Time-Dependent Chloride Binding Capacity of Various Types of Cement Pastes

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ABSTRACT: The aim of this paper is to investigate the time-dependent chloride binding capacity of various types of cement pastes. Three types of cement (type I, III and V) were used in this study. Cement paste specimens with different water to cement ratio, cement types, curing times and chloride exposure periods were tested. From the experimental results, the chloride binding capacity of cement paste exhibits time-dependent. It depends on the curing time prior to chloride attack and exposure period in chloride solution. Cement pastes having longer age prior to chloride exposure bind less amount of chloride than those exposed at the earlier age. Longer exposure period of paste results in larger content of bound chloride. Moreover, the chloride binding capacity also depends upon other factors, such as water to cement ratios and cement types. Higher water to cement ratio results in smaller amount of bound chloride than the lower one does. Type V cement binds less, but type III cement binds more amount of chloride than type I cement does.

KEYWORDS: time-dependent, chloride binding, cement, cement paste.

INTRODUCTION

One of the predominant causes of the corrosion of steel in concrete is chloride attack. Chloride ions may be present in concrete mixtures, either as a result of using contaminated ingredients or some chemical admixtures or as a result of penetration from external sources such as from seawater or de-icing salts. The ability of cement to bind chlorides from the pore solution in concrete is one of the important factors to control the initiation of chloride-induced corrosion of steel in concrete. This is because only free chlorides, present in the pore solution, can diffuse and initiate corrosion if the free chloride content around the steel reaches a critical value. Chloride binding reduces the amount of movable chloride and then reduces the chloride ingress. Therefore, the chloride binding capacity is a significant property of concrete for prolonging the service life of the reinforced concrete structures subjected to chloride attack.

There are many factors that govern the chloride binding capacity such as type of cement, water to cement ratio, curing time and so on.[1] Aluminate (C_3A) and aluminoferrite (C_4AF) phases in cement were found to be responsible for chemical binding of chloride.[2-6] These two phases form Friedel's salt ($Ca_6Al_2O_6.CaCl_2.10H_2O$) and calcium chloroferrite ($Ca_6Fe_2O_6.CaCl_2.10H_2O$). The chemical binding capacity was then considered to depend on the content of C_3A and C_4AF in cement. The increase of sulfate content in cement was found to reduce the chloride binding capacity since sulfates bind more strongly to C_3A than do chlorides.[7-8] While the chemical binding was discovered to depend on the content of aluminate and aluminoferrite phases in cement, the physical binding depended upon the content of hydrated products, particularly the content of C-S-H in concrete.[9-10] However, there were very few studies on the time-dependent behavior of chloride binding, especially for the various types of cement pastes.

The aim of this study is to investigate the time-dependent chloride binding capacity of various types of cement pastes by varying the curing time prior to chloride attack and the chloride exposure period. This study will be very useful for designing durable concrete structure located in marine environment with high content of chloride. Three types of cement were used in the preparation of cement pastes in this study. Furthermore, the compressive strength of cement pastes at 28 days and the pore structure of cement pastes at various ages were also investigated.

MATERIALS AND METHODS

Materials And Mix Proportions

Three types of cement (type I, III and V Portland cements) were used in this study. Those cements are widely used in concrete work nowadays, so it is needed to study time-dependent chloride binding capacity of those types of cement. In addition, type V cement has

been believed to be effective for use in marine environment. The study of chloride binding capacity will be very useful when using those cements for concrete structure located in environment with high content of chloride. The chemical composition and physical properties of the cements are given in Table 1.

Table 1. Chemical compositions and physical properties of Portland cements

Chemical Composition	Type I Portland cement	Type III Portland cement	Type V Portland cement
SiO_2 (%)	20.61	20.73	20.97
Al_2O_3 (%)	5.03	4.49	3.49
Fe_2O_3 (%)	3.03	3.32	4.34
CaO (%)	64.89	64.89	62.86
MgO (%)	1.43	1.25	3.33
SO_3 (%)	2.70	2.76	2.12
Na_2O (%)	0.22	0.24	0.12
K_2O (%)	0.46	0.32	0.47
Free lime (%)	0.79	0.57	1.01
Loss on ignition (%)	1.23	1.23	1.21
Physical properties			
Blaine fineness (cm^2/g)	3,190	4,770	3,760
Specific gravity	3.15	3.22	3.13
Bogue's potential compound compositions			
C_3S (%)	61.64	63.77	60.77
C_2S (%)	12.68	11.41	14.37
C_3A (%)	8.21	6.29	1.91
C_4AF (%)	9.21	10.29	13.19

The mix proportions of cement paste are shown in Table 2. Five different mixtures of cement pastes were prepared for this investigation. There were three mixtures for type I cement pastes, one mixture for type III cement paste and one mixture for type V cement paste.

Table 2. Mix proportions of cement paste

Mix designation	Cement type	Water to cement ratio
I30	Type I	0.30
I40	Type I	0.40
I50	Type I	0.50
III40	Type III	0.40
V40	Type V	0.40

Specimen preparation

Cube specimens of 50x50x50 mm size were produced for compressive strength and pore structure tests. After casting, specimens were sealed with plastic sheet to prevent drying for 24 hours. All specimens were cured in water immediately after removal from the molds. Curing times were 28 days for compressive

strength test, and 3, 7, 28 and 91 days for pore structure test, as shown in Table 3. Curing temperature was 30±2°C.

For sample preparation of chloride binding capacity test, thin disc specimens having 50 mm in diameter and 10 mm in thickness were cast in PVC molds. Thirteen specimens were prepared for each mixture at one curing time and one chloride exposure period, ten for expressing the pore solution and three for determining the evaporable water content. After casting, the specimens were sealed with plastic sheets to prevent drying for 24 hours. Except for the specimens to be exposed to chloride at 1 day, all specimens were cured in water immediately after removal from the molds. Curing times were 1, 7 and 28 days as presented in Table 3. Curing temperature was 30±2°C. The mixing procedure for all mixtures was performed according to ASTM C305.

Test Procedures

Compressive strength

The experimental conditions for compressive strength test are shown in Table 3. Only the 28-day compressive strength of cement paste was tested in this study. The compressive strength test of cement paste was performed according to ASTM C109.

Pore structure

In this study, the pore structure of cement pastes was investigated by using the mercury intrusion porosimetry (MIP) technique. The MIP was used to determine the average pore diameter and the total porosity in the cement paste. At the end of curing period (as shown in Table 3), specimen was removed from water and broken into small pieces by crushing machine. In order to prevent the heterogeneous effect of specimen, only middle parts inside the specimen were collected and investigated for the pore structure.

Chloride binding capacity

Five different mixtures of cement pastes were prepared for this investigation as shown in Table 3. The test parameters for investigation were water to cement ratio (w/c), type of cement, curing time and chloride exposure period. At the end of water curing, specimens were exposed to chloride by submerging in salt water containing 3.0 % (w/v) chloride ion for different exposure periods. Sodium chloride was used for making the chloride solution. The exposure periods were 28, 56 and 91 days as shown in Table 3. The volume of salt water (chloride solution) was 2.0 liters. The temperature during the chloride exposure period was also controlled at 30±2°C.

At the end of chloride exposure period, the specimens were removed from the salt water. Surfaces of the specimens were dried by using tissue paper. Pore

Table 3. Experimental conditions for compressive strength test, pore structure test and chloride binding capacity test

Mix designation	Compressive strength test	Pore structure test	Chloride binding capacity test	
	Curing time (day)	Curing time (day)	Curing time (day)	Chloride exposure period (day)
I30	28	3, 7, 28, 91	1, 7, 28	28, 56
I40	28	3, 7, 28, 91	1, 7, 28	28, 56, 91
I50	28	-	1, 7, 28	28, 56, 91
III40	28	3, 7, 28, 91	1, 7, 28	28, 56, 91
V40	28	3, 7, 28, 91	1, 7, 28	28, 56, 91

solution inside the specimens was obtained by using a pore expressing apparatus as shown in Fig 1. The maximum loading pressure for expressing the pore solution was about 500 MPa. Two or three cycles of loading and unloading were performed in order to get 3 to 5 cm^3 of pore solution. The evaporable water content of the three parallel specimens with the same mixture condition was immediately tested for free chloride content in the pore solution.

Total chloride content in the specimens was determined from the difference between initial chloride content in the submerging salt water at the start of

Fig 1. Pore expressing apparatus

exposure and its chloride content at the end of exposure, and then divided equally to all specimens that were submerged in the salt water. The free chloride content was determined from the chloride concentration in the pore solution expressed from specimen multiplied with the volume of the evaporable water. Finally, the fixed chloride content in the tested cement pastes can be determined by subtracting the total chloride content with the free chloride content. All chloride

concentrations were analyzed by potentiometric titration with $AgNO_3$ solution and chloride ion selective electrode.

RESULTS AND DISCUSSION

Compressive Strength

Test results of compressive strength of cement pastes at 28 days are presented in Fig. 2. Lower water to cement ratio of cement paste results in higher compressive strength (see mixtures I30, I40 and I50 for this comparison). At the same water to cement ratio of 0.40, type III cement paste (mixture III40) has nearly the same compressive strength at 28 days as type I cement paste (mixture I40) has. On the other hand, type V cement paste (mixture V40) has lower 28-day compressive strength than that of the type I cement paste.

Pore Structure

The results of average pore diameter and total porosity of cement paste from MIP test are shown in
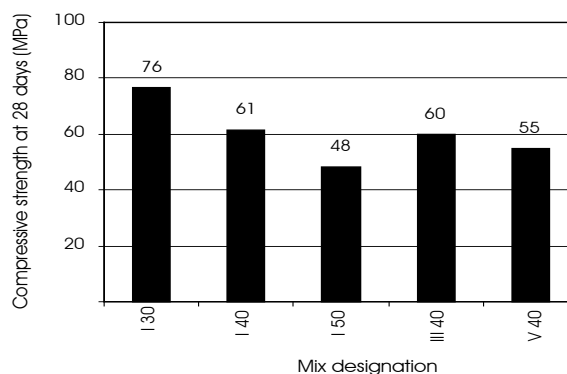

Fig 2. Compressive strength of cement paste at 28 days

Fig 3 and Fig 4, respectively. The average pore diameter and the total porosity of cement pastes decrease when the age of cement pastes increases, due to hydration of cement pastes. When age of pastes is longer than 30 days, the average pore diameter and total porosity of pastes still decrease at a lower rate. This is due to reduction in the rate of hydration at longer curing times. So, a smaller quantity of hydrated products, such as C-S-H, C-A-H, C-A-F-H, was produced, resulting in denser of pore structure. These results agree well with published results by Midley and Illston. [11]

From Fig 3, at the same water to cement ratio, type III cement paste (mixture III40) has the lowest average pore diameter when compared with other types of cement. Type I cement and type V cement pastes has nearly the same average pore diameter at all ages. When the water to cement ratio of cement paste decreases, the smaller average pore diameter can be achieved (compare I30 with I40). From Fig 4, the lower water to cement ratio of cement paste results in smaller total porosity. Type I cement and type III cement pastes have nearly the same total porosity at all ages, but type V cement paste has higher total porosity than do type I and type III cement pastes.

Chloride Binding Capacity

In this study, the test for chloride binding capacity was conducted based on the fact that in most cases, chlorides attack concrete from the outside environment. The test results of total chloride and fixed chloride are presented by bar charts in Fig. 5 and Fig. 6. The values in parenthesis above the bars indicate the fixed chloride ratios, which are the ratios of fixed chloride content to total chloride content in the paste.

Our results show that the chloride binding capacity of cement pastes exhibits a time dependent behavior. When considering samples with the same exposure
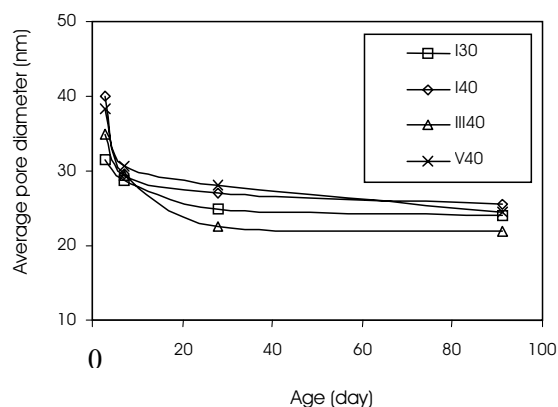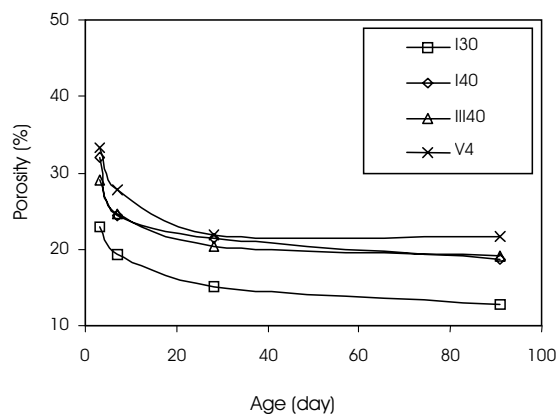

Fig 4. Total porosity of cement paste

period, pastes with shorter curing time have higher total and fixed chloride content than those with longer curing time. The reason for larger total chloride content in shorter curing time case is that younger paste had larger pore diameter and porosity (see Fig 3.and Fig 4), so larger amount of chloride can penetrate into the paste. The fixed chloride content is also higher because there are larger amount of unhydrated aluminate and aluminoferrite phases, which are accessible for chloride binding. On the contrary, considering pastes with the same curing time, longer exposure period in saltwater results in higher total and fixed chloride content. This observation concurs well with experimental results by Arya et al. [1] The higher total chloride content is due to the longer exposure period, while the larger amount of hydrated products produced during the longer exposure period can bind to more chlorides.

When comparing Fig 5(a) with Fig 5(b), it can be seen that at shorter exposure period, type III cement paste has a higher fixed chloride content than does type I cement paste. This is because type III cement had higher fineness than type I cement (see Table 1), so the hydration develops faster at early age and higher hydration products is produced. This results in higher fixed chloride content. However, when exposure period is longer, the binding capacity of type I cement and type III cement is nearly the same. On the other hand, when comparing Fig 5(a) with Fig 5(c), it can be observed clearly that type V cement pastes has a lower fixed chloride content than does type I cement pastes for all curing and exposure periods. This is mainly because the type V cement has lower content of C_3A than does type I cement (see Table 1), resulting in smaller chemical binding capacity. It is also found by the authors that cement pastes made from type V cement have larger porosity than the pastes made from type I cement, even though their average pore diameters are equivalent (see Fig 3 and Fig 4). So, these findings suggest that the use of type V cement in the marine environment must be carefully considered. In some occasions, type V

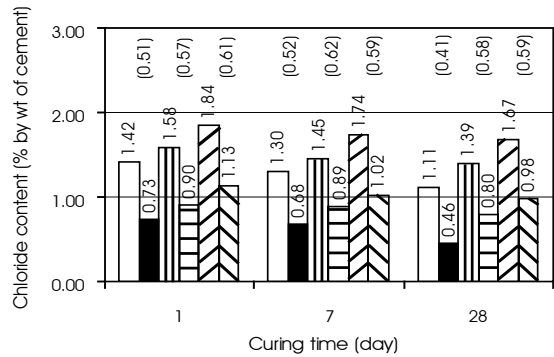**Fig 3.** Average pore diameter of cement paste
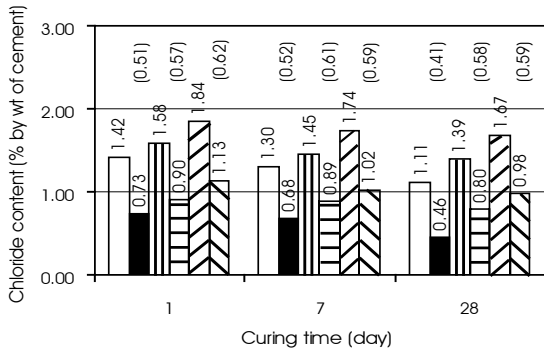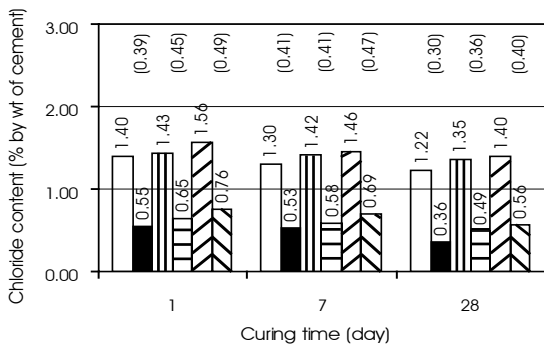
(a) I40: Type I cement paste (w/c=0.40)
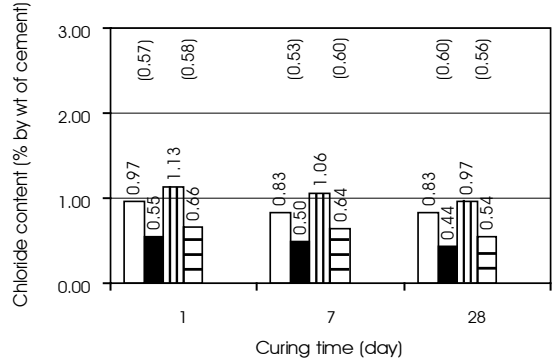
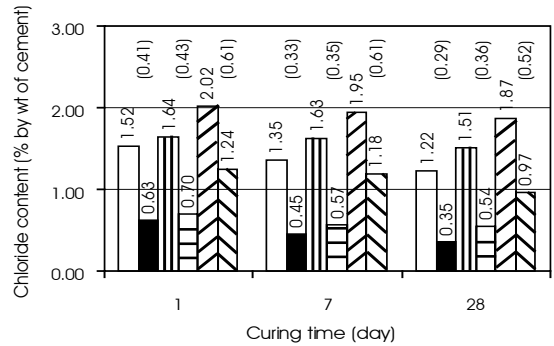(a) I30: Type I cement paste (w/c=0.30)
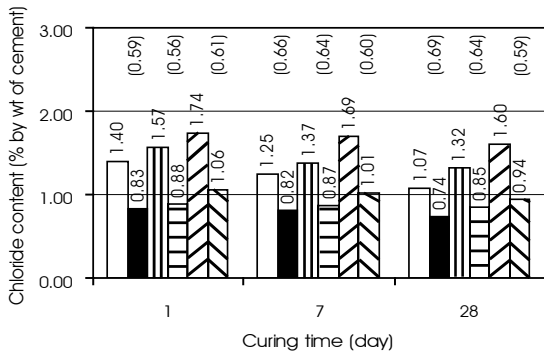
(b) III40: Type III cement paste (w/c=0.40)

(b) I40: Type I cement paste (w/c=0.40)

(c) V40: Type V cement paste (w/c=0.40)
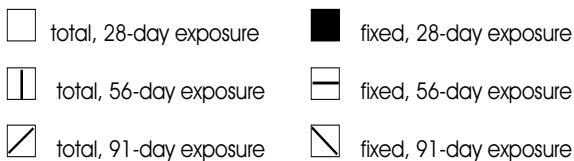

(c) I50: Type I cement paste (w/c=0.50)

☐ total, 28-day exposure   ■ fixed, 28-day exposure

▯ total, 56-day exposure   ⊟ fixed, 56-day exposure

▨ total, 91-day exposure   ◹ fixed, 91-day exposure

Fig 5. Chloride binding capacity of cement paste with different types of cement

☐ total, 28-day exposure   ■ fixed, 28-day exposure

▯ total, 56-day exposure   ⊟ fixed, 56-day exposure

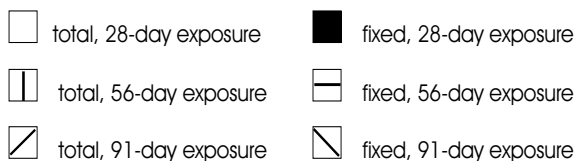▨ total, 91-day exposure   ◹ fixed, 91-day exposure

Fig 6. Chloride binding capacity of cement pastes with different water to cement ratios

cement was considered to be appropriate for concrete structure situated in the marine environment. This is not always correct. Type V cement is only good for protecting concrete from sulfate attack, but it may not be beneficial to steel in concrete when chloride attacks.

Fig 6 and Fig 7 show the effect of water to cement ratio on chloride binding capacity. With the increasing water to cement ratio, the ratio of fixed chloride content to total chloride content decreased, suggesting a reducing chloride-binding capacity. This may be because chloride can be easier retained, especially physically, in a denser paste.

Fig 8 shows the relationship between the 28-day compressive strength and the fixed chloride ratio of cement pastes at different curing times and chloride exposure periods. Generally, it can be seen that if the compressive strength of pastes is the same, type III cement paste has a higher fixed chloride ratio than does type I cement paste, while type V cement has the lowest fixed chloride ratio than type I cement paste.

CONCLUSIONS

Based on the experimental results, the following conclusions can be drawn.

1.	The behavior of chloride binding capacity of cement pastes is time-dependent. Chloride binding depends on the curing and chloride exposure periods. Pastes having longer curing times prior to chloride exposure bind less amount of chloride than do those exposed to chloride after shorter curing time. The longer exposure period of paste results in the larger content of bound chloride.

2.	Cement pastes with the higher water to cement ratio bind less amount of chloride than those with the lower water to cement ratio.

3.	Type V cement binds less amount of chloride than does type I cement. Type III cement binds more amount of chloride than type I cement at the early ages but the chloride binding capacity of both cements is similar as the exposure period increases.
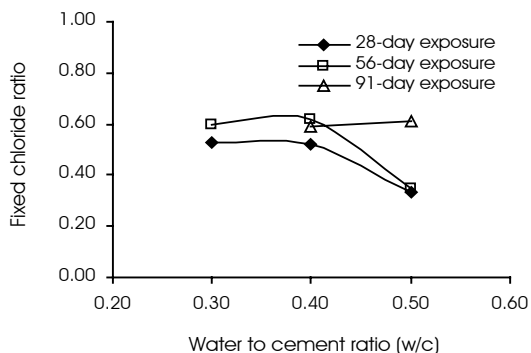
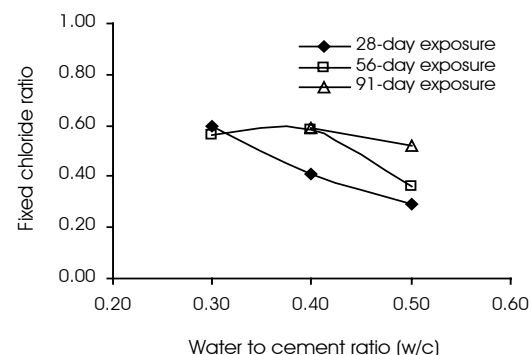## ACKNOWLEDGEMENTS

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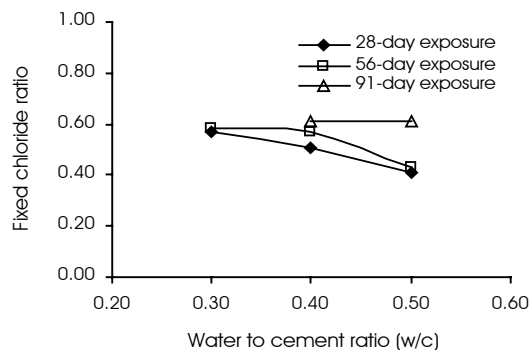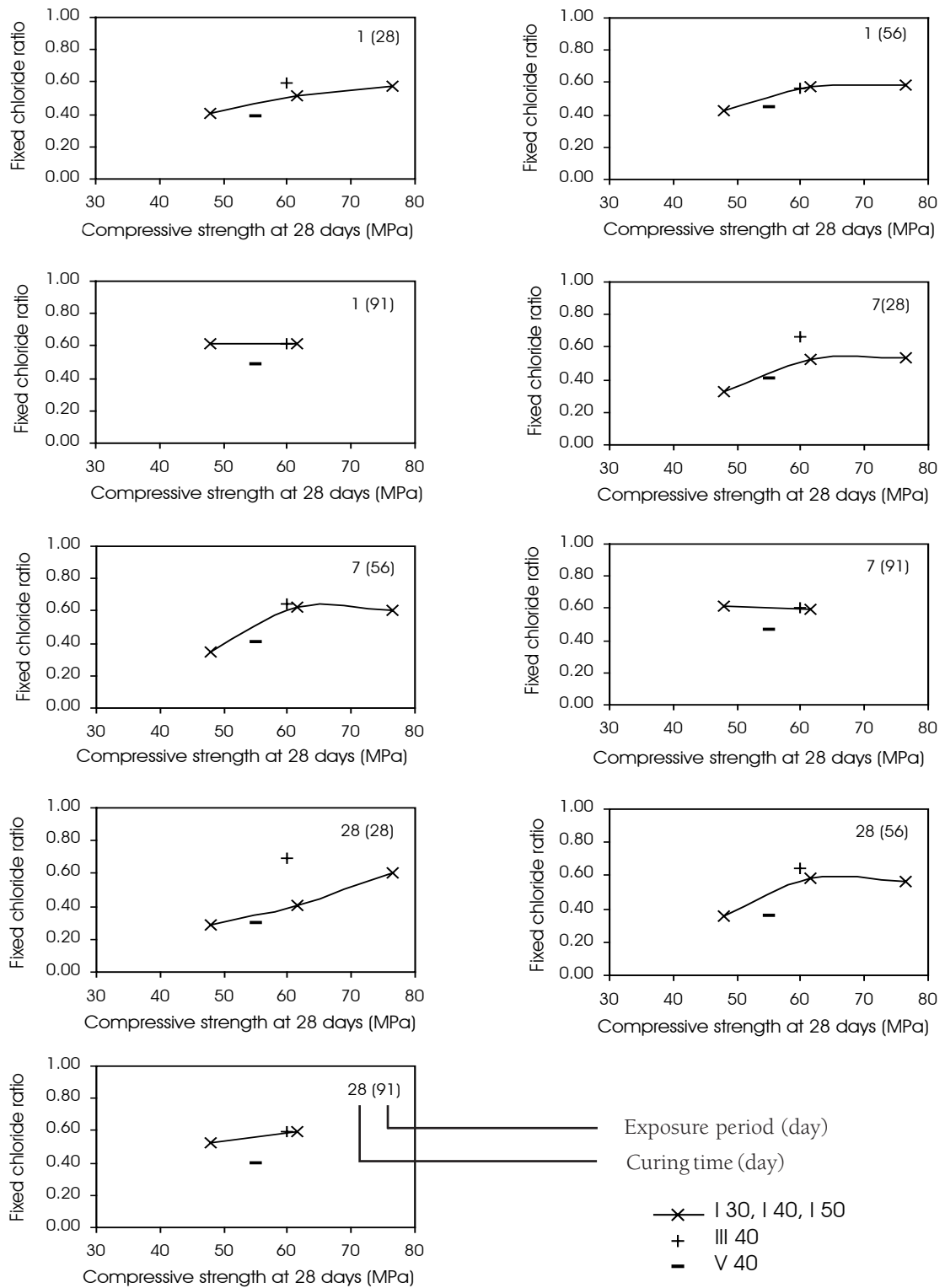

(a) 1-day cure

(b) 7-day cure

(c) 28-day cure

Fig 7. Effect of water to cement ratio on fixed chloride factor of cement pasteAverage pore diameter of cement paste

Fig 8. Relationship between fixed chloride ratio of cement paste at different curing times and chloride exposure periods and compressive strength at 28 days

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