

# **Influence of Membrane Potential on the Diffusion of Chloride Ion in the Paste**

Y. Elakneswaran, T. Nawa, K. Kurumisawa  
*Graduate School of Engineering, Hokkaido University, Sapporo, Japan*

## **Abstract**

Cement based materials can be regarded as a membrane from an electrochemical point of view, because they contain pore structures that are both variable and interconnected. The transport of ions through paste is affected by the physiochemical properties of pores. In this study, membrane potential between two surfaces of specimen, porosity and diffusion coefficient of chloride ion were measured for the paste blending Ground Granulated Blastfurnace Slag (GGBS). In the case of Ordinary Portland Cement (OPC) paste, membrane potential is increasing with curing period but the diffusion coefficient of chloride ion decreasing. For cement blending with GGBS, membrane potential is reducing at the later age. Diffusion coefficient of chloride ion is significantly reducing by adding of GGBS. The addition of GGBS to OPC makes a denser microstructure or lower porosity and change in electrochemical response, resulting in the great decrease in the diffusion coefficient of chloride ion.

## **1. Introduction**

A membrane has a porous structure with connected pores, through which ions and neutral molecules can pass. When it separates two electrolyte solutions with a different concentration, a potential difference will occur between the two surfaces of the membrane. The ionic species in the solution move through the membrane from a high concentration to low concentration to form an electroneutrality condition and develop a constant potential difference across the membrane. This is termed the membrane potential for that system. The membrane potential is independent of the geometrical shape of the membrane but depends on the properties of membrane. Membrane potential consists of diffusion potential within the membrane and phase boundary potentials. When ions diffuse into the ion exchange membrane, the faster counter ion tends to diffuse at higher rate. However, any excess charge transfer by faster counter ions builds up a space charge which slows down the faster ions and accelerates the slower ions. This develops the diffusion potential within the membrane. Diffusion of counter ions into membrane from the solution and diffusion of co-ions into solution from the membrane results an unbalance of charge between membrane and contact solution. The first few ions diffuse and build up an electrical potential, called Donnan

potential. The ion selective property of the membrane is usually determined by measuring the membrane potential. The surface charge influences the movement of the ions by electrostatic interaction between the ions and the surface charge. If the membrane has no surface charge, the membrane potential equals the diffusion potential within the membrane. On the other hand, membrane potential magnitude is dependent on the difference in ionic concentration of solution and its sign is determined by sign of surface charge.

Several attempts have been made to calculate the membrane potential [1 and 2]. Teorell, Meyer and Siveres developed a theory (T.M.S theory) to calculate the membrane potential of a charged membrane. According to the T.M.S theory, membrane potential consists of the diffusion potential within the membrane and phase boundary potentials (Donnan potentials). The unequal equilibrium distribution of mobile ions causes the Donnan potential to develop. Assume that all single ion activity coefficients are unity, and the surface charge concentration remains a constant for all external electrolyte solutions, then the membrane potential for 1, 1- valent electrolyte solution is given by the following equation:

$$\Delta f = f_d - f_0 = - \left[ \frac{RT}{F} \ln \frac{C_d \sqrt{X^2 + 4C_0^2} + X}{C_0 \sqrt{X^2 + 4C_d^2} + X} \right] - \left[ \frac{RT}{F} U \ln \frac{\sqrt{X^2 + 4C_d^2} + UX}{\sqrt{X^2 + 4C_0^2} + UX} \right] \quad (1)$$

where  $\Delta f$  is the membrane potential (V);  $C_d$  and  $C_0$  are the concentrations of the electrolyte solutions separated by membrane ( $\text{mol dm}^{-3}$ );  $f_d$  and  $f_0$  are the potentials of the reference electrodes immersed in solution with concentrations of  $C_d$  and  $C_0$  respectively;  $R$  is the gas constant ( $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ );  $T$  is the absolute temperature (K);  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ); and  $X$  is the surface charge concentration of membrane ( $\text{mol dm}^{-3}$ ).  $U$  is defined as follows;

$$U = \frac{u_+ - u_-}{u_+ + u_-} \quad (2)$$

where  $u_+$  and  $u_-$  are the mobility of cation and anion in the membrane respectively.

When the concentration of contact solution is smaller than that of surface charge, i.e.  $C < X/2$ , equation (1) is reduced to well known Nernst equation,

$$\Delta f_{\max} = -\frac{RT}{F} \ln\left(\frac{C_d}{C_0}\right) \quad (3)$$

where  $\Delta f_{\max}$  is the maximum potential across the membrane. On the other hand when  $C \geq X/2$ , equation (1) leads to

$$\Delta f = -(t_+ - t_-) \frac{RT}{F} \ln\left(\frac{C_d}{C_0}\right) \quad (4)$$

where  $t_+$  and  $t_-$  are the transport number of cation and anion in the membrane respectively.

From an electrochemical point of view, cement-based materials can be regarded as a membrane because it has continuous porous structure through which ions are migrating. The diffusion of chloride ions into cement-based material is an important issue in the durability of concrete structures, since the ingress of chloride ions induces corrosion in reinforced concrete structures. As for an assessment of the diffusion of chloride ions into cement based materials, parameters that influence on the diffusion of chloride ions are important issues. Cement based materials possess the electrochemical property such as surface charge on pore wall. It might give influence on transporting ions through the pore.

The electrochemical study is one of the emerging topics among the researchers in concrete field. There are substantial amount of research papers and thesis on chloride diffusion in cement based materials [3 and 4]. In addition, studies on measurement of membrane potential in cementitious materials have also been well articulated. However, none of them address the pore surface charge on membrane potential [5-8]. Though few researchers have highlighted that there are some influences of surface charges on diffusing ions [9-13], they have failed to elucidate the interaction of surface charges and transporting ions.

The sole seek of this study is to investigate the influence of electrochemical properties on the transporting ions through hardened cement paste blended with GGBS.

## 2. Experimental

The properties of materials such as Portland Cement (OPC) and Ground Granulated Blastfurnace Slag (GGBS), the details of sample preparation and the measurement of potential difference techniques are described in ref [14]. The diffusion cell experiment has been used to determine the diffusion coefficient of sodium and chloride. The experiment is carried out at room temperature of  $23\pm 2$  °C and an RH of 60%. The upstream compartment of the cell was filled with 0.5 mol/l NaCl solution and downstream compartment was filled with deionized water. The concentration gradient induces the flux of ions in across the sample. The chloride and sodium concentration in the downstream were measured with the use of Ion chromatography. Chloride and Sodium concentration are measured until the flux becomes constant, in other words, until they reach a steady state (Fig. 1). Measurement is taken in an interval of 7 days up to 35 days. The effective diffusion coefficient of ions can be calculated by using Fick's first law in the constant flow.

$$J_{e,Cl} = D_{e,Cl} \frac{C_{up}}{L} \quad (5)$$

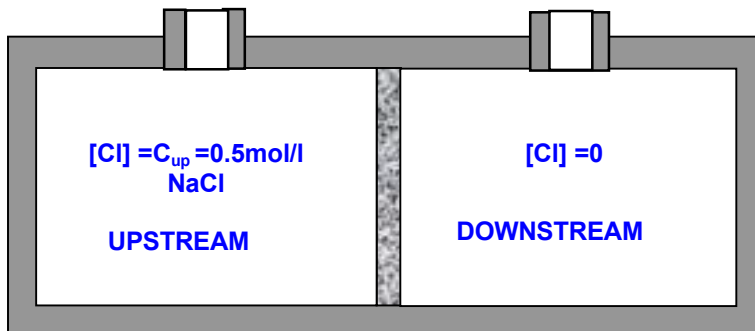


Fig.1. Diffusion test setup

The mercury intrusion method was employed to measure porosity and pore size distribution of the cement paste that had been broken into pieces between 2.36 mm and 4.76 mm. After curing was completed the samples were immersed into acetone to terminate the hydration. Prior to the porosity measurement, the samples were vacuumed at 0.1 MPa for one day at  $23\pm 2$  °C.

### 3. Results and Discussions

#### 3.1 Membrane Potential

##### 3.1.1 Membrane Potential for OPC Paste

According to the TMS theory, membrane potential can be considered as the sum of two Donnan potentials, at the interface of solution and membrane, and diffusion potential within the membrane. The membrane potential depends on the electrochemical characteristics of hardened cement paste in addition to the concentration difference of contact NaCl solution. Membrane potential of cement paste is also dependent on the mobility of all ions and their direction of diffusion. Membrane potential is a function of  $\ln(C_d/C_0)$  for different water to cement ratios for OPC paste at curing period of 28 and 56 days is shown in Fig.2. The membrane potential of paste for each curing period and the water to cement ratios are directly proportional to  $\ln(C_d/C_0)$ , follows equation (4). The gradient of the line rises with an increase in curing periods and/or a reduction in the W/C. Therefore, the gradient of the cement paste with a curing period of 28 days and a W/C of 0.4 is steeper than any other for OPC paste. The hydration of OPC is affected by change of W/C and curing periods. This leads to change of microstructure and surface properties especially surface charge concentration on pore walls. This reflects in change of membrane potential.

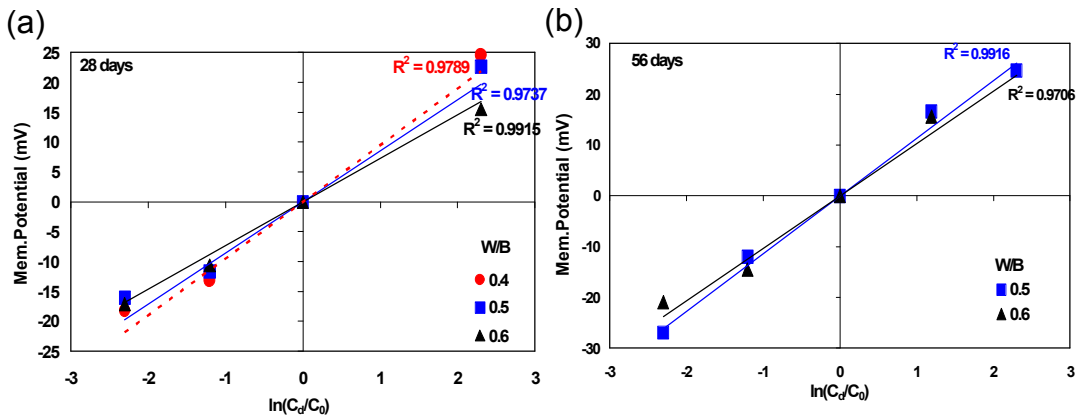


Fig.2 Membrane potential for different water to cement ratios for curing period of (a) 28 and (b) 56 days of OPC paste.

##### 3.1.2 Influence of GGBS Addition on Membrane Potential

The membrane potential of paste with W/B of 0.6 by addition of GGBS of 0%, 40% and 55% at curing periods of 28 and 56 days are shown in Fig.3 (a) and (b) respectively. A significant different in membrane potential is obtained when OPC is blended with GGBS. It gives the smaller value

when adding of GGBS to OPC at both curing period of 28 and 56 days. However, there is no difference in membrane potential for specimens when GGBS is added at 40% or 55% to OPC. Therefore, membrane potential is strongly dependent on the composition of cement binder. This indicates that the cement blending with GGBS changes the electrochemical properties of the paste due to the change of physiochemical properties of pores. The gradient of the straight line used to be determined the one electrochemical property, transport number.

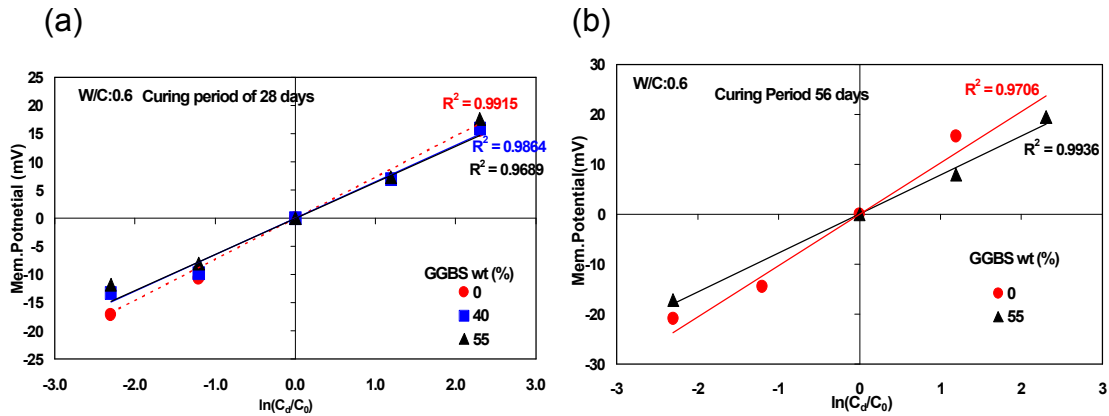


Fig.3. Membrane potential as a function of  $\ln(C_d/C_0)$  for different replacement ratio of GGBS and a W/B of 0.6 for curing periods of (a) 28 and (b) 56 days.

### 3.2 Determination of Surface Charge Concentration from Transport Numbers

From the T.M.S model, the transport number of  $\text{Cl}^-$  ion ( $t_-$ ) in the hardened cement paste is calculated by equation (4). The transport numbers of chloride ion are tabulated in table 1. The transport number of  $\text{Cl}^-$  ions in cement paste increases with a decrease in the W/B and/or an increase in curing period for OPC specimens. Transport number of chloride ion decreases when blending OPC with GGBS. From the table, the transport number of  $\text{Cl}^-$  ions in hardened cement paste is higher than the  $\text{Na}^+$  ion transport number (because the total transport number is equal to 1) for both OPC and GGBS paste specimens. It becomes evident that hardened paste has a positive electric charge for all water to cement ratios and curing periods whether GGBS was used or not. Therefore, hardened cement paste is an anion selective membrane for both with and without addition of GGBS. This result is consistent with previous study made for measurement of zeta potential of C-S-H and hydrated cements paste [15, 16]. The transport number of  $\text{Cl}^-$  ions in the hardened paste is larger than that in the bulk solution. This means that positive charge in the hardened paste pores selectively attracts  $\text{Cl}^-$  more than  $\text{Na}^+$ . In other words, there is repulsion between  $\text{Na}^+$  and the charge on the pore surface.

Table 1 Transport number of chloride ion

W/B, Curing period, GGBS (wt %)	t-	W/B, Curing period, GGBS (wt %)	t-
0.4,28,0	0.686	0.4,28,40	0.6397
0.5,28,0	0.6755	0.5,28,40	0.6407
0.6,28,0	0.6431	0.6,28,40	0.627
0.5,56,0	0.7287	0.4,28,55	0.6532
0.6,56,0	0.7022	0.5,28,55	0.624
		0.6,28,55	0.6253
Bulk solution	0.6037	0.5,56,55	0.6623
		0.6,56,55	0.6533

Permselectivity is a parameter of the extent to which counter ion migration is facilitated by ion-exchange membrane. Counter ions migrate due to charges in the membrane. The surface charge concentration,  $X$ , can be expressed in terms of permselectivity,  $P_s$  as follows [17-19].

$$X = \frac{2C_0 P_s}{\sqrt{1 - P_s^2}} \quad (6)$$

where  $C_0$  is the concentration of the electrolyte solution that makes contact with the membrane and  $P_s$ . It is expressed as follows:

$$P_s = \frac{t_i^m - t_i}{1 - t_i} \quad (7)$$

where  $t_i^m$  and  $t_i$  denote the transport number of counter ions  $i$  in the membrane and in the solution respectively.

Surface charge concentration on the pore wall of hardened paste can be calculated using the equations (6) and (7). Figure 4 shows the surface charge concentration of paste for curing period of 28 days. The absolute value of surface charge becomes lower when blending with slag and decreases with an increase in W/B for both OPC and GGBS cement paste specimens.

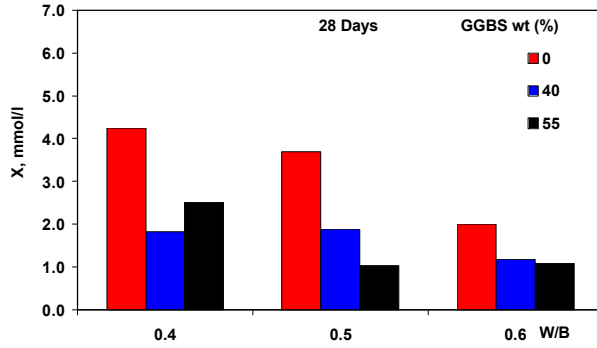


Fig.4. surface charge concentration for curing period of 28 days.

### 3.3 Diffusion Coefficient of Sodium and Chloride

The steady state ionic diffusion through the hardened cement paste is a strong function of W/B and curing period. This has been attributed to change in pore structure with curing period and W/B. The diffusion coefficient of sodium and chloride are similar to those in bulk aqueous solutions. Hardened cement paste with or without addition of GGBS shows greater resistance to ingress of sodium than chloride ion, shown in fig 5.

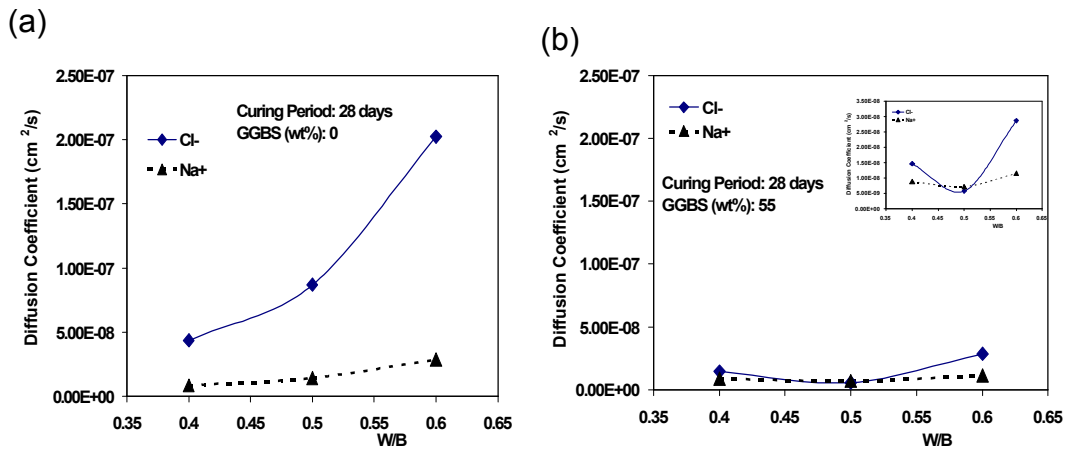


Fig.5. Diffusion coefficient of sodium and chloride as a function of W/B for (a) OPC and (b) GGBS of 55%.

Generally speaking, the difference in the rate of diffusion coefficient of both ions is greater in the cement paste without of GGBS addition and the rate reduces with addition of GGBS content. Both sodium and chloride diffusion coefficient are increasing with W/B for hydrated cement paste without GGBS and the difference in diffusion coefficient between these two ions are also increasing. Thus the diffusion coefficient of ions through the cement based materials strongly affects the mineral admixture



blended into cement. The diffusion coefficient of  $\text{Na}^+$  and  $\text{Cl}^-$  does not change significantly by W/B when the slag substitution ratio of 55%. Considerable reduction of diffusion coefficient of ions is obtained due to hydration and pozzolanic reaction of OPC and GGBS. The cement paste containing GGBS change the microstructure of hardened cement paste; there are more capillary pore which is filled with low density of C-S-H gel and reduce both the pore size and cumulative pore volume. In the later age cement paste, latent hydraulic reactions of GGBS make the microstructure of the cement matrix denser [20, 21].

### **3.4 Relationship between Diffusion Coefficient of Chloride ion and Surface Charge**

The diffusion coefficient of transporting ions depends not only on physical properties of pores but also on the electrochemical properties. The main electrochemical property of the pore is surface charge on pore walls, in other words electrical charge on C-S-H surface. The density of the surface charge is dependent on the charge on the surface of hydrated cement binders and pore solution concentration. The positive surface charge on pore walls is calculated and it changes with other parameters as explained in previous sections. The surface charge gives an influence of transporting ions through the pores. The surface charge influence on ionic diffusion through the hardened cement paste is shown in figures 6 and 7. Figure 6 represents how the effects of  $\text{SA} \times \text{X}$  (surface area \* surface charge) on the transporting chloride ion for OPC paste and GGBS replacement of 55% specimens. The hydrated cement paste considered as an assemblage of cementitious phase. The surface charge calculated by membrane potential measurement give the sum of the charge of each constituting phase. The product of total pore surface area into surface charge ( $\text{SA} \times \text{X}$ ) can be considered as surface charge density. The diffusion coefficient of chloride ion increases with  $\text{SA} \times \text{X}$  for OPC and GGBS cement paste with irrespective of W/B for both curing period of 28 and 56 days. The cement paste containing slag shows the lowest diffusion coefficient of chloride ion and surface charge. This means that GGBS is capable of influencing the electrochemical response of a pore solution in the cement system as well as its physical characteristics such as porosity and pore size distribution. It may be possible that blending with GGBS may change the properties of C-S-H gel. Figure 7 shows the ionic diffusion is influenced by surface charge for specimens cured at 28days. From figure 7, it is evident that diffusion coefficient of chloride ion increases with  $\text{SA} \times \text{X}$  but diffusion coefficient of sodium has not change significantly.

From the results, electrostatic interaction between diffusing ion and surface charge in a hardened cement paste is one of the major factors resulting in the change of diffusion coefficient. The interaction between surface charge and diffusing ions can be significant only in pores no wider than few times the value of electric double layer thickness. Thus the

surface charge interaction on ionic diffusion is mainly associated with transport of ions through gel pores than capillary.

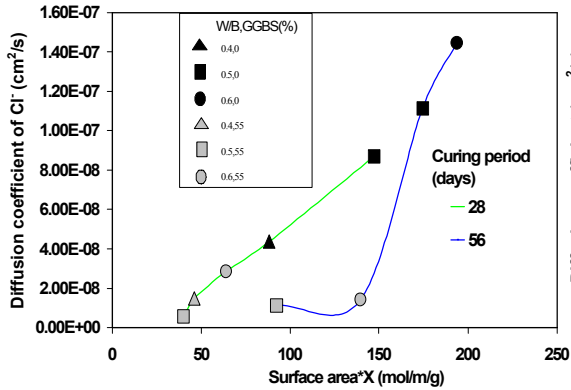


Fig. 6 Diffusion coefficient of  $\text{Cl}^-$  with production of surface area into surface charge

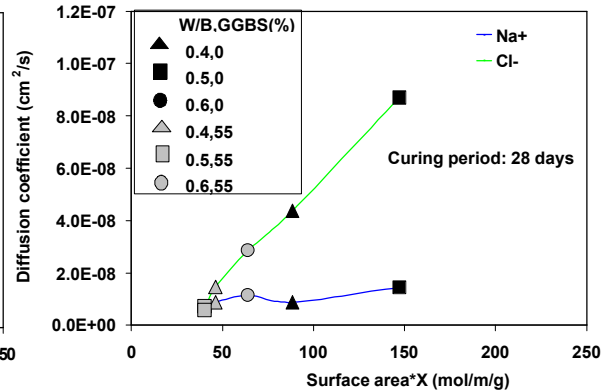


Fig. 7 Diffusion coefficient of  $\text{Na}^+$  and  $\text{Cl}^-$  with production of surface area into surface charge

#### 4. Conclusion

In this study, the membrane potential between two surfaces of specimen, porosity and diffusion coefficient of sodium and chloride were measured for later age paste made with OPC and cement blended with GGBS.

The membrane potential increases with a decrease in W/B, and/or an increase in the curing period for OPC paste. Membrane potential reduces at later age when blending with GGBS. Hardened paste, whether it contains GGBS or not, shows positive surface charge.

Hardened cement paste can be considered as electrochemical membrane and the physical and chemical properties of pore in hardened cement paste is affecting on the transport of ions. The steady state diffusion coefficient of transporting ions depends on porosity and the surface charge concentration on pore walls. Hardened cement paste has greater resistance to diffusing sodium ions than chloride ions. In later aged hardened cement paste, the introduction of GGBS to OPC changes the diffusion coefficient of chloride ion greatly. There is no significant difference in diffusion coefficient of chloride ion for cement containing 55% of GGBS with W/B.

## 5. References

- [1] M. Sakashita, Study on ion-selective property in precipitate membranes of hydrous Ni (II), Fe (III) and Cr (III) oxides, PhD thesis, Hokkaido University, Japan
- [2] F. Helfferich, Ion exchange, McGraw-Hill Book Company, Inc (1962)
- [3] T. OLIVIER, Prediction of Chloride Penetration into Saturated Concrete- Multi -species Approach, PhD thesis, Department of Building Materials CHALMERS UNIVERSITY OF TECHNOLOGY Goteborg, Sweden, 2000.
- [4] C.L Page, N. R short and A. El Tarras, Diffusion of chloride ions in hardened cement pastes, *Cem Concr Res* 11 (1981) 395-406.
- [5] N.R. Buenfeld, G.K. Glass, A. K. M. Hassenain and J. Z. Zhang, Chloride transport in concrete subjected to electric field, *Journal of Materials in Civil Engineering* 10 (1998) 220-228.
- [6] J.Z. Zhang, and N.R. Buenfeld, Membrane potential and its influence on chloride transport in cementitious materials. In: Andrade, C. and Kropp, J. Eds. Testing and modeling the chloride ingress into concrete, Proceedings of the 2<sup>nd</sup> International RILEM workshop. Cedex: RILEM publications S.A.R.L., (2000) 33-49.
- [7] J.Z. Zhang, and N.R. Buenfeld, Presence and possible implications of a membrane potential in concrete exposed to chloride solution, *Cem Concr Res* 17 (6) (1997) 853-859.
- [8] J.Z. Zhang, Jian Yun Li and N.R. Buenfeld, Measurement and modeling of membrane potentials across OPC mortar specimens between 0.5 M NaCl and simulated pore solutions, *Cem Concr Composites* 24 (5) (2002) 451-455.
- [9] M.Castellote, C. Alonso, C. Andrade, G.A. Chadbourn and C.L. Page, Oxygen and chloride diffusion in cement pastes as a validation of chloride diffusion coefficient obtained by steady-state migration tests, *Cem Concr Res* 31 (2001) 621-625.
- [10] S. Goto and D. M. Roy, Diffusion of ions through hardened cement pastes, *Cem Concr Res* 11 (1981)751-757.
- [11] V.T Ngala, C.L Page, L.J Parrott and S.W. Yu, Diffusion in cementitious materials: II. Further investigations of chloride and oxygen diffusion in well-cured OPC and OPC/30% PFA pastes, *Cem Concr Res* 21 (1991) 581-588
- [12] S.W. Yu and C.L Page, Diffusion in cementitious materials: 1. Comparative study of chloride and oxygen diffusion in hydrated cement pastes, *Cem Concr Res* 21 (1991) 581-588.
- [13] T. Zhang and Odd E. Gjorv, Diffusion behavior of chloride ions in concrete, *Cem Concr Res* 26 (1996) 907-917
- [14] Y.Elakneswaran, T. Nawa, K. Kurumisawa and K. Fushimi, Effect of GGBS on Membrane Potential of Paste, RILEM JCI international conference in Israel, 2006 March.

- [15] L. Nachbaur, P.C. Nkinamubanzi, A. Nonat and J.C. Mutin, Electrokinetic properties which control the coagulation of silicate cement suspensions during early age hydration, *Journal of Colloid and Interface Science* 202 (1998), 261-268.
- [16] H. Viallis-Terrisse, A. Nonat and J.C. Petit, Zeta-Potential study of calcium silicate hydrates interacting with alkaline cations, *Journal of Colloid and Interface Science* 244 (2001), 58-65.
- [17] V.K. Shahi, G.S. S.K Thampy, and R. Rangarajan, Studies on transport properties of surfactant immobilized anion-exchange membrane, *Journal of membrane Science* 158 (1999) 77-83.
- [18] V.K. Shahi, G.S. Trivedi, S.K Thampy, and R. Rangarajan, Studies on the electrochemical and permeation characteristics of asymmetric charged porous membranes, *Journal of Colloid and Interface Science* 262 (2003) 566-573.
- [19] K. Singh, and A.K Tiwari, Studies on the electrochemical characterization of cellulose acetate and Dowex-50 membranes for uni-univalent electrolytes in aqueous solutions, *Journal of Colloid and Interface Science* 210 (1998) 241-250
- [20] W.-C. Jau and D.-S. Tsay, A study of the basic engineering properties of slag cement concrete and its resistance to seawater corrosion, *Cem Concr Res* 28 (10) (1998) 1363-1371
- [21] D.M. Roy, W. Jiang and M.R. Silsbee, Chloride diffusion in ordinary, blended, and alkali-activated cement pastes and its relation to other properties, *Cem Concr Res* 30 (2000) 1879-1884.