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A Discussion of the Paper "A BOLTZMANN-MATANO ANALYSIS OF CHLORIDE DIFFUSION" by P.J. Tumidajski, G.W. Chan, R.F. Feldman and G. Strathdee*

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Tumidajski et al have used Boltzmann-Matano modification of Fick's 2nd law to analyze their chloride diffusion data. From this analysis they have concluded that the chloride ion diffusivity depends on time and concentration/depth and is linear function of the Boltzmann variable. The Fick's laws and their variants are valid strictly for non-ionic diffusants and the equations relevant for ionic diffusants are Nernst and Nernst-Planck equations and their variants (1). Using Nernst diffusivity and Kohlrausch conductivity equations the following relationship, between the

$$D_i=D_0-A\sqrt{c}\ldots\ldots\ldots\ldots(1)$$

diffusivity of an ion and its concentration in solution, can easily be drawn (2). This relationship has been found to be valid for previously reported results (3) of NaCl and LiCl diffusion through Na and Li-montmorilonite clay plugs respectively (4). These are cases of pure diffusion as all clay-salt interactions had occurred during the preparations of the Na and Li-montmorilonite samples. The equation 1 shows that the ionic diffusivity increases with decreasing solution concentration. In concrete the corresponding states will be deeper layers. However, the case of concrete is not so simple as chloride ion binding is also occurring whilst diffusion is proceeding. Moreover there is an electrostatic interaction between the cement hydration products and the diffusing ions which Fick's laws and their variants ignore (5). Furthermore neither Boltzmann-Matano equation nor Nernst-Planck equation explains why chloride ion has a higher diffusivity than any alkali ion in the case of a Portland cement paste but not in the case of a blastfurnace slag cement paste or through a granite membrane.

Beside the above general comments there are other comments as well. For easy reference and discussion their primary chloride concentrations have been collected in tables 1 and 2. In these

$$C=Ae^{-Bx}\ldots\ldots\ldots\ldots\ldots(.2)$$

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tables the values in () refer to the 28 day fog room cured samples.

Table 1
Chloride Profiles (%) for 3 and 28 Day Cure Exposed to Bath 1.

Depth mm	3 months	6 months	12 months	18 months	24 months
0-4	0.60 (0.99)	1.07 (1.31)	1.43 (1.45)	1.17 (1.38)	1.20 (1.08)
6-10	0.49 (0.34)	0.61 (0.66)	0.72 (0.69)	0.73 (0.76)	0.83 (0.82)
12-16	0.28 (0.26)	0.43 (0.41)	0.46 (0.50)	0.59 (0.62)	0.59 (0.61)
18-22	0.15 (0.15)	0.28 (0.21)	0.21 (0.41)	0.42 (0.43)	0.45 (0.47)
24-28	0.08 (0.07)	0.15 (0.08)	0.21 ((0.24)	0.27 (0.29)	0.44 (0.36)
30-34	0.06 (0.04)	0.11 (0.06)	0.10 (0.15)	0.12 (0.14)	0.32 (0.29)
36-40		0.08 (0.06)	0.05 (0.08)	0.07 (0.07)	0.19 (0.15)
42-46			0.05 (0.04)	0.06 (0.06)	0.11 (0.10)
48-52				0.05 (0.05)	0.06 (0.07)
54-58				0.01 (0.01)	0.05 (0.06)
60-64					0.05

1) The logical difficulty of applying Boltzmann-Matano to ionic diffusion is similar to that of the error function fitting. Boltzmann-Matano function, being a backward fitting function (see equation 7 of the original), requires a preliminary data smoothing so as to avoid errors in the tail end of the concentration profile being propagated to the high concentration side. The authors have used an exponential equation (the equation 8 of the original paper) to smooth their data. From the text it is not clear what had actually been done. If they have smoothed their data column by column then there is a misprint in their equation 8. The equation should read as in the equation 2 where A and B are constants as in their equation 8. This formulation is consistent with each column of the primary results i.e chloride concentration increases as depth decreases. (There are other similar misprints in the paper e.g. 12 months and 18 months chloride concentrations for 3 day cured sample in the Bath 2 are identical. These misprints are obvious to data analysts and do not cause any problem). The constancy of B in the equation 2 (or in their equation 8) in itself assumes a constancy in the rate of chloride penetration into concrete whereas the authors' Boltzmann-Matano analyses show that the diffusivity is concentration/depth dependent. Thus there is an

internal logical contradiction in the mathematical processing of the data. In other words logically B has to be concentration/depth dependent. In that case the situation is back to the stage of the equation 3 of the original paper with all that involves.

Table 2
Chloride Profiles (%) for 3 and 28 Day Cure Exposed to Bath 2.

Depths (mm)	3 months	6 months	12 months	18 months	24 months
0-4	1.18 (0.82)	1.05 (1.26)	0.94 (1.47)	0.94 (1.91)	1.21 (1.93)
6-10	0.43 (0.41)	0.59 (0.63)	0.67 (0.72)	0.67 (0.88)	0.73 (0.96)
12-16	0.23 (0.30)	0.35 (0.39)	0.47 (0.52)	0.47 (0.65)	0.59 (0.81)
18-22	0.12 (0.13)	0.17 (0.24)	0.29 (0.43)	0.29 (0.47)	0.46 (0.54)
24-28	0.06 (0.06)	0.08 (0.12)	0.15 (0.29)	0.15 (0.40)	0.37 (0.35)
30-34	0.04 (0.04)	0.05 (0.08)	0.06 (0.15)	0.06 (0.38)	0.28 (0.23)
36-40		0.05 (0.07)	0.04 (0.07)	0.04 (0.32)	0.15 (0.14)
42-46			0.04 (0.04)	0.04 (0.17)	0.11 (0.06)
48-52			0.04	0.04 (0.08)	0.04 (0.005)
54-58			0.04	0.04 (0.07)	0.004 (0.005)
60-64			0.01	--- (0.07)	

The error function can also be used in a step-wise fashion ; in that case it shows variations in the diffusivity with depth (6). However both increasing and decreasing diffusivity with depth have been observed depending on the nature and history of the samples.

2) Concentrations in the tables 1 and 2 give an impression that they could be linearly related to depths. Linear regression analyses show that after 24 months exposure 3 and 28 day cured samples in bath 1 and 3 day cured sample in bath 2 have correlation coefficients of about 0.94 and for the 28 day cured sample in bath 2 it is 0.88. These correlation coefficients indicate a high degree of linearity. This is most probably due to the averaging over 4 mm thick samples. This is further substantiated by an error function fitting to all 24 months exposed samples. In each case C_0 value comes very close to the average value of 0-4 mm section i.e. these C_0 are not the real C_0 values of the samples which should be much higher than the average values of 0-4 mm sections. In the error

function C_0 plays a very important part. Thus the reported concentrations are not suitable for any error function fitting. One would expect that a backward fitting function like the Boltzmann-Matano will be more susceptible to this averaging artefact.

A careful examination of tables 1 and 2 shows that for each bath the chloride concentration at each depth, with the exception of 0-4 mm depth, is essentially independent of the initial curing period. This is particularly so in prisms stored in bath 1 which is essentially a mixed alkali chloride solution. Even in 0-4 mm slice a longer curing 28 days mostly increased the chloride concentrations compared to 3 day curing. This is a rather unusual observation and runs against a generally held view that a longer curing is essential for a better reinforcements protection. The authors' comment on this point will be useful.

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