

Potentiometric Determination of Free Chloride in Cement Paste – an Alternative Method for Low-Budget Laboratories

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ABSTRACT

Corrosion of rebar in concrete is commonly associated with, and to a large degree influenced by, the free chloride concentration in the pore water. The amount of chloride in concrete is important because chloride can promote corrosion of steel reinforcement when moisture and oxygen are present. A potentiometric procedure that makes use of direct measurement with a chloride ion selective electrode has been developed to analyze free chloride in the pore water extracted from cement paste.¹⁶ The accuracy and reliability of this analytical technique has been checked against a certified reference material, Merck sodium chloride solution. Confidence levels ($CL_{0.95}$), of 0.03 and relative standard deviations of 0.2 % for chloride were determined for ordinary Portland cement (OPC) chloride binding capacity.

KEYWORDS

OPC, free chloride, potentiometry.

1. Introduction

Chloride analysis in fresh or hardened concrete and its raw materials is of great importance for quality control and life expectancy of existing structures due to corrosion of the rebars by free chloride ions.^{1–5} Chloride compounds occur widely in nature and are abundant in both liquid and solid form, especially chlorinated municipal drinking water used in the building industry in South Africa.

Chlorides, whether added during mixing or later transported into concrete, can be bound by hydrated products in concrete by physisorption, chemisorption or entrapment. This is called the chloride binding capacity of cement.^{6,7} The unbound or free chloride in the cement paste matrix can be extracted by means of a pore water expression device.^{8,9}

The analytical determination of chloride can be accomplished in various ways, including gravimetric, volumetric, colorimetric analysis,¹⁰ X-ray fluorescence (XRF),¹¹ and ion chromatography.¹² The use of ion selective electrode (ISE) is limited to field determinations due to perceptions that it is less accurate and is dependent upon the ionic strength and composition of the solution. It is also reported that direct potentiometric readings are known to be less accurate than potentiometric titrations.¹³ The working range of potentiometric titrations are dependent upon the nature of the ISE and reference electrode used.¹⁴ In this study the accuracy and reliability of the proposed direct potentiometric analysis with a chloride ISE was investigated. The method is particularly suitable for low-budget laboratories.

2. Experimental Design

2.1. Sample Preparation

For this study only OPC and four different chloride concentrations (0.25, 0.5, 1 and 2 % were used. The procedure for 0.25 % chloride in cement paste is as follows: First 16.49 g (± 0.01 g accuracy) of chloride (in the form of NaCl) was weighed and dissolved in 2400 g (± 0.01 g accuracy) de-ionized H₂O. The chloride solution was placed in a Hobard A150 (India) blender. A mass of 4000 g (± 0.01 accuracy) of OPC was slowly added to the bowl while mixing. The blender was left on for another 5 min to ensure that a homogeneous mixture was achieved. The mixture was then cast in pre-prepared plastic bags that were sealed and placed in sample cylinders and tumbled for 12 h for homogeneous setting.

The curing of the samples was done at ambient temperature for 1, 7, 14, 28, 56 and 84 days.

2.2. Mass Loss and Pore Water Expression

After each time interval (1, 7, 14, 28, 56 and 84 days), three samples were taken from the bulk and a quarter of each sample was chiselled off and weighed. The quartered samples were placed in a Labotech, 40 L, EcoTherm, oven at 50 °C and left for 12 h to dry, after which the sample was weighed again. The percentage water mass loss was then determined and captured (Table 1).

The water mass loss percentage is the percentage mass loss

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Table 1 Combined data of chloride bound in cement paste samples taken at 84 days.

% Chloride: Sample	0.25 % Cl ⁻		0.5 % Cl ⁻		1.0 % Cl ⁻		2.0 % Cl ⁻	
	mV	Cl/g mL ⁻¹	mV	Cl/g mL ⁻¹	mV	Cl/g mL ⁻¹	mV	Cl/g mL ⁻¹
A (Calibration 6)	188	0.001	182	0.001	169	0.003	143	0.009
B	190	0.001	183	0.001	171	0.002	142	0.010
C	188	0.001	181	0.001	171	0.002	143	0.009
Av.		0.001		0.001		0.002		0.010
V/%		6		6		6		3
% Mass loss	8		8		9		11	
Mass correction		0.001		0.001		0.002		0.009
σ /%		0.0		0.0		0.1		0.2
CL _{0.95}		0.03		0.03		0.09		0.18
% Free Cl ⁻		16		12		13		26
% Binded Cl ⁻		84		88		87		74

A, B, C = the set of three samples.

Av = the average of the three values.

V% = coefficient of variance.

σ (%) = calculated percentage standard deviation.

CL_{0.95} = 95 % confidence level.

determined from the initial sample before drying and the sample after drying and was calculated as follows:

$$M_1 = \frac{(M_{i0} - M_o)}{M_{i0}} \times 100 ,$$

where: M_{i0} = the initial sample mass before drying, and M_o = the sample mass after drying.

The rest of the specimen was placed in the pore water express device and the pressing procedure was followed to extract the pore water from the sample according to the procedure describe by Tritthart and Diamond.^{8,9} The expressed water was placed in a 10 mL plastic bottle.

2.3. Direct Chloride ISE Measurements

From the pore water, 1.00 mL of the sample was pipetted into a 100 mL beaker and 50 mL of de-ionized water added. The beaker was then placed on a Metrohm, Titrand 902, Switzerland, magnetic stirrer and stirred while the chloride selective electrode and a Ag/AgCl reference electrode was placed in the solution. Three individual measurements were taken of each solution and the average value was captured (Table 1).

Two Metrohm electrodes, namely the chloride ISE(6.0502.120) and the Ag/AgCl reference electrode (6.0726.107) were used in

the electrode assembly. The saturated KCl electrolyte in the reference electrode was replaced by saturated analytically pure KNO₃ to prevent contamination of the expressed chloride ion solution *via* the membrane of the electrode. This was done by ultra pure chloride free de-ionized water saturated with analytically pure KNO₃. The electrode assembly was left for three days in de-ionized water to reach equilibrium.

The electrode assembly was calibrated by means of a series of standard solutions that were made from analytically pure NaCl (Merck, USA) in ultra-pure de-ionized water. From data obtained, a calibration curve was generated and the regression determined (Fig. 1). The data was also verified by means of a Merck 0.1 M NaCl Titrisol (9945) standard solution (data point round marker in calibration graph). The percentage coefficient of variance between the standard Merck solution and the prepared series of solutions was calculated to be 0.1 %. The electrode assembly was calibrated each time before a particular set of results.

3. Calculations

3.1. Calculation of Chloride Concentration

The chloride concentration in gram per mL in the sample and was calculated as follows:

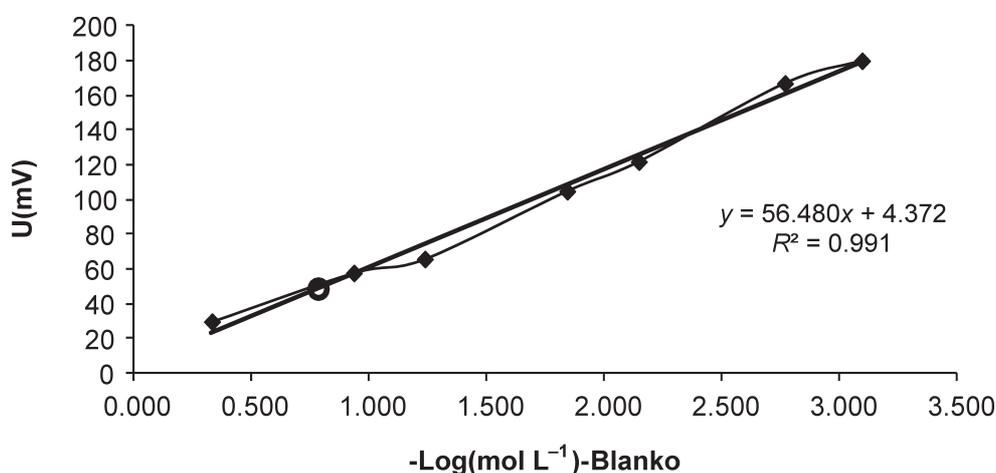


Figure 1 Selective chloride electrode calibration 1 with regression values and Merck standard data point (round marker).

$$\text{Cl}^{-}(\text{g mL}^{-1}) = \frac{(V_s \times M_{\text{Cl}}) \left[-\log \left(\frac{U_s - U_v}{U_c} \right) \right]}{V_c},$$

where: V_s = the total volume of the sample, 1 mL of the pore water sample added to the 50 mL de-ionized water, M_{Cl} = molecular mass of chloride (35.45 g mol⁻¹), U_s = chloride ISE reading of each sample, U_v = y-axis intercept value of the regression equation of the calibration curve, U_c = correlation coefficient value of the regression equation.

3.2. Calculation of Mass Correction

The mass correction calculation takes the mass loss of the evaporated water in the sample during the hydration of cement curing into account. This value is the true gram chloride per millilitre in the sample.

$$\text{Mass corrected Cl}^{-1}(\text{g mL}^{-1}) = \frac{C_a \times (100 - M_1)}{100}$$

where: C_a = calculated chloride concentration value obtained in paragraph 3.1, and M_1 = water mass loss percentage value.

3.3. Calculation of Percentage Free Chloride

The percentage free chloride in the sample is the amount of chloride left after the hydration of cement paste sample. Chloride binding is mainly influenced by the amount of tricalcium aluminate (C_3A) content in the concrete and the binding efficiency of tetracalcium aluminoferrite (C_4AF) is lower than that of C_3A at the same chloride content.¹⁵

Therefore:

$$\% \text{ Free Cl}^{-1}(\text{g mL}^{-1}) = \frac{C_m}{\left(\frac{m_{\text{Cl}}}{2400 \text{ g}} \right)} \times 100,$$

where: C_m = Calculated mass corrected value (g mL⁻¹) obtained in paragraph 3.2, m_{Cl} = The initial mass (g) of chloride added in the sample, and 2400 g = the amount of water added in the sample.

4. Conclusions

Based on the results obtained in our work the following conclusions can be made:

- The cement bound 84 % of the 0.25 % chloride, 88 % of the 0.5 % chloride, 87 % of the 1.0 % chloride and 74 % of the 2.0 %

chloride added to the cement samples.

- By replacing the saturated KCl electrolyte in the reference electrode with saturated analytically pure KNO₃, the contamination of the sample with chloride from the tip-membrane of the ISE was prevented.
- The accuracy of the chloride ISE measurements were checked by using a standard solution. It correlated well with the values of the standard solutions that were made (Fig. 1). The regression value of the calibration was 0.991.
- The calculated percentage standard deviation of the 0.25, 0.5, 1.0 and 2.0 % chloride additions ranged from 0 to 0.2 %.
- The 95 % confidence level obtained for the four chloride additions were between 0.03 and 0.18.
- To conclude, the use of direct chloride ISE measurements is an inexpensive, easy and reliable method without a large capital layout (R60 000).

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