Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1995–1998

Communication

Aggregate influence on chloride ion diffusion into concrete

D.W. Hobbs*

British Cement Association, Century House, Telford Avenue, Crowthorne, Berkshire RG45 6YS, UK

Received 28 May 1999; accepted 20 August 1999

Abstract

An attempt is made to predict the probable effect of the aggregate on chloride ion diffusion into saturated concrete. It is shown that if the chloride ion diffusion coefficient of an aggregate ranges from 0.2 to 10 times that of the cement paste matrix, then this could result in variations in the concrete chloride ion diffusion coefficient of up to 10:1. Such a variation is equivalent to a change in free water-cement ratio from 0.77 to 0.45.

Keywords: Diffusion; Chloride; Aggregate volume concentration; Elastic moduli; Permeability

1. Introduction

It is sometimes assumed that ingress of external chloride ions into concrete is dependent solely on the quality of a concrete's cement paste fraction. In reality the rate at which chloride ion ingress into saturated concrete occurs depends on the chloride ion diffusion coefficient of the concrete's cement paste and aggregate fractions and the aggregate volume concentration. Additionally the rate of ingress will be influenced by paste/aggregate interfacial effects and internal cracks.

Very limited data exists on the role the aggregate plays in influencing chloride ion ingress. Page et al. [1] expressed pore fluid under pressure from concretes, containing limestone and quartzite coarse aggregate, exposed to external chlorides and found the limestone aggregate contained up to 2% chloride by mass compared to less than 0.1% in the quartzite aggregate. Page et al. concluded that in the limestone concrete it appears that chlorides can be transported through the aggregate as well as through the surrounding cement paste.

Carbonation and water permeability data indicate that the aggregate could play an important role in influencing chloride ingress into concrete. For example, Brown and Beeby [2] observed that carbonation depths for Portland cement concretes of similar water-cement ratios subjected to sheltered external exposure were on average 90% greater for concretes containing a lightweight coarse aggregate (sintered pulverized fuel ash) than for concretes containing dense coarse aggregate. Additionally, Swamy and Jiang [3] observed that replacing two thirds of expanded slate fines in a lightweight concrete with fine sand could result in a substantial reduction in 10-year carbonation depths in high water-cement ratio concretes stored externally.

In the case of water permeability, Ruettgers and Vidal [4] observed an average range in water permeability of 30:1 when the water-cement ratio was held constant and the maximum aggregate size was reduced from 230 to 0.64 mm, using an aggregate with a water absorption of 0.6%. In this comparison the cement content was also a variable. The difference in observed water permeability can be attributed to aggregate-paste interfacial effects and/or fine cracking. In addition, Powers et al. [5] have shown that the water permeability of aggregates can vary widely (Table 1) and that the water permeability of a mature paste with water-cement ratio of 0.48 can be between 10 to 0.001 times that of an aggregate likely to be used in concrete. In the case of mature cement paste the water permeability of a paste of water-cement ratio 0.71 could be 10,000 times that of a paste of water-cement ratio 0.38 (see Table 1), which is two orders of magnitude greater than that for concretes with a similar range of water-cement ratios [4], indicating that the aggregate is a major influence.

According to Hobbs and Matthews [6] the concrete chloride ion diffusion coefficient, D_c, for mature concrete exposed to a marine environment is related to water-cement ratio, w/c, by Eq. (1):

$$D_c = 0.04(1166^{w/c}) \times 10^{-12} \qquad (r = 0.693) \tag{1}$$

which, for concretes of w/c ratio 0.71 and 0.38, gives diffusion coefficients differing by 10:1—an order of magnitude less than the corresponding change in water permeability [4].

---

*Corresponding author. Tel.: +44-1344-725705; fax: +44-1344-722676.
E-mail address: dhobbs@bca.org.uk (D.W. Hobbs)

0008-8846/99/$ – see front matter
PII: S0008-8846(99)00188-X

Table 1
Comparison between permeabilities of rocks and cement pastes

Type of rock	Coefficient of permeability (m/s)	Water/cement ratio of mature paste of the same permeability
Dense trap	3.45×10^{-15}	0.38
Marble	9.2×10^{-15}	0.41
Quartz diorite	1.15×10^{-14}	0.42
Quartz feldspar	1.26×10^{-14}	0.42
Limestone	1.72×10^{-14}	0.44
Limestone/marble	3.34×10^{-14}	0.48
Limestone/marble	8.05×10^{-13}	0.66
Quartzite	1.15×10^{-12}	0.68
Limestone	2.30×10^{-12}	0.69
Granite	7.48×10^{-12}	0.70
Porous sandstone	1.72×10^{-11}	0.71
Granite	2.18×10^{-11}	0.71

The chloride ion diffusion coefficient of the cement paste is dependent on w/c ratio and degree of hydration, but if its diffusion coefficient is lower than that of the aggregate, then, ignoring interfacial effects, chloride ion ingress will increase with increasing aggregate volume. Similarly, if the aggregate has a lower diffusion coefficient than the cement paste, the resulting concrete will have a lower diffusion coefficient than the cement paste and chloride ion ingress will decrease with increasing aggregate volume. Consequently, to achieve a specified working life, controls are necessary both on the quality of a concrete's paste fraction and its aggregate.

In this note attempts are made to predict the probable aggregate effect on chloride ion diffusion into saturated concrete. The role of the paste/aggregate interface in influencing chloride ingress is not considered. The approach used is not applicable to situations where water absorption determines the rate at which chloride ions ingress into the concrete.

2. Concrete diffusion coefficient

Fick's law of diffusion may be stated as given in Eq. (2):

$$Q = -D_c \frac{dn}{dx} \tag{2}$$

where Q is the mass of chloride ions carried across a unit area in the normal direction of diffusion in unit time, n is the concentration of chloride ions at depth x and dn/dx is the rate of decrease in chloride ion concentration in the direction of diffusion. D_c is the chloride ion diffusion coefficient for concrete at a concentration n, which can be expressed by Eq. (3):

$$D_c = f(D_p, D_a, V_a) \tag{3}$$

where D_p and D_a are the chloride ion diffusion coefficients for the paste and aggregate, respectively, and V_a is the aggregate volume concentration.

The two simplest prediction models for D_c are based on the assumptions that first the decrease in chloride ion concentration is the same in both the paste and aggregate, and that second the mass of chloride ions carried across a unit area is the same in both the paste and aggregate. The former assumption gives an upper bound for the diffusion coefficient, D_{cu}, and the latter a lower bound, D_{cl}. The two models are illustrated in Figs. 1 and 2. These two models are equivalent to the Voigt and Reuss models used for bounding the elastic modulus of two-phase materials [7], where $D_c \equiv E_c$, the Young's modulus of concrete, $Q \equiv \sigma$, the applied stress, and $dn/dx \equiv \epsilon$, the induced strain. The models result in the following solutions for D_{cu} [Eqs. (4) and (5)] and D_{cl} [Eq. (6) and (7)]:

$$D_{cu}\frac{dn}{dx} = (1 - V_a)D_p \cdot \frac{dn}{dx} + V_a D_a \frac{dn}{dx} \tag{4}$$

giving

$$D_{cu} = (1 - V_a)D_p + V_a D_a \qquad \text{(upper bound)} \tag{5}$$

and

$$\frac{Q}{D_{cl}} = \frac{V_a}{D_a}Q + \frac{(1 + V_a)Q}{D_p} \tag{6}$$

giving

$$D_{cl} = 1/[V_a/D_a + (1 - V_a)/D_p] \qquad \text{(lower bound)} \tag{7}$$

Clearly, if the diffusivity of the aggregate and paste fractions are not the same, then chloride ion mass flow and chloride ion concentration gradient are nowhere near uniform across a concrete section in the normal direction of diffusion.

Eq. (8) closely fits the elastic modulus for concrete [7,8]:

$$E_c = \frac{[(E_a - E_p)V_a + (E_p + E_a)]E_p}{(E_p + E_a) + (E_p - E_a)V_a} \tag{8}$$

If in the arguments and assumptions made in deriving Eq. (8), the applied stress is replaced by mass of chloride ions transported, Q, and the induced strain is replaced by concentration gradient dn/dx, then Eq. (8) becomes Eq. (9):

$$D_c = \frac{[(D_a - D_p)V_a + (D_p + D_a)]D_p}{(D_p + D_a) + (D_p - D_a)V_a} \tag{9}$$

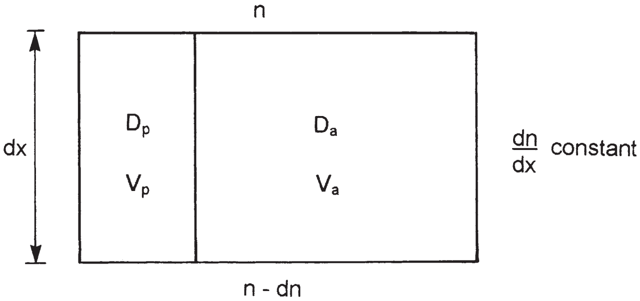

Fig. 1. Constant decrease in chloride ion concentration model.

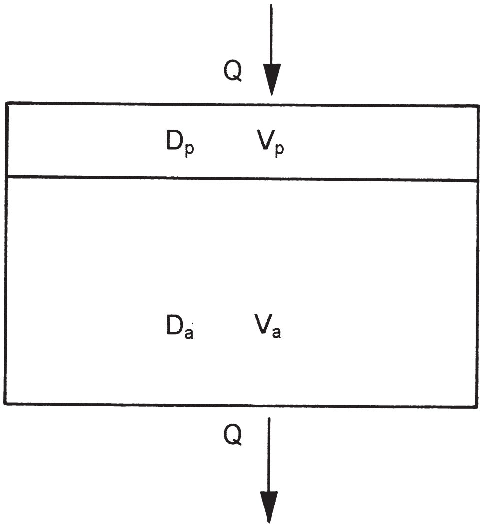

Fig. 2. Constant mass of chloride ions model.

3. Effect of the aggregate on the concrete diffusion coefficient

From Eq. (9), assuming the chloride ion diffusion coefficient for aggregates employed in concrete could range from 0.2 to 10 times that of a mature paste of w/c ratio 0.45, gives chloride ion diffusion coefficients for concrete shown in Eq. (10):

$$D_c = \frac{(3 - 2V_a)}{3 + 2V_a} D_p \qquad (10)$$

and Eq. (11), approximately

$$D_c = \frac{(9V_a + 11)}{11 - 9V_a} D_p \qquad (11)$$

respectively.

Thus, at $V_a = 0.70$, the diffusion coefficient, D_c, predicted from Eqs. (10) and (11), are in the ratio 0.36:3.68, which implies that if the assumptions are correct, the concrete chloride ion diffusion coefficient could vary by a factor of 10 due to variations in the aggregate, which from Eq. (1) is equivalent to the change produced by a change in concrete w/c ratio from 0.45 to 0.77.

4. Effects of variations in cement content

Replacing V_a in Eqs. (10) and (11) with $1 - V_p$ gives Eq. (12):

$$D_c = \frac{(1 + 2V_p)}{5 - 2V_p} D_p \qquad (12)$$

and Eq. (13):

$$D_c = \left(\frac{20 - 9V_p}{2 + 9V_p}\right) D_p \qquad (13)$$

Two extremes of cement content for concretes of w/c ratio 0.45 are 400 and 300 kg/m^3 and correspond with cement paste volumes of 31 and 23%, respectively. From Eq. (12), paste volumes of 31 and 23% result in concrete diffusion coefficients of 0.37 D_p and 0.32 D_p, respectively. Thus, when the diffusion coefficient of the paste is five times that of the aggregate, the reduction in cement content results in a predicted reduction in the concrete diffusion coefficient of 14%. For concretes subject to marine exposure, this is from Eq. (1), equivalent to a reduction in free w/c ratio of 0.02.

From Eq. (13), paste volumes of 31 and 23% result in concrete diffusion coefficients of 3.59 and 4.41 D_p, respectively. Thus, when the diffusion coefficient for the paste is 0.1 times that of the aggregate, the reduction in cement content results in a predicted increase in the concrete diffusion coefficient of 23%. For concretes subject to a marine exposure, this is from Eq. (1), equivalent to an increase in free w/c ratio of 0.03.

5. Conclusions

Ignoring cement paste/aggregate interfacial effects, for saturated concrete subject to external chlorides, the following predictions can be made.

1. If the chloride ion diffusion coefficient of the aggregate ranges from 10 to 0.2 times that of a cement paste of w/c ratio 0.45, then this could result in variations of 10:1 in the concrete chloride ion diffusion coefficient.
2. Reductions in concrete cement content, depending on the chloride ion diffusion coefficient of the aggregate, may result in an increase or a reduction in the concrete chloride ion diffusion coefficient.

6. Recommendations

If the above conclusion 1 is valid, then in situations where reinforced concrete is exposed to external chlorides, consideration should be given to placing a limit on an aggregate's water absorption, or alternatively on the compressive strength of concrete, to ensure that only dense aggregates are used and that the maximum specified free w/c ratio is not exceeded. A further possible alternative is to relate the maximum specified free w/c ratio of a concrete to the water absorption of the aggregate employed. However, for such an approach to be adopted, it would be necessary to establish that chloride ion ingress into concrete is dependent on the aggregate's water absorption or, for a given binder type, dependent on the concrete's compressive strength.

References

[1] C.L. Page, P. Lambert, P.R.W. Vassie, Investigations of reinforcement corrosion. 1. The pore electrolyte phase in chloride-contaminated concrete, Materiaux et Constructions 24 (1991) 243–252.

[2] J.H. Brown, A.W Beeby, Exposure site carbonation depth measure-

ments, BCA Report for Building Research Establishment, Building Research Establishment, Garston, UK, 1992.

[3] R.N. Swamy, E.D. Jiang, Pore structure and carbonation of lightweight concrete after 10 years exposure, in: Proceedings of a Conference on Structural Lightweight Aggregate Concrete Performance, A. Holm, Alexander M. Vaysburd (Eds.), ACI SP-136, 1992, pp. 377–395.

[4] A. Ruettgers, E.N. Vidal, An investigation of the permeability of mass concrete with particular reference to Bolder dam, Proc ACI 31 (1935) 382–416.

[5] T.C. Powers, L.E. Copeland, J.C. Hayes, H.M. Mann, Permeability of Portland cement paste, Proc ACI 51 (1954) 285–298.

[6] D.W. Hobbs, J.D. Matthews, Minimum requirements for concrete to resist deterioration due to chloride induced corrosion, in: Minimum Requirements for Durable Concrete, D.W. Hobbs (Ed.), British Cement Association, Crowthorne, UK, 1998, pp. 43–89.

[7] Z. Hanshin, S. Shtrikman, A variational approach to the theory of the elastic behaviour of multi-phase materials, J Mech Phys Solids 11 (1963) 127–140.

[8] D.W. Hobbs, The dependence of the bulk modulus, Young's modulus, creep, shrinkage and thermal expansion of concrete upon aggregate volume, Materiaux et Constructions 4 (1971) 107–114.