EFFECT OF SALINITY LEVEL ON EARLY-AGE ELECTRICAL PROPERTIES OF CEMENT PASTE

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ABSTRACT

Salinity is the great problem for coastal regional structures. It has a capability to damage the structure externally and internally as well as it also can break the strong chemical structures of binding materials. This study investigates the early-age electrical resistivity and conductivity of cemtitious materials. Assuming constant water/cement ratio, the test is performed for distill water, 0.5%, 1.0%, 2.0%, and 3.0% salt solution. A ring shape mold is used to execute the test. Constant power supply is applied and monitored the reading of voltage and current. Results of the rate of electrical resistivity on early age cement hydration have a great impact. Distill water sample provide larger resistivity than other salt induced sample. A 3.0% salt induced sample gives 76.21%, 63.23%, 37.32% and 9.5% more electrical conductivity than distill water, 0.5%, 1.0%, and 2.0% salt induced samples at the beginning stage. Finally, higher salinity level increases the conductivity of cementitious material that can degrade the structure by affecting long term concrete strength and originating corrosion process in future.

Keywords: Cement, Cement Hydration, Resistivity, Conductivity, Salinity.

1. INTRODUCTION

Early-age properties of cement-based materials play an important role in determining the construction process and concrete durability. Concrete related construction is highly depended on cementitious materials. It has adhesive and cohesive properties which make it capable of binding material. It also has a high chemical structure. So, hydration reaction occurs between cementitious material and water. It produces concrete like hard compound. The hydration of cement based materials leads to a continuous decrease in the amount of porosity due to the increase in hydration products. There are many methods to measure the hydration of cement, such as electrical method, calorimetry, chemically bonded water, X-ray diffraction and image analysis. However, different methods provide different results for the degree of hydration due to the different parameters of cementitious materials and water (Ye, 2003). Electrical conduction occurs primarily due to ion transport through the pore solution in a cement paste. It is highly dependent on both pore solution conductivity (McCarter, et al., 2003). Electrical methods have been applied to find out the early stage resistivity in hydrating cement based material systems (Christensen, et al., 1994).

The service life of concrete structures depends on the environmental conditions and on the quality of concrete. Durability of concrete to chloride attack is one of the environmental problems. It damages the formation of ettringite $(Ca_6Al_2(SO4)_3(OH)_{12}.26H_2O)$ and gypsum. It is generally attributed to the formation of expansive product named Friedls salt (3CaO.Al_2O_3.CaCl_2.10H_2O). The process of chloride attack on concrete may be explained by the following series of chemical reaction (Ben-Yair, 1974 and Islam et al., 2005).

Ca(OH) ₂ +	2NaCl	\rightarrow	CaCl ₂	+	2NaOH
Calcium Hydroxide	Sodium Chloride	e	Calcium Chlor	ride	Sodium Hydroxide
$C_{2}C_{1}$ +	$3C_{2}O_{1}A_{1}O_{2}+$	10H O	$\rightarrow 3C_{2}OAlc$		10년 0
CaCI ₂	$3CaO.Al_2O_3$	101120	\rightarrow 3CaO.Al ₂ C	73.CaCl	2.101120
Calcium	Tri-Calcium		Calcium ch	loroalu	minate
Chloride	Aluminate		Fr	iedls sa	ılt

 $MgCl_2$ after reacting with $Ca(OH)_2$ of hydrated cement forms calcium chloride, which being soluble, gets leached out leading to material loss and weakening (Metha ,1986). Possible reactions are given below:

$Ca(OH)_2$	+	$MgCl_2 \rightarrow$	CaCl ₂ +	$Mg(OH)_2$
Calcium		Magnesium	Calcium	Magnesium
Hydroxide		Chloride	Chloride	Hydroxide

Electrical resistivity measurement is a way to find out the rate of hydration of cement paste. With time, cement paste starts to harden and block the way of transportation of ions through the solution. Early age properties of cement paste gives an indication of its performances. The objectives of this paper are to measure of early stage electrical resistivity of cement paste and also find out the effect of various salinity level on electrical resistivity and conductivity.

2. METHODOLOGY

The experimental work was carried out to the study the electrical resistivity of early-age cement hydration using different concentration of saline water over a period of 8 hours. The variable parameters studied and materials and calculation formula involved were as follows:

2.1 Materials

The experimental program consists of main three types of materials. These are mainly Cement Type I (Ordinary Portland Cement), pure distilled water and sea salt.

2.1.1 Cement

Specification of this cement is ASTM C-150, Type-I. Composition of this cement is (95-100) % clinker, and (0-5) % gypsum. Cement Type-I, Ordinary Portland Cement was used as a binding material. Ordinary Portland cement is supplied by King Brand Cement Company, Bangladesh. The oxide compositions of ordinary Portland cement are summarized in Table 1. A 200g cement was measured for every sample.

Table 1: Chemical composition of ordinary portland cement

Compound	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
Conc. Unit	0.183%	2.310%	5.633%	22.69%	0.147%	1.4%	0.491%	65.32%	0.206%	3.009%

2.1.2 Saline Solution

Artificial saline water was made by mixing up distilled water with exact amount of principal salts found in natural sea water. Chemical composition of sea salt is given in Table 2. Different salinity level solutions were prepared by using various percentage weights of sea salt. Composition of cement paste is given in Table 3.

Table 2: Chemical composition of sea salt

Compound	NaCl	MgCl ₂	MgSO ₄	CaSO ₄	K ₂ SO ₄	CaCO ₃	MgBr ₂	
Conc. Unit	77.71%	10.86%	4.86%	3.43%	5.57%	0.28%	0.85%	

Table 3: Composition of cement paste

Sample ID	Percentage of Salt	Weight of Cement	Weight of water
SL 0.0%	0%	200 g	80 g
SL 0.5%	0.5%	200 g	80 g
SL 1.0%	1.0%	200 g	80 g
SL 2.0%	2.0%	200 g	80 g
SL 3.0%	3.0%	200 g	80 g

2.2 Test Setup and Procedure

Present study involves the construction of five ring shape mold to determine the electrical properties of cement paste at early stage for different concentration of salinity. Diameter of the outer ring was 8.0cm and height was 4.0cm and internal ring diameter was 2.5cm and height was 4.0cm. Dimension of ring shape mold is shown in Figure 1.



Figure1: Dimension of ring shape mold.

For one sample 200g cement and 80g salt solution was mixed properly by hand and poured into the mold. Where water/cement ratio was 0.4. Composition of cement paste is illustrated in Table 3. After placing the cement paste, constant electrical voltage was supplied from a DC power supply according to the following Figure 2. Constant input 18V was supplied from DC power supply and reading of output current and voltage were measured from the connected digital ammeter and voltmeter with respect to time distance. The measurement of voltage and current were stopped after 8 hours from starts.



Figure 2: Electrical circuit diagram for resistance measurement (a) schematic diagram, (b) pictorial diagram.

Ring shaped specimen were made by using insulator and current allows passing through it. The goal of this new approach is to find out useful information of the hydration process of the cement-based material using its electrical resistivity. Generaly, with increasing the degree of hydration, the resistivity of the cement paste also increase. The increasing resistivity refers that the cement paste becoming solid and bond among the cement particle become stronger. The principle of measuring resistance, in which DC current is transmitted through the cement slurry by two metal electrodes, is shown in Figure 2. When the voltage drop over the electrodes (V) and the current through the sample (I) are known, Resistance (R) can be calculated from the Ohm's law.

 $\mathbf{R} = \mathbf{V}/\mathbf{I}.$

And the resistivity of the cement paste can be calculated by the following formula

 $\rho = AR/1....(2)$

Where, ρ is the resistivity (ohm-m), A is the cross sectional area, and l is the distance between the voltage electrode.

Conductivity = $1/\rho$ (3)

3. RESULTS & DISCUSSION

The purpose of this subdivision is to report the results gathered from the measurement of voltage and current passing through cement paste. By the measurement of voltage and current, electrical resistances are calculated and by using equation (2). Electrical resistivity of cement pastes with respect to time is plotted in Figure 3. It explains the rate of electrical resistivity of cement paste during early age cement hydration. The resistivity was along vertical direction. After applying DC power, voltage is gradually increased and current flow is decreased with time distance. As a result, resistance is progressively increased with respect to time. Resistivity departed gradually to the upward direction of each sample. After applying DC voltage into the cement paste, water acted as a conductive medium and then cements paste performed like an electrochemical cell. Ions were flowed through this electrolyte. With passing time, immersed water of cement paste slowly decreased for hydration reaction. For this, ions passing conducting medium shorted and resistance of cement paste slowly increased. SL 0.0% specimen shows more rate of electrical resisvity than SL 0.5% and vice versa. Electrical resistivity of the cement paste is affectd by the ionic flow. Diffusion rate of chloride ions through cement paste is increased by the application of electric field and cocentation of ions also acclerate the rate of diffusion (Nisson and Tang, 1995). It also depends upon the capillary pore size, pore system complexity and moisture contents. Chloride affects on resistivity as the hydroxyl ions from the cement dissolved in pore water outnumber the free chloride ions (Broomfield and Millard, 2002). For this reason, more ions passed through the SL 3.0% and more salinity levels affect the early hydration reaction.



Figure 3: Electrical resistivity (ohm-m) at early stage of cement hydration

It has been also shown in Figure 4 that relation between salinity level and electrical resistivity for different time interval. Below electrical resistivity of 20 ohm-m, the graph lines are nearly straight line for all specimens. And above 20 ohm-m, it has turned into non-linear part. It is also important that electrical resistivity of SL 3.0% and SL 2.0% specimens have no major change with respect to time duration. And this change have stared from 1% salinity level. The range of resistivity change for SL 1.0% salinity is visibly not more significant. Substantial change has happened for SL 0.5% and SL 0.0% specimens with respect to time duration. The change of resistivity for SL 0.5% are approximately nearly 15 ohm-m to 40 ohm-m. But it changes from nearly 20 ohm-m to 100 ohm-m for SL 0.0% specimen. So, Figure 4. clearly shows that higher salinity level increases the passing rate of ions. It decreases rate of resistivity that means hydration rate with time duration.



Figure 4: Relation between electrical resistivity (ohm-m) vs salinity levels (%).

Figure 5 shows the electrical coductivity of of cement paste during cement hydration. Electrical conductivity is reverse of electrical resistivity and it was calculated by using equation (3). When the concentration of salineity is increased then the production of $CaCl_2$ is naturally increased. High productions of $CaCl_2$ produce more Friedls salt (3CaO.Al₂O₃.CaCl₂.10H₂O) (Broomfield and Millard, 2002). This Friedls salt increased the electrical conductivity rate of each sample shows decreasing nature. After 3 hours later, the conductivity of SL 0.0% specimen reached near to the zero level. High salinity induced specimens show more conductivity and it assure lower hydration rate.



Figure 5: Electrical conductivity (S/m) of cement paste during cement hydration

Relative average conductivity for different salinity levels are shown in Figure 6. Relative conductivity measured with respect to SL 3.0% specimen and it was assumed 100% conductivity for SL 3.0%. The graphical representation shows that specimen SL 0.0%, SL 0.5%, SL 1.0%, SL 2.0% offer 76.21%, 63.23%, 37.32% and 9.5% lower conductivity than SL 3.0%. Finally the experimental study demonstrated that percentages of NaCl and MgCl₂ have a great impact on early age cement hydration.



Figure 6: Relative avgerage conductivity exposed to different salinity level

4. CONCLUSIONS

The main conclusions can be drawn as follows:

- 1. Electrical resistivity with respect to time shows a good result. Larger concentration of salinity level shows lower rate of electrical resistivity.
- 2. Time dependent relation between electrical resistivity and salinity level shows a good aggrement for SL 0.0% but there have no responce for SL 3.0%.
- 3. SL 3.0% specimen shows 76.21% more conductivity than SL 0.0%. It indicates that higher salinity levels degrade the hydration reaction.

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