride ingress methods used as well. First of all, 5% CO_2 environment was selected for the carbonation exposure in this study, whereas for the Cl^- ingress test, 165 g/L NaCl solution was used. Secondly, phenolphthalein was used for testing the depth of carbonation, which specifies a pH of 9 as the threshold value between carbonated and uncarbonated samples, and the measured depth must be theoretically lower than the true carbonation depth^[24]. In contrast, the Cl^- ingress depth is tested by the AgNO_3 solution, which can identify the location with a Cl^- concentration of 0.01%–0.4% by mass of the cementitious material^[37], which can basically be considered as the true Cl^- ingress depth. Therefore, direct comparison between the two ingress depths does not make sense.

In addition, the influence of the tensile and compressive stresses on the CO_2 and Cl^- transport was similar (it can be attributed to the impact of stress on the size of the transport paths), but the dotted lines in Fig 7 show that Cl^- transport was more sensitive to stress than CO_2 , *i.e.*, under the effect of a same tensile/compressive stress, the change in the Cl^- ingress is deeper than in the carbonation depth (e.g., the Cl^- ingress depth reduced to 54% of the unstressed state under the effect of 40% f_c , whereas for carbonation it decreased to 66%). This phenomenon might be due to the following reasons:

- It is reported that a decrease in pore dimension due to the effect of compressive stress will lead to an enhancement of the physical (capillary action) and chemical interaction between minerals at the pore surface and the Cl^- existing in the pore solution^[29-31]. In comparison, CO_2 is transported via pores in the form of gas molecules, and the geometrical variation caused by the stress affects the movement of CO_2 but has a limited effect on the reaction between CO_2 and the hydrated materials.
- The dimension of the transported particle will influence the ingress speed. For the two ingress processes, Cl^- and CO_2 have a diameter of 181 pm and 330 pm, respectively. However, it has been widely accepted that during the movement of Cl^- in the pore solution, one Cl^- ion will be wrapped by six water molecules, forming a $\text{Cl}^-+6\text{H}_2\text{O}$ polar molecular group with an overall diameter of 700 pm^[38]. This might explain why the chloride ingress result is more sensitive to the external loads than the carbonation.

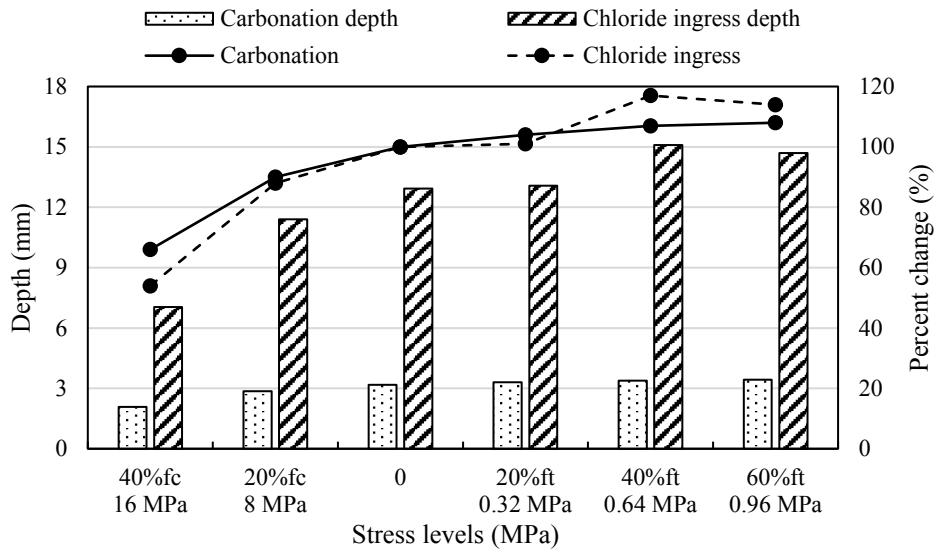


Fig 7 Comparison of carbonation and chloride ingress into mortar samples under loads

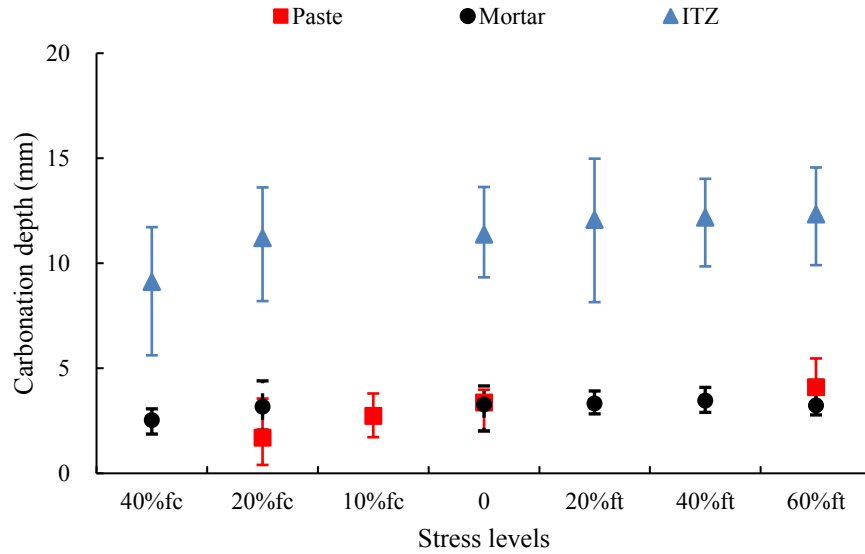
3.2 Effect of loads on transport properties of different components in concrete

The results of carbonation and chloride ingress into paste, mortar and ITZ samples under loads are presented in Fig 8 to Fig 10. Fig 8 shows the carbonation depth of the loaded samples after 4 weeks of CO₂ exposure. Fig 8(a) shows the relationship between the carbonation depth and the different stress levels tested and Fig 8 (b) displays the relationship between the carbonation depth and the stress magnitude. It can be seen from the results that:

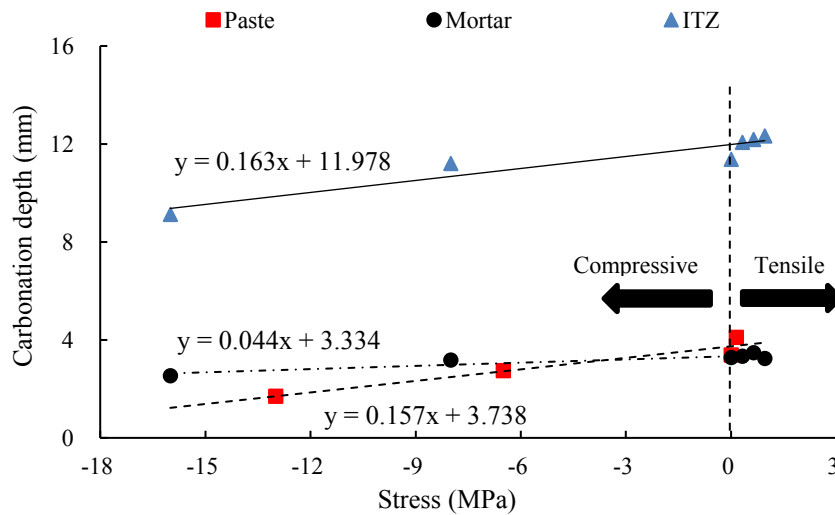
- 1) Carbonation depths in the ITZ samples were much higher than those in the paste and mortar samples, and the values for the latter two samples are closed to each other.
- 2) As the applied loads changed from 40% f_c to 60% f_t , the carbonation depth exhibited an approximately linear trend with the load value for all samples.
- 3) The linear trend between the carbonation depth and the applied load was the most obvious in the ITZ samples and was relatively weak in the mortar samples.
- 4) Within the three types of specimens, the measured carbonation depths in the ITZ samples had the highest scatter, while variations of the paste and mortar specimens were relatively small.

Fig 9 shows the depth of Cl⁻ ingress after 4 weeks in paste, mortar and ITZ subjected to different stresses. The results show that (continuing the numbering of the previous results):

- 5) The depth of Cl⁻ ingress into the three types of materials followed a descending sequence of ITZ, mortar and paste.
- 6) The Cl⁻ ingress depth and the stress magnitude again presented a linear relationship, but its correlation was weaker than that shown for the carbonation result (Fig 8-b). When the samples were subjected to a low tensile load, the Cl⁻ ingress depth already exhibited a comparatively obvious change. With a continuous increase in the tensile load, the further increase in the Cl⁻ ingress depth was less significant. In contrast, the depth of Cl⁻ ingress decreased linearly with the applied load until it reached 40% f_c for the samples under compressive loads. The ITZ sample had the most significant decrease when compressed, in which the chloride ingress depth decreased to 41% of that in the unstressed sample.
- 7) The ITZ samples presented the strongest influence of the load, whereas that of the paste samples was not so sensitive.
- 8) Test results of the Cl⁻ ingress depth presented a more noticeable fluctuation than those of the carbonation depth.



(a) Relationship between carbonation depth and stress levels



(b) Relationship between carbonation depth and stress magnitude

Fig 8 Depth of carbonation in paste, mortar and ITZ under stress (4 weeks)

Comparing the results of Fig 8 and 8, it can be deduced that transport of CO_2 and Cl^- in the three different types of samples follow several similar trends, but with different characteristics under some conditions. The similarities include:

- The ITZ samples had the fastest CO_2 and Cl^- transport speeds which might be due to its loose microstructure containing a significant amount of CH crystals [39] that can lead to a higher regional porosity.
- The ITZ sample had the highest sensitivity to the applied loads. This is also related to its loose microstructure, which gave the most significant volumetric deformation of the samples under the loads and the most obvious influence on changes in its transport paths. Consequently, the change in the ingress depth for the ITZ was clearly identified. This loose microstructure can also explain the presented largest discreteness in the carbonation results for the ITZ samples.

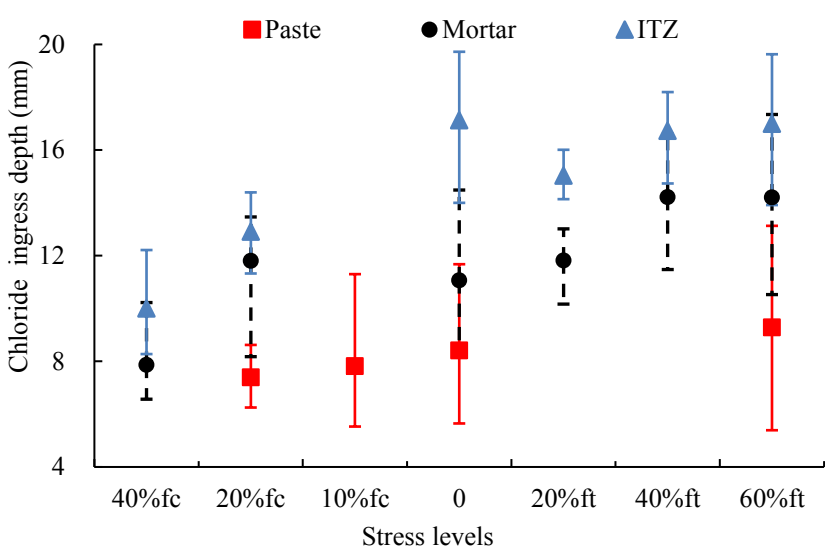
The differences in the CO_2 and Cl^- transport include:

- In the three tested phases, the results for Cl^- ingress had greater discreteness than those of CO_2 . This is caused by the differences in the test sensitivity between the two test methods (as has been explained in

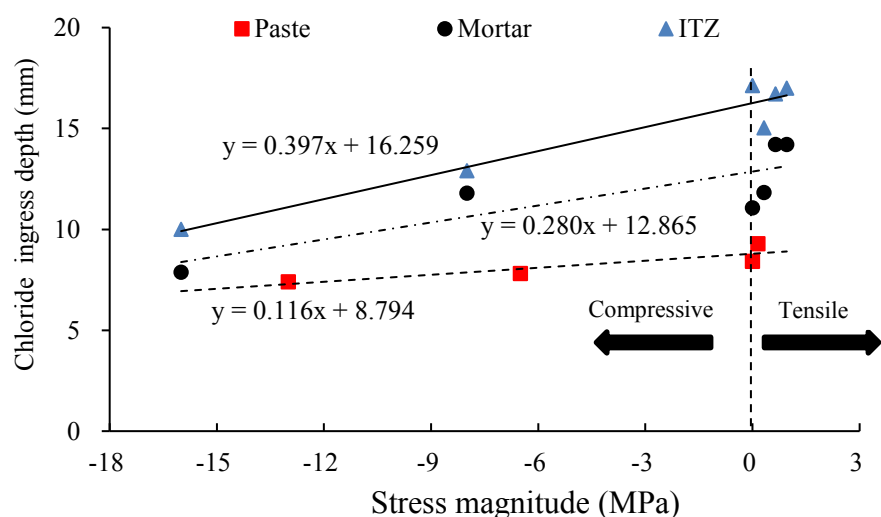
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the previous section). Compared with the use of phenolphthalein for the depth of carbonation, using an AgNO₃ solution for the chloride ingress depth has a high accuracy.

- d. The depths of carbonation in the mortar and the paste samples were similar, while the differences were found for depths of Cl⁻ ingress. As the Cl⁻ ingress depth in the mortar is higher than in the paste, it can be concluded that the interface between hardened cement paste and fine aggregate in the mortar definitely has an influence on the transport of substances. Comparatively, the limited difference in the results of the carbonation depth in the two types of samples might be related to the following two reasons: (i) the low sensitivity of the phenolphthalein method, once the samples are carbonated to a limited degree; (ii) compared with Cl⁻, CO₂ can quickly react with CH at the interface zone, preventing the further movement of CO₂ into the sample.



(a) Relationship between chloride ingress depth and stress level



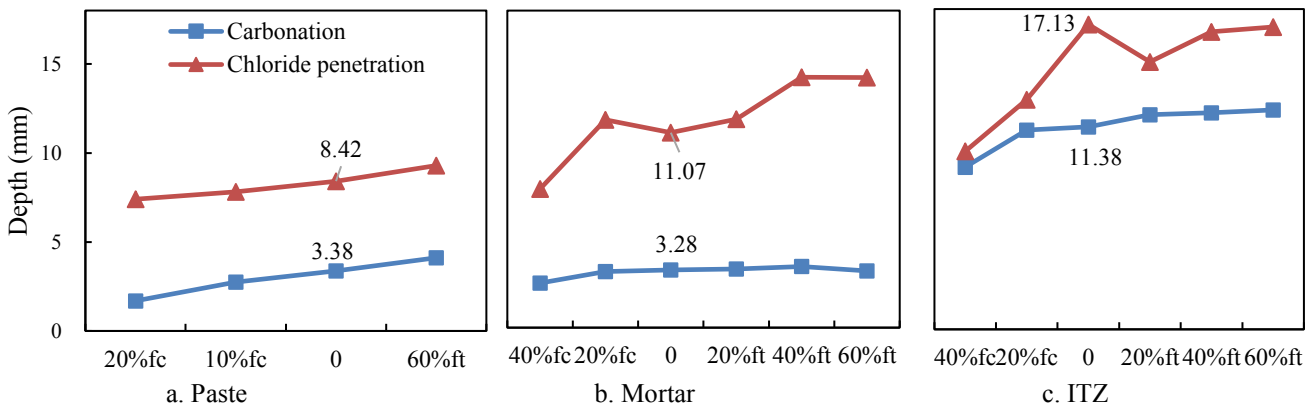
(b) Relationship between chloride ingress depth and stress magnitude

Fig 9 Ingress of chloride ions in paste, ITZ and mortar samples under stress

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The differences in the carbonation and chloride ingress into paste, mortar and ITZ samples under loads are given in Fig 10. The results indicate that within the range of load studied (continuing the numbering of the previous results):

- 376 9) In hardened cement paste without any coarse or fine aggregates (Fig 10-a), the influences of load on the carbonation and Cl^- ingress depths (*i.e.*, the slope of the linear regression curve obtained) were relatively similar. However, the effect of the loads on chloride ingress was significantly higher than on the depth of carbonation for mortar (Fig 10-b) and ITZ (Fig 10-c) samples that involved sand and coarse aggregates. This is consistent with reason (d) as mentioned during the differences in the CO_2 and Cl^- transport of the analyses of Fig 8 and Fig 9, *viz.*, in the samples containing interfaces, the ingress of Cl^- was affected by the applied loads to a more obvious extent.
- 383 10) The depths of chloride ingress were higher than the depths of carbonation in all tested samples. It should be noted that the two ingress depths had the smallest difference in the ITZ sample and the difference can be omitted, once the ITZ samples were under the 40% f_c load. This indicates that Cl^- ingress had a greater sensitivity to the loads than carbonation. This should be related to the larger dimensions of the $\text{Cl}^- + 6\text{H}_2\text{O}$ cluster compared to the CO_2 , as described in section 3.1.3.
- 388 11) Within the range of the loads applied, the carbonation results presented a clear increasing trend, whereas the results of Cl^- ingress were not constant, especially in the mortar and ITZ samples. As shown previously in section 3.1.3, this should be related to the different sensitivities of the test methods used.



393 Fig 10 Comparison of carbonation and chloride ingress into paste, mortar and ITZ

397 4. Conclusion

399 The ingress of Cl^- and carbonation into the three components of concrete (paste, mortar and ITZ) under the effects of non-destructive axial loads, was investigated in this study. The results obtained proved that due to the different physical and chemical properties of the three types of samples, the ingress of Cl^- and carbonation shows different trends in the samples. Also, the applied tensile and compressive loads had different influences on the depth of carbonation and Cl^- ingress. Based on knowledge from the literature and the results obtained, the following conclusions can be drawn:

- 405 1) As the ITZ formed between coarse aggregate and hydrated cement had the most porous structure, the change in its transport properties under the effects of loading was most obvious. In comparison, in mortar samples, the interface between fine aggregates and hardened cement paste also affected the transport properties but to a relatively low extent. In the ITZ, there is a high content of CH which has higher reaction kinetics with CO_2 than Cl^- . Therefore, the progress of carbonation should be more difficult than the ingress of Cl^- in the ITZ. This different reaction kinetics might lead to the fact that the ingress of Cl^- into the ITZ and mortar samples was more sensitive to the applied loads than the carbonation process.
- 412 2) Within the level of the applied loads, there were approximately linear relationships between the load value and the depth of carbonation and chloride ingress. The linear relationship obtained from carbonation

414 results had a strong correlation, whereas that for the chloride ingress presented obvious fluctuations,
415 especially in the mortar and the ITZ samples. This should be a combined effect from the high sensitivity
416 of the AgNO_3 method in testing the depth of chloride ingress, the loose structure and poor tensile property
417 of these materials and the poor chloride binding capacity of the minerals in the ITZ.

- 418 3) The effect of loads on the transport properties is mainly reflected as a change in the dimensions of the
419 transport paths. Compared with tensile loads, compressive loads can significantly inhibit the ingress of
420 CO_2 and Cl^- at the latter stage of exposure. This decrease in the degree of carbonation and chloride ingress
421 was the most obvious in the ITZ part of concrete. The linear relationship between the depth of carbonation
422 and the square root of the erosion time was not observed in the loaded samples. This might be an effect
423 from the change in the dimensions of the transport paths due to both the applied loads and the reaction of
424 CO_2 with CH in the matrix.
- 425 4) It can be deduced that with the aspect of substance transport, loaded concrete should be regarded as a
426 material composed of various phases with different properties. Even if the load applied does not exceed
427 the macro-cracking limit of the composite material, unevenly distributed stress will be generated, leading
428 to cracking in certain phases and resulting in apparent changes in transport properties. This may cause
429 predictable deviations in the results, if it is assumed that the diffusion coefficient of all of the components
430 is changed to the same degree.

431 Based on the linear relationships obtained between the external loads and the ingress depths of CO_2 and
432 Cl^- , we suggest that in future simulation studies, the diffusion coefficient of the three components can be
433 linearly revised according its magnitude in the unstressed state and the value of the load applied. Under the
434 effect of tensile loads, its change in diffusion coefficient from the unstressed state can be neglected and the
435 diffusion coefficient remains unchanged, until the local stress reaches the corresponding ultimate tensile
436 capacity. In addition, the reaction of Cl^- , CO_2 and other transport substances with the different components of
437 the concrete should also be considered in a precise simulation. When studying the transport of substances that
438 are highly reactive with CH, such as CO_2 and SO_4^{2-} , the chemical reaction kinetics need to be introduced to
439 modify the transport coefficient of the ITZ.

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