Journal of Metals, Materials and Minerals, Vol.21 No.1 pp.57-66, 2011

Corrosion Prevention of Rebar in Concrete due to Chloride

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Abstract

In coastal and brackish areas, black rebar in concrete structures suffers from chloride corrosion which leads to spalling of the concrete. The "Half Cell Potential Measurement" technique has been applied to study the corrosion behavior of both black and galvanized deformed rebar in different concretes. Additives in the concretes vary from pozzolan, calcium nitrite, to pozzolan plus calcium nitrite. Rebar which has higher half cell potential possesses better corrosion resistance. It has been found that concrete cover thickness has no significant effect on the half cell potential of either rebar; that for both types of rebar, the half cell potential is highest in concrete coming from cement + fly ash, and finally, that the half cell potential of galvanized rebar is lower than that of black rebar because zinc has lower electro-chemical potential at -763 mV than steel at -440 mV.

Key words: Rebar, Chloride induced corrosion, Pozzolan, Calcium Nitrite, Half cell potential measurement

Introduction

Reinforced concrete is concrete incorporate with steel bars. While the concrete resists compression, the rebar withstands tension of the load. Concrete can be made into almost any shapes and sizes. Without steel reinforcement, many concrete structures would not have been possible.

Steel reinforced concrete structures suffer in coastal and brackish areas due to chloride induced corrosion onto the rebar. The phenomenon weakens the structures, and reduces their load carrying capacity and durability. When steel corrodes to form rust, its volume expands 4 to 6 times causing concrete to spall. The detachment of rebar from concrete and the reduction of load bearing cross section of rebar may cause the structures to tumble down.

When high pH wet cement contacts rebar, a hydration reaction occurs with the formation of $Fe(OH)_2$ passive film on the steel surface. As long as this film persists, the rebar does not corrode. However, depassivation of rebar may be caused by carbonation and especially by chloride attack (1). (See Figure 1)

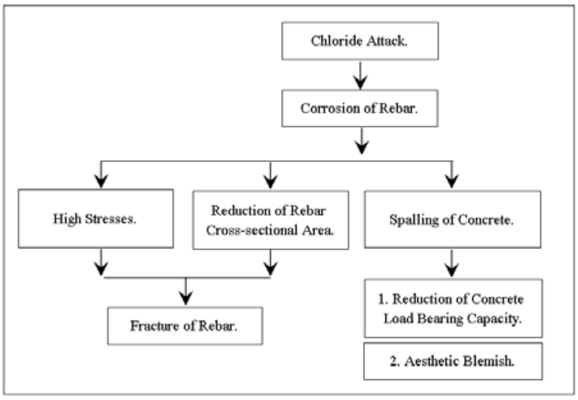

Figure 1. Chloride attack–effects on rebar and concrete (1).

Corrosion Prevention of Rebar

It may be achieved by the following actions (2).

1. Design concrete to obtain low water permeability. This trait which retards diffusion of chloride ions is the result from having a low water to binder ratio. The addition of "filter" materials to cement such as silica fume and pozzolanic fly ash at appropriate quantities not only reduces permeability of concrete, but also "sieges" chloride ions much more effectively than cement alone. The thickness of concrete layer around rebar and proper curing of the wet binder are also vital to the marine environment resistance of the rebar.

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2. Use surface-coated rebar in concrete. In this aspect, galvanized rebar is quite widely used. Compared to steel, zinc has a corrosion resistance in the region of 17-80 times better than steel, depending on the environment in which it is applied. Moreover, the electro-chemical potential of zinc is -763 mV compared to -440 mV of steel. Hence for galvanized steel bar, when the zinc is intact, it provides barrier protection to the steel substrate. But when some areas of the zinc coating are damaged, the zinc still protects the steel via cathodic protection mechanism.

3. Add corrosion inhibitors to binder. One such popular chemical is calcium nitrite which provides another passive layer of $2NO.Fe_2O_3$ on rebar in case the previous mentioned $Fe(OH)_2$ film is destroyed by chloride ions. The reaction may be represented by the following equation (3).

$$2\,Fe^{2+}\ 2OH^{-} + 2(\,NO_2)^{2-} \rightarrow 2NO = Fe_2O_3 + H_2O + 2e^{-} \qquad \text{-----}\ (1)$$

Half Cell Potential Measurement (ASTM C 876)

It is a non-destructive electro-chemical method applied to find out the corrosion tendency of rebar in concrete. The technique directly measures the potential of rebar using a high-impedance voltmeter as in Figure 2. The meter has 2 terminals, one of which goes straight to the rebar in concrete, while the other is connected to a copper/copper sulfate reference cell with a porous sponge end. During the measurement process, the sponge is guided to slide over the surface of the concrete, and readings from the voltmeter are registered (4).

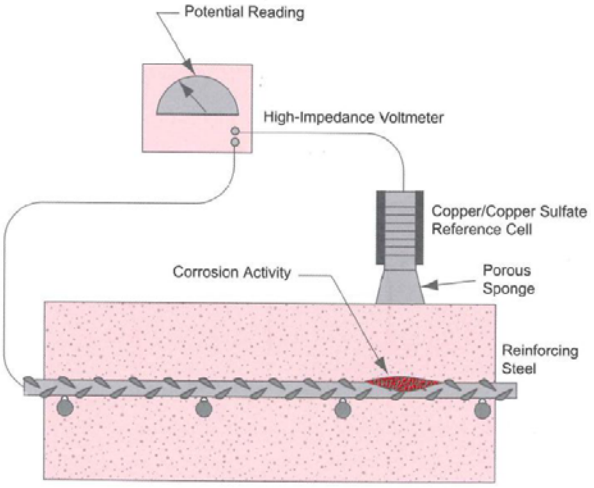


Figure 2. Copper/copper sulfate half cell (4).

ASTM C 876 has provided guidelines on the relationship between half cell potential and tendency of rebar corrosion as follows (5).

1. If potentials over an area are more positive than -200 mV, there is a greater than 90% probability that no reinforcing steel corrosion is occurring in that area at the time of measurement.

2. If potentials over an area are in the range of -200 mV to -350 mV, corrosion activity of the reinforcing steel in that area is uncertain.

3. If potentials over an area are more negative than -350 mV, there is a greater than 90% probability that reinforcing steel corrosion is occurring in that area at the time of measurement.

Base Lines

For concrete structures, the Engineering Institute of Thailand has specified for the code of concrete that the maximum water to binder ratio is 0.45, and that cover thickness on rebar for floors and beams should not be less than 5 cm (6) for concrete which requires high resistance to chloride diffusion under severe corrosion environment. The design for this experimental work is based upon the construction code above.

In this work, 4 different concrete mixes with different additives such as fly ash and calcium nitrite are designed. The compositions of the mixes are displayed in Table 1.

Experimental Procedures

1. Evaluate properties of the 4 concretes.

1.1 Tests for Slump according to ASTM C 143.

1.2 Tests for Compressive Strengthaccording to BS 1881: Part 4.

2. Appraise corrosion severity of rebar in the concretes due to chloride.

2.1 Prepare black and galvanized deformed bars, grade SD 40 according to TIS 24, with 12 mm diameter.

2.2. Prepare sample cubes of dimensions 15 * 15 * 15 cm^3. The deformed bars are placed in the cubes having concrete cover thickness of 3 cm and 5 cm. Four concrete mixes are used.

2.3. Place the cubes in NaCl solution at 12% w/w concentration for 98 days to accelerate rebar corrosion. After a period of 2 days, the cubes are taken out from the solution which is now renewed, and the cubes are let to settle for 2 hours before the half cell potential measurement is carried out. All results are recorded.

2.4 When 98 days have elapsed and the corresponding work has all been completed, the cubes are crushed to expose the rebar. Severity of corrosion as well as the chloride content on the surface of rebar are examined and measured respectively. The chloride contents are examined according to ASTM C 1218 Standard Test Method for Water-Soluble Chloride in Mortar and Concrete.

Experimental Results

1. Properties of concrete from the 4 mixes:
(See Table 2)
2. Test results of half cell potential vs. submersion time:

The test results are depicted in the form of graphs from Figures 3 to 14. The Figures are further divided into 4 sub-groups which are named as A, B, C and D.

On those graphs, brown dot lines and brown dashed lines are drawn at potential -200 mV and -350 mV, respectively. This is to graphically display the essence of ASTM C 876 mentioned in the **Introduction** section that areas above the brown dot line would not see rebar corrosion, and areas below brown dashed line would encounter severe corrosion on steel reinforcement. The remaining domain between brown dot lines and brown dashed lines means that corrosion of rebar would be uncertain.

Figures 3 and 4 for black rebar show that Mixes 1, 2, and 3 have similar half cell potential. It can also be seen that Mix 4 provides the lowest performance. At the beginning of the test the potential of Mix 2 is lower than potentials of Mixes 1 and 3; it is rather puzzling, however, that the reverse is true for both cover thicknesses at the end of the test.

Figures 5 and 6 for galvanized rebar show that the half cell potential for all mixes has the same trend. It may also be concluded that the order of corrosion resistance of the mixes ranging from high to low is Mix 2, Mix 3, Mix 1 and Mix 4.

Apart from Mix 4, group C for black rebar displays that concrete cover thickness of 3 and 5 cm does not create a difference in terms of half cell potential of the other 3 mixes. For Mix 4, it is clear that the thicker cover contributes more corrosion protection to rebar than its thinner counterpart. This finding may well imply that Mix 4 is rather “weak” for chloride attack, and has to resort to concrete thickness to raise its half cell potential.

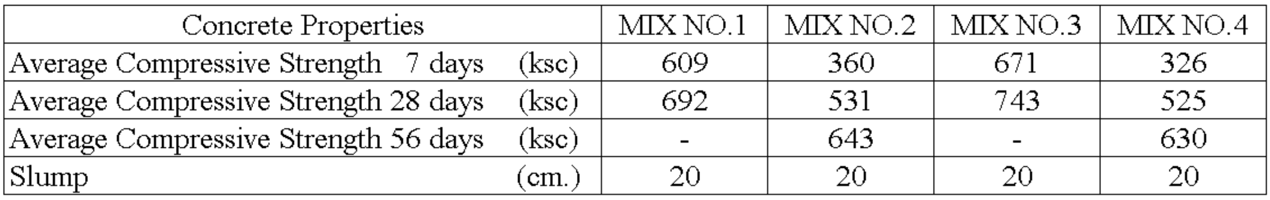
Group D for galvanized rebar shows that concrete cover thickness of 3 and 5 cm makes virtually no difference on the half cell potential of all mixes. It should also be noted that nearly all half cell potentials fall below the brown dashed line, and that galvanized surface brings the potential of 3 and 5 cm cover thickness of Mix 4 to the same proximity in contrast to what black steel surface does.

Table 1. Ingredients of the 4 concrete mixes used in the work.

MIX INGREDIENTS		MIX NO.1	MIX NO.2	MIX NO.3	MIX NO.4
Type 1 Cement	(kg.)	356	178	356	178
Pulverized Fly Ash	(kg.)	-	178	-	178
Water	(l.)	160	160	160	160
w/b Ratio		0.45	0.45	0.45	0.45
Calcium Nitrite	(l.)	-	-	20	20

* Coarse and fine aggregates added to make up to one cubic meter of concrete.
** Type D and F admixtures added to improve workability.

Table 2. Properties of concrete from the 4 mixes.



Concrete Properties		MIX NO.1	MIX NO.2	MIX NO.3	MIX NO.4
Average Compressive Strength 7 days	(ksc)	609	360	671	326
Average Compressive Strength 28 days	(ksc)	692	531	743	525
Average Compressive Strength 56 days	(ksc)	-	643	-	630
Slump	(cm.)	20	20	20	20

Group A: *Containing Figures 3 and 4*

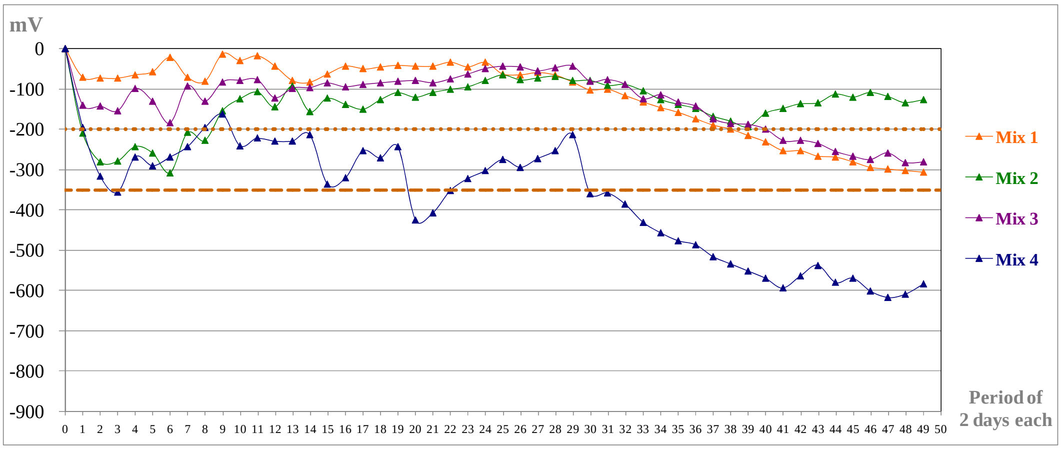


Figure 3. mV of black deformed bar in the 4 mixes vs. submersion period with 3 cm cover.

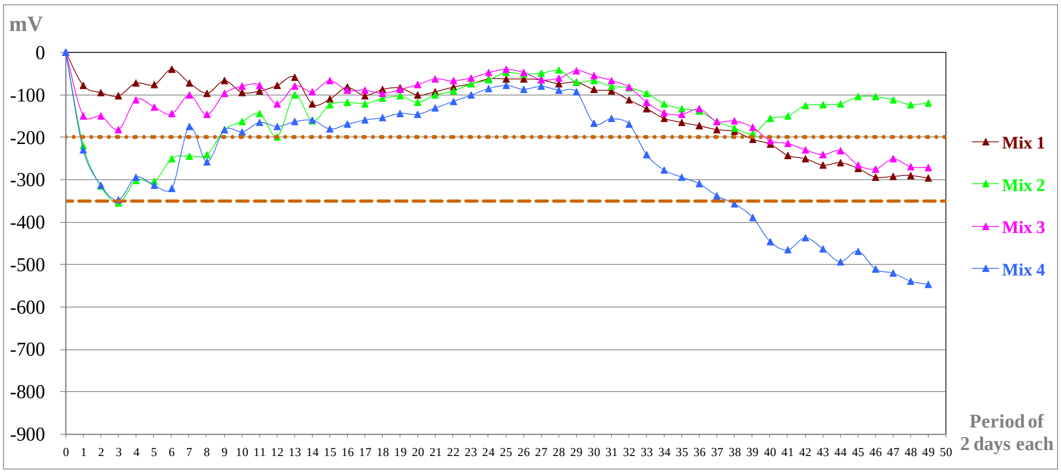


Figure 4. mV of black deformed bar in the 4 mixes vs. submersion period with 5 cm cover.

Group B: *Containing Figures 5 and 6*

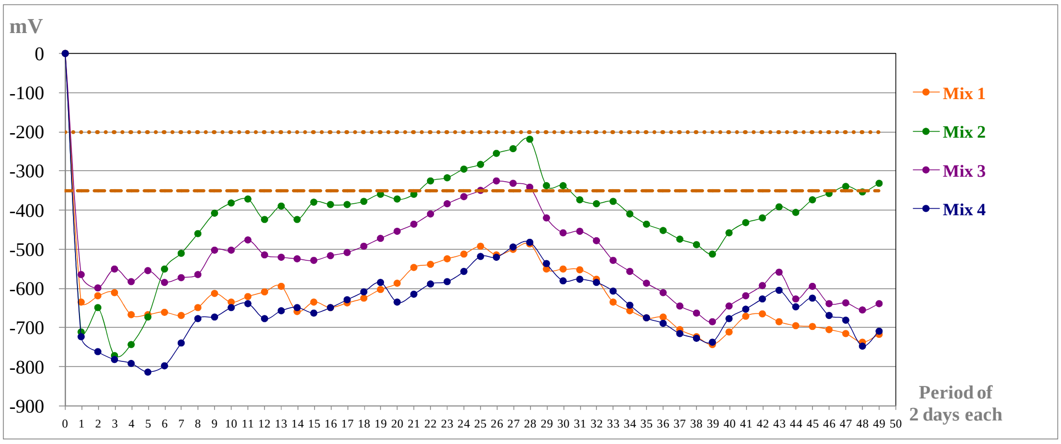


Figure 5. mV of galvanized deformed bar in the 4 mixes vs. submersion period with 3 cm cover.

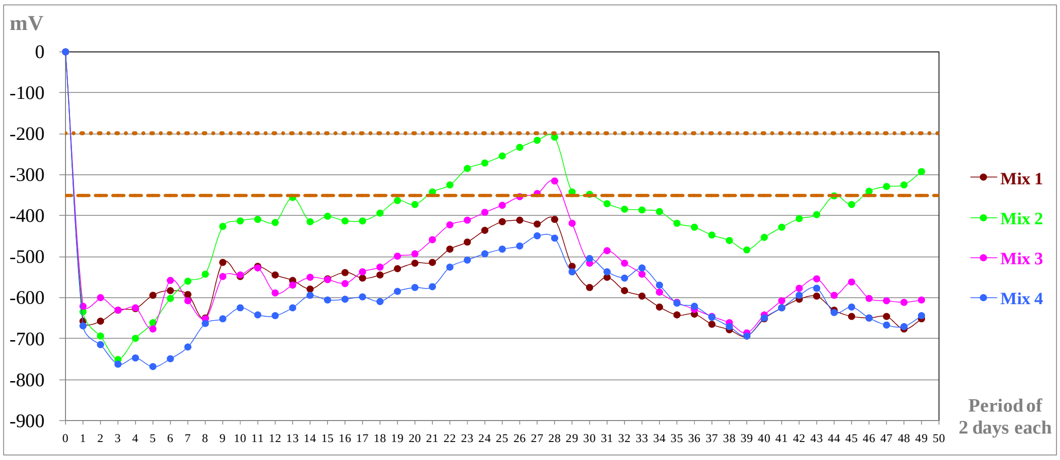


Figure 6. mV of galvanized deformed bar in the 4 mixes vs. submersion period with 5 cm cover.

Group C: *With Figures 7 to 10 inclusive*

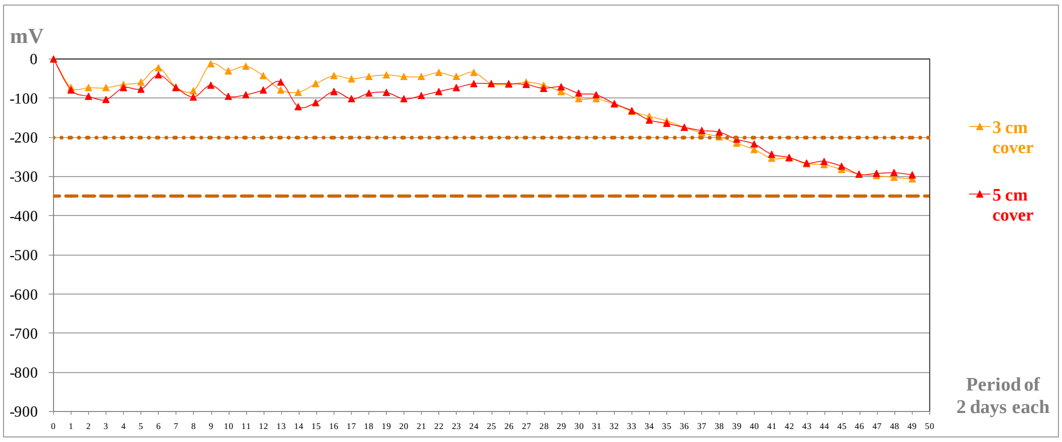


Figure 7. mV of black deformed bar in mix 1 vs. submersion period with 3 and 5 cm cover.

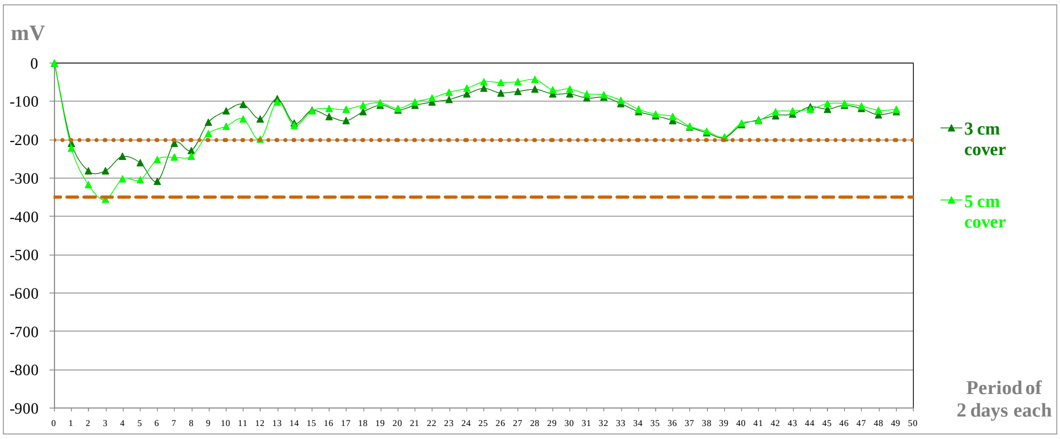


Figure 8. mV of black deformed bar in mix 2 vs. submersion period with 3 and 5 cm cover.

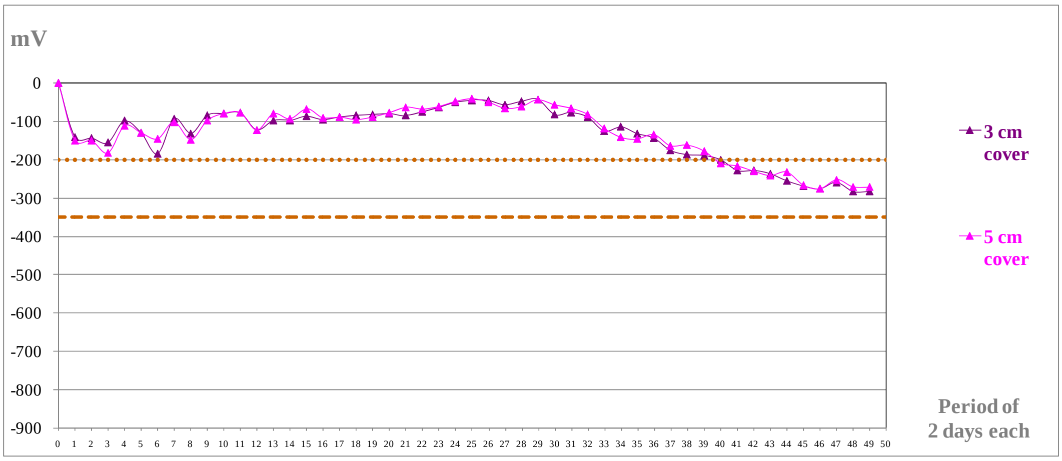


Figure 9. mV of black deformed bar in mix 3 vs. submersion period with 3 and 5 cm cover.

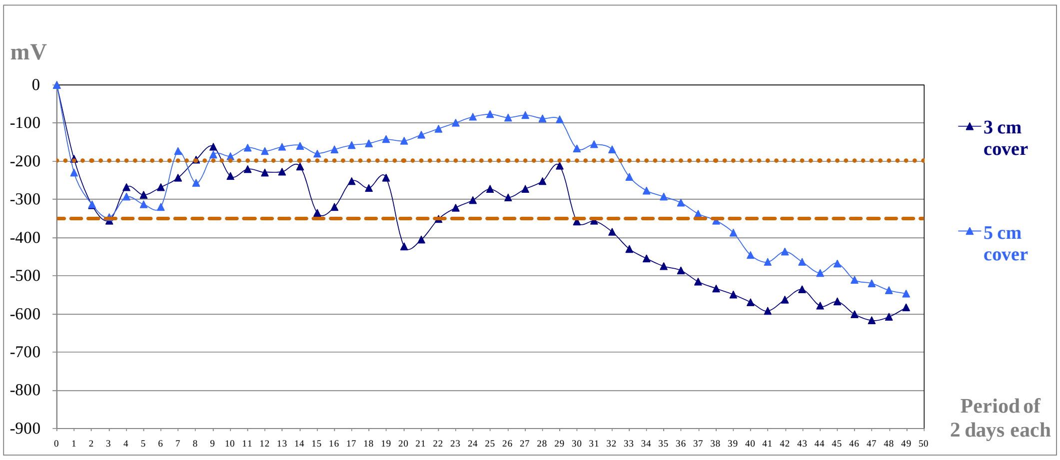


Figure 10. mV of black deformed bar in mix 4 vs. submersion period with 3 and 5 cm cover.

***Group D:** With Figures 11 to 14 inclusive*

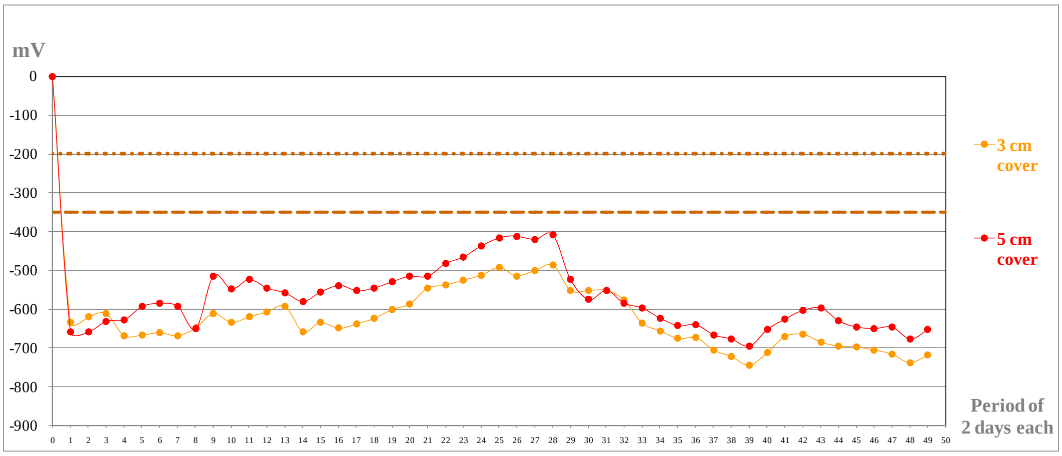


Figure 11. mV of galvanized deformed bar in mix 1 vs. submersion period with 3 and 5 cm cover.

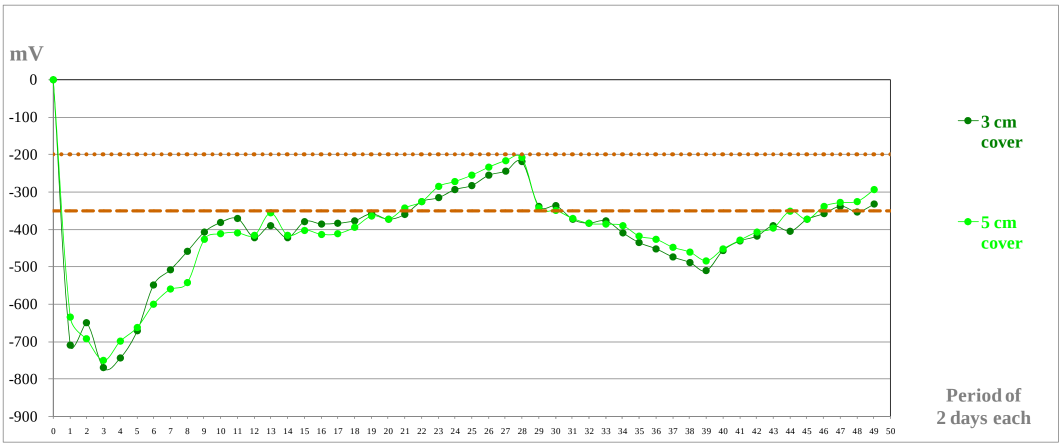


Figure 12. mV of galvanized deformed bar in mix 2 vs. submersion period with 3 and 5 cm cover.

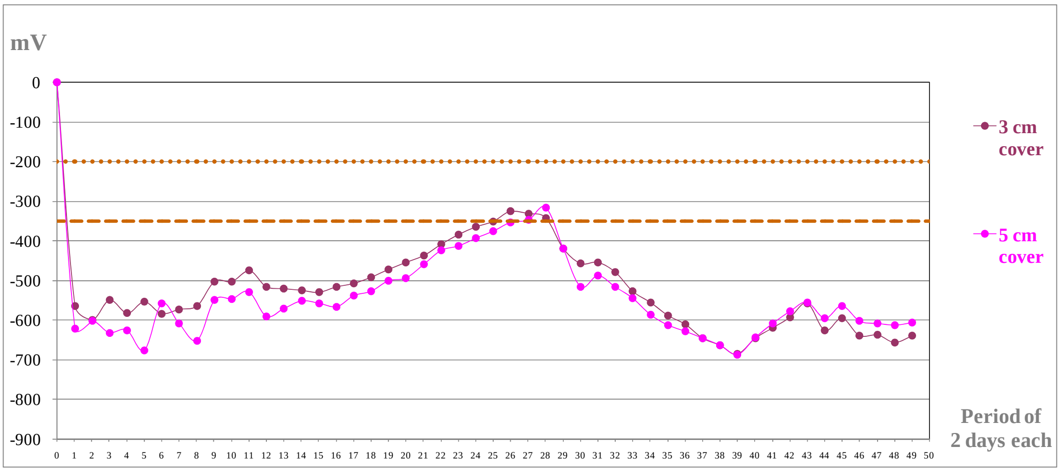


Figure 13. mV of galvanized deformed bar in mix 3 vs. submersion period with 3 and 5 cm cover.

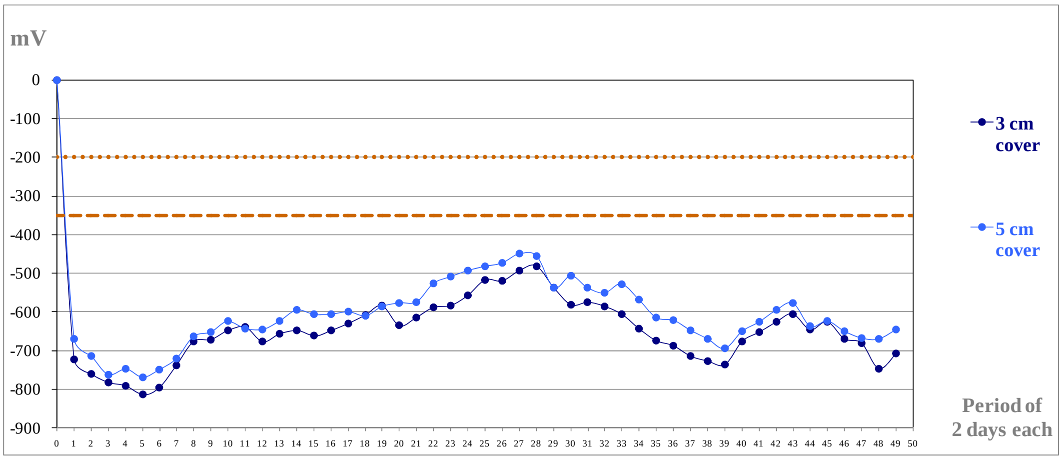


Figure 14. mV of galvanized deformed bar in mix 4 vs. submersion period with 3 and 5 cm cover.

3. The extent of rebar corrosion in the 4 mixes:

Figure 15. Exposed black deformed bar in mix 4 with 3 and 5cm cover (some rust).

Figure 16. Representative exposed black deformed bar in mixes 1, 2 and 3 with 3 and 5 cm cover, (no rust).

Figure 17. Exposed galvanized deformed bar in the 4 mixes, (no rust at all).

4. The chloride contents in the vicinity of rebar surface of the 4 mixes:

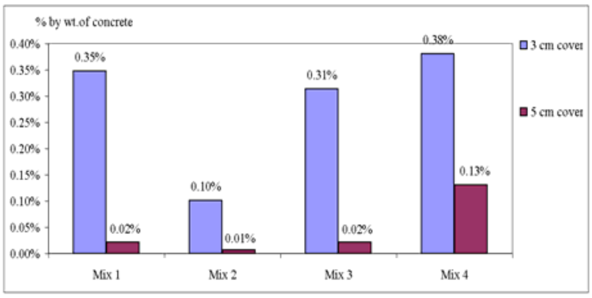


Figure 18. Chloride contents in concrete in close proximity to rebar surface of the 4 mixes.

It is observed that for all the 4 mixes with 3 cm cover, chloride content at the rebar surface is higher than 5 cm cover. Mix 4 has the highest chloride content at rebar surface.

Discussions

1. Experimental results in Table 2 display average compressive concrete strength of the 4 mixes from no.1 to no. 4 as follows.

	1	2	3	4
Curing time 7 days (ksc):	609	360	671	326
Curing time 28 days (ksc):	692	531	743	525
Curing time 56 days (ksc):	-	643	-	630

At 28 days curing, the order from high to low of concrete compressive strength is cement + calcium nitrite (3), cement (1), cement + fly ash (2) and cement + fly ash + calcium nitrite (4), respectively. The reason for the low strength phenomenon of concretes with fly ash at this curing time is that the full impact of pozzolanic reaction is not yet realized. With sufficiently long curing at 56 days, the expected high compressive strength of the concretes is then obtained. On strength alone, the 4 different mixes may all be considered as acceptable.

High concrete compressive strength may also imply high concrete cover density which provides a good physical barrier protecting the steel from chloride induced corrosion (7). The notion can then be used to explain why the half cell potential of rebar in Mix 2 with fly ash is lower than that of Mixes 1 and 3 at the beginning, but climbing up to the same level as the 2 mixes at 56 days or at 28th interval on the y-axis in Figures 3 and 4.

However, reference (7) also states that a dense concrete cover limits oxygen diffusion process in a way that the oxygen in the rebar/concrete interface could be very low, that the corrosion potential could shift too a more negative value, and that the potential could not be used to indicate a high probability of steel corrosion.

In total, this work suggests that the high compressive strength of concrete retards diffusion of chloride ions and contributes a high corrosion potential to rebar.

Mix 4 having 3 cm concrete cover in Figure 3 displays poor corrosion potential; but Figure 4 reveals that thicker cover at 5 cm does help retard chloride diffusion. It may be concluded that cement + fly ash + calcium nitrite is a bad combination when corrosion of rebar is concerned.

2. Based on ASTM C 876 about half cell potential and tendency of corrosion as indicated by the 2 horizontal lines, one at -200 mV and the other at -350 mV, discussion on corrosion behavior of the deformed rebar in different mixes is proceeded as follows:

2.1 Figures 3 and 4 demonstrate that Mixes 1, 2 and 3 provide similarly good corrosion resistance for black rebar at the same concrete thickness, be it at 3 cm or 5 cm, while Mix 4 is a poor candidate. It is anticipated that only black rebar from Mix 4 would suffer from corrosion when the concrete-cubes are crushed at the end of the test. The notion comes from the graphs in that the half cell potential is lower than -350 mV. Examination on Figures 15 and 16 proves that this is in fact the case.

2.2 Figures 5 and 6 show that regardless of the cover thickness, the order of effectiveness in protecting galvanized deformed rebar ranges from Mix 2, Mix 3, while Mix 1 and Mix 4 take the same ranking. It should be noted that no rebar is corroded as can be seen in Figure 17 although virtually all of the half cell potential readings are lower than -350 mV. This is the real advantage of having rebar galvanized.

2.3 Figures 7, 8, and 9 show that concrete cover thickness of Mixes 1, 2 and 3 play no significant role on the potential of black deformed bar. The same cannot be maintained for Mix 4 in that the black deformed bar potential does depend to a certain degree on concrete cover thickness as shown in Figure 10.

2.4 Figures 11, 12, 13 and 14 display the fact that the concrete cover thickness of the 4 mixes has no effect on the potential of galvanized deformed bar at all.

2.5 As for the extent of corrosion on black rebar, Figure 15 clearly demonstrates Mix 4 is unacceptable even the concrete cover is 5 cm. Figure 16 shows that Mixes 1, 2 and 3 have good corrosion resistance. And lastly in Figure 17, it is obvious that galvanized rebar will not corrode regardless of concrete mixes.

3. Chloride content at vicinity of rebar surface

Figure 18 reveals that the water soluble chloride contents on rebar surface of 3 cm concrete cover is much higher than that of the 5 cm counterpart. The reason for this discovery can be that chloride ions have a shorter distance to diffuse to rebar surface at 3 cm cover in comparison to the 5 cm cover.

Conclusions

1. Thickness of concrete cover has no significant effect on half cell potential of both black and galvanized deformed bar.

2. For black deformed bar, the half cell potential ranging from high to low for the 4 mixes of binder is shown below:
   - Cement + Fly ash
   - Cement + Calcium Nitrite, Cement only
   - Cement + Fly ash + Calcium Nitrite

3. For galvanized deformed rebar, the half cell potential ranging from high to low for the 4 mixes of binder is as follows:
   - Cement + Fly ash
   - Cement + Calcium Nitrite
   - Cement + Fly ash + Calcium Nitrite, Cement only

4. The reason why the half cell potential of galvanized steel is lower than that of black steel is because zinc has lower electro-chemical potential at -763 mV than steel at -440mV.

5. Being a non-destructive testing method, the half cell potential approach can be considered as very useful in monitoring the corrosion severity of rebar, especially in marine environment. It is recommended that more research be carried out to investigate the extent of rust formation at different concrete depths so as to obtain more reliable information in field practice.

6. To protect rebar from chloride induced corrosion, there are good reasons to believe that it should be galvanized.

7. Half Cell Potential Measurement, the extent of rebar and the water soluble chloride content reveal that Calcium Nitrite should not be added in concrete containing fly ash.

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