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Rapid estimation of chloride diffusion coefficient in concrete

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The Authors have presented an interesting paper in a very important area of concrete technology. The introduction reviews previous work on accelerating chloride ion diffusion in concrete, but overlooks work that has been in progress at Imperial College since September 1986. The Imperial College work has involved developing, optimizing and validating an accelerated chloride ion diffusion (ACID) test and then applying it to investigate a number of factors that could not have been studied using existing techniques. The optimized test method was fully described in a paper published in 1988.[1] The ACID test is based on the same principal as that used by the Authors. There are a number of differences between the two methods; the most significant of these are discussed below. The ACID test has been used for commercial testing since 1987. This work formed the basis of El-Belbol's PhD studies; he completed the first draft of his thesis in April 1990 and was awarded a PhD[2] in February 1991. Two papers on the validation of the test have been presented.[3,4] The ACID test apparatus is available commercially and a comprehensive paper on the application of the ACID test is to be published soon.

In this discussion we first address the test technique used by the Authors and then discuss their interpretation of the results. The Authors tested concrete with a maximum aggregate size of 20 mm. Inevitably this aggregate could have contained elongated particles that passed through the 20 mm sieve, yet had a maximum of considerably more than 20 mm. The concrete specimens tested were 25 mm thick. It is therefore likely that some coarse aggregate particles spanned, or nearly spanned, between opposite faces of a specimen. This is undesirable, as there is good evidence to suggest that for many concretes the aggregate/cement paste interface provides a relatively easy flow path in relation to the cement paste or the aggregate particles alone. This is not a major problem in the context of a study comparing the result of concentration-driven diffusion with electrical-potential-driven diffusion where the same concrete and thickness of specimen are used throughout. However, in other applications it is suggested that the specimen thickness should be several times the maximum aggregate size to eliminate any distortion of results due to this phenomenon. The ACID test uses 50 mm thick specimens, since, in most chloride-rich environments, a concrete cover of around 50 mm is generally specified.

A consequence of increasing the specimen thickness is an increase in the test duration. Our work shows that doubling the specimen thickness should lead to an approximate doubling of t_0. If it is felt that this makes the test duration unacceptably long, the applied voltage may be increased. Increasing the voltage may also be appropriate if specimens with high resistance to chloride ion diffusion are to be tested, e.g. very low water/cement concretes, concretes incorporating ggbs or an integral waterproofer, or surface-treated concrete. If 10 V were used for these materials the test duration could be 8 to 10 times greater than that reported here, i.e. up to 15 weeks. The ACID test uses a potential of 40 V. The Authors report chlorine gas evolution and graphite electrode dissolution at voltages of 20 V and higher, and hence they restricted the applied voltage to 10 V. These problems are exacerbated at higher voltages if the choice of 'neutral solution' (cell reservoir liquid) is incorrect. If the neutral solution is not sufficiently alkaline, chlorine gas and hypochlorous and hydrochloric acids are formed. Chlorine gas and hypochlorous acid formation consume a proportion of the chloride ion present, resulting in misleadingly low chloride ion diffusion values. Furthermore, acid formation results in attack of the cement paste microstructure. The Authors use distilled water as neutral solution, and it is therefore likely that these effects are still present at 10 V but are less dramatic than those observed at higher voltages. The way to avoid such problems is to use a neutral solution of relatively high pH. The ACID test (inappropriately named in this context!) uses a neutral solution of 0·3 M NaOH. This has the added appeal of more accurately simulating cement paste pore solution, thereby reducing leaching.

We are very concerned that passing a direct current through concrete for several days would lead to changes in the cement paste microstructure such that the results would not be representative of the original concrete. We too carried out parallel diffusion cell tests (10 mm thick specimens) and ACID tests (50 mm thick specimens) on both mortar and cement pastes and found a good correlation. We also compared the microstructure of tested and untested specimens using backscattered electron imaging in the SEM. We found that, with the exception of the surface 100 μm in contact with the neutral solution, no microstructural changes could be identified.

The Authors use a chloride ion selective electrode to measure chloride concentration in the cell reservoir. In our early experiments we also used this method, with a datalogger automatically taking measurements. However, we found that this was inaccurate. Firstly there was an error associated with the applied voltage and hence we developed an arrangement whereby the applied voltage was switched off a certain time before readings were taken. Then we observed that trace quantities of metal ions, leached from the specimen well before any chloride ions had penetrated the full thickness of the specimen, interfered with the electrode, resulting in a chloride reading higher than the chloride concentration actually present.

We monitored leaching for a range of neutral solutions and found that the effect was at its most severe when the neutral solution was distilled water. We also found that it was impossible to test mixes containing ggbs using a chloride ion selective electrode in this way because the sulphide ion readily released from ggbs poisons the electrode. We therefore resorted to manual sampling and potentiometric titration remote from the test cell; this is more labour-intensive, but produced results in which we were far more confident.

The 'diffusion cell' used by the Authors, and in particular the method of sealing specimens into it, results in less than 90% of the specimen cross-sectional area being in contact with the solutions on either side of the specimen. Hence the flow path taken by chloride ions, the 'transmission area', is poorly defined; a sealing method is required[1] that allows the specimen to be sealed on its curved face alone, allowing the full cross-sectional area of the specimen to be exposed to chloride diffusion.

The title of the paper, together with a statement in the introduction that 'A fundamental parameter describing the resistance of a particular concrete to the transport of chlorides is the coefficient of diffusion D, from which the depth of penetration of chlorides over a period of time may be estimated', suggests that this test may be used to predict directly chloride penetration depths into concrete. Care must be taken when quoting 'the diffusion coefficient' to indicate which one is being considered. The CD test results in an *intrinsic* diffusion coefficient. The good correlation observed between the CD and PD tests therefore allows estimation of the *intrinsic* diffusion coefficient. The depth of penetration of chlorides over a period of time is described by an *apparent* diffusion coefficient. To our knowledge, no relationship has yet been proven that allows the depth of penetration of chlorides over a period of time to be calculated from an *intrinsic* chloride ion diffusion coefficient, although this is an area in which we are presently active.

Figure 4 presents the 'Ideal form of chloride ion transmission through test specimens for CD and PD tests'. We are unsure about the sense in which this is ideal. It shows the chloride concentration in the cell reservoir increasing from the moment the test is started. Clearly this is impossible, as it takes a considerable time for the first ions to diffuse across the full thickness of the specimen. Fig. 5 confirms this.

Comparison of a calculated and the true value of C_1 is stated as being a method of checking that the assumptions made and the experimental procedure are correct. The calculated value is based on extrapolating the graph of $\ln(C_1 - C_2)$ against $t_n - t_0$ back to the y-axis ($t_n - t_0 = 0$) to calculate $\ln C_1$ and hence C_1. C_1 is around 177 250 ppm and in the CD tests, for the results shown, C_2 is considerably less than 0·5% of this concentration, even at the end of the tests. We would suggest that the variation in $C_1 - C_2$ (i.e. $< 0{\cdot}5\%$) over the duration of a test is less than the accuracy with which C_1 can be controlled/measured and it is therefore difficult to see how this "check" is useful. Perhaps the Authors should comment on this, particularly with regard to the methods of chloride analysis used.

The first paragraph on p. 182 compares mass transport in the CD and PD tests; the difference is of course two (not one) orders of magnitude. It is stating the obvious to say that the results obtained with the PD test cannot be taken directly as coefficients of diffusion; if they could, the test method would not have accelerated the diffusion process, and the object of the exercise would not have been achieved.

Finally two queries regarding Fig. 9. Firstly, was there any reason why the regression line in Fig. 9 was not forced through the origin? Secondly, there are many more PFA datapoints in Fig. 9 than in Fig. 8; are Figs 8 and 9 based on the same data.?

References

1. El-Belbol S. and Buenfeld N. R. Accelerated chloride ion diffusion test. *Materials Research Society Symposium—Pore Structure and Permeability of Cementitious Materials.* Boston, November 1988. *MRS Proceedings*, Vol. 137, 203–208.
2. El-Belbol S. Accelerating chloride ion diffusion in concrete. London University PhD thesis, 1991.
3. El-Belbol S. M. T. and Buenfeld N. R. Comparison of chloride ion diffusion in concrete driven by chemical and electrical potentials. *Concrete Materials Research Seminar*, Imperial College, 17–18 July 1990.
4. El-Belbol S. M. T. and Buenfeld N. R. An accelerated chloride ion diffusion test for concrete. *Institute of Metals Conference on The Microstructure of Cement and Concrete.* 19–20 September 1990, University of Oxford.

Reply by the authors

We thank Drs Buenfeld and El-Belbol for their comments on our Paper on what is a subject of great importance in the field of concrete technology. We will discuss the points in the order in which they have been raised.

We were aware of the work that Drs Buenfeld and El-Belbol have carried out, as published in the proceedings of a conference held in Boston, USA in November 1988.[1] However, their Reference 2 postdates our publication, and References 3 and 4 only amount to summaries of oral presentations and are not catalogued in any library system. Moreover, their published work was of no direct relevance to our study of chloride diffusion in concrete.

We are surprised that Drs Buenfeld and El-Belbol call their test method, described in their reference 1, optimized, presumably indicating that this is the final version of the voltage driven chloride diffusion test (VDCD) or ACID test. In that reference only the results of mortars were reported and no correlations with the coefficient of chloride diffusion *D* were presented. Their work was on mortar samples, but they mentioned the importance of the coarse aggregate/matrix bond zone as a major flow path for Cl-transmission.

Since the inception of our work in 1985 we have not concentrated on the use of pastes and mortars, as our aim has been to develop a test of relevance to the concrete construction industry. Our test method has been shown to work and we believe it provides a sound basis for further application in laboratory and site investigations. Our particular test arrangement allows multiconcurrent tests to be easily carried out, which is not possible with the Imperial College method, except by numerous 'ACID' test units.

The gravel aggregate we used had an elongation index of $< 1\%$, and we can confirm that no coarse aggregate particle spanned the full thickness of the test specimens. Any specimen thickness can be used with our proposed test method, since the depth of the locating collar of the test cell could be easily manufactured to accommodate any specimen thickness.

We have for the time being rejected the use of thicker test specimens than we have used, as we wish to build up a more complete picture of the variability within the cover concrete in 25 mm thick layers (assuming 20 mm matrix aggregate). This has numerous advantages, since it does not require producing and controlling an upstream alkaline solution or the use of high potential differences. More importantly, thinner specimens allow the relative effects of curing etc. to be measured on the first 25 mm and subsequent layers. We are sure that Drs Buenfeld and El-Belbol would not advocate using specimens even thicker than 50 mm, for example, up to 300 mm as used in some offshore structures.

We have described, in detail, the way in which we have used the ion-selective electrode (ISE) previously[1] and have not experienced any problems in its use in this context. We would make it clear that the ISE is only used when the power is switched off and is not left in the test cells after use. A calibration check is made against a reference buffer solution before and after each test. Comparisons against titration of an aliquot of the solution confirmed that with the materials we have used the ISE is the most simple and straightforward test method. In addition, with the ISE there is no depletion of solution in the upstream reservoir. We note that when ggbs concrete is used some difficulty using an ISE may be experienced. We would, however, generally recommend the use of a well-calibrated and maintained ISE measuring system for simplicity, particularly for use in situ.

With regard to sealing the test specimen, we tried petroleum jelly and many other methods and found the sealing to be totally inadequate. We therefore utilized O-rings and silicone sealant.

It is possible to estimate the chloride depth after some period of time, using the intrinsic value of *D*. Without being able to carry out such a calculation we doubt that any rapid test has much use for engineers.

Table 1. Characteristics of PFA used

Property	Pulverized-fuel ashes					
	P31/F*	P31/H*	P31/I†	P31/L†	P13P*	P31P*
Major oxides: %						
SiO_2	45·7	45·0	46·0	48·2	46·7	46·8
Al_2O_3	33·9	33·0	32·4	31·6	25·6	33·3
Fe_2O_4	6·8	7·2	7·0	6·9	9·1	7·5
CaO	3·4	3·6	3·8	3·8	4·8	3·7
LOI	1·8	4·8	4·0	4·8	4·4	3·6
Mineralogical composition: %						
Glass	63·3	61·3	59·6	55·8	75·2	58·0
Mullite	26·4	26·3	27·4	2·68	10·2	29·3
Quartz	4·1	2·9	4·7	7·1	3·9	5·7
Hematite	1·7	1·5	1·8	1·8	2·2	2·3
Magnetite	2·7	2·9	2·5	3·7	4·1	2·5
Physical properties: %						
Fineness: % ret 45 μm	1·6	7·1	12·8	23·0	11·8	5·7
Water requirement‡	87	89	91	96	90	91
Pozzolanic activity index‡	126	102	100	76	92	101

*Complying with BS 3892: Part 1.
†Complying with BS 3892: Part 2.
‡with respect to OPC Control.

We have demonstrated that the PD index correlates well with D (Figs 8 and 9 on p. 185). However, following this publication we have developed nomograms for this purpose and their use has recently been published.[2]

Figure 4 on p. 181 is purely schematic, therefore no time unit was given. The figure is used to represent the most important period of chloride transmission in this case, i.e. when steady-state conditions occur. The period before or after this is not significant to the Paper, although it is highly significant to the durability of the structure.

As it should be, the calculation method we have adopted is simple and straightforward. The use of the intercept value $\exp(\ln C_1)$ is a useful way of checking that, in general terms, the operator has properly carried out the test, for example no leakages occurred, etc., and that no arithmetic error was made in the calculation. Given the accuracy of the ISE, as we have already discussed, we therefore do not see any problem with this approach.

Table 2. Mix proportions of concrete

PFA code	Mix constituents: kg/m^3			
	OPC	PFA	Water	Aggregates*
20 N/mm^2				
P31/I	175	75	165	1945
P13P	175	75	165	1945
40 N/mm^2				
P31/F	220	145	160	1840
P31/H	235	130	165	1830
P31/L	280	85	173	1835
P31P	235	130	165	1830

*General coarse aggregate (10 and 20 mm sizes) and natural sand (Zone M, BS 882).

We do not understand how Drs Buenfeld and El-Belbol consider the differences in concentrations of chlorides transported in the CD and PD tests to be two orders of magnitude. This is quite clearly, as shown in Fig. 5 on p. 183, one order of magnitude, as stated in the Paper. There is also an order of magnitude difference in the time taken in each test but it is incorrect to add these together to give two orders of magnitude.

It is strange that Drs Buenfeld and El-Belbol should comment in the way they have on not taking directly the PD results as D. It seems perfectly sensible to make a cautionary comment in a paper, even though it may seem to be obvious to experts. Surely it is desirable to minimize the risk of the reader misinterpreting the results of an accelerated test.

The regression line in Fig. 9 on p. 185 is a best fit and as such did not go through the origin; we attach no significance to this. There could be more points in Fig. 9 as data becomes available from another investigation which utilized a larger number of cement and concrete variables. Since these tended to support the

Table 3. Curing conditions for concrete test specimens

Code	Curing conditions*
E1	20% water for 28 days
E2	20°C water for 3 days followed by air curing
E3	Air curing for 28 days

*Including initial 24 h under damp hessian after casting.

Table 4. Relationship between coefficient of diffusion D with PD index

PFA code	Concrete grade: N/mm^2	Curing	Coefficient of diffusion D: cm^2/s × 10^{-9}	PD index cm^2/s × 10^{-6}
P31/F	40	E3	17·4	2·3
P31/H	40	E3	24·1	3·2
P31/I	20	E1	37·3	4·1
P31/L	40	E3	21·9	2·9
P13P	20	E1	33·2	3·8
P31P	40	E2	20·2	2·9

trends shown we chose to use these estimated results for good measures, but without further comment in order not to cloud the fundamental issues regarding the test methodology. Details of additional materials, mix proportions, curing and D and PD results are given in Tables 1–4, respectively.

As a final point, we note that the ACID test equipment is available commercially. The question arises as to whether this is an adequate validation of the quality of the ACID test.

References

1. Dhir R. K. *et al.* Determination of total and soluble chlorides in concrete. *Cem. Concr. Res.*, 1990, **20**, No. 4, 579–590.
2. Dhir R. K. *et al.* Concrete durability: estimation of chloride concentration during design life. *Mag. Concr. Res.*, 1991, **43**, No. 154, March, 37–44.