

# CHLORIDE TRANSPORT IN CONCRETE EXPOSED TO MARINE ENVIRONMENT

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## ABSTRACT

The purpose of this research is to predict transportation behavior of chloride ions in concrete under marine environment. Marine environment phases are modeled in laboratory and a series of experiments have been performed with different combinations of chloride concentrations, temperature variations, and wetting/drying spell cycle durations. The chloride transport profiles thus generated are compared with analytical results by DuCOM. The experimental and analytic results verify the chloride and moisture surface flux models and their coupling under varying wetting and drying environments.

**Keywords:** Chloride transportation, moisture migration, service life prediction in marine environment.

## 1. INTRODUCTION

Concrete is a forefront heavy construction material parallel to steel, but far excels in bulk use. Perfection of construction in concrete is fraught with inhibited disabilities of concrete of multifarious nature and extent. On top of all porosity/permeability is the most grievous. Thus the ingress of deleterious materials (chlorides and sulphates etc.) is facilitated to troublesome extent. In past, research was mainly done on chloride transport in saturated concrete (completely submerged), where diffusion governs. But in reality concrete surfaces are exposed to wetting and drying environments, where main transportation of chloride is through convection. In this research the chloride movement as a combined affect of diffusion and convection is considered. Four hygral environment conditions in laboratory-controlled climate are designed. The experimental results are compared with the analytical results obtained by the DuCOM model for its verification.

## 2. DUCOM-THERMODYNAMIC DURABILITY SIMULATOR MODEL

In this research DuCOM model is used,

which is the durability computation model developed by Concrete Laboratory-The University of Tokyo, Japan. The originality of this model comes from the fact that DuCOM is a composite multipurpose model, which predicts the state of the concrete from its birth, to its entire life. It comprises several sub-models, which work together and are interlinked. The development of multi-scale micro-pore structures at early age is obtained for average degree of cement hydration in the mixture. For any arbitrary initial and boundary conditions, the vapor pressure in pores, relative humidity (RH), and moisture distribution are mathematically simulated according to a moisture transport model that considers both vapor and liquid phases of mass transport. The moisture distribution, RH, and micro-pore structure characteristics in turn control the  $Cl^{-1}$ ,  $CO_2$  and  $O_2$  diffusion and rate of carbonation under arbitrary environmental conditions. In this study the chloride transport with moisture migration is the primary focal point. [3]. Association map of the whole model is summarized as Fig. 1

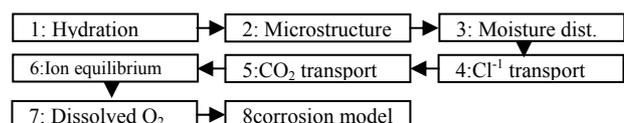


Fig. 1 Basic Frame of DuCom

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## 2.1 Modeling of Chloride Transport

Chloride transport in cementitious materials under usual conditions is an advective-diffusive phenomenon. In modeling, the advective transport due to bulk movement or pore solution phase is considered, as well as ionic diffusion due to concentration gradients. Mass balance for free (moveable) chlorides can be expressed as shown in Eq. 1 [1, 2, 5]

$$\frac{\partial}{\partial t}(\phi SC_{cl}) + \text{div}J_{cl} - Q_{cl} = 0, \quad (1)$$

Where  $(\phi SC_{cl})$  is the potential term, (is the capacity of the system to hold moisture and chloride ions), from which the porosity and saturation is directly obtained by thermo-hygro physics.  $Q_{cl}$  is the sink term for modeling of equilibrium between free and bound chloride, and  $\text{div}J_{cl}$  is the chloride flux term. The relationship between free and bound chlorides under equilibrium conditions is model based on several experiments by Ishida et al [7] by measuring concentration of free chlorides by the extracted pore liquid and bound chlorides by XRD. The model is based on Langmuir equation

$$C_b = 11.8C_f / (1 + 4C_f) \quad (2)$$

Eq. 2 represents the relation between free and bound chlorides for ordinary cement (mass percentage of mineral composition as  $C_3A$ ,  $C_3S$ ,  $C_4AF$ ,  $C_2S$  and mono-sulfate are 8.64%, 49.70%, 9.4%, 23.9%, 3.40% respectively). Where:  $C_b$ : bound chloride concentration (kg Cl/kg cement),  $C_f$ : free chloride concentration (kg Cl/kg cement) [8]

$$J_{cl} = -\frac{\phi S}{\Omega} \delta D_{cl} \nabla C_{cl} + \phi S \cdot u \cdot C_{cl} \quad (3)$$

Eq. 3 represents the flux term. Where:  $J_{cl}$ : chloride flux (mol/m<sup>2</sup>.s),  $\Omega$ : tortuosity (reduction factor in terms of complex micro-pore structure)  $\delta$ : constrictivity (takes the effect of pore radius and density of ions)  $D_{cl}$ : Diffusion coefficient of chloride ion in the pore solution (m<sup>2</sup>/s),  $C_{cl}$ : concentration of chloride ions in the pore solution phase (mol/l),  $u^T = [u_x \ u_y \ u_z]$ : the advective velocity of ions due to the bulk movement of pore solution phase (m/s),  $\phi$ : Porosity of the porous media (m<sup>3</sup>/m<sup>3</sup>).[5]

At the boundary level, the surface flux of chloride ions has been modeled taking into account the diffusion and quasi-adsorption flux (Maruya et-al) [4]. It has been experimentally known that the concentration of chlorides in the concrete near exposure surface is higher than that

of the submerged environment. To simulate this phenomenon, Maruya proposed the condensation model at the surface.

It considers the diffusive movement due to the concentration gradient and the quasi-adsorption phase by electro-magnetic attractive force between the positively charged pore walls and the negatively charged chloride ions. The flux of free chlorides through the boundary surface  $q_{cl}$  (mol/m<sup>2</sup>.s) is described as the summation of the diffusive component  $q_{diff}$  and the contribution of quasi-adsorption  $q_{ads}$ . It is expected that the quasi-adsorption flux will decrease as the free and adsorbed chlorides increases, because the migrating chlorides neutralize positive charges on the pore wall. In this system, the flux of quasi-adsorption is described by the following function, in which the flux decreases as a function of the chlorides in the porous medium.

$$Q_{cl} = q_{diff} + q_{ads} \quad (4)$$

$$q_{diff} = E_{cl}(C_{pore} - C_{cl}) \quad (5)$$

$E_{cl}$  has been given a fixed value of  $1.0 \times 10^{-3}$  m/s based on sensitivity analysis

$$q_{ads} = K_{cl}(C_{cl}/0.51)2exp(-1.15C_{cl}) \quad (6)$$

$C_{cl}$ : Chloride concentration at the exposure surface,  $C_{pore}$ : chloride concentration in the pore. (mol/l). For ordinary Portland cement  $K_{cl} = 1.5 \times 10^{-3}$  m/s

Coefficients in the above equations are determined by experiments using 100% Portland cement. To examine the performance of the chloride surface flux model coupled with moisture transport a comprehensive experimentation series is carried out under laboratory-controlled conditions. In addition to this equation, moisture conductivity in concrete is very important in this regard, since the chloride transportation is dependent on it, as the increase in moisture flux will indirectly affect the diffusion and convection parameters of chloride penetration model.

## 2.2 Moisture Conductivity Process

The moisture transport model for cementitious materials considers the multiphase dynamics of liquid and gas phases. The contributions of the diffusive as well as bulk movements of moisture have been combined in the model. The total porosity of the cementitious material is divided into interlayer, gel and capillary porosity. The moisture model considers the contributions from each of these components from a thermodynamic viewpoint. The macroscopic moisture transport characteristics of flow, such as conductivity are obtained directly from the microstructure of the porous media, and

this is achieved by considering the mass conservation of moisture capacity, conductivity, pore-structure development, and hydration loss.

The moisture capacity is obtained from pore structures, summation of gel, capillary and interlayer. Moisture conductivity comprises of liquid and vapor phases computed from pore structure. Pore structure development is based on cement particle expansion, and average degree of hydration, and lastly moisture loss due to hydration is directly obtained from hydration model of DuCOM. The moisture flux for both vapor and liquid water can generally be expressed as Eq. 7 [3, 2, 5 and 6]

$$J = -(D_p \nabla P_l + D_T \nabla T) \quad (7)$$

Where,  $D_p$ : moisture conductivity (kg/Pa.m.s) with respect to the pore pressure gradient, and  $D_T$ : moisture conductivity (kg/Pa.m.s) with respect to temperature gradient. Capillary and gel pores are idealized as cylindrical pores. Liquid transport in the porous network would be only through the pores which are capillary condensed. Integrating the liquid flux over the complete microstructure using random pore distribution model, the equation of moisture flux was proposed. A general frame work of mass and moisture equilibrium, flux of moisture in liquid and vapor phases, and overall moisture balance of concrete equations have been presented elsewhere in detail by Maekawa & Ishida 2003 [5]

Since convection (transport of chloride ions with moisture flow in concrete) is one of the major causes of chloride transport in wetting and drying marine environments, hence in this research, the emphasis is laid on the moisture surface mass flux, which consists of a moisture emissivity coefficient, and is formulated after experimentation and much sensitivity analysis. A value of  $5 \times 10^{-5}$  is given to this constant. The mathematical equation for moisture surface flux  $E_b$  is given by Eq. 8

$$E_b = 5 \times 10^{-5} (RH_{bound} - RH_{surf}) \quad (8)$$

$RH_{bound}$  = relative humidity of the interior

$RH_{surf}$  = humidity of the surrounding environment.

In the above Eq. 8, the moisture surface mass flux expression is simplified by considering 99.95% RH (fully saturated air environment) as water submergence conditions. The other way to simulate is to apply saturated pore pressure at the surface nodes of the elements. For simplicity, in this paper, the moisture migration results have been obtained from the simplified expression of Eq. 8 [3]

### 3. EXPERIMENT

To verify the chloride surface flux model coupled with moisture surface mass flux model, a comprehensive series of experimentation is conducted.

#### 3.1 Materials and Specimen Preparation

Ordinary Portland cement, regular tap water, coarse sand and a W/C of 50% was provided to all specimens. The mix proportion of cement to sand was kept at 1:2.25. Cement content  $580 \text{ kg/m}^3$ , water  $290 \text{ kg/m}^3$  and sand  $1305 \text{ kg/m}^3$  were used. Specimens consist of cylinders 50mm diameter and 100mm height. Curing was done for 28 days in sealed condition at  $20^\circ\text{C}$ . After curing, the top 10mm slice from the surface of all the specimens was removed to minimize the surface disturbances. Dry cutting was done for Slicing of the specimens. Two levels of salt concentrations 3% ( $0.51 \text{ mol/L}$  of  $\text{Cl}^-$  ions) and 6% ( $1.02 \text{ mol/L}$  of  $\text{Cl}^-$  ions) by mass of water were selected.

For the determination of chloride profiles, specimens were tested after 1 and 7 months exposures by potentiometer titration technique. In this experiment, slicing method was used for the determination of chloride contents. Slicing was done by power driven concrete cutter. Thickness of each slice ( $10 \pm 2 \text{ mm}$ ) was measured and specimen loss due to the blade thickness of the cutter was accounted for in measuring the depth of each slice from the surface. After this, the slices of respective specimens were grounded and tested for the chloride contents according to the relevant ASTM standard C1152/C1152M-04 (for acid soluble chloride). The same information was input in DuCOM which simulates the conditions from hydration, microstructure development, to moisture distribution and chloride transport without any fitting technique.

#### 3.2 Specimen Variables

For each exposure and time duration, same set of temperature and salt concentration is repeated as shown in Table 1

Table 1 Specimen identification table

Environment	Exposure	Temperature	NaCl
Submerged 33hr/9hr/1hr	1 month	$20^\circ\text{C}$ & $40^\circ\text{C}$	3%
	7 months		6%

#### 3.3 Environment Exposure Cycle

After removing the top surface slice, all specimens were exposed to laboratory controlled simulated marine environmental conditions. For

this purpose, four hygral cycles of 3 days recurring duration were designed as shown in Table 2.

Table 2 Environment exposure table

Exposure cycle	Wetting in 3days period (hr)	Drying in 3days period (hr)
Submerged	72	0
33hr wetting	33	39
9hr wetting	9	63
1hr wetting	1	71

#### 4. ANALYTICAL BOUNDARY CONDITION

The boundary conditions in the modeling were simulated as precise as in the experiment. In the modeling, only one surface was exposed to the environment to simulate the sealed specimen with one face exposed. For the initial curing period the moisture flux in and out of the specimen was restricted, whereas the heat flux was allowed during curing and environment exposure conditions. The submerged wetting cycle was modeled by providing 99.95% Relative humidity, and drying environment corresponds to 60% RH.

#### 5. EXPERIMENT RESULTS AND DISCUSSION

Experimental and analytical results of chloride transport profile by DuCOM are presented and compared for verification of the model. Due to space limitation, results for 3% NaCl by weight of water are not shown.

##### 5.1 Chloride Penetration Experiment Results

##### 5.1.1 Submerged case: 1 and 7months exposure

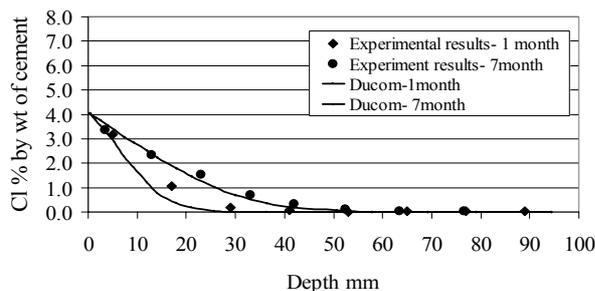


Fig. 2 Results for chloride penetration profiles for 40°C and 6%NaCl- Submerged case

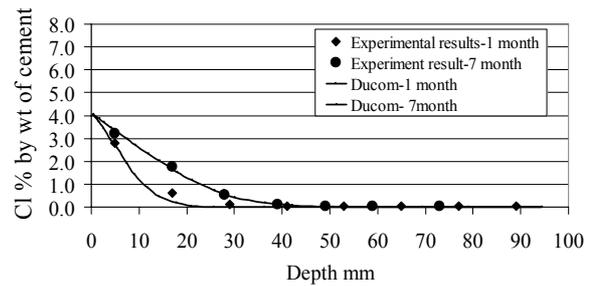


Fig. 3 Results for chloride penetration profiles for 20°C and 6%NaCl- Submerged case

The experiment results show very good agreement with the analytical model results of DuCOM for 20°C and 40°C with 6%NaCl exposure environment as shown in Fig. 2 and 3. The good prediction by the analysis can be seen both for 1month as well as 7months environmental exposures. Since completely submerged case corresponds to the pure diffusion, therefore the validity of model in diffusion-dominated environments is confirmed. Same trend was observed in case of 3% NaCl concentration exposures.

##### 5.1.2 33hr wetting case: 1 and 7months exposure durations

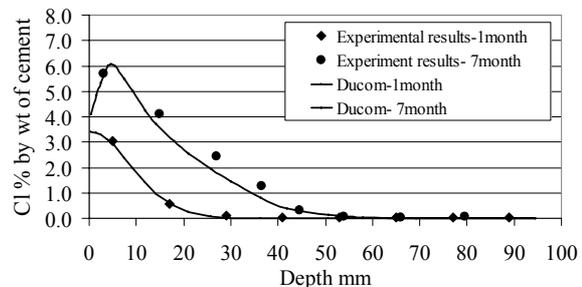


Fig. 4 Results for chloride penetration profiles for 40°C and 6%NaCl- 33hr wetting case

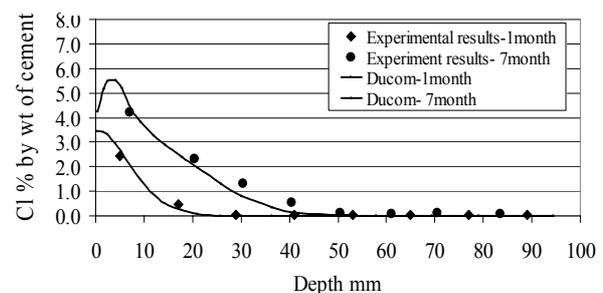


Fig. 5 Results for chloride penetration profiles for 20°C and 6%NaCl- 33hr wetting case

The results of experiment and model in Fig. 4 and 5 are in good agreement like that of submerged zone for 1month and 7month exposures. The same trend was observed for 3%NaCl environment exposures. In this case, the wetting time was nearly equal to that of the drying time, and diffusion and convection phenomenon worked simultaneously for the buildup of chloride ions. A visible peak is formed, which may be due to the simultaneous two-way movement of chloride ions during the drying period. Here the temperature affects become more pronounced as compared to submerged environment, due to the wetting and drying cycle, which generates strong moisture flux, responsible for the convection movements of chloride ions. For 1month testing, the specimens were picked up after the end of drying period; however for 7months exposure time, the specimens were tested after end of wetting cycle. Both of the above mentioned testing conditions were very nicely predicted by the analytical results of DuCOM, which verify the ability of this model to predict under any variable hygral environment.

### 5.1.3 9hr & 1hr wetting case: 1 and 7months exposure durations

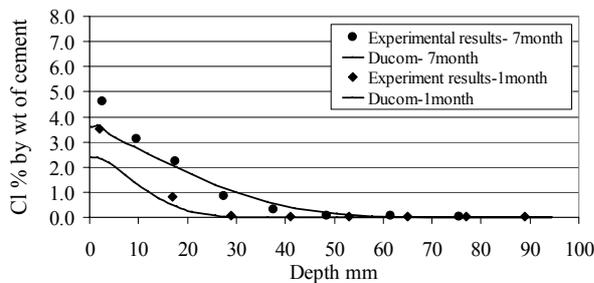


Fig. 6 Results for chloride penetration profiles for 40°C and 6%NaCl- 9hr wetting case

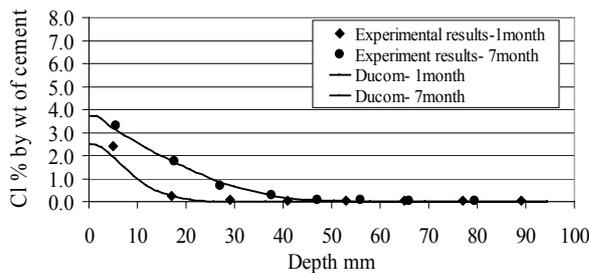


Fig. 7 Results for chloride penetration profiles for 20°C and 6%NaCl- 9hr wetting case

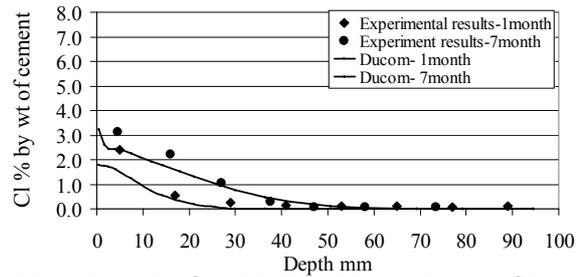


Fig. 8 Results for chloride penetration profiles for 40°C and 6%NaCl- 1hr wetting case

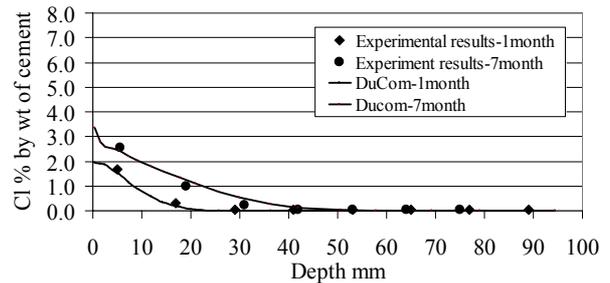


Fig. 9 Results for chloride penetration profiles for 20°C and 6%NaCl- 1hr wetting case

In these cases DuCOM prediction is also in good agreement with the experiment; however for high temperature environments under-estimation is seen near the surface. Here only 6% NaCl results are shown, whereas 3% also follow the same trend. (Fig. 6 to 9). In case of high temperature environment, the surface moisture flux in and out of the specimen is very strong, as shown by the moisture migration results in the succeeding section 5.2; therefore the high surface mass convection flux of moisture drags with it a large amount of chloride ions. However the analytical results do not show this strong temperature affect as seen in the preceding graphs for 33hr wetting. This small under-estimation may be related to the fact that the moisture surface mass flux has been modeled by considering the simplified surface flux Eq. 8, wherein the submergence is simulated by 99.95% RH, instead of the induced saturated pore pressure, at the surface elements at each cycle.

## 5.2 Moisture Migration Experiment Results

Moisture absorption of the specimens was also measured during drying and wetting cycles for 1hr, 9hr and 33hr, and the experimental values were compared with the analytical values computed by DuCOM. Due to space limitation, moisture migration results for 20°C are not shown in this paper.

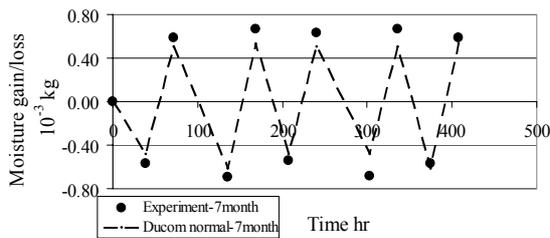


Fig.10 Results for moisture migration 33hr wet 40°C during wetting and drying

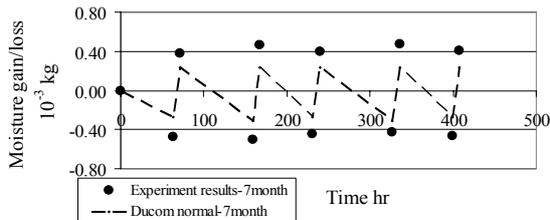


Fig.11 Results for moisture migration 9hr wet 40°C during wetting and drying

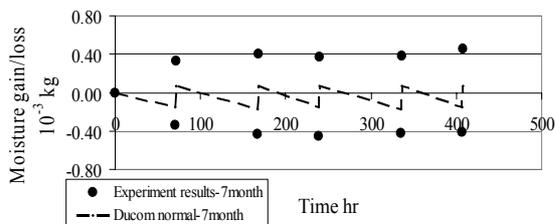


Fig.12 Results for moisture migration 1hr wet 40°C during wetting and drying

The Fig. 10 to 12 corresponds to the moisture surface mass flux movement in and out of the specimen at 40°C temperature. The analytical results for moisture gain/loss were directly obtained in units of kg/m<sup>3</sup> and converted to gm by multiplying it with the actual volume of the specimens used in this experiment. The zero on the y-axis does not correspond to the absolute saturation condition, and is taken as the starting point of drying cycle after 7months exposure. The analytical result for 33hr wetting at 40°C is in good agreement with that of experiment. However for 9hr and 1hr wetting cycles, there is a slight under-estimation between experiment and analytical results. The underestimation of results for 9hr and 1hr wetting cases could be due to the usage of simplified moisture surface mass flux Eq.8 instead of applying saturated pore pressure as explained earlier.

## 6. CONCLUSIONS

The experimental and analytic results verify the DuCOM chloride surface flux model coupled with moisture surface mass flux model under

varying wetting and drying environments. Advective movement of Cl<sup>-1</sup> ions is difficult to study, as pure convection is not easy to obtain, as compared to diffusion. In all the wetting and drying cases the diffusion and convection affects takes place simultaneously and make thing complicated. The chloride distribution is simulated without fitting any model parameter, and by directly coupling the chloride penetration with the moisture migration model, which is based on logical and physical laws of convection and diffusion movements.

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