Effect of temperature on transport of chloride ions in concrete

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ABSTRACT: Chloride-induced corrosion is the major durability issue of reinforced concrete structures along seacoast and in cold areas where de-icing salts are used. Various service life prediction models based on chloride induced corrosion have been developed. Temperature plays an important role in modeling chloride transport in cement-based materials. However, it is often overlooked. In this paper, the effect of temperature on non-steady-state migration and diffusion coefficients of chloride ion in concrete with water-to-cement ratios of 0.35, 0.48 and 0.6 were investigated. Non-steady-state migration coefficient was measured at 20°C and 5°C following NT build 492. Non-steady-state diffusion coefficient was measured at 5°C, 20°C and 40°C according to NT build 443. The effect of temperature on migration/diffusion coefficient is examined by using Arrhenius Equation. The results show that higher temperatures result in higher diffusion/migration coefficients. Temperatures alter the chloride penetration depth, but not the trend of chloride profile. The activation energy obtained from non-steady-state migration coefficient is quite comparable to Samson and Marchand's results (Cement and Concrete Research, V37, 2007, 455–468), which is around 20 kJ/mol, and independent of water-to-cement ratio. However, the activation energy obtained from non-steady-state diffusion tests ranges from 17.9 to 39.9 kJ/mol, which seems dependent on water-to-cement ratio. The surface chloride concentration is also affected by water-to-cement ratio and temperature.

1 INTRODUCTION

Chloride-induced corrosion is the major durability issue of reinforced concrete structures along seacoast and in cold areas where de-icing salts are used. Various service life prediction models (Anna 1993, Mangat 1994, Magne 1996, Tang 1996, Xi 1999, Samson 2007) based on chloride induced corrosion have been developed. In Maage's and Mangat's models, the chloride profiles were obtained from existing buildings, which were fitted to Fick's second law's error function solution. Two parameters were obtained from the profile fitting, i.e. the apparent diffusion coefficient and the surface chloride concentration. The time dependency of diffusion coefficient was also taken into account. Very recently, Tang (2007) pointed out that Maage's and Mangat's models were oversimplified. Actually, all the environmental factors in their models, such as temperature, the exposure chloride concentration, chloride binding and humidity etc., are lumped in the apparent coefficient and the surface chloride concentration. The model is practical for the service life prediction of existing buildings, but not suitable for new buildings. In the Duracrete model, a curing factor and an environmental factor were introduced to a similar equation to Maage's model. The migration coefficient obtained from NT build 492 was employed in the model. However, models based on the actual physical or chemical/electrochemical processes would be better than those based on simple Fick's second law (Tang 2007).

In the physical/chemical-based model, the effect of temperature on the chloride diffusivity was taken into account, which was often expressed by Arrhenius law (Anna 1993, Tang 1996, Xi 1999):

$$D_2 = D_1 e^{\left(\frac{Ea(T_2 - T_1)}{RT_2 T_1}\right)} \tag{1}$$

where D_1 and D_2 are the diffusion coefficients at T_1 and T_2; E_a is the activation energy of chloride transport in concrete, R is the gas constant. Only few data on activation energy are available.

In (Goto 1981, Page 1981, Atkinson 1983), steady state diffusion tests were used to measure the activation energy of cement paste. Goto (1981) obtained an activation energy of 50.2 kJ/mol for paste with a water-to-cement ratio of 0.4. Page (1981) found that the activation energy was dependent on water-to-cement ratio, 41.8 kJ/mol for paste with water-to-cement ratio of 0.4, 44.6 kJ/mol for paste with water-to-cement ratio of 0.5, and 32 kJ/mol for paste with water-to-cement ratio of 0.6. Collepardi (1972) and McGrath (1996) determined non-steady-state diffusion coefficients at different temperatures. Collepardi obtained an activation energy of 35.6 kJ/mol for paste with water-to-cement ratio of 0.4, and McGrath obtained 32.8 kJ/mol for paste with water-to-cement ratio of 0.3. Samson (2007) obtained migration coefficients by regularly measuring current passing through sample over a 200-hour period at 4, 23 and 40°C respectively. The migration coefficients were used to fit the following relationship:

$$D = D^{ref}e^{\partial(T-T^{ref})} \tag{2}$$

where ∂ is the constant, which was found to be independent on water-to-cement ratio and cement type.

As can be seen, there is a variation in the published activation energy, and most activation energies were obtained from cement paste, not concrete. Different methods used to measure diffusion coefficients might be partly responsible for the variation. Normally, diffusion tests are regarded as reference testing method, but need a long testing duration. Electrical fields are widely used to shorten the duration. Several studies (Andrade 2000, Tang 2007) have been carried out on the relationship between diffusion coefficients and migration coefficients. However, no report was found on studying the difference between the effect of temperature on migration and diffusion coefficients. Temperature affects the transport of chloride ions in concrete in two aspects. On one hand, the movement of chloride ions can be accelerated by increasing the temperature, or slowed down by decreasing the temperature; On the other hand, the reaction between chloride and cement hydration products can be influenced by temperature. Chloride ions can exist in concrete in three forms: chemically bound to cement hydration products, physically bound to C-S-H and free chloride. These three types of chloride are in a dynamic equilibrium. The equilibrium can be influenced by temperature. Zibara (2001) found that at a low chloride concentration (0.1 M, 1.0 M), an increased temperature resulted in a decreased binding; while at high chloride concentration (3.0 M), an increased temperature results in an increased binding. Larsson (1995) and Roberts (1962) found that the amount of bound chloride decreased as temperature increases. Theoretically, the movement of free chloride ions and the chemical reaction between chloride ions and Al-bearing phase are accelerated by increasing temperature. However, it also may increase the solubility of the reaction products (Friedel's salt), resulting in more reactants free at the equilibrium. For a physical adsorption, an elevated temperature increases the thermal vibration of absorbates, resulting in more unbound chloride. In the case of diffusion, chemical gradient is the driving force, while electrical field is the main driving force in the case of migration. The effect of temperature on the driving forces, as well as chloride binding, might be different. Thus, the effect of temperature on the chloride diffusion and migration in concrete might be different.

The surface chloride concentration is an important parameter for the service life prediction of reinforced concrete structures subjected to chloride environment, which is not a measured value of the chloride concentration at the surface, but a value obtained from non-linear regression analysis. The surface chloride concentration is time dependent; several empirical equations have been proposed to describe the time dependency of surface chloride concentrations (Amey 1998, Kassir 2002). However, few studies were found on the effect of temperature on the surface chloride concentration.

The purpose of this paper is to investigate the difference between the effect of temperature on migration/diffusion coefficient, and the effect of temperature and water-to-cement ratio on the surface chloride concentration.

2 EXPERIMENTAL

An ordinary Portland cement (CEM I 52.5 N), complying with EN 197-1 (2000), was used in this study. Its chemical composition is shown in Table 1. The fine aggregate has a size range of 1–4 mm. The gravel with a size range of 5–16 mm was used as the coarse aggregate. Dry ingredients were first added to a 200 L capacity flat pan mixer and mixed for 1 min. Water and water reducing admixture (if needed) were then added into the mixer and mixed for 2 min. After mixing, the concrete was cast in molds, and a rod was used to consolidate the concrete mixture. The specimens

Table 1. Chemical compositions of cement.

CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3	SO_3	Loss on Ignition
62.21	19.12	3.79	0.86	5.39	3.06	1.65
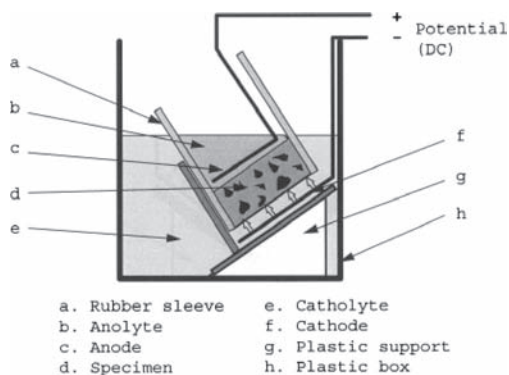
Figure 1. Testing setup of NT build 492.

a. Rubber sleeve   e. Catholyte
b. Anolyte   f. Cathode
c. Anode   g. Plastic support
d. Specimen   h. Plastic box

Table 2. Details of concrete mixes.

Mix	Mix proportions (kg/m³)		
	B6	B48	B35
Water	218	182	140
Cement	363	380	400
Gravel	1162	1217	1281
Sand	559	627	660
Water reducer	–	–	0.94%
	Properties of concrete		
Slump (mm)	250	172	200
Density (kg/m³)	2478	2487	2481
Air content	1.2%	1.1%	0.6%
Strength at 56 d (MPa)	37.8	46.7	81.7
Porosity accessible to water (% by volume)	15%	14.1%	10.2%

were demolded after 24 hours, and then cured in a standard curing chamber for 13 days. Specimens with the dimensions of $150 \times 150 \times 150$ mm were cast for compressive strength. Five cores were drilled from prismatic specimens ($150 \times 150 \times 600$ mm) at the age of 14 days. The central portions of cylindrical cores ($\Phi100$ mm $\times 50$ mm) were cut for chloride diffusion or migration tests. Labeled the surface nearer to the cast surface, which is the one exposed to the chloride solution.

Before migration and diffusion tests, all the specimens were vacuum-saturated with saturated calcium hydroxide solution following the procedure described in NT build 492. The testing setup is shown in Figure 1. The details of the concrete are shown in Table 2.

The migration and diffusion tests were carried out on concrete at the age of 56 days. Migration tests were performed at 5°C and 20°C according to NT build 492, in which an electrical field is applied through the specimen to accelerate chloride transport in concrete. After the migration test, the specimens were split into two parts, and then the penetration depth of chloride was measured by spraying 0.1 M silver nitrate solution. The migration coefficient of chloride ion can be calculated by (NT build 492, 1999):

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t}\left(x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{U-2}}\right) \quad (3)$$

where x_d is the average chloride ion penetration depth (mm), which is measured by the spraying silver nitrate solution method; D_{nssm} is the non-steady-state migration coefficient ($\times10^{-12}$ m²/s); U is the absolute value of the applied voltage (V); T is the average of the initial and final temperatures in the anolyte solution (°C); L is the thickness of the specimen (mm); and t is the test duration (hour).

Diffusion tests were conducted at 5, 20 and 40°C by following NT build 443. The sample grinding after the diffusion test was performed by Profile Grinder 1100. The grinding area is 73 mm in diameter. Exact depth increments are adjustable, between 0.5 mm and 2.0 mm. The depth increments are accurate within 2% and the variation is less than 1%. The produced powder was collected with a small vacuum cleaner. For every depth increment of 0.5 mm approximately 5 grams of powder is obtained for analysis. Nitric acid soluble chloride was determined as total chloride content. Since salt may precipitate on the concrete surface, the first layer was omitted. 6 to 8 points were used for regression analysis. The values of C_s and D_{app} are determined by fitting the chloride profile to the error function solution of Fick's second law by means of a non-linear regression analysis in accordance with the method of least squares fit.

$$C = C_S - C_S \cdot \text{erf}(x / \sqrt{4D_{app}t}) \quad (4)$$

where C(x,t) is the chloride concentration measured at the depth x at the exposure time t (mass %); C_s is the surface chloride concentration (mass %); x is the depth below the exposed surface (m) (to the middle of a layer); D_{app} is non-steady-state diffusion coefficient (m²/s); t is the exposure time (s); and erf is error function.

3 RESULTS AND DISCUSSION

3.1 *Migration/diffusion coefficients*

The results of the migration tests are given in Table 3. The results show that a higher temperature results in a higher migration coefficient. The migration coefficients

measured at 5χC and 20°C were used to calculate the activation energy of chloride ion transport in concrete according to Equation 1, as shown in Table 3.

A comparison of the chloride profiles at different temperatures is shown in Figure 2. It can be clearly seen that the trend of the chloride profiles don't change with temperature. Only the penetration depth decreased with decreased temperature. The detailed

Table 3. Chloride ion migration coefficient and activation energy.

Mix	Temperature	Migration coefficient ($\times 10^{-12}$ m^2/s)	Activation energy (kJ/mol)
B6	8.5*	14	15.5
	20	18.15	
B48	8	5.98	26.7
	19.5	9.55	
B35	7.5	3.46	24.9
	20.6	5.65	

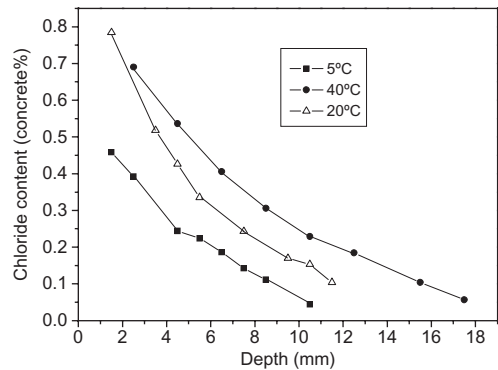*due to the joule effect, the temperature increased slightly.

Figure 2. Chloride profile of concrete at different temperatures.

chloride concentrations at different depths are given in Tables 4–6. The diffusion coefficients of chloride ion and the correlation coefficient are given in Table 7. A plot of lnD versus 1/RT was plotted to obtain the activation energy, as shown in Table 7. The activation energy obtained from non-steady-state diffusion tests are 23, 17.9 and 39.9 kJ/mol for concretes with water-to-cement ratios of 0.35, 0.48 and 0.6, respectively, which seem dependent on water-to-cement ratio, and are lower than the published data (Goto 1981, Page 1981, Atkinson 1983, Collepardi 1972, McGrath 1996). It is worth to mention that the previous published data were obtained from cement past, not concrete. Chloride transport in concrete might be different from that in paste due to the inclusion of aggregate and the interface transition zone (ITZ). ITZ is characterized by high porosity and high permeability. For a normal concrete, the mass of aggregate is almost five times as that of cement. Chloride ions only transport in the pore solution of concrete. Temperature only affects the transport of chloride ions in cement paste. Thus, the activation energies obtained from cement paste might be different from those obtained from concrete.

Migration tests were carried out only at two different temperatures, 5°C and 20°C. However, the activation energy obtained from two rapid migration tests ranges from 15.5 to 26.7 kJ/mol, which is very comparable to the data obtained from migration test ranging from 17.9 to 21.2 kJ/mol by Samson and Marchand (2007), which is obtained by regularly measuring current passing through sample over a 200-hour period at 4, 23 and 40°C respectively. The activation energy of chloride ion transport in concrete calculated based on Samson and Marchand's data on type 10 cement are shown in Table 8. The activation energy seems independent of water-to-cement ratio.

The activation energy of chloride ion transport in concrete with various water-to-cement ratios and measured by migration tests were given in Figure 3. Despite of water-to-cement ratio, the activation

Table 4. Chloride profile of mix B6 after exposure to 165 g/l NaCl solution for 42d (% by concrete mass).

5°C			20°C			40°C		
Depth(mm)	1	2	Depth(mm)	1	2	Depth(mm)	1	2
2–3	0.447	0.445	2–3	0.484	0.596	1–2	0.408	0.502
4–5	0.292	0.362	4–5	0.410	0.508	4–5	0.347	0.334
6–7	0.218	0.302	8–9	0.341	0.355	7–8	0.288	0.291
8–9	0.173	0.199	12–13	0.136	0.200	10–11	0.262	0.273
10–11	0.112	0.138	16–17	0.048	0.087	13–14	0.230	0.252
12–13	0.059	0.086	18–19	0.015	0.042	16–17	0.167	0.195
14–15	0.029	0.036	20–21	0.009	0.014	19–20	0.130	0.158
			21–22	0.011	0.010	21–22	0.127	0.153

energy is very close to 20 kJ/mol, which is different from the results obtained from diffusion tests. This probably means that the effect of temperature on the diffusion process and the migration process is different and need further investigation.

3.2 *Surface chloride concentration*

The surface concentrations obtained from diffusion tests are shown in Table 7, which were obtained from non-linear regression analysis. For a given temperature, the chloride surface concentration seems

Table 5. Chloride profile of mix B48 after exposure to 165 g/l NaCl solution for 42d (% by concrete mass).

5°C			20°C			40°C		
Depth(mm)	1	2	Depth(mm)	1	2	Depth(mm)	1	2
1–2	0.490	0.458	1–2	0.784	0.751	2–3	0.690	0.554
2–3	0.401	0.392	3–4	0.518	0.564	4–5	0.536	0.482
4–5	0.278	0.244	4–5	0.426	0.432	6–7	0.405	0.375
5–6	0.206	0.224	5–6	0.335	0.355	8–9	0.306	0.279
6–7	0.164	0.186	7–8	0.243	0.217	10–11	0.229	0.206
7–8	0.136	0.142	9–10	0.170	0.122	12–13	0.184	0.135
8–9	0.108	0.111	10–11	0.153	0.099	15–16	0.104	0.066
10–11		0.044	11–12	0.104	0.066	17–18	0.057	0.034

Table 6. Chloride profile of mix B35 after exposure to 165 g/l NaCl solution for 42d (% by concrete mass).

5°C		20°C			40°C	
Depth(mm)	1	Depth(mm)	1	2	Depth(mm)	1
0.5–1	0.320	0.5–1	0.277	0.341	0.5–1	0.397
1–1.5	0.312	1–1.5	0.242	0.298	1–1.5	0.358
1.5–2	0.276	1.5–2	0.199	0.288	1.5–2	0.338
2–2.5	0.218	2.5–3.5	0.204	0.251	2.5–3	0.286
2.5–3	0.197	3.5–4	0.183	0.216	3–3.5	0.272
3–3.5	0.171	4–4.5	0.170	0.188	4–4.5	0.228
3.5–4	0.131	4.5–5	0.135	0.188	4.5–5	0.218
4–4.5	0.121	5–5.5	0.107	0.152	5–5.5	0.207

Table 7. Diffusion coefficient, surface concentration and activation energy of chloride transport in concrete.

Mix	Condition	Apparent diffusion coefficient ($\times 10^{-12}$ m²/s)		Chloride surface concentration (% concrete)	Correlation coefficient	Activation energy (kJ/mol)
B6	40°C	55.3	54.8	0.43	0.989	39.9
			55.8	0.467	0.900	
	20°C	13.24	13.56	0.75	0.991	
			12.92	0.62	0.966	
	5°C	8.2	9.3	0.59	0.984	
			7.11	0.57	0.987	
B48	40°C	12.8	12.7	0.85	0.996	17.9
			12.9	0.72	0.994	
	20°C	8.13	8.13	0.77	0.987	
	5°C	5.38	5.05	0.60	0.996	
			5.7	0.56	0.992	
B35	40°C	7.22	7.22	0.42	0.988	23.0
	20°C	6.35	6.3	0.29	0.900	
			6.4	0.36	0.980	
	5°C	2.31	2.31	0.39	0.980	

Table 8. Activation energy calculated from (Samson 2007).

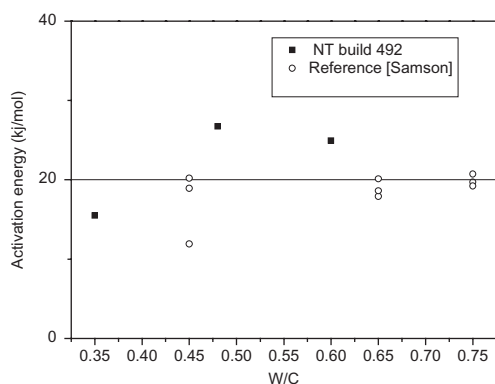| w/c	Age (days)	Activation energy (kJ/mol)
0.45	28	18.9
	91	11.9
	365	20.2
0.65	28	17.9
	91	20.1
	365	18.6
0.75	28	19.7
	91	20.7
	365	19.2

Figure 3. Activation energy of chloride ion transport in concrete with different water-to-cement ratios.

increases with increased water-to-cement ratio. This is partly because that concrete with higher water-to-cement ratio has more pore voids than concrete with low water-to-cement ratio. Free chloride in the pore voids is counted into total chloride. Another possible reason for this is that higher water-to-cement ratio results in higher chloride binding. The surface chloride concentration also shows temperature dependency. Increased temperature seems result in higher surface chloride concentration.

4 CONCLUSIONS

Based on above analysis and experimental results, the following conclusions can be drawn:

1. Higher temperature results in higher diffusion/ migration coefficient. Temperatures alter the chloride penetration depth, but not the trend of chloride profile.
2. The activation energies obtained from migration tests and diffusion tests are different. For the concrete without supplementary cementing materials, the activation energy around 20 kJ/mol was obtained from migration tests, which is independent of water-to-cement ratio. However, the activation energy obtained from diffusion tests seems water-to-cement dependent.
3. Chloride surface concentration obtained from non-linear regression analysis after immersion testing increases with water-to-cement ratio. Increased temperature seems result in higher chloride concentration.

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