Available online at www.sciencedirect.com

ScienceDirect

Cement and Concrete Research 37 (2007) 1544–1550

Cement and Concrete Research

Methods of obtaining pore solution from cement pastes and mortars for chloride analysis

L.J. Buckley [a], M.A. Carter [b,*], M.A. Wilson [b], J.D. Scantlebury [c]

[a] Mott MacDonald, 33 Stamford St, Altrincham, Cheshire WA14 1ES, UK
[b] School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, PO Box 88, Manchester M60 1QD, UK
[c] School of Materials, The University of Manchester, PO Box 88, Manchester M60 1QD, UK

Received 22 February 2006; accepted 15 August 2007

Abstract

Two techniques for the recovery of pore solution from cement mortars are examined: pore solution expression and miscible displacement using a high pressure permeameter. In the former, the pore solution is expressed from the mortar by crushing; in the latter, it is eluted from the mortar over 30 min by miscible displacement with water. Experimental results are presented for a range of cement pastes and mortars into which known amounts of chloride ion have been incorporated by using sodium chloride solution as the mix water. The results show that both eluted and expressed solutions exhibit a decrease in chloride ion concentration as the cement matrix ages, with the elution method showing a greater sensitivity to mix composition. Both methods show a decrease in chloride concentration as the water: cement ratio of the mix is increased. Overall, the high pressure elution method is capable of recovering a significantly higher proportion of the incorporated chloride. The application of these techniques to pore solution analysis is discussed.

Keywords: Chloride; Pore solution; Miscible displacement; Cement paste; Mortar

1. Introduction

When cement undergoes hydration an interconnected pore structure is produced. These pores contain solution, the composition of which may be significant in respect of the formation of hydrated solid phases, binding of waste materials and reactions leading to deterioration of concrete, not least of which are corrosion processes occurring in the reinforcing steel. Analysis of pore solution is therefore an important tool in understanding these processes. Chloride ions are particularly important as their presence leads to loss of corrosion protection in embedded steel reinforcement [1].

The purpose of this paper is to compare pore solution expression, in which a mechanical pressure is used to force the pore solution from the material, with an alternative method in which pore solution is removed by miscible displacement with water in a high pressure Hassler cell permeameter. In each case the resultant solution is analysed for chloride ion concentration, the chloride having been deliberately introduced into the mortar by using a sodium chloride solution of known concentration as the mix water.

Each method provides very different information. Pore solution expression allows analysis of the pore solution at a particular age and condition of sample and provides a "snapshot" of existing concentrations at the time. However, as hydration proceeds the yield obtainable is progressively reduced [2]. In contrast to this, high pressure permeametry removes diluted pore solution from cored mortar samples which have been vacuum saturated with water prior to being "flushed" with flowing water under pressure. Initially, the pore solution is in contact with a calcium silicate hydrate (C-S-H) gel of high surface area and there is a dynamic equilibrium between the two. On dilution of the pore solution by vacuum saturation, equilibrium ion concentration will be restored by further dissolution from the solid phases. Of interest here is the dissolution of chloride ions which are bound by the cement as Friedel's salt and its solid solutions with other calcium aluminate and sulphate hydrates. The timescales involved in permeametry are likely to be sufficient for soluble species to

---

* Corresponding author.
E-mail address: margaret.carter@manchester.ac.uk (M.A. Carter).

0008-8846/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2007.08.009

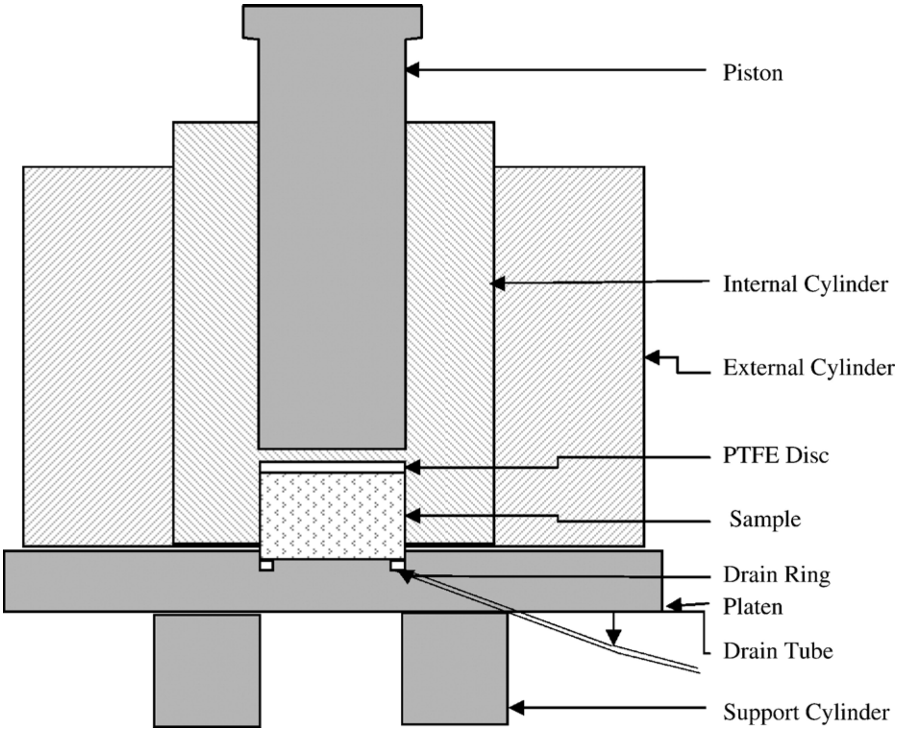
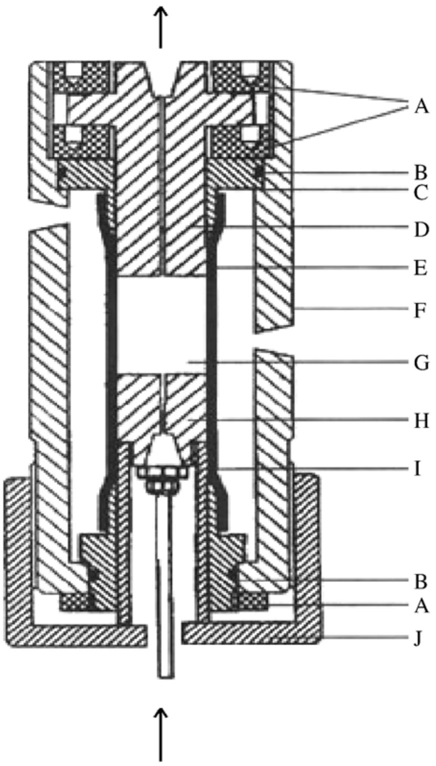


Fig. 1. Schematic diagram of pore solution expression apparatus [12].

readjust their concentrations and chloride ions, previously bound by the cement paste, can be released, eluted in the diluted pore solution and their concentration determined. This technique does not provide an estimate of the chloride concentration in the pore solution at a particular stage of cement hydration, but rather is a way of establishing the proportion of chloride that can be recovered from the sample. A key factor with regard to corrosion is the chloride available in solution.

The most widely used technique for obtaining pore solution from cementitious materials is pore solution expression. Analysis



KEY:

A: Retaining ring,
B: Nitrile rubber O ring,
C: Sleeve carrier,
D: Fixed platen,
E: Nitrile rubber sleeve,
F: Stainless steel case,
G: Sample,
H: Movable platen,
I : Platen carrier,
J: End cap.

Fig. 2. Hassler cell permeameter [15].

Table 1
Mortar mix proportions (by mass) together with the calculated volumes of mix water and amount of chloride ion contained in an 84 cm^3 sample

Water: cement ratio	Composition (cement: sand)	Initial volume of water in sample (cm^3)	Quantity of Cl$^-$ in sample (mg)
0.5	1:0	28	339
0.5	1:1	16.8	203
0.5	1:2	12	145
0.5	1:3	9.33	113
0.5	1:4	7.6	92
0.6	1:0	31.5	381
0.6	1:1	19.4	235
0.6	1:2	14	169
0.6	1:3	11	133
0.6	1:4	9	109
0.7	1:3	12.5	151
0.7	1:3.5	11.3	137
0.7	1:4	10.3	125

of recovered solution provides a means of tracking changes in species concentration as a cementitious material ages. Pore solution expressed from Portland cement pastes has been shown to have initially high concentrations of Na, K, Ca, and sulphate and hydroxyl ions [3]. The concentrations of both Ca and sulphate ions diminish after several hours as the heavily hydrated calcium sulphoaluminate, ettringite, forms. Thereafter the alkali metal concentrations rise together with the pH. The concentrations of Al, Fe and Si however are initially low and remain so. This study [3], which included TG and XRD on the residual solid, did not include an examination of chloride ion concentration.

2. Experimental methods

2.1. Pore solution expression

Pore solution expression was originally developed by Longuet *et al.* [4] as a relatively simple method of removing pore solution from a cementitious material by using mechanical pressure. The technique has since been applied in the study of pore solution compositions of cement pastes, mortars and blended cements [5–14]. Following expression, the pore solution may be analysed for specific ions.

The pore solution expression experimental arrangement is shown schematically in Fig. 1 [12]. The equipment consists of a die body of two concentric thick-walled steel cylinders, the inner cylinder being a close fit to the bore of the outer cylinder. The die body is seated on a platen, with both components ground so as to be exactly on a level plane and thus to allow even pressure transfer across the body of the equipment. The test core is placed inside the inner cylinder and a PTFE disk placed on top of this followed by a piston to which pressure is applied. The pressure is increased gradually and pore solution is expressed via a drain ring in the base platen where it is collected and stored in a sealed container to prevent reaction with atmospheric carbon dioxide.

Using this technique it is inevitable that some pore solution will remain in the sample after being crushed and the residual material remains damp to the touch. For this reason pore solution expression is considered by many within the field of corrosion to provide an accurate measure of the pore solution composition of the sample, but not necessarily an accurate measure of its volume.

2.2. Hassler cell permeameter

The Hassler cell permeameter is shown in Fig. 2. Full details of the experimental arrangement and associated equipment are given in [15]. The Hassler cell is a high pressure axial-flow permeameter designed to accommodate a cylindrical core 25 mm in diameter and between 25 and 75 mm in length. Before being loaded into the Hassler cell the sample must be saturated with water. The core is encased in a nitrile rubber sleeve to which a containing pressure is applied such that the containing pressure exceeds the pressure of the liquid, in this case deionised water, flowing through the sample. The containing pressure seals the circumferential face of the sample and ensures axial-flow. A chromatography pump provides a

Table 2
Volume and chloride content of pore solution obtained from each mortar sample by pore solution expression

Age of sample	1 day			7 Days			14 days			28 days		
Composition (Cement: sand, w/c)	Volume (ml)	Chloride content (ppm)	Chloride content (mg)	Volume (ml)	Chloride content (ppm)	Chloride content (mg)	Volume (ml)	Chloride content (ppm)	Chloride content (mg)	Volume (ml)	Chloride content (ppm)	Chloride content (mg)
1:0, 0.5	7.7	13415	103	4.7	5650	27	2.8	3800	11	1.5	4200	6
1:1, 0.5	7.4	11425	85	3.0	7750	23	2.5	9200	23	1.1	7200	8
1:2, 0.5	1.5	11550	17	1.0	10400	10	–	8300	–	–	–	–
1:3, 0.5	1.0	9830	10	–	6400	–	–	–	–	–	–	–
1:0, 0.6	8.0	7150	57	6.2	3865	24	5.4	3350	18	3.4	3025	10
1:1, 0.6	7.9	7000	55	6.5	3800	25	5.4	3150	17	5.0	3015	15
1:2, 0.6	7.1	6565	47	5.0	3800	19	5.6	3550	20	2.8	3800	11
1:3, 0.6 [a]	3.7	9237	34	2.4	3715	9	1.3	4065	5	1.0	1950	2
1:4, 0.6	4.2	7900	33	1.0	4400	4	–	–	–	–	–	–
1:3, 0.7	6.4	8835	57	5.4	4415	24	4.6	4115	19	2.3	4835	11
1:3.5, 0.7	5.9	9215	54	3.8	4935	19	4.2	5000	21	1.0	7725	8
1:4, 0.7	4.7	9035	42	2.5	4600	12	1.5	6388	10	–	–	–

[a] Values in this row are those used in Fig. 8 and Table 3.

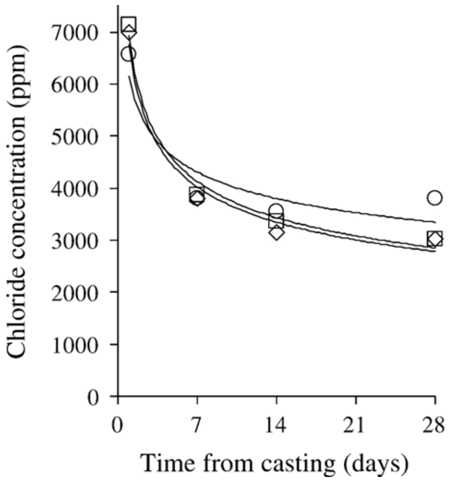


Fig. 3. Chloride ion concentration in expressed pore solution for a cement paste and two cement mortars measured at 1, 7, 14 and 28 days after casting. □, cement: sand = 1:0; ◇, cement: sand = 1:1; ○, cement: sand = 1:2. Water: cement ratio = 0.6 in each case.

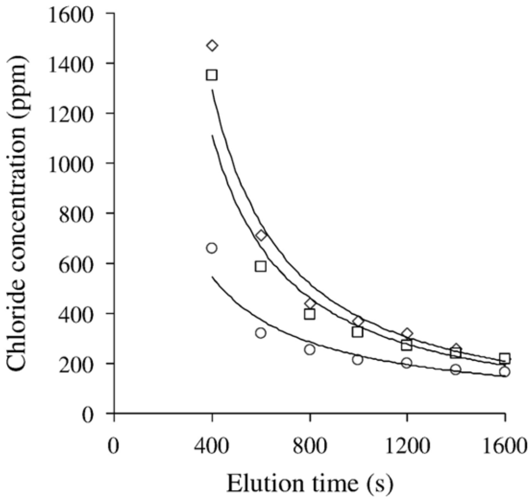


Fig. 5. Change in chloride ion concentration with elution time for three cement mortars 1 day after casting. ◇, water: cement ratio = 0.5; □, water: cement ratio = 0.6; ○, water: cement ratio = 0.7. Cement: sand ratio = 1:3 in each case.

pulse-free constant flow rate of liquid through the sample and the pressure necessary to maintain this flow (the fluid pressure) is recorded. The containing pressure is typically set to four times the fluid pressure. Both containing and fluid pressures are measured using pressure transducers. For the pumped and saturating liquids being completely miscible, as is the case here, the latter is eventually completely displaced [16,17]. The pore solution is thus eluted by the pumped liquid, collected, and may then be analysed for ions such as chloride. In contrast to the pore solution expression method the samples remain intact, but may not for long elution times.

3. Experimental work

3.1. Sample preparation

Experiments were carried out on the range of ordinary Portland cement pastes and mortars shown in Table 1. The mix water used in each case was a 2% solution (2 g per 100 ml) of sodium chloride in deionised water to ensure that a measurable chloride ion concentration would be present in the pore solution of the set mixes [12]. This 2% solution is equivalent to a concentration of 2×10^4 ppm of sodium chloride in the mix water, giving an initial chloride ion concentration of 1.21×10^4 ppm. The amount of chloride ion (in mg) contained in any sample may thus be calculated from the volume of water incorporated as indicated by the mix proportions. These values are also shown in Table 1. A number of samples for both pore solution expression and Hassler cell elution were prepared from each freshly-mixed batch of mortar. Samples for pore solution expression were cast in cylindrical moulds with a volume of 84 cm^3 and slightly smaller in diameter than the inner cylinder of the pore solution expression equipment. Following casting each sample was sealed with polymer film to prevent both evaporation of the mix water and

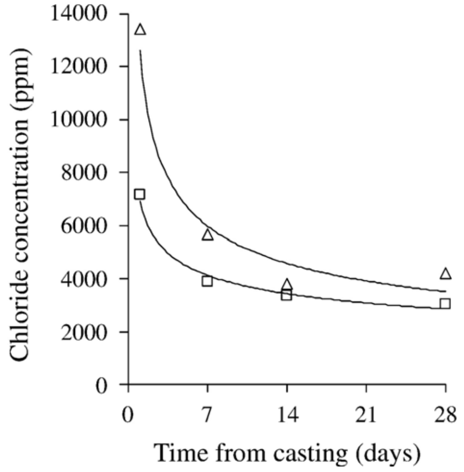


Fig. 4. Chloride ion concentration in expressed pore solution for two cement pastes measured at 1, 7, 14 and 28 days after casting. □, water: cement ratio = 0.6; △, water: cement ratio = 0.5.

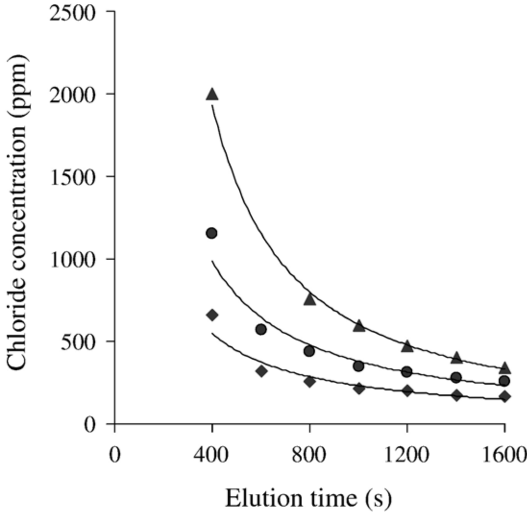


Fig. 6. Change in chloride ion concentration with elution time for three cement mortars of water: cement ratio = 0.7, 1 day after casting. ◆, cement: sand = 1:3; ●, cement: sand = 1:3.5; ▲, c:s = 1:4.

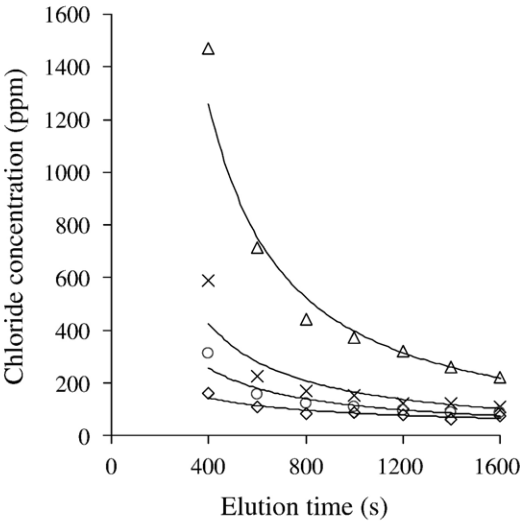


Fig. 7. Change in chloride ion concentration with elution time for a cement mortar (cement: sand ratio = 1:3 and water: cement ratio = 0.5) at 1 day, △; 7 days, ×; 14 days, ○; 28 days, ◇, after casting.

carbonation, and remained sealed until immediately prior to crushing. Samples for the Hassler cell were cast in 100 × 70 × 70 mm moulds which were also sealed until immediately prior to the removal of 25 mm diameter cores. To produce flat surfaces a 5 mm slice was removed from the end of each core with a circular saw resulting in a sample size of approximately 30 cm^3. Sample preparation, curing, coring and subsequent measurements were carried out at a room temperature of approximately 20 °C.

Table 3
The total chloride content of a pore solution obtained following both miscible displacement and pore solution expression for a 1:3 cement: sand mortar of water: cement ratio 0.6

Age of sample	1 day		7 days		14 days		28 days	
Elution time (s)	Cl^- (ppm)	Cl^- (mg)	Cl^- (ppm)	Cl^- (mg)	Cl^- (ppm)	Cl^- (mg)	Cl^- (ppm)	Cl^- (mg)
400	1350	9.00	885	5.90	480	3.20	400	2.66
600	585	1.94	440	1.46	280	0.93	200	0.66
800	395	1.31	190	0.63	190	0.63	160	0.53
1000	325	1.08	143.5	0.47	133	0.44	140	0.46
1200	270	0.89	120	0.39	103.5	0.34	120	0.39
1400	240	0.79	106.5	0.35	86.5	0.28	120	0.39
1600	220	0.73	100	0.33	80	0.26	110	0.36
1800	190	0.63	93.5	0.31	73.5	0.24	120	0.39
Total Cl^- eluted (mg) in 30 min using Hassler cell		16.41		9.88		6.35		5.94
Total Cl^- (mg) in pore solution expressed from same mix. Factored by the volume ratio 30/84		12.14		3.21		1.79		0.71

3.2. Pore solution expression

Samples were tested at 24 h, 7, 14 and 28 days from casting. Each sample was placed in the pore solution expression apparatus and loaded to 750 N mm^{-2} at a rate of 0.375 N mm^{-2} s^{-1} (taking about 30 min) and then held at this pressure for 30 min. The total volume of expressed pore solution was measured and analysed for chloride within 10 min of collection. For the analysis 1 ml of expressed pore solution was diluted to 50 ml with deionised water before being measured using a silver/silver chloride redox electrode that had been calibrated, using stock solutions, for voltage versus chloride concentration. Mixes composed of the higher cement: sand ratios (1:3 and 1:4) did not yield a measurable volume of pore solution when the mortars were older than 7 days.

3.3. Hassler cell permeameter

Cores were tested at 24 h, 7, 14 and 28 days from casting. Each core was vacuum saturated with water before being placed in the Hassler cell and flushed with deionised water for 30 min. A flow rate of 1 ml min^{-1} was used in each case, resulting in fluid pressures ranging between 0.1 and 1 MPa depending on the mortar composition. The containing pressure was held constant at 4 MPa. The eluent was collected over the first 400 s and subsequently over 200 s intervals for a total of 30 min. Thus 6.67 ml of liquid was collected after the first 400 s and 3.33 ml at the end of each 200 s interval, giving a total of 30 ml of deionised water passing through the sample. For a typical porosity of 35% and a sample size of 30 cm^3 this amount of liquid is equivalent to about 3 pore volumes. Analysis for chloride was undertaken as for the pore solution expression except that 1 ml of eluent was diluted to 10 ml with deionised

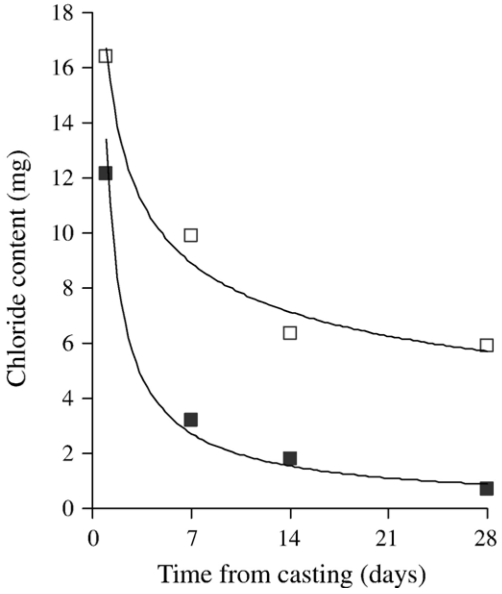


Fig. 8. Total chloride content established from Hassler cell elution, □, and pore solution expression, ■, for a 1:3 cement: sand mortar of water: cement ratio 0.6 at various ages from casting. The latter were calculated from Table 2 and multiplied by the volume ratio of the samples (30/84).

water. Not all the mix compositions of Table 1, notably those of the two lower water: cement ratios and lower cement: sand ratios, were amenable to this technique as measurable flow through the samples could not be achieved.

4. Experimental results and discussion

4.1. Pore solution expression

The volume and measured chloride concentration (ppm) of expressed pore solution for each mortar composition examined are shown in Table 2. Table 2 shows that the volume of pore solution decreases markedly with age from casting. This would be expected as hydration and curing proceed. Further, for a given water: cement ratio the volume of pore solution that can be expressed from a mortar at any age decreases as the proportion of sand is increased until it is not possible to express a measurable amount.

Fig. 3 shows the change in concentration of chloride ions in the expressed pore solution with age of mortar for mixes of a range of cement: sand ratios each with the same water: cement ratio of 0.6. The decrease in chloride ion concentration indicates that the cement matrix retains chloride as it cures, as has been shown by previous workers [18]. Fig. 3 also shows that the cement: sand proportions make little difference to the chloride concentration of the expressed pore solution. Fig. 4 shows the change in chloride ion concentration with age for cement pastes of two different water: cement ratios. The data exhibit the same decrease in chloride ion concentration with age as Fig. 3 but show the water: cement ratio to have a marked effect on chloride concentration, with the paste of lower water: cement ratio having a higher chloride concentration at all times. It can be seen from Table 2 that both these compositional effects were observed for all the mortars. Further, Fig. 4 shows a chloride concentration of 1.34×10^4 ppm in the expressed pore solution at 24 h for the cement paste of water: cement ratio 0.5. This is in excess of the 1.21×10^4 ppm incorporated into the mix water and may be due to the effects of hydration reactions at early times removing water thus leaving behind a higher concentration of chloride, and possibly other ions, in the pore solution. (As a rough estimate, some 10.7% of the mix water will have been removed by the hydration reactions).

4.2. Hassler cell

Fig. 5 shows the change in chloride ion concentration with elution time for 1:3 cement: sand mortars of different water: cement ratios determined at 24 h after casting, and collected over the time intervals already described. Consistent with the pore solution expression results shown in Fig. 4, the chloride ion concentration of the eluent increases as the water: cement ratio is reduced. Fig. 6 shows the chloride ion concentration of solution eluted from a range of cement: sand mortars all with a water: cement ratio of 0.7, also at 24 h after casting. In contrast to the pore solution expression results shown in Fig. 3, the Hassler cell results of Fig. 6 show that mortar composition does have a significant and systematic effect on the chloride ion concentration of the eluted solution and shows a clear increase in chloride ion concentration as the cement content is reduced. This effect is to be expected as there is less cement available to bind the chloride. These differences could not be detected using the pore solution expression technique. Fig. 7 shows the chloride ion concentration of solutions eluted from 1:3 cement: sand mortars of water: cement ratio 0.5 at 24 h, 7, 14 and 28 days after casting. The chloride ion concentration in the eluents decreases with the age of mortar and is consistent with the pore solution expression results shown in Figs. 3 and 4.

Since the flow rate through the sample in the Hassler cell was held constant at 1 ml min^{-1}, it is possible to calculate the volume of water passing through a sample during each elution interval. Thus 6.67 ml of water passed through the sample during the first 400 s and 3.33 ml during each subsequent 200 s interval. The quantity of chloride eluted (in mg) during each time interval may therefore be calculated from the product of the measured chloride concentration (ppm) and the volume of each elution. The sum of these quantities is equal to the total amount of chloride eluted in 30 min. Table 3 compares the total amount of chloride eluted in 30 min using the Hassler cell to the total amount of chloride obtained using pore solution expression for the 1:3 cement: sand mortar of water cement ratio 0.6. (To account for the difference in sample volume, the pore solution expression results from row 8 of Table 2 have been factored by 30/84). These data are plotted in Fig. 8 from which it can be seen that, compared to pore solution expression, the Hassler cell is capable of recovering a significantly higher proportion of the incorporated chloride as curing proceeds.

5. Conclusions

Both eluted and expressed pore solutions exhibit a decrease in chloride ion concentration as cement pastes and mortars cure (Figs. 3 and 7). This is to be expected and indicates that the chloride binds to the matrix as the material ages. However, the elution method shows a greater sensitivity to mix composition (specifically cement content) than the pore solution expression method (Figs. 3 and 6). Both methods show a decrease in chloride concentration as the water: cement ratio of the mix is increased. This effect is due to water being taken up during the hydration reaction. The lower the water: cement ratio, the higher the proportion of water taken up during hydration and the higher the concentration of chloride left behind in the residual pore solution. Overall, the high pressure elution method is capable of recovering a significantly higher proportion of incorporated chloride than pore solution expression.

Pore solution expression is an established technique which allows direct analysis of the chemical composition of the pore solution itself. High pressure elution is an indirect method which provides a more subtle means of examining pore solution species. The main limitation of the pore solution expression technique is the range of mixes over which sufficient pore solution may be obtained, with the higher cement: sand ratios not yielding measurable volumes. This is due to the incompressibility of the sand component of the mix and the yield is not likely to be improved by increasing the pressure. The main limitation of the

Hassler cell is that cements of lower water: cement and cement: sand ratios are too impermeable to allow measurable flow.

Pore solution expression, followed by analysis, gives the concentration of (in this case) chloride ions and thus reflects the existing equilibrium in the sample at the time of measurement. In contrast, the samples for high pressure elution are deliberately saturated with water prior to measurement. This dilution of the pore solution will cause the components present to readjust their equilibria to the much wetter conditions and will result in some of the bound chloride being released from the matrix and subsequently recovered in the eluted solution.

We suggest therefore that a combination of the two techniques described here could extend the scope of pore solution analysis, particularly in respect of leaching, studies of alternate wetting and drying and dynamic pore solution/cement interactions upon which many durability issues depend. Although the high pressure elution work reported here has focused on chloride ion concentrations, there is a clear scope to extend the work to other anion species such as sulphate and hydroxyl in which the changes in equilibria due to dilution may be even more pronounced. There is further application in the monitoring of cation species such as those of metals which are important in waste immobilization.

References

[1] C.L. Page, K.W.J. Treadaway, Aspects of the electrochemistry of steel in concrete, Nature 297 (1982) 109–115.

[2] R.S. Barneyback Jr., S. Diamond, Expression and analysis of pore fluids from hardened cement pastes and mortars, Cement and Concrete Research 11 (1981) 279–285.

[3] B. Lothenbach, F. Winnefeld, Thermodynamic modeling of the hydration of Portland cement, Cement and Concrete Research 36 (2006) 209–226.

[4] P. Longuet, L. Burglen, A. Zelwer, La phase liquide du ciment hydrate, Revue Materiaux Construction Travaux 676 (1973) 35–41.

[5] S. Diamond, Effects of two Danish fly ashes on alkali contents of pore solutions of cement fly ash pastes, Cement and Concrete Research 11 (1981) 383–394.

[6] S. Diamond, Chloride concentrations in concrete pore solutions resulting from calcium and sodium chloride admixtures, Cement and Concrete Aggregates 8 (1986) 97–102.

[7] S. Diamond, F. Lopez-Flores, Fate of calcium chloride dissolved in concrete mix water, Journal of the American Ceramic Society 64 (1981) 162–164.

[8] C.L. Page, P. Lambert, P.R.W. Vassie, Investigations of reinforcement corrosion 1: the pore electrolyte phase in chloride contaminated concrete, Materials and Structures 24 (1991) 243–252.

[9] C.L. Page, O. Vennesland, Pore solution chemistry and chloride binding of silica fume cement, Materials and Structures 16 (1983) 19–25.

[10] P. Lambert, C.L. Page, N.R. Short, Pore solution chemistry of the hydrated system tricalcium silicate sodium chloride water, Cement and Concrete Research 15 (1985) 675–680.

[11] K. Byfors, C.M. Hansson, J. Tritthart, Pore solution expression as a method to determine the influence of mineral additives on chloride binding, Cement and Concrete Research 16 (1986) 760–770.

[12] T. Yonezawa, V. Ashworth, R.P.M. Procter, Pore solution composition and chloride effects on the corrosion of steel in concrete, Corrosion Engineering 44 (1988) 489–499.

[13] C. Arya, N.R. Buenfeld, J.B. Newman, Factors influencing chloride binding in concrete, Cement and Concrete Research 20 (1990) 291–300.

[14] S. Rasheeduzzafar, S.E. Hussain, S.S. Al-Saadoun, Effect of cement composition on chloride binding and corrosion of reinforcing steel in concrete, Cement and Concrete Research 21 (1991) 777–794.

[15] K.M. Green, W.D. Hoff, M.A. Carter, M.A. Wilson, J.P. Hyatt, A high preessure permeameter for the measurement of liquid conductivity of porous construction materials, Review of Scientific Instruments 70 (1999) 3397–3491.

[16] C. Hall, Barrier performance of concrete: a review of fluid transport theory, Materials and Structures 27 (1994) 291–306.

[17] C. Hall, W.D. Hoff, Water Transport in Brick, Stone and Concrete, SPON, London, 2002.

[18] A.M. Neville, Properties of Concrete, Longman, 1996.