Pergamon

Cement and Concrete Research 31 (2001) 1567–1572

CEMENT AND CONCRETE RESEARCH

Effects of metakaolin and the interfacial transition zone on the diffusion of chloride ions through cement mortars

A.H. Asbridge[a,*], G.A. Chadbourn[b], C.L. Page[c]

[a]Imerys Minerals Ltd, John Keay House, St. Austell, Cornwall PL25 4DJ, UK
[b]School of Engineering and Applied Science, Aston University, Birmingham B4 7ET, UK
[c]School of Civil Engineering, University of Leeds, Leeds LS2 9JT, UK

Received 14 December 2000; accepted 22 June 2001

Abstract

The effects of metakaolin and variations in aggregate volume content on the diffusion kinetics of chloride ions in hydrated Portland cement model mortars were studied. Chloride diffusion was monitored under both steady- and non-steady-state conditions, and capillary porosity data were obtained for the specimens under investigation. The observed variations in chloride diffusivity were interpreted in terms of the pozzolanic effect of metakaolin and the influence of an increasing proportion of paste–aggregate interfacial transition zone (ITZ) material as aggregate volumes increase. Metakaolin reduced the rate of chloride diffusion through the hydrated cement matrix and also tended to enhance the resistance to chloride transport of the ITZ material within the mortars. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Interfacial transition zone; Diffusion; Chloride; Metakaolin; Mortar

1. Introduction

Metakaolin is produced by the thermal activation of the mineral kaolinite. This pozzolanic material has been extensively investigated, particularly in relation to its effects on the durability and properties of Portland cement composites [1]. Specifically, metakaolin has been shown to provide advantages with respect to chloride penetration [2], deterioration due to alkali–silica reaction (ASR) [3], sulphate attack and acid erosion [4].

Portland cement mortars and concretes consist of two principal components namely hydrated cement paste (hcp) and aggregate. However, it is widely acknowledged that there exists a third morphologically distinct constituent at the hcp–aggregate boundary [5]. This region, often termed the interfacial transition zone (ITZ), has been studied directly by electron microscopy [6] and microhardness [7,8], and indirectly by gas [9] and liquid permeation [10] techniques. Wide, although not universal, agreement exists that the ITZ is a zone characterised by a higher porosity [11] and differing chemical and mineralogical composition [12] than the bulk hcp. It has been suggested that these properties of the ITZ can be detrimental to some composite properties, including resistance to chloride transport [13]. It has also been shown that pozzolanic materials, such as metakaolin, can affect the chemistry and microstructure of the ITZ [14] and, thus, impact, potentially beneficially, on transport properties [15].

The aim of the work to be described was to examine the influence of metakaolin on chloride diffusion kinetics in mortars with systematically varied volume fractions of aggregate and, hence, varied proportions of ITZ material. The approach used to evaluate the contribution of the ITZ was similar to that described in previous work and involved using model mortars containing nominally single-sized spherical glass bead aggregates [16].

2. Experimental

Work was undertaken in two stages, viz. (i) steady-state diffusion studies and (ii) non-steady-state studies. Whilst different Portland cements and metakaolins were used for each of the stages their properties were not significantly dissimilar. The Portland cements used were commercial

---

* Corresponding author. Tel.: +44-1726-818116; fax: +44-1726-623019.

E-mail address: tony.asbridge@imerys.com (A.H. Asbridge).

PII: S0008-8846(01)00598-1

Table 1
Properties of Portland cements and metakaolins

	Portland cement		Metakaolin	
	Steady state (mass%)	Non-steady state (mass%)	Steady state (MetaStar 500) (mass%)	Non-steady state (MetaStar 501) (mass%)
SiO_2	20.3	20.8	51.8	55.4
Al_2O_3	5.44	5.2	42.3	40.9
Fe_2O_3	2.8	2.0	2.99	0.64
CaO	63.7	63.8	0.08	0.01
MgO	1.44	1.6	0.13	0.23
SO_3	2.9	2.5		
K_2O	0.77	1.1	0.61	0.81
Na_2O	0.09	0.1	0.01	0.01
LOI	0.94		1.3	0.7
Pozzolanic reactivity (mg $Ca(OH)_2$/g)			1050	1050

products (CEN I: 42.5 N), and were sieved at 150 μm to remove any coarser particles or agglomerates prior to use. The metakaolins were also commercially available products (MetaStar 500 and 501 from Imerys Minerals). Chemical and physical properties of the Portland cements and the metakaolins used are shown in Table 1. The aggregate used to prepare the model mortars was a silicate glass bead of similar composition to that used elsewhere [16] and supplied by British Optical. The physical properties of the beads are shown in Table 2. To ascertain the potential for reaction between the beads and the alkaline pore solution encountered in Portland cement systems, beads were either contacted with 10 M NaOH solution at elevated temperature or autoclaved with a 10-M NaOH solution. Results are also shown in Table 2 and suggest that degradation by pore solution under normal conditions would be negligible. This performance was in contrast to that of other glass beads considered, which were marketed as zirconia but which were actually a blend of ZrO_2 and SiO_2. These beads disintegrated under the autoclave conditions. It is suspected that the silicate composition of the glass beads gave them greater resistance to alkali attack than the silica component of the beads that disintegrated.

The compositions of pastes and mortars are given in Table 3. Metakaolin was used as a 10 mass% partial replacement for Portland cement. The aggregate quantity was adjusted to give aggregate volume fractions as tabulated. Samples prepared for steady-state diffusion experiments also contained a superplasticiser addition (1% by binder mass of a sulphonated naphthalene formaldehyde condensate). A planetary mixer was used to prepare all samples. In all cases, the cement and metakaolin were preblended. Details of sample processing and storage conditions are given in Table 4. Duplicate samples were prepared for non-steady-state diffusion and four replicate samples for steady-state diffusion experiments.

Table 2
Properties of model aggregate (glass beads)

Typical bead size (mm)	1.00–1.25
Bead specific gravity (kg/m^3)	2.57
Loss in mass on exposure to 10 M NaOH at 80 °C for 24 h (mass%)	0.4
Loss in mass on autoclaving for 24 h with 10 M NAOH (mass%)	11.7

Table 3
Mix descriptions

	Steady state	Non-steady state
Binder	PC/MK	PC, PC/MK
Water/binder ratio	0.35	0.40
Aggregate contents (vol.%)	0, 15, 30, 40, 50, 55	0, 15, 35, 55

After the initial curing periods, the following procedures were followed. For steady-state measurements, discs (2.5–3 mm thick) were cut from central portion of the cylinder and then lightly polished and mounted between the two compartments of a diffusion cell [17]. The compartments contained 1 M NaCl/0.035 M NaOH and 0.035 M NaOH, respectively. The increase in chloride concentration in the compartment containing dilute NaOH was monitored by periodically removing 100-μl aliquots for chloride determination by colorimetric analysis [18]. Plotting chloride concentration as a function of time allowed subsequent calculation of effective chloride diffusivity by the application of Fick's first law.

For non-steady-state measurements, the top (cast face) 12 mm was removed using a diamond saw. The remnant was reimmersed in NaOH for about 24 h. The cut face was then polished with P600 grade wet polishing paper and the sides and base of the cylindrical section sealed with paraffin wax. The wax-coated cylindrical samples were then placed horizontally (noncoated surface vertical and exposed) in a sealed vessel containing a mixture of 0.032 M NaOH and 1 M NaCl for 168 days. The area of each exposed face was 28.3 cm^2 and the volume of solution per sample was 1.5 dm^3 (exposed area to volume ratio of 18.9 cm^2 dm^{-3}). After exposure, the wax coating and circumferential 4 mm of the samples were removed and profile grinding was performed in 3-mm increments from the exposed surface. All "grindings" were dried at 105 °C and then combined to give 5–10 aliquots per sample. Portions of these aliquots

Table 4
Experimental conditions

	Steady state	Non-steady state
Casting	Cast into cylindrical moulds with vibration to remove air. Samples covered with polythene, sealed, and rotated slowly end-over-end (8–10 rpm for 24 h)	
Nominal temperature (°C)	22	20
Mould diameter (mm)	49	60
Demould (h)	168	24
Initial curing regime	0.035 M NaOH solution, 84 days	0.032 M NaOH solution, 60 days
Aggregate contents (vol.%)	0, 15, 30, 40, 50, 55	0, 15, 35, 55

(5 g) were then dissolved in boiling HNO_3 (100 ml of 10% concentration), filtered, and the filtrate analysed for chloride content using a chloride ion selective electrode calibrated against sodium chloride standards. For each sample, a chloride penetration profile was constructed and the corresponding apparent chloride diffusivity calculated assuming Boltzmann's solution of Fick's second law [19].

To aid in the interpretation of the diffusion data, the 'capillary pore volumes' of all samples were determined prior to exposure to chlorides. As in earlier investigations [20], 'capillary porosity' was taken to be the volume fraction represented by the loss of water on drying specimens from a saturated condition to a condition of equilibrium at 90.7% RH (obtained by storage over a saturated solution of barium chloride at 20 °C). This particular measure of 'capillary porosity' corresponds to pores wider than about 30 nm [21].

3. Results and discussion

3.1. Steady-state diffusion

Mortar-paste diffusivities were estimated on the assumption of Maxwell's relationship and using measured effective chloride diffusivities. The Maxwell relationship (Eq. (1)) strictly applies to a composite of effective diffusion coefficient (D_{eff}), consisting of a previous matrix of diffusion coefficient, D, containing periodically spaced, impervious spheres of volume fraction, ϕ [16].

$$\mathrm{D}_{\mathrm{eff}} = 2\mathrm{D}(1-\phi)(2+\phi)^{-1} \qquad (1)$$

Fig. 1 shows that the effective diffusion coefficient of chloride in the mortars diminishes with increasing aggregate volume fraction as would be expected for an impermeable aggregate. Estimations of the mortar-paste diffusivities, obtained using the Maxwell equation, compensated for the reduced diffusion cross-sectional area resulting from the presence of the impervious aggregate. The data show that for the range of aggregate volume contents investigated, the mortar-paste diffusivity did not change significantly. It would be expected that with increasing aggregate volume content, there would be a gradual predominance of the microstructural characteristics of the ITZ over the bulk paste. That the mortar-paste diffusivity does not increase with aggregate volume content indicates that no gross percolation is occurring when a metakaolin is used as a partial cement replacement.

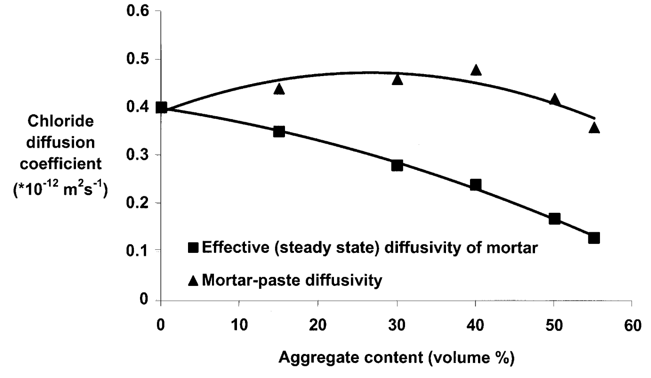

Fig. 1. Variation in effective (steady state) diffusivity with aggregate content (Portland cement/metakaolin binder).

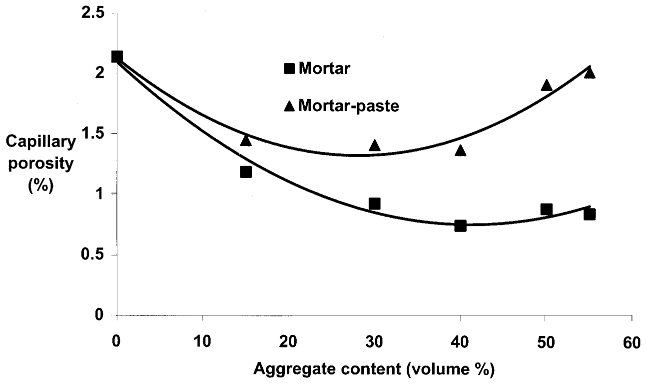

Fig. 2. Variation in capillary porosity with aggregate content (Portland cement/metakaolin binder).

Page and Ngala [16] reported effective mortar and mortar-paste diffusivities about one order of magnitude higher for model mortars prepared with only Portland cement at a similar water/binder ratio (cured at 38 °C for 10 weeks). Observed increases in mortar-paste diffusivity with increasing aggregate content were considered a possible indication of some percolation occurring at high aggregate volume fractions.

Mortar capillary porosity (Fig. 2) decreases with increasing aggregate volume as would be expected. The calculated mortar-paste capillary porosities show a decrease in volume with aggregate contents between 15 and 40 vol.%. This may be due to aggregate improving dispersion of the pozzolan, thus, facilitating a more efficient pozzolanic reaction. The increases in capillary porosity at 50 and 55 vol.% possibly

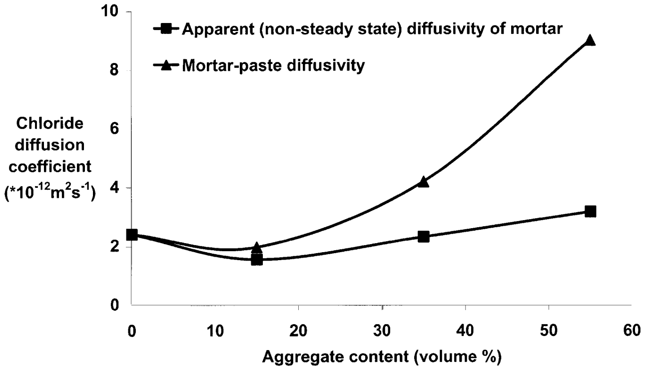

Fig. 3. Variation in apparent (non-steady state) diffusivity with aggregate content (Portland cement binder).

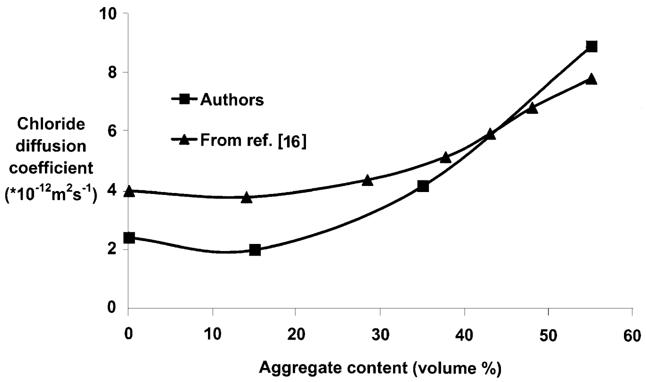

Fig. 4. Comparison of mortar-paste diffusivities (Portland cement binder).

indicate ITZ effects, but these are not reflected in the diffusion data obtained.

3.2. Non-steady-state diffusion

Fig. 3 shows that for the "control" samples, the apparent diffusivity remains almost constant with increasing aggregate content, despite the reduced paste volume available for chloride transport. The corresponding calculated mortar-paste diffusivities increase sharply as the aggregate volume fraction is increased over the range 35–55%. This trend is supportive of the hypothesis that some percolation may be occurring as a result of the overlap of more porous ITZ regions when higher aggregate contents are used in Portland cement model mortars as reported previously [16].

Mortar-paste diffusivities from this and the previous work are compared in Fig. 4, although it should be noted that only the trends and not the absolute values are relevant here as the data from Ref. [16] are steady-state 'effective diffusivities'. That the data from two sources correlate well, however, supports the view that increasing aggregate content, and, hence, the quantity of ITZ material, is detrimental to the chloride permeability characteristics of the mortar paste.

Fig. 5 shows the effect on apparent diffusivity of the incorporation of 10 wt.% metakaolin as a partial substitute for Portland cement. Compared with those of the control specimens, apparent diffusivities are reduced by approximately one order of magnitude. Mortar-paste diffusivities show little variation with aggregate contents. This trend suggests that the ITZ produced in samples containing metakaolin does not differ significantly from the bulk paste

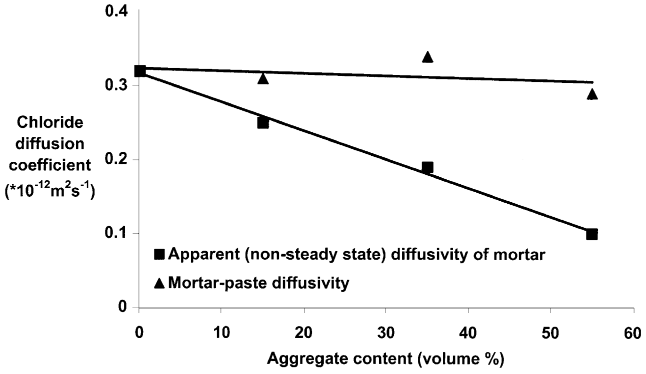

Fig. 5. Variation in apparent (non-steady state) diffusivity with aggregate content (Portland cement/metakaolin binder).

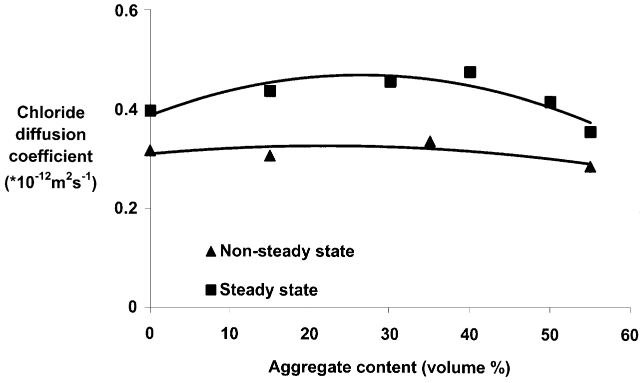

Fig. 6. Comparison of mortar-paste diffusivities (Portland cement/metakaolin binder).

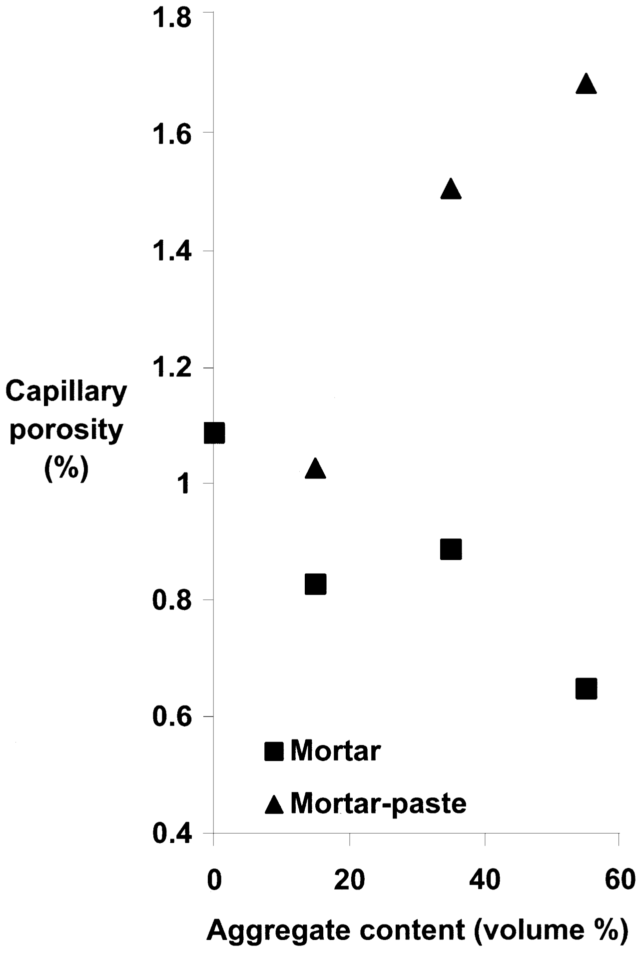

Fig. 7. Variation in capillary porosity with aggregate content (Portland cement binder).

in terms of its chloride diffusion resistance. Therefore, the apparent diffusivity of the mortar composite decreases continuously with increasing aggregate content.

It is also interesting to compare the steady- and non-steady-state diffusion data obtained for samples prepared with metakaolin in this work. Fig. 6 shows that despite the use of different methods, i.e. steady and non-steady state, there is agreement in terms of general trends.

It is acknowledged that the ITZ formed by Portland cements can contain a higher concentration of calcium hydroxide than the bulk paste [22], and it is therefore possible that these higher-than-average reactant levels would increase the extent of the metakaolin–calcium hydroxide reaction in the ITZ. Greater reaction between metakaolin and the calcium hydroxide would produce more finely dispersed products of the pozzolanic reaction, thus, increasing the diffusion path tortuosity and further limiting chloride ingress.

Figs. 7 and 8 compare the mortar and mortar-paste capillary porosities of the two sets of non-steady-state samples. Samples incorporating metakaolin have lower measured capillary porosities than their "control" counterparts. The data indicate that the use of metakaolin reduced the capillary porosity of the bulk paste and ITZ pore structures although the ITZ were still more porous than the bulk paste. This effect of metakaolin on porosity has been widely reported and is attributed to the products of the metakaolin–lime pozzolanic reaction, which have higher molecular weight silicate chains than those characteristic of the CSH phase of hydrated Portland cements [23]. These reductions in capillary porosity are a contributing factor to the lower mortar-paste diffusivities observed for samples incorporating metakaolin. However, the contribution that the metakaolin could make to the chloride binding capacity of the hcp is also potentially another important factor in reducing chloride penetration [24,25].

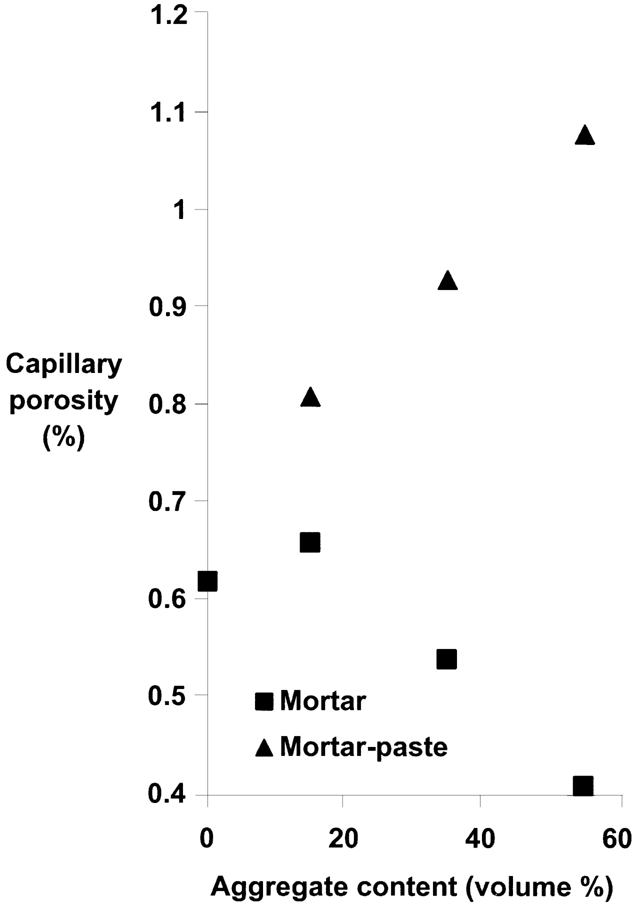

Fig. 8. Variation in capillary porosity with aggregate content (Portland cement/metakaolin binder).

4. Conclusions

The steady-state diffusivity of chloride ions in mortar pastes incorporating metakaolin did not vary significantly with aggregate volume fractions. Mortar-paste capillary porosity data only showed some increases at aggregate volume fractions greater than 40%. Metakaolin has been reported to act as a pozzolan and produce cementitious products that refine paste pore structure. In this case, it appears that metakaolin has also refined the pore structure of the ITZ so that its chloride diffusion characteristics differ little from those of the bulk paste.

Non-steady-state chloride diffusivities of mortar pastes increased with aggregate volume content in samples with only Portland cement as binder. The capillary porosity of the mortar paste increased with aggregate volume, indicating that the ITZ had a higher overall porosity than the bulk paste. The chloride diffusivity increased relatively sharply at aggregate volume fractions above 35%, whereas capillary porosities increased broadly linearly with aggregate content. This is suggestive of some interconnection of higher porosity ITZ regions results in percolation, thus, facilitating chloride diffusion.

The use of 10 mass% metakaolin as a partial replacement for Portland cement reduced non-steady-state chloride diffusivities by approximately one order of magnitude relative to those of samples with only Portland cement as binder. Mortar-paste diffusivities did not vary significantly with variations in aggregate content. Relative to control samples, metakaolin reduced mortar-paste capillary porosities although the latter still increased with increasing aggregate volumes. The lack of variation in mortar-paste diffusivity and rising capillary porosity with increasing aggregate content supports the hypothesis that the use of metakaolin increases permeation path tortuosity and inhibits percolation.

Acknowledgments

The authors would like to thank T.R. Jones of Imerys Minerals for his contribution to this research.

References

[1] J.A. Kostuch, G.V. Walters, T.R. Jones, High performance concretes incorporating metakaolin — a review, in: R.K. Dhir, M.R. Jones (Eds.), Concrete 2000, vol. 2, E & FN Spon, London, 1993, pp. 1799–1811.

[2] G.A. Chadbourn, PhD Thesis, School of Engineering and Applied Science, Aston University, Birmingham, UK, 1997.

[3] G.V. Walters, T.R. Jones, Effect of metakaolin on alkali–silica reaction in concrete manufactured with reactive aggregate, in: V.M. Malhotra (Ed.), Proceedings of the 2nd International Conference on the Durability of Concrete, 1991, pp. 941–953.

[4] A.H. Asbridge, T.R. Jones, G.J. Osborne, High performance metakaolin concrete: Results of large-scale trials in aggressive environments, in: R.K. Dhir, P.C. Hewlett (Eds.), Radical Concrete Technology, Proceedings of the International Conference on Concrete in the Service of Mankind, Dundee 1996, E & FN Spon, London, 1996, pp. 13–24.

[5] D. Breton, A. Carles-Gibergues, G. Ballivy, J. Grandet, Contribution to the formation mechanism of the transition zone between rock–cement paste, Cem. Concr. Res. 23 (2) (1993) 335–346.

[6] B.D. Barnes, S. Diamond, W.L. Dolch, The contact zone between Portland cement paste and glass "aggregate" surfaces, Cem. Concr. Res. 8 (2) (1978) 233–244.

[7] L. Struble, J. Skalny, S. Mindess, A review of the cement–aggregate bond, Cem. Concr. Res. 10 (2) (1980) 277–286.

[8] S. Igurashi, A. Bentur, S. Mindess, Microhardness testing of cementitious materials, Adv. Cem. Based Mater. 4 (1996) 48–57.

[9] U. Costa, M. Facoetti, F. Massazza, Permeability of the cement–aggregate interface: Influence of the type of cement, water/cement ratio and superplasticizer, Proceedings of the RILEM International Symposium, 1990, pp. 392–401.

[10] P. Halamickova, R.J. Detwiler, D.P. Bentz, E.J. Garboczi, Water permeability and chloride ion diffusion in Portland cement mortars: Relationship to sand content and critical pore diameter, Cem. Concr. Res. 25 (1995) 741–751.

[11] B. Bourdette, J.P. Ollivier, E. Revertegat, Transfer properties of interfacial transition zones and mortars, Mater. Res. Soc. Symp. Proc., vol. 370, 1995, pp. 449–455.

[12] K.L. Scrivener, P.L. Pratt, Characterisation of interfacial microstructure, in: J.C. Maso (Ed.), Interfacial Transition Zone in Concrete, RILEM Report 11, E & FN Spon, London, 1996.

[13] A. Delagrave, J.P. Bigas, J.P. Ollivier, J. Marchand, M. Pigeon, Influence of the interfacial zone on the chloride diffusivity of mortars, Adv. Cem. Based Mater. 5 (1997) 86–92.

[14] A. Goldman, A. Bentur, Properties of cementitious systems containing silica fume or nonreactive microfillers, Adv. Cem. Based Mater. 1 (1994) 209–215.

[15] J.A. Larbi, PhD Thesis, Materials Science Group, Faculty of Civil Engineering, Technical University of Delft, 1991.

[16] C.L. Page, V.T. Ngala, Steady-state diffusion characteristics of cementitious materials, in: L.O. Nilsson, J.P. Ollivier (Eds.), Proceedings of the RILEM International Workshop on 'Chloride penetration into concrete', RILEM Publishing, Cachan, 1997, pp. 77–84.

[17] C.L. Page, N.R. Short, A. El Tarras, Diffusion of chloride ions in hardened cement pastes, Cem. Concr. Res. 11 (1981) 395–406.

[18] A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, fourth ed., Longman, London, 1978.

[19] E.L. Cussler, Diffusion: Mass Transfer in Fluid Systems, Cambridge Univ. Press, Cambridge, 1984.

[20] V.T. Ngala, C.L. Page, L.J. Parrott, S.W. Yu, Diffusion in cementitious materials: II. Further investigations of chloride and oxygen diffusion in well-cured OPC and OPC/30%PFA pastes, Cem. Concr. Res. 25 (4) (1995) 819–826.

[21] L.J. Parrott, Variations of water absorption rate and porosity with depth from an exposed concrete surface: Effects of exposure conditions and cement type, Cem. Concr. Res. 22 (1992) 1077–1088.

[22] S. Diamond, Cement paste microstructure in concrete, Mater. Res. Soc. Symp. Proc., vol. 85, 1987, pp. 21–31.

[23] A.M. Dunster, J.R. Parsonage, M.J.K. Thomas, The pozzolanic reaction of metakaolinite and its effects on Portland cement hydration, J. Mater. Sci. 28 (1993) 1345–1350.

[24] A. Delagrave, J. Marchand, J.P. Ollivier, S. Julien, K. Hazrati, Chloride binding capacity of various hydrated cement paste systems, Adv. Cem. Based Mater. 6 (1997) 28–35.

[25] N.J. Coleman, C.L. Page, Aspects of the pore solution chemistry of hydrated cement pastes containing metakaolin, Cem. Concr. Res. 27 (1) (1997) 147–154.