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Effect of cement type on the corrosion of reinforcing steel bars exposed to acidic media using electrochemical techniques

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Abstract

The effect of different percentages of cement components (tricalcium aluminate C_3A) on the corrosion of embedded reinforcing steel bars was studied in presence of 5% NaCl or 5% $MgSO_4$ solutions. Different electrochemical techniques namely; half-cell potential measurement, impressed voltage method and impressed current method were used. The C_3A in cement reduced greatly the corrosion of steel bars embedded in concrete subjected to chloride or sulphate solutions. In chloride solution, as the percent of C_3A increased in cement from 2% to 10% the steel corrosion decreased proportionally. The rate of corrosion in 5% $MgSO_4$ solution was decreased as the percent of C_3A increased from 2% to 6%. From 6% to 10% the steel corrosion rate was rapidly accelerated. In general the presence of chloride and sulphate solutions in surrounding media reduced the destructive effect of sulphate ions on embedded steel bars.

Keywords: Cement; C3A; Corrosion; Reinforcement; Electrochemical; Sulphate attack

1. Introduction

The durability of reinforced concrete depends on the surrounding environmental and exposure conditions. The alkaline phase from hydrated cement has a protective action for the embedded reinforcing steel bars. The corrosion of steel produced as rusting, pitting, or/and galvanic corrosion [1].

Steel corrosion may occur directly through oxidation of metals or by acid attack or indirectly by electrochemical corrosion. Electro-chemical corrosion processes are initiated due to the difference in the reinforced concrete composition, or non-uniformity of chemical or physical reactions between the concrete and surrounding medium [2].

The cement which is alkaline (pH 13.5) oxidizes embedded steel bars, forming a chemically and electrically inactive layer (passive film) of ferric oxide [2]. Corrosion of the reinforcing steel bars is initiated to form inactive thin layer which can be broken when immersed in carbonate, chloride or sulphate solutions. Carbonates, chlorides and sulphates media can be found in concrete when using contaminant aggregates, or adding $CaCl_2$ (as an accelerator) during the mixing step or they are found under the effect of sea-water or ground-water on concrete and they can also result from attack of concrete by the surrounding environment in coastal regions [3]. Carbonates destroy the protective oxide layer presented on the surface of embedded steel in concrete leading to corrosion. Carbonation of concrete takes a long time, depending on the thickness of the cover concrete [4].

Chao et al. [5] suggested that chlorides formed metal holes at the film interfaces. Leek and Poole [6] reported that activation by chloride was attributed to dissolution of the portland layer followed by de-stabilizations of the film bond by migrating through ions, with little or no chemical dissolution of the film occur at this stage. Trittart [7] proposed that chloride ions induced corrosion of steel reinforcement in concrete requires a minimum concentration of free chloride ions in the vicinity of the bar.

Sulphates attack concrete by reacting with free $Ca(OH)_2$ to produce calcium sulphate and with aluminate hydrate to produce calcium sulphoaluminate and thus severe cracking

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and disintegration of the cement strength. C_3A is a portland cement compound that reacts with sulphates and chlorides in ground water and/or soil forming an insoluble compound, thus slowing down their destructive effect on reinforcing steel [8]. The C_3A in cement contributes little or nothing to the strength of cement, and when hardened cement paste is attacked by sulphates, expansion due to the formation of calcium sulphoaluminate from C_3A lead to disruption of the hardened paste.

The passive protective film is destroyed when the concentration of chloride ions in contact with the surface of embedded steel bar in concrete increases than threshold limits, making steel electrically negative and leading to the formation of narrow pits in its surface, which begins to function as cathodes [2]. Electrons liberated in the anodic areas, move through steel toward the cathodic area creating in the steel bar an electric current, I_{corr}, and the final product is hydrated red rust, which precipitates forming the corrosion [3].

The present study investigates the effect of different percentage (from 2% to 10%) of tricalcium-aluminate (C_3A) in cement on corrosion of reinforcing steel bars when subjected to chloride and/or sulphate media using different electrochemical techniques. Also try to estimate the corrosion rate, and find the correlation between the corrosion and the cover thickness of reinforced steel bars embedded in cement paste were investigated.

2. Experimental

Portland cement is classified by (American Standard for Testing Materials) ASTM C-150 into five types (I, II, III, IV and V) according to the percentage of C_3A. The types of used cement were supplied from Tora Company for Cement in Helwan, Cairo, Egypt. Chemical analysis of the different used types of cement was done at Tora Company and data are given in Table 1. It complies with ASTM C-150 specification for cement.

The actual quantities of various compounds forming cement varied from one type of cement to another within acceptable ranges. To calculate the percentage of main compounds percent in cement, Bogue's equations [9] were applied using the percentage of cement oxide. Results are given in Table 2.

2.1. Sample preparations

Cubic of cement paste specimens of dimension 70×70×70 mm were prepared to investigate the compressive strength of different types of cement mixed with 40% of water. Other cylinder specimens of 60, 85 and 110 mm in diameter and 100, 113 and 125 mm in height were cast with an embedded steel bar (yield stress 38.8 MPa) of 10.0 mm diameter for corrosion test. The steel bars were fixed at a distance of 25, 38 and 50 mm (1, 1.5 and 2 in.) from both bottom and sides of the mould. The steel bars were mechanically polished to remove the firmly adherent mill scales on the surface and then coated with wax in such a manner that a pre-determined area was always exposed.

2.2. Corrosion measurements

Three different electrochemical methods were used to evaluate the corrosion rate of reinforcing steel bar.

2.2.1. Half cell potential

Half-cell potential of steel bar in cement was found to be a rapid indicator of corrosion activity in either chloride or sulphate solutions. The change in potential occurred when the corrosion-inducing agent diffused to the steel surface through cement and initiated corrosion. The method provides good information on the passive film repair or the passive film breakdown. This technique can compare specimens by measuring the time taken until change in potential occurs. Fig. 1 illustrates a simple cell for half-cell potential measurements.

2.2.2. Impressed voltage method

In this method a constant positive potential was applied to the steel bar embedded in cement and the current from the reinforcing steel bar to counter electrode is measured periodically. A sharp increase in current indicates the corrosion effect [9]. The anode is the tested specimen and a steel bar of same dimension is the cathode. The current impressed into steel bar was obtained from a direct constant current (DC) power

Table 1
Chemical analysis of different portland cement types

Cement type					
ASTM description British description	Type I Ordinary	Type II Modified	Type III Rapid hardening	Type IV Low heat	Type V Sulphate resisting
Oxide compositions					
CaO	58	62	63	62	65
SiO_2	18	21	19	20	22
Al_2O_3	4.5	3.3	6	5	5
Fe_2O_3	6	1.5	3.5	3	5.5
MgO	3.5	5.5	4.0	2.5	0.3
SO_3	2.5	1.7	2.3	2	1.7

Table 2
Calculated compound compositions percent of different types of cement

Compound compositions					
British description	ASTM description				
	Cement type				
	Type I Ordinary	Type II Modified	Type III Rapid hardening	Type IV Low heat	Type V Sulphate resisting
$3CaO \cdot SiO_2$ (C_3S)	53	63	60	28	51
$2CaO \cdot SiO_2$ (C_2S)	12	13	10	49	25
$3CaO \cdot Al_2O_3$ (C_3A)	2	6	10	8	4
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (C_4AF)	18	5	11	9	17

supply at (5 V). Fig. 2 illustrates a simple cell for current–time measurement at constant voltage. The corrosion rate was calculated [10] using Farady's law (Eq. (1)):

$$W = K(I.t) \qquad (1)$$

where W is the mass of substance liberated, (I) is the intensity of corrosion and (t) is the prolonged time, (K) is a proportional constant equal to 0.0167 g/A min for steel. ($I.t$) represents the area under the current–time relationship. The weight loss (w) of steel bar was determined quantitatively from the above equation and it is proportional to the area under current–time curve ($I.t$).

2.2.3. Impressed current method

A constant current density about 20 $\mu A/cm^2$ was passed between the specimen and stainless steel counter electrode. The electrode potential of the specimen was measured as a function of time. This method is the most accelerated reliable corrosion test to determine whether a given medium is corrosive or inhibitive.

3. Results

3.1. Compressive strength

Table 3 shows the compressive strength (MPa) of different types of cement mixed with 40% water and immersed in different acidic solutions for 72 days after 28 days of water curing.

Results showed that, there was no significant effect of C_3A concentration on compressive strength of cement paste while the media surrounding cement paste (especially sulphate media) had a decreasing effect on compressive strength. Results indicated also that the compressive strength of samples immersed in chloride or sulphate media was slightly decreased as C_3A% increased in cement. In general, the compressive strength of cement specimens immersed in 5% NaCl solution decreased by 7–10% while when specimens were immersed in 5% $MgSO_4$ solution the compressive strength decreased by 15–20%.

3.2. Corrosion measurements

3.2.1. Half-cell potential measurements

Fig. 3a and b show the variation of corrosion potential of reinforcing steel bar embedded in cement paste of different percentages of C_3A with time (days) and immersed in 5% NaCl and 5% $MgSO_4$ solutions, respectively. The half-cell potential of reinforcing steel bar in portland cement was found to be good indicator of corrosion activity. If the half-cell potential between saturated calomel electrode (SCE)

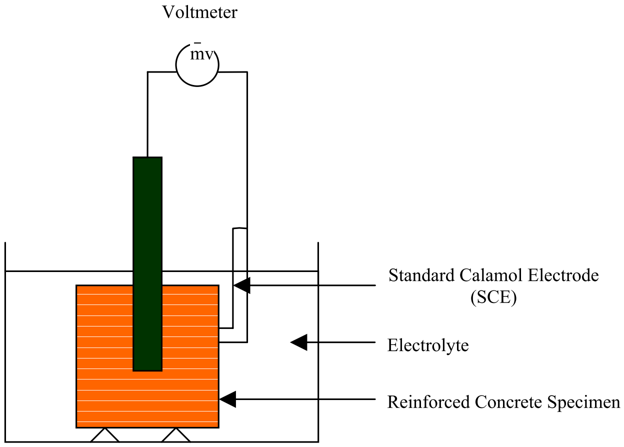

Fig. 1. Half cell potential measurement.

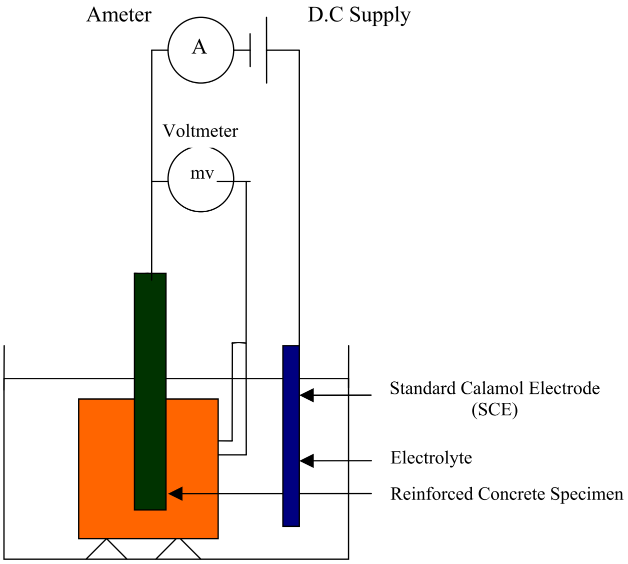

Fig. 2. Current–time measurements at constant voltage (5 V).

Table 3
The maximum compressive strength (MPa) of different types of cement immersed in different acidic media

Cement type	I	II	III	IV	V
C_3A %	2	6	10	8	4
Immersed ionic media	*Compressive strength (MPa)*				
Water	76	78	79	73	72
5% NaCl	70	72	71	66	67
5% $MgSO_4$	64	65	63	62	61

Table 4
Active potential time (days) of different C_3A due to different cover thickness (mm) immersed in 5% of NaCl or 5% of $MgSO_4$ solution

Active potential time (days)						
Media	NaCl			$MgSO_4$		
Cover thickness (mm)	25	38	50	25	38	50
% of C_3A						
2	31	36	43	–	–	–
4	37	41	50	–	–	–
6	43	50	69	–	–	–
8	46	56	72	9	11	14
10	107	115	135	6	9	12

and steel bar was more positive than −200 mV, it is considered a non corrosion (passive) state for steel, while if the value was more negative than −250 mV this indicates active corrosion. Between −200 and −250 mV, the steel surface may be active or passive [3,11]. Samples immersed in 5% NaCl solution, (Fig. 3a) attained active potential and the time of active potential increased with increasing C_3A in the specimen. Regarding specimens immersed in 5% $MgSO_4$ solution, (Fig. 3b) a steady state potential was observed and remained passive in the range of 4–6% of C_3A. The values of active potential times of different percentage of C_3A due to different cover thickness (mm) of specimens immersed in 5% NaCl or 5% $MgSO_4$ solution are given in Table 4. It can be observed that the active potential time increased with increasing the percentage of C_3A in 5% NaCl solution while in case of 5% $MgSO_4$ solution the active potential time has a significant value for specimens having 6% C_3A and more according to the cover thickness. As cover thickness increased the active potential time increased. The active potential time increased by 8–19% when the cover thickness increased by 50% while as the cover thickness increased by 100% the active potential time increased in a range from 30% to 60%. Results showed that there was no relation between corrosion potential time and cover thickness measured by half-cell potential method.

Generally samples with low percentage of C_3A (2%) immersed in 5% NaCl solution have more negative potential

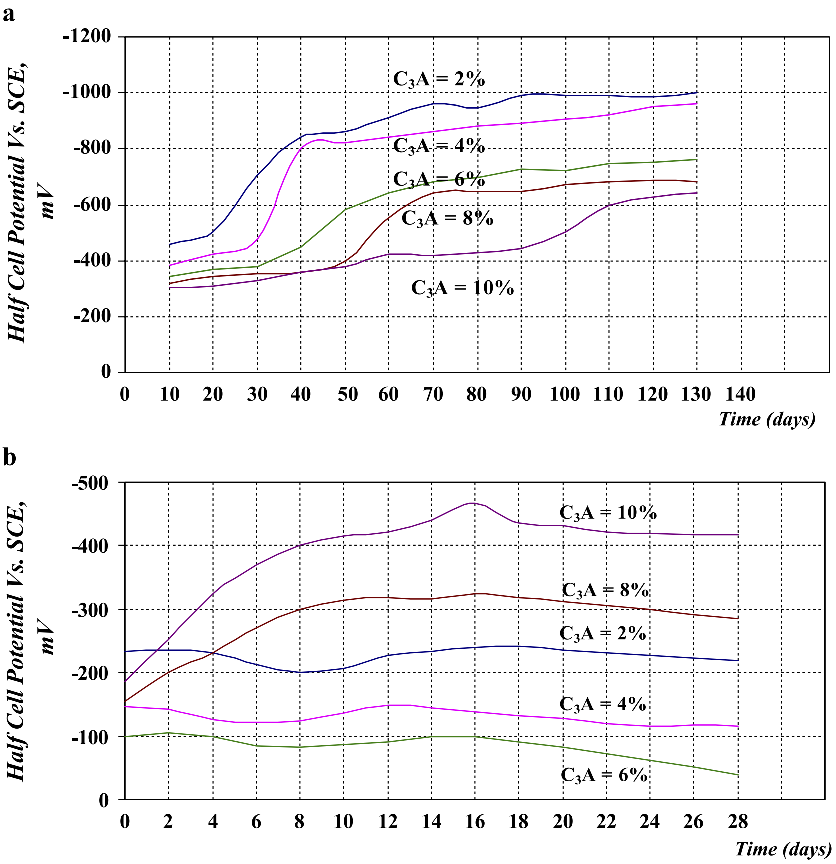

Fig. 3. (a) Variation of corrosion potential of reinforcing steel bar immersed in solution of 5% NaCl (using different percentages of C_3A in cement). (b) Variation of corrosion potential of reinforcing steel bar immersed in solution of 5% $MgSO_4$ (using different percentages of C_3A in cement).

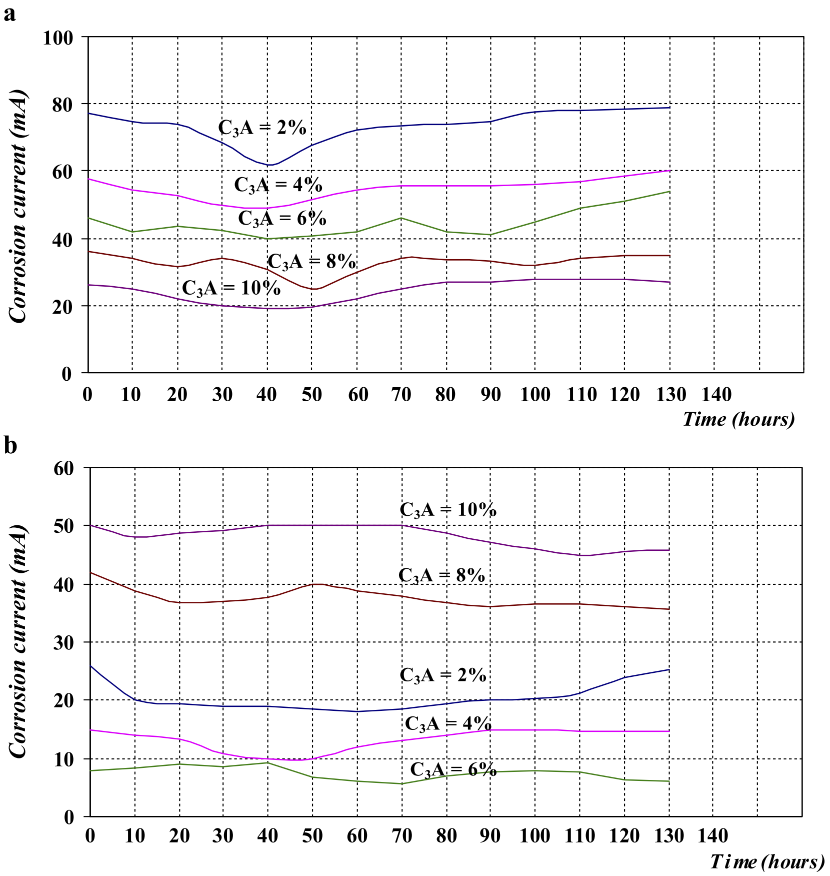

Fig. 4. (a) Current–time relationship at constant voltage of 5 V of reinforcing steel bar immersed in solution of 5% NaCl (using different percentages of C_3A in cement). (b) Current–time relationship at constant voltage of 5 V of reinforcing steel bar immersed in solution of 5% $MgSO_4$ (using different percentages of C_3A in cement).

(about ≈ -850 mv) but they have less negative values (about ≈ -200 mv) if immersed in 5% $MgSO_4$ solution.

3.2.2. Impressed voltage method

Fig. 4a and b show the current–time relationship for reinforcing steel bars embedded in cement paste with different percentage of C_3A and immersed in 5% NaCl or 5% $MgSO_4$ solutions at constant voltage of 5 V, respectively. The area under the current–time curve decreased as the percent of C_3A increased when the samples were immersed in 5% NaCl solution. Regarding specimens immersed in 5% of $MgSO_4$ solution the area under the curve was lowest as the concentration range of C_3A% in cement was from 4% to 6%.

The considerable change in current values can be divided into three stages. The first stage was characterized by an initial decrease in current values with time and this can be attributed to the formation of iron oxide layer, which protects steel temporarily. The second stage was characterized by an increase in current due to the intimation of micro-crack which resulted from steel corrosion. In this stage resistively decreased and ions penetrate into the steel. The third stage was characterized by relatively small current variation since resistively reached constant values. In this stage the corrosion rate and failure mode were dependent on the percentage of C_3A and nature of ions (Cl^- or SO_4^{--}), which effect the nature and strength of the passive film [2].

Table 5 shows the different amount of iron dissolved due to corrosion of anodic steel bar used in the cell of different C_3A % immersed in 5% NaCl or 5% $MgSO_4$ solutions for 130 h for different cover thickness [weight loss (W_{loss}) expressed as=initial weight−final weight].

Table 5
Weight loss percent (m g) at different percentage of C_3A immersed in chloride or sulphate media for 130 h

Weight loss						
Surround media	5% NaCl			5% $MgSO_4$		
Cover thickness (mm)	25	38	50	25	38	50
% of C_3A						
2	0.962	0.911	0.772	0.903	0.810	0.612
4	0.851	0.815	0.393	0.791	0.701	0.486
6	0.643	0.623	0.321	0.342	0.532	0.342
8	0.512	0.419	0.214	0.713	0.315	0.256
10	0.432	0.381	0.183	0.861	0.437	0.842

Results indicated that the weight loss decreased as the percent of C_3A increased when immersed in NaCl solution, but when immersed in $MgSO_4$ solution the weight loss decreased as the percent of C_3A increased up to 6% then the weight loss started to increase as the percent of C_3A increased. It was also observed that as cover thickness increased the weight loss decreased.

3.2.3. Impressed current method

Fig. 5a and b show the potential–time curve for reinforced cement paste specimens immersed in 5% NaCl or 5% $MgSO_4$ solutions at constant impressed current of 20 μA/cm^2, respectively. The steel potential rose very slowly from 5 to 40 days towards the noble direction in case of samples immersed in 5% NaCl solution. While samples immersed in 5% $MgSO_4$ solutions the steel showed sharp rise in potential (from 15 to 65 min) to the noble direction and shorter time to reach passivity state (non-corrosion).

Measurements of stationary potential anode polarization of reinforced steel bar in cement paste under impressed current gives more information about the electrochemical behavior of steel bars and helps to demonstrate the dependence of the corrosive process on cement moisture. Results indicated that the steel bar takes more time to reach passivity state when immersed in chloride solution than when immersed in sulphate media.

4. Discussion

The results of the present work showed that each electrochemical technique provide some but not all information about the corrosion resistance of steel bars embedded in cement in exposed to aggressive media.

Results showed that the major cement component responsible for chloride binding is C_3A. Aluminates in C_3A react with chloride forming an insoluble compound of calcium chloro-aluminate $3\ CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10\ H_2O$. Monochloro-aluminate hydrate and trichlor-aluminate hydrate $3\ CaO \cdot Al_2O_3 \cdot 3\ CaCl_2 \cdot 32\ H_2O$, thus slowing down detrimental effect of chlorides on corrosion of reinforcing steel [6]. In general reinforcing steel bars embedded in cement of low C_3A suffer more corrosion than that embedded in cement of higher C_3A. Results also indicated that the time to initiate corrosion of cement type III (10% C_3A) was triple that for cement type I (2% C_3A) when exposed to moderate chloride contents. The active potential times of cement immersed in NaCl solution increased as the percentage of C_3A increased. Moreover

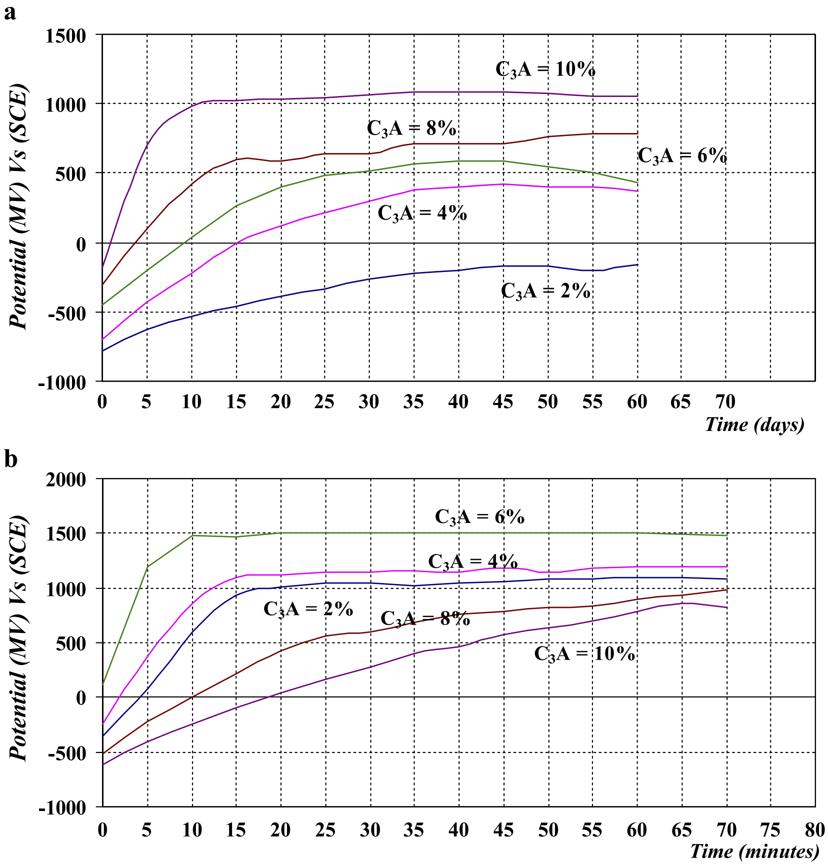

Fig. 5. (a) Potential–time relationship at impressed current of 20 μA/cm^2 of reinforcing steel bar immersed in solution of 5% NaCl (using different percentages of C_3A in cement). (b) Potential–time relationship at impressed current of 20 μA/cm^2 of reinforcing steel bar immersed in solution of 5% $MgSO_4$ (using different percentages of C_3A in cement).

the amount of iron dissolved due to corrosion of steel bar at different percentage of C_3A in cement immersed in 5% NaCl solution decreased with increasing C_3A% as indicated by impressed voltage method. The increased C_3A% is not always favorable because beyond a certain limit it has a harmful effect on concrete in marine environment [8].

In the present study the effect of sulphate ions on the corrosion of steel was different from that of chloride ions. Sulphate ions resisted various type of portland cement depending on C_3A%. Result showed that when exposed to sulphate environments (5% $MgSO_4$) corrosion increased if C_3A% was higher than 6%. On the other hand, 4% C_3A was found to be the most suitable percent to minimize steel bar corrosion. Results indicated that when immersed in 5% $MgSO_4$ solution the active potential time (days) for cement decreased as the percentage of C_3A increased while the steel weight loss increased as the percent of C_3A increased in cement. This can be attributed to the existing original passive film which may be replaced by a thin protective film. Modification of the original film by sulphate ions may lead to the formation of ion sulphate, and reduces the ability of protective film than the original passive film [7].

The presence of other ions than sulphate in solution (such as chlorides) increased the solubility of the constituent part of hardened cement and of hydro-sulpho-aluminate, which reduced the corrosion action of such solution on steel bars. The results indicated that the great amount of chloride ions in sulphate solution reduced the risk of sulpho-aluminate attack on reinforcing in concrete.

5. Conclusions

From the obtained results it can be concluded that :

(1) Chloride ions are more aggressive for steel bars in cement than sulphate ions. However, sulphate ions attack cement of more than 6% of at C_3A forming a weak protective film.
(2) Tricalcium-aluminate (C_3A) plays an important role in reducing the corrosion of steel in cement exposed to chloride or sulphate media.
(3) Concrete made with cement of low percentage of C_3A suffers more corrosion compared to concrete made with cement of high C_3A.
(4) Increasing the percent of C_3A from 2% to 10% decreases the corrosion of reinforcing steel immersed in 5% NaCl solution.
(5) C_3A% from 2 to 6 decreases the corrosion rate of reinforced steel bar of samples immersed in 5% $MgSO_4$ solution, while C_3A% from 6 to 10 accelerates the corrosion rate of reinforcing steel bar.
(6) The presence of chlorides together with sulphate ions reduces the effect of sulphate attack.
(7) The optimum percentage of C_3A to control corrosion of reinforcing steel in both chloride and sulphate containing media is 6%.
(8) Steel corrosion rate is a function of cement cover thickness over the reinforcement and bar diameter.

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