Pergamon

Cement and Concrete Research, Vol. 25, No. 7, pp. 1556-1566, 1995
1995 Elsevier Science Ltd
Printed in the USA. All rights reserved
0008-8846/95 $9.50+.00

0008-8846(95)00149-2

A BOLTZMANN-MATANO ANALYSIS OF CHLORIDE DIFFUSION

P.J. Tumidajski, G.W. Chan, R.F. Feldman and G. Strathdee*

Institute for Research in Construction
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6
and
*Potash Corporation of Saskatchewan, Inc.
Suite 500, 122-1st Avenue South
Saskatoon, Saskatchewan, Canada S7K 7G3

(Refereed)
(Received February 2, 1995)

ABSTRACT

The Boltzmann-Matano methodology has been applied to calculate the non-steady state chloride diffusion coefficients for concrete. It was found that the chloride diffusion coefficients depend on time and concentration/depth. The chloride diffusion coefficients were expressed as a linear function of the Boltzmann variable.

Introduction

With increased acceptance of life cycle cost analysis of concrete structures, service life prediction models based on the depth of chloride ingress in concrete were developed (1,2) based on non-steady-state chloride diffusion described by Fick's Second Law in one dimension as,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad [1]$$

where, C represents chloride concentration, t is time, x is distance, and D is the chloride diffusion coefficient or diffusivity. The solution of Eq.[1] for an infinite concrete beam immersed in a bath of constant chloride composition is (3),

$$C(x,t) = C_0 \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \qquad [2]$$

where erf represents the statistical error function and C_0 is the chloride concentration at the beam surface. Eq.[2] is valid for a constant diffusion coefficient. But, this is seldom true for concrete systems. For example, Buenfeld and Newman (4) and Mangat and Molly (5,6) showed that chloride diffusion coefficients depended on time. In the latter case, a relationship was proposed where the chloride diffusion coefficient was expressed as an explicit function of time.

Chloride diffusion coefficients can also vary with composition (or equivalently with the depth of chloride penetration into the concrete). In this case, Eq.[1] becomes,

$$[3] \qquad \frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) = \frac{\partial D}{\partial x}\cdot\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2}$$

The equation is inhomogeneous, and a generic solution in closed form is impossible. However, a special case, where conditions are simplified by the Boltzmann variable $u = x/\sqrt{t}$, transforms Eq.[3] to a solvable homogeneous differential equation.

$$[4] \qquad -\frac{u}{2}\cdot\frac{dC}{du} = \frac{d}{du}\left(D\cdot\frac{dC}{du}\right)$$

With appropriate simplifications, the integral of Eq.[4] between C=0 and $C=C^*$ ($0<C^*<C_o$) is,

$$[5] \qquad -\frac{1}{2}\int_{C=0}^{C=C^*} u\cdot dC = \left[D\cdot\frac{dC}{du}\right]_{C=0}^{C=C^*}$$

Since, chloride concentration profiles are routinely obtained at fixed time intervals, then Eq.[5] can be expressed in terms of the chloride profile parameters as,

$$[6] \qquad -\frac{1}{2}\int_0^{C^*} x\cdot dC = D\cdot t\cdot\left[\frac{dC}{dx}\right]_{C=0}^{C=C^*} = D\cdot t\cdot\left(\frac{dC}{dx}\right)_{C=C^*}$$

The $D\cdot t\left(\frac{dC}{dx}\right)_{C=C^*}$ term is a consequence of an infinite beam where $\frac{dC}{dx} = 0$ at C=0. The concentration dependent diffusion coefficient, $D(C^*)$, can be isolated in Eq.[6] as,

$$[7] \qquad D(C^*) = -\frac{1}{2t}\cdot\left(\frac{dx}{dC}\right)_{C^*}\cdot\int_0^{C^*} x\cdot dC$$

Eq.[7] was first used by Matano (7) to calculate diffusion coefficients in metallurgical systems. Gummerson et al (8) determined hydraulic diffusivities for ordinary Portland cement mortars using Eq.[7]. This paper represents the first attempt to apply the Boltzmann-Matano methodology to determine chloride diffusion coefficients as a function of time and distance/concentration for concrete exposed to chloride solutions.

Experimental

The concrete mix design is given in Table 1. The coarse aggregate was crushed limestone (<19 *mm*), and graded silica sand was the fine aggregate. The slump was 114 *mm* and the entrained air was 5.0%.

TABLE 1.
Mix Design (*kg/m*^{3})

Type 50 Cement	Water	Coarse Agg.	Fine Agg.	Air Agent (Darex)	Superplacticizer (40% Disal)
369.96	147.98	1107.01	737.95	0.93	4.64

Beams of dimension 75 *mm* x 75 *mm* x 300 *mm* were cast and cured at 100% *rh* for 3 and 28 days. Subsequently, the beams were waxed on five sides and immersed into baths. The composition of the baths is given in Table 2.

TABLE 2
Ion Concentrations of Baths (%)

	Bath 1	Bath 2
K^+	4.68	4.32
Cl^-	16.82	16.98
SO_4^{2-}	0.18	0.16
Ca^{2+}	0.134	0.154
Mg^{2+}	0.107	1.46
Na^+	7.76	5.44

At 3, 6, 12, 18 and 24 months, the beams were removed from the baths. The chloride contents (ASTM C114) were determined at various penetration depths by measuring total chloride in specimens 4 *mm* thick (i.e., specimens were taken at 0-4, 6-10, 12-16, etc. *mm* from the specimen surface).

Results and Discussion

The chloride penetration data are presented in Tables 3 to 6. For each curing condition, bath exposure and time, the chloride profiles in Tables 3 to 6 were fitted to an equation of the form,

$$C = A \cdot e^{-B/x} \qquad [8]$$

where, A and B represent constants, and C is the concentration of chloride. Values for A and B were determined by minimizing the chi-squared values using the Levenberg-Marquardt algorithm (9). Subsequently, Eq.[7] was used to calculate the chloride diffusion coefficients. These values have been summarized in Tables 7 to 10 and Figures 1 to 4.

There is both a time and concentration/depth dependence for the chloride diffusion coefficient. In all cases, the chloride diffusion coefficient increases further into the bulk concrete. However, for longer exposure times, the concentration/depth dependence of the chloride diffusion coefficients is less pronounced. It is probable that components of the bath solutions interact with the concrete and hinder chloride diffusion. At the outset, the interaction is mainly confined to the

TABLE 3.
Chloride Profiles (%) for 3 Day Cure Exposed to Bath 1.

Depth (*mm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0-4	0.60	1.07	1.43	1.17	1.20
6-10	0.49	0.61	0.72	0.73	0.83
12-16	0.28	0.43	0.46	0.59	0.59
18-22	0.15	0.28	0.21	0.42	0.45
24-28	0.08	0.15	0.21	0.27	0.44
30-34	0.06	0.11	0.10	0.12	0.32
36-40		0.08	0.05	0.07	0.19
42-46			0.05	0.06	0.11
48-52				0.05	0.06
54-58				0.01	0.05
60-64					0.05

TABLE 4.
Chloride Profiles (%) for 28 Day Cure Exposed to Bath 1.

Depth (*mm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0-4	0.99	1.31	1.45	1.38	1.08
6-10	0.34	0.66	0.69	0.76	0.82
12-16	0.26	0.41	0.50	0.62	0.61
18-22	0.15	0.21	0.41	0.43	0.47
24-28	0.07	0.08	0.24	0.29	0.36
30-34	0.04	0.06	0.15	0.14	0.29
36-40		0.06	0.08	0.07	0.15
42-46			0.04	0.06	0.10
48-52				0.05	0.07
54-58				0.01	0.06

TABLE 5.
Chloride Profiles (%) for 3 Day Cure Exposed to Bath 2.

Depth (*mm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0-4	1.18	1.05	0.94	0.94	1.21
6-10	0.43	0.59	0.67	0.67	0.73
12-16	0.23	0.35	0.47	0.47	0.59
18-22	0.12	0.17	0.29	0.29	0.46
24-28	0.06	0.08	0.15	0.15	0.37
30-34	0.04	0.05	0.06	0.06	0.28
36-40		0.05	0.04	0.04	0.15
42-46			0.04	0.04	0.11
48-52			0.04	0.04	0.04
54-58			0.04	0.04	0.004
60-64			0.01		
66-70			0.02		

TABLE 6.
Chloride Profiles (%) for 28 Day Cure Exposed to Bath 2.

Depth (*mm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0-4	0.82	1.26	1.47	1.91	1.93
6-10	0.41	0.63	0.72	0.88	0.96
12-16	0.30	0.39	0.52	0.65	0.81
18-22	0.13	0.24	0.43	0.47	0.54
24-28	0.06	0.12	0.29	0.40	0.35
30-34	0.04	0.08	0.15	0.38	0.23
36-40		0.07	0.07	0.32	0.14
42-46			0.04	0.17	0.06
48-52				0.08	0.005
54-58				0.07	0.005
60-64				0.07	
66-70				0.07	
72-76				0.07	

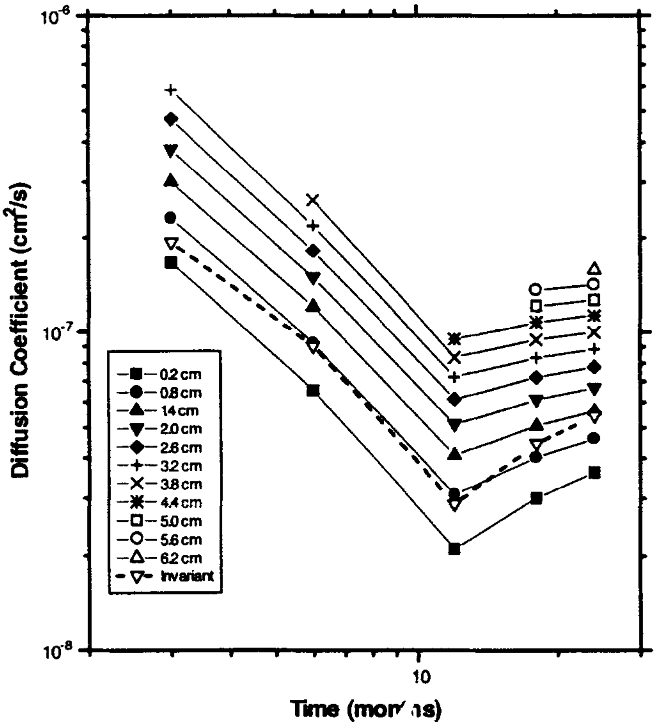

FIGURE 1.
Cured for Three Days and Exposed to Bath 1.

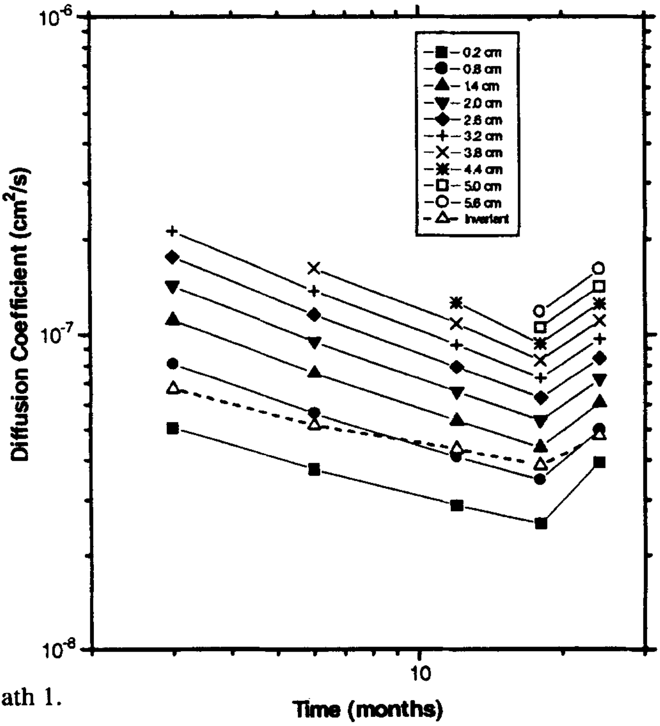

FIGURE 2.
Cured for 28 Days and Exposed to Bath 1.

TABLE 7.
Chloride Diffusion Coefficients for 3 Day Cure Exposed to Bath 1.

	Diffusion Coefficient (cm^2/s)				
Depth (*cm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0.2	$1.6582\text{x}10^{-7}$	$6.5478\text{x}10^{-8}$	$2.0891\text{x}10^{-8}$	$3.0062\text{x}10^{-8}$	$3.6184\text{x}10^{-8}$
0.8	$2.3027\text{x}10^{-7}$	$9.2123\text{x}10^{-8}$	$3.0882\text{x}10^{-8}$	$4.0294\text{x}10^{-8}$	$4.6193\text{x}10^{-8}$
1.4	$3.0022\text{x}10^{-7}$	$1.1986\text{x}10^{-7}$	$4.0921\text{x}10^{-8}$	$5.0651\text{x}10^{-8}$	$5.6382\text{x}10^{-8}$
2.0	$3.7863\text{x}10^{-7}$	$1.4935\text{x}10^{-7}$	$5.1063\text{x}10^{-8}$	$6.1171\text{x}10^{-8}$	$6.6787\text{x}10^{-8}$
2.6	$4.7002\text{x}10^{-7}$	$1.8162\text{x}10^{-7}$	$6.1350\text{x}10^{-8}$	$7.1947\text{x}10^{-8}$	$7.7525\text{x}10^{-8}$
3.2	$5.8128\text{x}10^{-7}$	$2.1832\text{x}10^{-7}$	$7.1953\text{x}10^{-8}$	$8.3053\text{x}10^{-8}$	$8.8487\text{x}10^{-8}$
3.8		$2.6213\text{x}10^{-7}$	$8.3102\text{x}10^{-8}$	$9.4758\text{x}10^{-8}$	$1.0008\text{x}10^{-7}$
4.4			$9.5202\text{x}10^{-8}$	$1.0720\text{x}10^{-7}$	$1.1265\text{x}10^{-7}$
5.0				$1.2079\text{x}10^{-7}$	$1.2618\text{x}10^{-7}$
5.6				$1.3606\text{x}10^{-7}$	$1.4101\text{x}10^{-7}$
6.2					$1.5781\text{x}10^{-7}$
Invariant	$1.9273\text{x}10^{-7}$	$9.0158\text{x}10^{-8}$	$2.8806\text{x}10^{-8}$	$4.4463\text{x}10^{-8}$	$5.4479\text{x}10^{-8}$

TABLE 8.
Chloride Diffusion Coefficients for 28 Day Cure Exposed to Bath 1.

	Diffusion Coefficient (cm^2/s)				
Depth (*cm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0.2	$5.0573\text{x}10^{-8}$	$3.7352\text{x}10^{-8}$	$2.8796\text{x}10^{-8}$	$2.5257\text{x}10^{-8}$	$3.9138\text{x}10^{-8}$
0.8	$8.0720\text{x}10^{-8}$	$5.6224\text{x}10^{-8}$	$4.0866\text{x}10^{-8}$	$3.4518\text{x}10^{-8}$	$4.9785\text{x}10^{-9}$
1.4	$1.1123\text{x}10^{-7}$	$7.5335\text{x}10^{-8}$	$5.3129\text{x}10^{-8}$	$4.3843\text{x}10^{-8}$	$6.0724\text{x}10^{-8}$
2.0	$1.4253\text{x}10^{-7}$	$9.4896\text{x}10^{-8}$	$6.5713\text{x}10^{-8}$	$5.3263\text{x}10^{-8}$	$7.2057\text{x}10^{-8}$
2.6	$1.7556\text{x}10^{-7}$	$1.1529\text{x}10^{-7}$	$7.8814\text{x}10^{-8}$	$6.2829\text{x}10^{-8}$	$8.3917\text{x}10^{-8}$
3.2	$2.1230\text{x}10^{-7}$	$1.3722\text{x}10^{-7}$	$9.2772\text{x}10^{-8}$	$7.2618\text{x}10^{-8}$	$9.6491\text{x}10^{-8}$
3.8		$1.6209\text{x}10^{-7}$	$1.0811\text{x}10^{-7}$	$8.2746\text{x}10^{-8}$	$1.1002\text{x}10^{-7}$
4.4			$1.2574\text{x}10^{-7}$	$9.3395\text{x}10^{-8}$	$1.2483\text{x}10^{-7}$
5.0				$1.0484\text{x}10^{-7}$	$1.4136\text{x}10^{-7}$
5.6				$1.1748\text{x}10^{-7}$	$1.6021\text{x}10^{-7}$
Invariant	$6.7270\text{x}10^{-8}$	$5.1565\text{x}10^{-8}$	$4.3331\text{x}10^{-8}$	$3.8309\text{x}10^{-8}$	$4.7752\text{x}10^{-8}$

TABLE 9.
Chloride Diffusion Coefficients for 3 Day Cure Exposed to Bath 2.

	Diffusion Coefficient (cm^2/s)				
Depth (*cm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0.2	$4.0663\text{x}10^{-8}$	$4.2274\text{x}10^{-8}$	$3.7974\text{x}10^{-8}$	$2.5524\text{x}10^{-8}$	$3.1144\text{x}10^{-8}$
0.8	$6.7022\text{x}10^{-8}$	$6.2613\text{x}10^{-8}$	$5.1779\text{x}10^{-8}$	$3.4842\text{x}10^{-8}$	$4.0426\text{x}10^{-8}$
1.4	$9.3416\text{x}10^{-8}$	$8.3327\text{x}10^{-8}$	$6.5588\text{x}10^{-8}$	$4.4224\text{x}10^{-8}$	$4.9899\text{x}10^{-8}$
2.0	$1.1989\text{x}10^{-7}$	$1.0471\text{x}10^{-7}$	$7.9406\text{x}10^{-8}$	$5.3707\text{x}10^{-8}$	$5.9638\text{x}10^{-8}$
2.6	$1.4657\text{x}10^{-7}$	$1.2730\text{x}10^{-7}$	$9.3236\text{x}10^{-8}$	$6.3340\text{x}10^{-8}$	$6.9743\text{x}10^{-8}$
3.2	$1.7371\text{x}10^{-7}$	$1.5205\text{x}10^{-7}$	$1.0709\text{x}10^{-7}$	$7.3206\text{x}10^{-8}$	$8.0361\text{x}10^{-8}$
3.8		$1.8067\text{x}10^{-7}$	$1.2097\text{x}10^{-7}$	$8.3422\text{x}10^{-8}$	$9.1691\text{x}10^{-8}$
4.4			$1.3489\text{x}10^{-7}$	$9.4172\text{x}10^{-8}$	$1.0401\text{x}10^{-7}$
5.0			$1.4888\text{x}10^{-7}$	$1.0573\text{x}10^{-7}$	$1.1771\text{x}10^{-7}$
5.6			$1.6297\text{x}10^{-7}$	$1.1853\text{x}10^{-7}$	$1.3307\text{x}10^{-7}$
Invariant	$5.1689\text{x}10^{-8}$	$5.7836\text{x}10^{-8}$	$5.4099\text{x}10^{-8}$	$3.6047\text{x}10^{-8}$	$4.7065\text{x}10^{-8}$

TABLE 10.
Chloride Diffusion Coefficients for 28 Day Cure Exposed to Bath 2.

	Diffusion Coefficient (cm^2/s)				
Depth (*cm*)	3 Months	6 Months	12 Months	18 Months	24 Months
0.2	$8.3829x10^{-8}$	$4.1342x10^{-8}$	$3.1224x10^{-8}$	$2.6118x10^{-8}$	$1.6667x10^{-8}$
0.8	$1.2525x10^{-7}$	$6.1408x10^{-8}$	$4.3892x10^{-8}$	$3.5467x10^{-8}$	$2.3125x10^{-8}$
1.4	$1.6855x10^{-7}$	$8.1823x10^{-8}$	$5.6804x10^{-8}$	$4.4811x10^{-8}$	$2.9610x10^{-8}$
2.0	$2.1526x10^{-7}$	$1.0287x10^{-7}$	$7.0109x10^{-8}$	$5.4150x10^{-8}$	$3.6136x10^{-8}$
2.6	$2.6814x10^{-7}$	$1.2504x10^{-7}$	$8.4044x10^{-8}$	$6.3478x10^{-8}$	$4.2726x10^{-8}$
3.2	$3.3217x10^{-7}$	$1.4927x10^{-7}$	$9.8988x10^{-8}$	$7.2791x10^{-8}$	$4.9420x10^{-8}$
3.8		$1.7718x10^{-7}$	$1.1555x10^{-7}$	$8.2083x10^{-8}$	$5.6273x10^{-8}$
4.4			$1.3470x10^{-7}$	$9.1340x10^{-8}$	$6.3379x10^{-8}$
5.0				$1.0055x10^{-7}$	$7.0879x10^{-8}$
5.6				$1.0967x10^{-7}$	$7.8995x10^{-8}$
Invariant	$1.1490x10^{-7}$	$5.7027x10^{-8}$	$4.7352x10^{-8}$	$4.0926x10^{-8}$	$2.5788x10^{-8}$

surface layers with the consequent large variation in chloride diffusion coefficients from the surface layer to the bulk. At longer exposure times, the interior of the concrete sample experiences the same phenomenon and there is less variation of the chloride diffusion coefficients across the sample. It has been suggested that the initial formation of $Mg(OH)_2$, prior to the onset of cracking, can decrease the permeability of concrete (10). The presence of Mg^{2+} in the baths would indicate that such a mechanism is possible.

For exposure to Bath 1, the smaller values of the chloride diffusion coefficients at longer

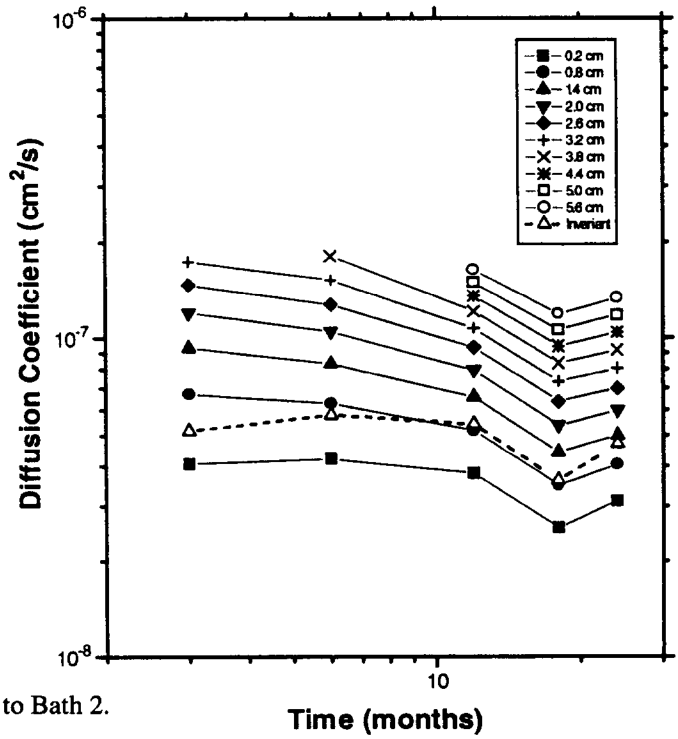

FIGURE 3.
Cured for Three Days and Exposed to Bath 2.

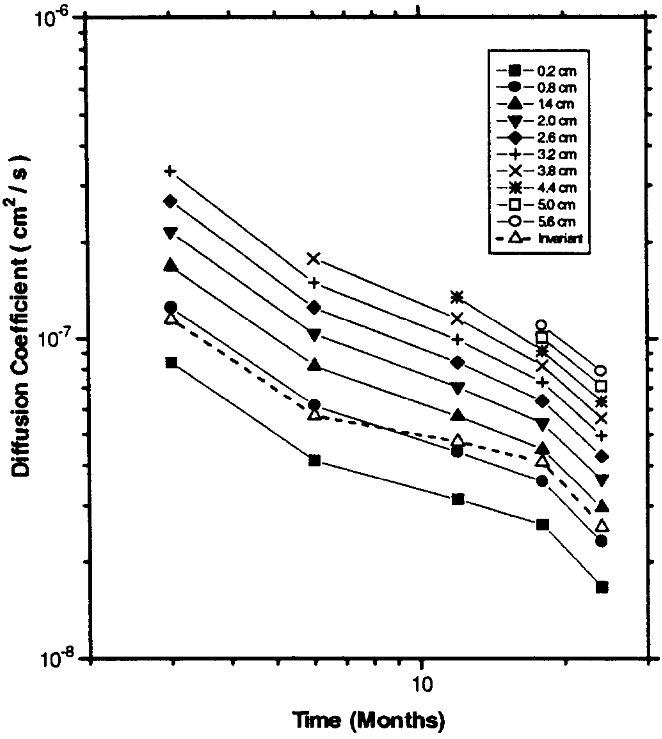

FIGURE 4.
Cured for 28 Days and Exposed to Bath 2.

curing times is indicative of a less permeable concrete in agreement with general principles of cement hydration. In contrast, for the more concentrated Mg^{2+} Bath 2, the data indicate that the influence of curing is not as significant on the chloride diffusion coefficient. But, chloride penetration depths were always less than the 3 day cured concrete.

Except for concrete cured for 28 days and exposed to Bath 2, all chloride diffusion coefficients had a peculiar time dependence. Initially, chloride diffusion coefficients decreased with time. Then, following 12 to 18 months exposure, the chloride diffusion coefficients increase with exposure time. There are two possibilities to explain this behavior: either the precipitated insoluble $Mg(OH)_2$ has caused a sufficient number of microcracks which has allowed chloride to penetrate more quickly, or a sufficient amount of $Ca(OH)_2$ has been leached which renders the concrete more porous. The concrete cured for 28 days and exposed to Bath 2 will continue to be monitored. It is anticipated that the behavior described above will manifest with the next several months. In any case, any prediction of a service life based on chloride diffusion coefficients determined at the earlier times would seriously overestimate the time required for the chloride to penetrate to the depth of the reinforcing steel. The time dependence of the chloride diffusion coefficients proposed previously (6) is not obeyed in this work. This work represents true diffusion measurements in the fully saturated condition, whereas the previous workers (5,6) exposed samples to the cyclic conditions of the tides where imbition of the chloride may compromise their diffusion calculations. The chloride diffusion coefficients in this investigation have been plotted against the Boltzmann variable. Figure 5 is an example plot for concrete cured

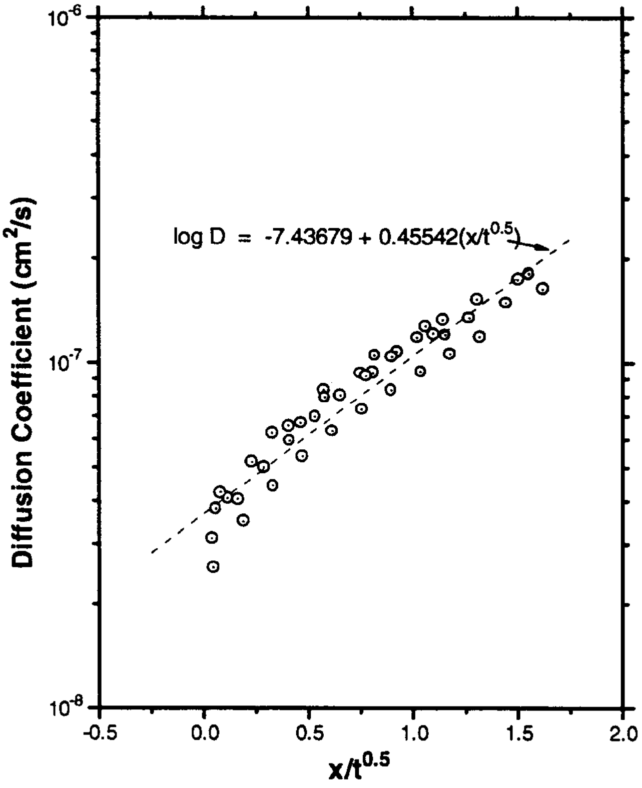

FIGURE 5.
Chloride Diffusion Coefficient Versus the Boltzmann Variable for Three Day Cured Concrete Exposed to Bath 2.

for 3 days and exposed to Bath 2. It can be seen that the chloride diffusion coefficients are well represented by the indicated least squares lines. In all cases, all data fell to within ±10% of the least squares lines. The results have been summarized in Table 11. Therefore, it is possible to calculate the chloride diffusion coefficient at any time and any depth using the equations described in Table 11.

The composition independent chloride diffusion coefficients calculated with Eq.[2] have also been included in Tables 7 to 10 and Figures 1 to 4. These values are comparable to those

TABLE 11.
Chloride Diffusion Coefficients as a Function of the Boltzmann Constant
(x=cm, t=months)

	$\log D = A + B \cdot (x / \sqrt{t})$	
System	A	B
Bath 1, 3 day cure	-7.4070	0.5365
Bath 1, 28 day cure	-7.4276	0.4515
Bath 2, 3 day cure	-7.4368	0.4554
Bath 2, 28 day cure	-7.5204	0.5304

values calculated with Eq.[7] for the surface layer. Clearly, any life prediction based on chloride diffusion coefficients calculated with Eq.[2] is questionable.

It should be emphasized that the mathematical development in this paper has been applied to experimental data on acid soluble chlorides in concrete. While it is true that it is the free chloride concentration gradient which is the thermodynamic driving force for diffusion, there is considerable doubt whether the chloride concentration of expressed pore solutions are valid representations of the true free chloride concentration in concrete. The expression of pore solution involves the application of pressure with a consequent temperature increase. Hence, there must be an increase in chloro-complex solubility which will contribute to the chloride concentration of the expressed pore solution. As such, the total acid soluble chloride concentration is a good first approximation to the diffusional concentration gradient.

Conclusions

- The Boltzmann-Matano methodology for the calculation of chloride diffusion coefficients can be applied to concrete systems.
- There is both a time and concentration/depth dependence of the chloride diffusion coefficient.
- The chloride diffusion coefficient can be expressed as linear function of the Boltzmann variable, $x/\sqrt{t}$.
- Values of the non-steady state chloride diffusion coefficient, calculated with the assumption that the values are independent of concentration, are not representative of the bulk concrete. And, lifetime predictions based on these values overestimate the time needed for chloride to diffuse to the level of the reinforcement.

Acknowledgment

The authors are grateful to the Saskatchewan Potash Producer's Association for their assistance and financial support.

References

1. K. Tutti, *Corrosion of Steel in Concrete*, Swedish Cement and Concrete Research Institute, Stockholm (1982).
2. R.D. Browne, *Design Prediction of the Life of Reinforced Concrete in Marine and Other Chloride Environments,* Durability of Building Materials **1**, 113-125 (1982).
3. J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, Chapters 2 and 3 (1983).
4. N.R. Buenfeld and J.B. Newman, *Examination of Three Methods for Studying Ion Diffusion in Cement Pastes, Mortars and Concrete*, Materials and Structures **20**, 3-10 (1987).
5. P.S. Mangat and B.T. Molloy, *Factors Influencing Chloride-Induced Corrosion of Reinforcement in Concrete,* Materials and Structures **25**, 404-411 (1992).

6. P.S. Mangat and B.T. Molloy, *Prediction of Long Term Chloride Concentrations in Concrete*, Materials and Structures **27**, 338-346 (1994).
7. C. Matano, Japan. Phys., 8, 109 (1933).
8. R.J. Gummerson, C. Hall, W.D. Hoff, and R. Hawkes, *Water Flow Within Porous Materials Observed by NMR Imaging*, Nature **281**, 56-57 (1979).
9. W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, *Numerical Recipes in C, The Art of Scientific Computing*, Cambridge University Press, New York (1988).
10. R.F. Feldman and V.S. Ramachandran, New *Accelerated Methods for Predicting Durability of Cementitious Materials*, ASTM STP-691, 313-325 (1978).