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Critical polarization resistance in service life determination

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Abstract

The service life of concrete exposed to chloride environments was measured experimentally, and polarization resistance and half-cell potential values were used to monitor corrosion. Service life was considered as the combination of the initiation phase and a part of the propagation phase in which the degree of corrosion is lower than an "tolerable" degree of corrosion. Polarization resistance corresponding to this tolerable degree of corrosion was termed the "critical polarization resistance," or CPR. Subsequently, CPR was used to establish the service life of four grades of concretes prepared from four cements; the influence of the type of cement was also studied. Polarization resistance was found to be a much more useful and reliable technique in service life evaluation than the half-cell potential.

Keywords: Corrosion; Electrochemical properties; Polarization resistance; Service life; Long-term performance

1. Introduction

The service life of concrete in marine environments is commonly divided into two phases: the initiation phase and the propagation phase. In the initiation phase, no corrosion is observed, but the chloride ions are migrating from the aggressive environment to the reinforcement. At the end of the initiation phase, the concentration of chloride ions at the reinforcement is greater than a critical threshold concentration, which leads to depassivation, and subsequently corrosion starts, and this is considered as the propagation phase. Various researchers have further subdivided the propagation phase depending on the rate of corrosion [1–3].

The effect of the type of cement on the duration of the initiation phase is the subject of numerous studies [4–7]. The general approach is to carry out ponding tests and evaluate the resistance of concrete to the penetration of chloride ions. The resistance of various concretes to chloride penetration is either evaluated by chloride profiles or by the apparent diffusion coefficient calculated by Fick's second law [6,8]. Subsequently, the implication of the chloride profile or apparent diffusion coefficient on the initiation phase or service life is evaluated [4,9,10]. Thereby, the effect of the type of cement on service life is indirectly established.

In this study, the service life of concretes prepared from different cements was experimentally measured and thereby the effect of the type of cement on service life was established.

An estimate of service life would be the initiation phase during which no repairs are required. However, such an estimation is too conservative and a more realistic service life would be the combination of the initiation phase and the part of the propagation phase in which the degree of corrosion is lower than a tolerable degree of corrosion. It is difficult to determine this "tolerable" degree of corrosion and it is complicated by the fact that the values would differ from structure to structure. The tolerable degree of corrosion is also expected to vary within a structure and within structural elements. In this study, the tolerable degree of corrosion has been defined as the stage of propagation phase corresponding to significant corrosion and just before the appearance of rust stains on the surface of the sample or before spalling occurs.

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2. Experimental details

2.1. Materials

In this study, concretes were prepared from four cements as detailed below:

- General purpose (GP) portland cement concrete: concretes prepared from a GP portland cement conforming to Australian Standard AS 3972 and similar to ASTM Type I.
- High-slag cement concrete: concretes prepared from a high slag cement (nominally 65% ground granulated blast furnace slag and 35% GP portland cement) (GP/BS).
- Silica fume concretes: concretes prepared from 93% GP portland cement and 7% silica fume (GP/SF).
- Fly ash concretes: concretes prepared from 30% fly ash (ASTM Class F) and 70% GP portland cement (GP/FA).

2.2. Details of concrete mixes

Concretes of similar 28-day strengths were prepared from the four cements listed above. Concrete mixes of characteristics strength of 15, 20, 40, and 50 MPa (mean strength 22, 27, 47, and 57 MPa, respectively) or of strength grade 15, 20, 40, and 50 were prepared. The coarse aggregate was a crushed river gravel and the sand used was a river sand. A water-reducing agent (WRA) was added to all mixes at a rate of 400 ml per 100 kg of cement. The WRA was a modified sodium salt lignosulfonic acid. Table 1 presents the water-to-cementitious materials ratio (W/CM) and 28-day compressive strengths of the mixes cast. The specimens were cast vertically.

Table 1
Details of the mixes

	GP	GP/BS	GP/FA	GP/SF
Nominal grade 15				
W/CM	0.65	0.65	0.65	0.87
28-day cylinder strength (MPa)	23.0	18.5	21.5	18.5
CPR	14	14	14	8
Nominal grade 20				
W/CM	0.59	0.54	0.56	0.70
28-day cylinder strength (MPa)	24.0	26.0	26.5	30.0
CPR	19	22	20	14
Nominal grade 40				
W/CM	0.52	0.40	0.43	0.52
28-day cylinder strength (MPa)	49.5	46.0	40.5	49.5
CPR	24	39	34	24
Nominal grade 50				
W/CM	0.42	0.34	0.38	0.50
28-day cylinder strength (MPa)	56.0	51.0	50.5	52.5
CPR	33	52	39	23

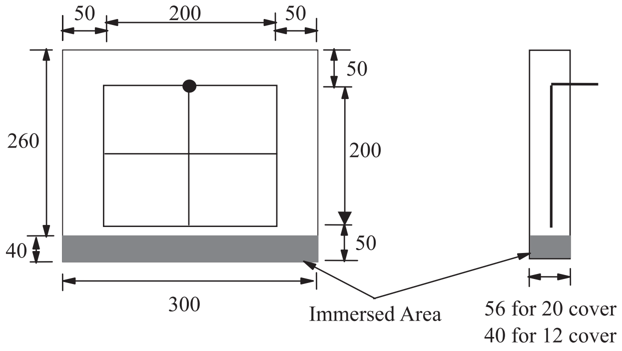

Fig. 1. Concrete slab with steel reinforcement mesh (dimension in mm).

2.3. Sample configuration

Fig. 1 shows the schematic diagram of a slab specimen that was used to measure service life. The sample represents a small section of a structural element typically used in various concrete structures. The 300-mm^2 slabs were 40 and 56 mm thick for concrete covers of 12 and 20 mm, respectively. An F81 (8-mm bars and 100-mm centers) mesh was used as reinforcement for the slabs.

Concretes of grades 15 and 20 are seldom expected to be used in a marine environment and also covers of 12 and 20 mm are low compared to cover requirements in specifications, however, these concretes were selected for the study as their service life is practical to measure. Some of the results of higher grade concretes are presented and the remaining results will be published later. It is anticipated that the trend (effect of the type of cement on service life) observed in higher grade concretes would be similar to the trend observed in lower grade concretes. Long-term data will be essential to conclusively establish the trends in service life.

Before the slabs were cast, the surfaces of the reinforcement meshes were cleaned by sandblasting to remove the oxidation products. Two slabs were cast from each mix, one with a concrete cover of 20 mm and the other with a cover of 12 mm. The slabs were subjected to 7 days of sealed curing followed by storage in laboratory (23 ± 2 °C) to the age of 28 days. At the age of 28 days, the specimens were partially immersed to a depth of 40 mm in a 3% sodium chloride solution in the laboratory.

2.4. Measurement of corrosion and service life

Corrosion rate was indirectly evaluated by measuring the polarization resistance. Furthermore, attempts have been made to determine the polarization resistance that corresponds to the tolerable degree of corrosion, as defined in Section 1, and subsequently, the service life has been calculated for concrete prepared from various cements.

Concretes of similar 28-day strength were immersed in 3% NaCl solution to a depth of 40 mm (Fig. 1) and their corrosion

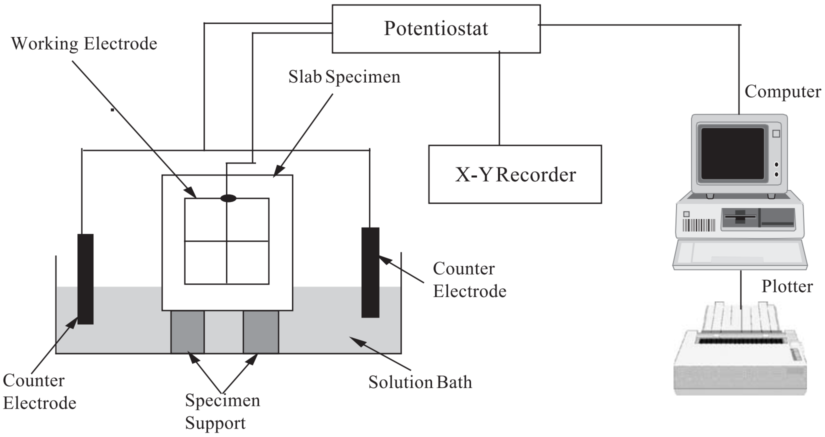

Fig. 2. Setup for the measurement of polarization resistance and half-cell potential.

rate was monitored. The corrosion of the reinforcement was monitored by measuring the half-cell potentials and polarization resistance. Such electrochemical techniques for the nondestructive assessment of metal loss due to corrosion have been employed extensively by many researchers [11–14]. A polarization resistance, which corresponds to the tolerable degree of corrosion, was established as the "critical polarization resistance," or CPR. Subsequently, CPR was used to estimate the service life of concrete.

Fig. 2 shows the experimental setup used for the measurement of half-cell potential and polarization resistance. As shown in Fig. 2, a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat was used for the experiments. This was coupled to a PAR Model 175 Scanner. Modules for IR compensation were built into the system. Real-time data were recorded on an $X-Y$ plotter. Data were also digitized and stored on disk for later computer analysis. A spreadsheet was used to calculate half-cell potential and polarization resistance.

Potentiodynamic anodic/cathodic polarization scans were carried out between the potential (ΔE) of $+50$ and -50 mV with respect to the rest potential (E_{corr}). The potential was applied at a scan rate of 0.5 mV/s and the current (ΔI) required to maintain the overpotential was measured. The reinforcement in the slab was the working electrode, and the counter-electrodes were two graphite rods partially immersed in the solution. A saturated calomel reference (SCE) electrode was located next to the prism and was immersed in the solution to the depth of the bottom of the reinforcement. The specimens were immersed in 3% NaCl solution to a depth of 40 mm during the measurement of polarization resistance. The junction of the anodic and cathodic polarization curve was considered as the rest potential and its potential values as half-cell potential. Half-cell potential values were measured with respect to SCE. Polarization resistance is equal to ($\Delta E/\Delta I$) and is essentially the slope of the potentiodynamic curve between applied potential and applied current measured close to the corrosion potential. A spreadsheet was used to calculate ($\Delta E/\Delta I$) and an average value of polarization resistance was calculated for a range of overpotentials. The spreadsheet was also used to calculate half-cell potential values.

3. Results and discussion

3.1. Half-cell potential values

Figs. 3–10 show the half-cell potential values of concretes of nominal grades 15 to 50 with cover values of 12 and 20 mm. As mentioned earlier, the half-cell potentials were measured with respect to SCE and are reported in volts.

3.2. Polarization resistance values

Figs. 11–18 show the polarization resistance of various concretes.

3.3. Measurement of corrosion

Both half-cell potential and polarization values were used to assess corrosion. According to ASTM C 876, if the half-cell potential value is lower than -270 mV (-0.27 V) with respect to SCE (-350 mV with respect to copper–

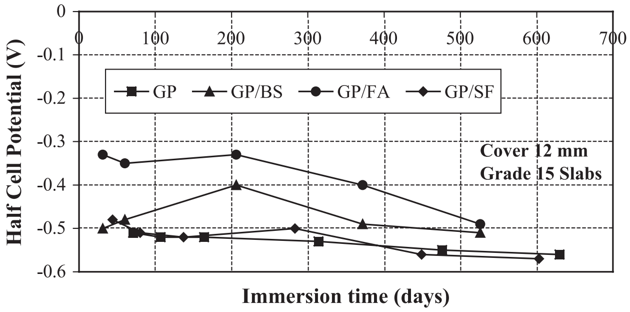

Fig. 3. Half-cell potential values of concretes of grade 15 and a cover of 12 mm.

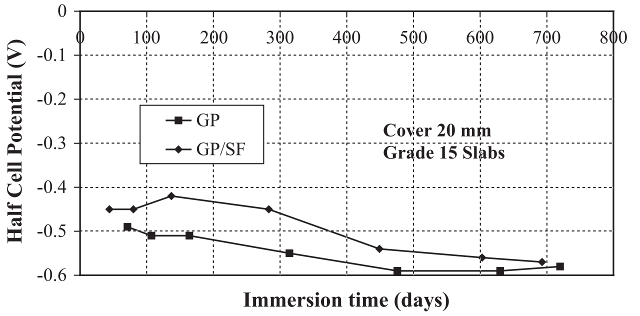

Fig. 4. Half-cell potential values of concretes of grade 15 and a cover of 20 mm.

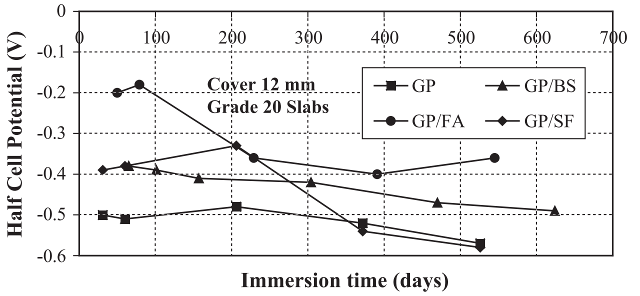

Fig. 5. Half-cell potential values of concretes of grade 20 and a cover of 12 mm.

copper sulfate electrode), there is a 90% probability that the reinforcement is corroding. In addition, polarization resistance (R_p) can be correlated to the corrosion current density (I_{corr}) by the Stern–Geary equation [11,12]. The Stern–Geary equation is shown below (Eq. (1)):

$$I_{corr} = \beta_a \times \beta_c / [2.3 \times R_p \times (\beta_a + \beta_c)] \qquad (1)$$

where β_a and β_c are anodic and cathodic Tafel constants, respectively.

3.4. Service life of concretes

As mentioned earlier, the service life of a concrete in a marine environment can be divided into two phases: corrosion initiation and corrosion propagation. Service life equivalent to just the initiation phase is a conservative estimate, and realistically, service life should include a part of the propagation phase as well. According to Ahmed and Bhattacharjee [2], the end of service life is when the spalling occurs and requires repair actions. In the opinion of the authors, the occurrence of spalling and the need of repairs may jeopardize the safety and integrity of structure and thus the spalling is the upper limit of service life. Thus, a practical, realistic, and safe service life would be less than the time period corresponding to the occurrence of spalling. Such a service life has been defined as the initiation phase and the part of the propagation phase in which the degree of corrosion is below a tolerable degree of corrosion. Such an approach of tolerable or acceptable

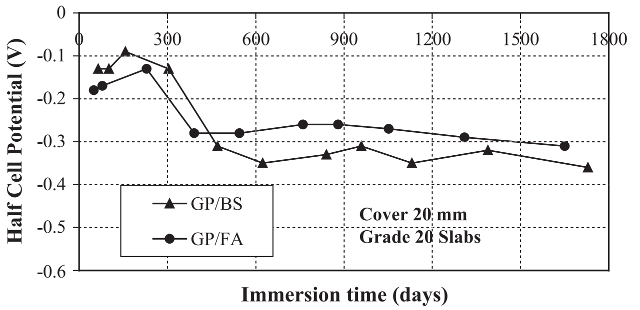

Fig. 6. Half-cell potential values of concretes of grade 20 and a cover of 20 mm.

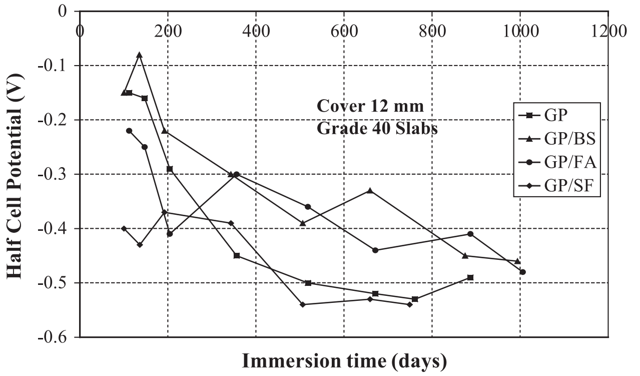

Fig. 7. Half-cell potential values of concretes of grade 40 and a cover of 12 mm.

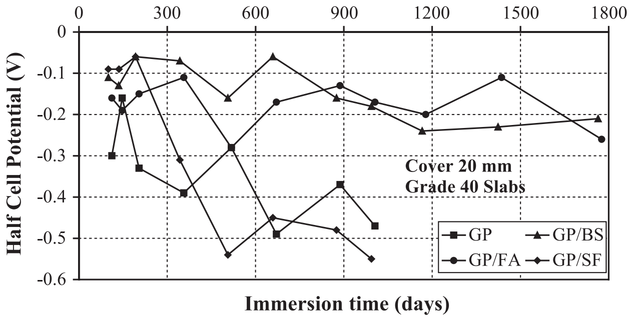

Fig. 8. Half-cell potential values of concretes of grade 40 and a cover of 20 mm.

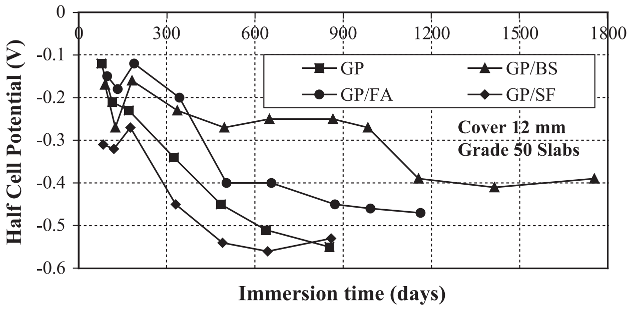

Fig. 9. Half-cell potential values of concretes of grade 50 and a cover of 12 mm.

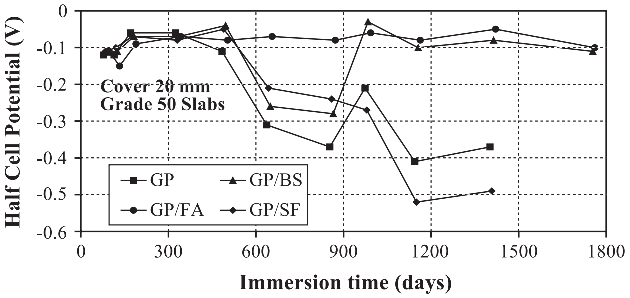

Fig. 10. Half-cell potential values of concretes of grade 50 and a cover of 20 mm.

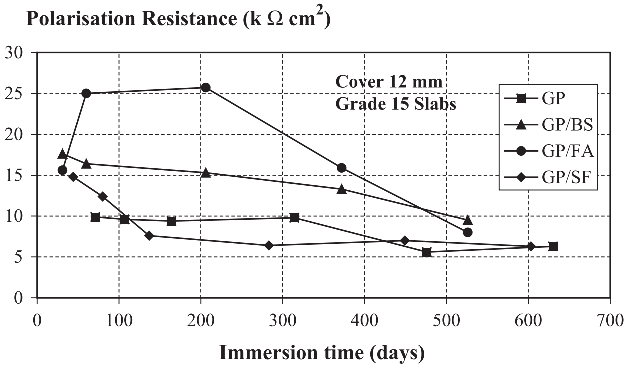

Fig. 11. Polarization resistance of concretes of grade 15 and a cover of 12 mm.

degree of corrosion to calculate service life has been used by other researchers also [15–17]. It is difficult to define this ‘‘tolerable’’ degree of corrosion as it is not expected to be the same for all structures. A tolerable degree of corrosion was arbitrarily defined as the stage of propagation phase corresponding to significant corrosion and just before the appearance of rust stains on the surface of the sample, or the occurrence of spalling. This was considered to be the tolerable degree of corrosion as it will not result in immediate spalling, after which a rehabilitation strategy and repairs will be required. Also, it is expected that a significant reduction in the area of reinforcement bars would not have occurred thus far and consequently will not jeopardize the structural integrity or the safety [18,19]. Such an tolerable degree of corrosion was used to determine the service life.

Thus, the tolerable degree of corrosion would correspond to a particular value of polarization resistance, and this is called CPR. A polarization resistance value higher than CPR signifies that the degree of corrosion is lower

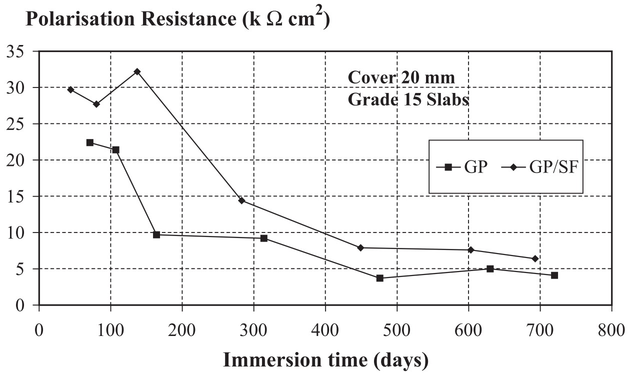

Fig. 12. Polarization resistance of concretes of grade 15 and a cover of 20 mm.

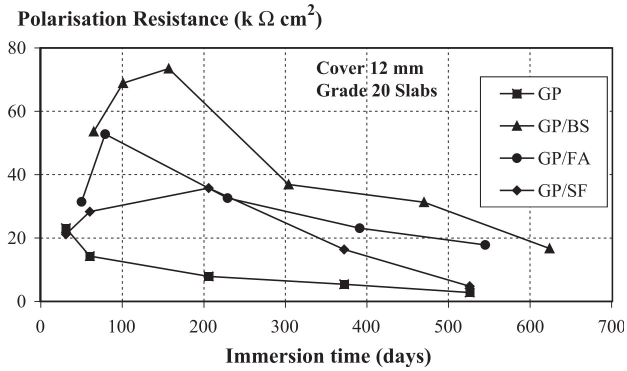

Fig. 13. Polarization resistance of concretes of grade 20 and a cover of 12 mm.

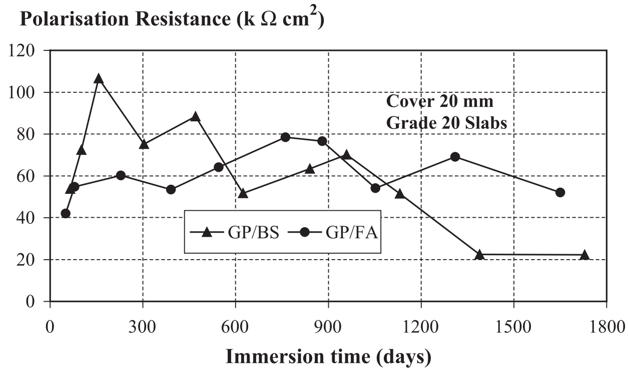

Fig. 14. Polarization resistance of concretes of grade 20 and a cover of 20 mm.

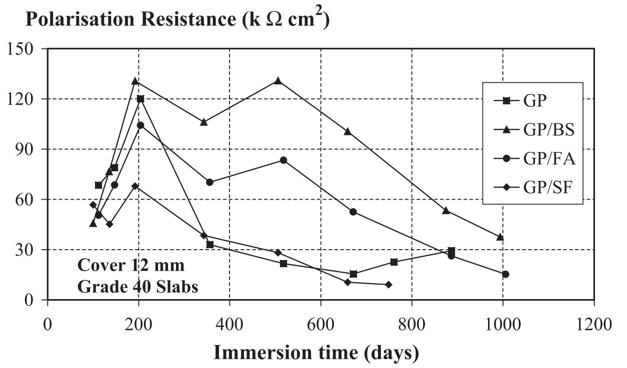

Fig. 15. Polarization resistance of concretes of grade 40 and a cover of 12 mm.

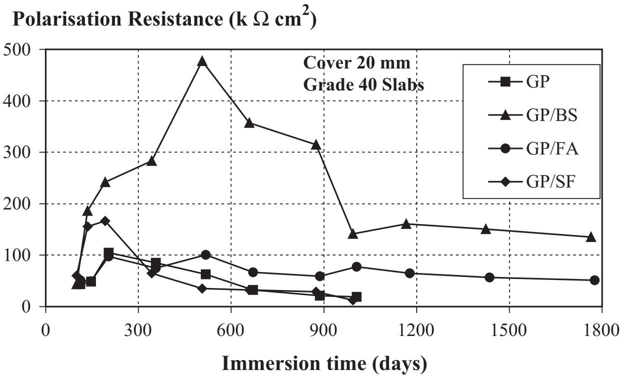

Fig. 16. Polarization resistance of concretes of grade 40 and a cover of 20 mm.

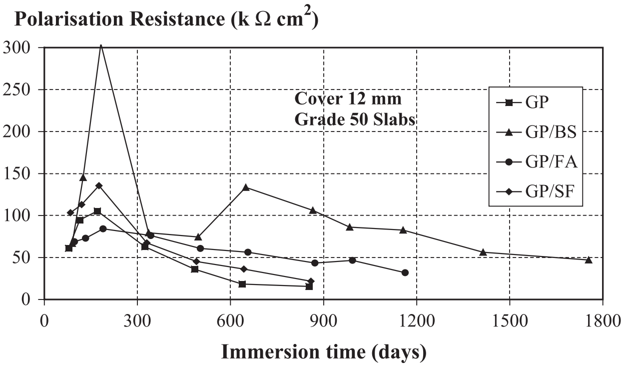

Fig. 17. Polarization resistance of concretes of grade 50 and a cover of 12 mm.

than the tolerable limit of corrosion, which in turn means that the end of service life has not yet been reached. On the other hand, a polarization value lower than CPR indicates that service life has already been exceeded.

Half-cell potential values (Figs. 3–10) and polarization resistance values (Figs. 11–18) were analyzed to determine service life. Half-cell potential should be lower than – 270 mV and the polarization resistance should be lower than CPR to ensure that tolerable degree of corrosion is achieved. Service life would be the time period when both these conditions are achieved.

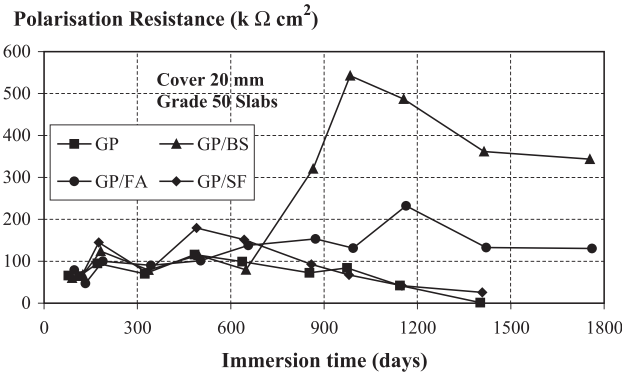

Fig. 18. Polarization resistance of concretes of grade 50 and a cover of 20 mm.

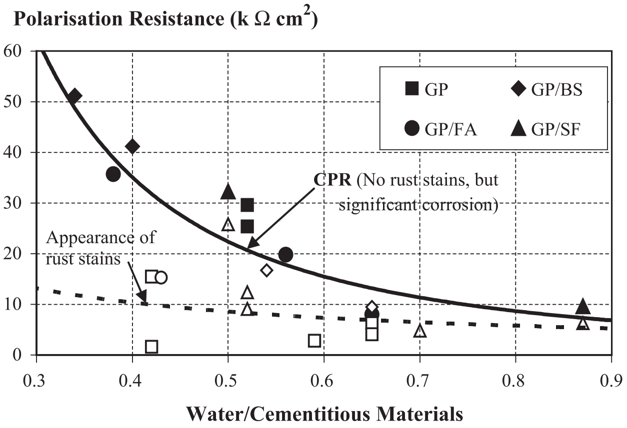

Fig. 19. Variation of CPR and polarization resistance corresponding to the appearance of rust stains with W/CM.

The next step in the evaluation of service life is the determination of CPR. Once CPR for various grades of concretes is known, half-cell potential values, CPR values, and Figs. 3–18 can be used to assess service lives. During the initial part of this study, the values of CPR were not known and the only clue for CPR was from the literature [20]. Hence, the samples were continuously immersed in salt solution until rust stains were visible on the surface of the sample. The appearance of rust stains is beyond the end of service life and hence the actual value of CPR is

Table 2
Immersion time (days) for half-cell potential to decrease below – 0.27 V and polarization to decrease below CPR

Nominal grade of concrete and 28-day F_c	GP		GP/BS		GP/FA		GP/SF	
	Cover (mm)		Cover (mm)		Cover (mm)		Cover (mm)	
	12	20	12	20	12	20	12	20
Half-cell potential < – 0.27 V								
Grade 15	31	31	31	–	31	–	44	44
28-day F_c	23		18.5		21.5		19.0	
Grade 20	71	–	65	430	150	390	31	–
28-day F_c	24.0		26.0		26.5		30.0	
Grade 40	190	190	330	>1764	180	518	100	310
28-day F_c	49.5		46.0		40.5		49.5	
Grade 50	260	600	1000	820	420	>1761	180	1000
28-day F_c	56.0		51.0		50.5		53.0	
Polarization resistance (k Ω cm²) < CPR								
Grade 15	50	150	330	–	430	–	130	440
28-day F_c	23		18.5		21.5		19.0	
Grade 20	71	–	610	>1729	530	>1650	400	–
28-day F_c	24.0		26.0		26.5		30.0	
Grade 40	500	880	970	>1764	840	>1776	600	930
28-day F_c	49.5		46.0		40.5		49.5	
Grade 50	520	1210	1540	>1754	1030	>1761	840	1280
28-day F_c	56.0		51.0		50.5		53.0	

expected to be higher than the polarization values corresponding to the appearance of rust stains. Polarization resistance on the appearance of rust stains can be considered as the lower limits of CPR.

As mentioned above, in the initial stages of the study, the samples were immersed until the observation of rust stains. After establishing few values of the lower limits of CPR, immersion of samples was stopped when their polarization resistance reached the anticipated CPR. The samples were then broken to examine the reinforcement and to confirm that it was indeed corroding. In all cases, the reinforcement was found to be corroding. These values were considered to be CPR and are plotted against W/CM in Fig. 19. The tolerable degree of corrosion was defined as the stage of the propagation phase corresponding to significant corrosion and just before the appearance of rust stains. It is likely that the immersion of samples is stopped significantly before the appearance of rust and not just before the appearance of rust. Thus, the actual value of CPR could be lower than the value of CPR selected in this study. Consequently, this selected CPR value may yield a service life that is lower than the accurate estimation of the service life. In spite of the measured service life being lower than the accurate estimation of service life, the measured service life would be of immense value in comparing the service life of concretes prepared from different cements.

Fig. 19 shows the variation of selected CPR with W/CM for all four types of concrete. The figure also shows the polarization resistance corresponding to the appearance of rust stains (the individual values are in open symbols and the trend line is the broken curve). It can be seen from the figure that CPR is independent of the type of cement, and also CPR decreases with an increase in W/CM. The W/CM of various mixes (given in Table 1) was used to evaluate the CPR, and their CPR values are also given in Table 1.

Table 3
Service life and 28-day compressive strength of concretes of various grades and cover values of 12 and 20 mm

Nominal grade of concrete and 28-day	Service life (days) and 28-day strength (MPa)							
	GP		GP/BS		GP/FA		GP/SF	
	Cover (mm)		Cover (mm)		Cover (mm)		Cover (mm)	
	12	20	12	20	12	20	12	20
Grade 15	50	150	330	–	430	–	130	440
28-day F_c	23		18.5		21.5		19.0	
Grade 20	71	–	610	>1729	530	>1650	400	–
28-day F_c	24.0		26.0		26.5		30.0	
Grade 40	500	880	970	>1764	840	>1776	600	930
28-day F_c	49.5		46.0		40.5		49.5	
Grade 50	520	1210	1540	>1754	1030	>1761	840	1280
28-day F_c	56.0		51.0		50.5		53.0	

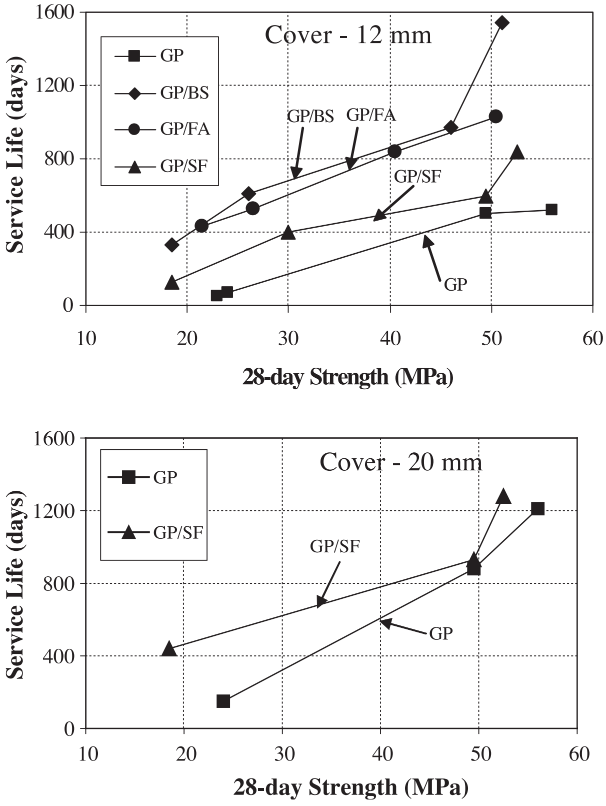

Fig. 20. Variation of service life with 28-day compressive strength.

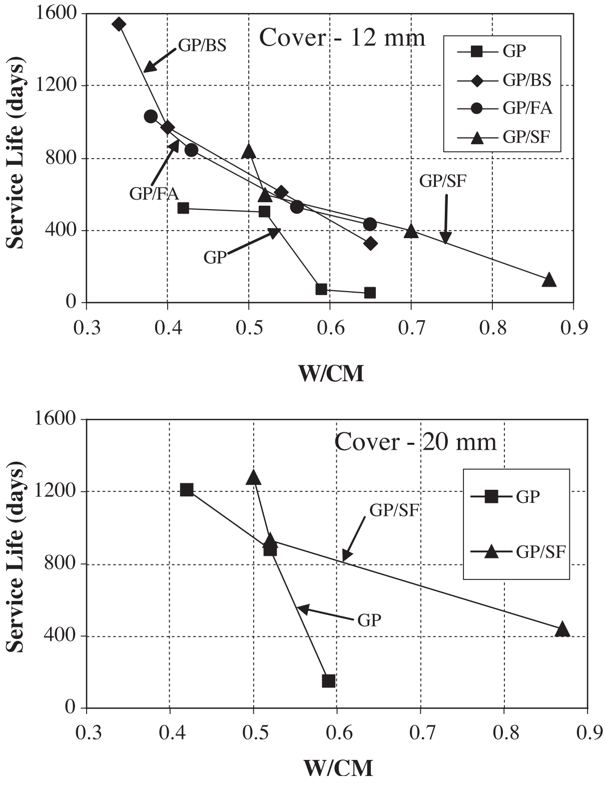

Fig. 21. Variation of service life with W/CM.

Figs. 3–10 were used to estimate the time of immersion for the half-cell potential to decrease below − 270 mV (− 0.27 V), and those immersion times are given in Table 2. Also, the CPR values listed in Table 1 were used in conjunction with Figs. 11–18 to evaluate the immersion time to reach CPR. They are also tabulated in Table 2. For both half-cell potential and polarization resistance, the immersion times are the interpolated values.

As mentioned earlier, service life is the immersion time when half-cell potential is less than − 0.27 mV and polarization resistance is less than CPR. It can be seen from Table 2 that the immersion time for half-cell potential to decrease below − 270 mV is always either lower or similar to the immersion time for polarization resistance to decrease below CPR. Furthermore, in many cases, the immersion time required for half-cell potential to decrease below − 270 mV is significantly less than the time required for polarization resistance to become less than CPR. Thus, service life is essentially the time period corresponding to the immersion time when the polarization resistance decreases to a value less than the CPR. This indicates that the polarization resistance is a much more reliable and useful technique than half-cell potential values. Also, service life estimations based on half-cell potential would be a conservative estimates and would be much lower than those based on CPR.

The service life (essentially the time period for polarization to decrease below CPR) is given in Table 3 and is plotted against the 28-day compressive strength in Fig. 20 and against W/CM in Fig. 21. For similar strengths, the service life of concretes GP/BS and GP/FA is superior to that of concretes GP and GP/SF, and the service life of concrete GP/SF is more than that of concrete GP. On the other hand, for similar W/CM, the service life of concretes GP/BS,GP/FA, and GP/SF is similar and greater than that of concrete GP. Thus, the influence of the type of cement on service life can be studied.

4. Conclusions

A concept of CPR was successfully used as a nondestructive technique to measure the service life of four nominal grades of concretes prepared from four cements. Thereby the influence of the type of cement can be studied. CPR was found to be independent of the type of cement. Also, a decrease in CPR was observed with an increase in water to cement ratio. Polarization resistance was found to be more useful in the evaluation of service life than half-cell potential.

Acknowledgements

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References

[1] K.Y. Furusawa, Inspection of deterioration and prediction of residual service life for a 15 year old structure, Proceedings of the 4th CANMET/ACI/JCI International Conference on Recent Advances in Concrete Technology, 7–11 June, Tokushima, Japan, Supplementary Papers, 1998, pp. 13–24.

[2] S. Ahmad, B. Bhattacharjee, Assessment of service lives of reinforced concrete structures subjected to chloride-induced rebar corrosion, J. Struct. Eng. 23 (4) (1997) 177–182.

[3] Y. Liu, R.E. Weyers, Modelling the time-to-corrosion cracking in chloride contaminated reinforced concrete structures, ACI Mater. J. 25 (6) (1998) 675–681.

[4] E.C. Bentz, C.M. Evans, M.D.A. Thomas, Chloride diffusion modeling for marine exposed concretes, Proceedings of the 3rd International Symposium on Corrosion of Reinforcement in Concrete Construction, Society for Chemical Industry, London, UK, 1996, pp. 136–145.

[5] P.B. Bamforth, W.F. Rice, Factors influencing chloride ingress into marine structures, in: U.K. Dundee, R.K. Dhir, M. Roderick Jones (Eds.), Proceedings of the International Conference on Concrete 2000, E&FN Spon, UK, 1993, pp. 1105–1118.

[6] R.K. Dhir, M.R. Jones, H.E.H. Ahmed, Concrete durability: estimation of chloride concentration during a design life, Mag. Concr. Res. 43 (154) (1991) 37–44.

[7] A. Kumar, D.M. Roy, Diffusion through concrete, Concrete (1987 January) 31–32.

[8] C.L. Page, N.R. Short, A. El-Tarras, Diffusion of chloride ions in hardened cement paste, Cem. Concr. Res. 11 (3) (1981) 395–406.

[9] K.C. Liam, S.K. Roy, D.O. Northwood, Chloride ingress measurements and corrosion potential mapping study of a 24-year old reinforced concrete jetty structure in a tropical marine environment, Mag. Concr. Res. 44 (160) (1992) 205–215.

[10] S. Helland, M. Maage, J.E. Carlsen, Service life prediction of marine structures, Proceedings of the Conference of the Concrete Institute of Australia, FIP, Brisbane, Australia, 1995 (October), pp. 243–250.

[11] P.S. Mangat, B.T. Molloy, Influence of PFA, slag and microsilica on chloride induced corrosion of reinforcement in concrete, Cem. Concr. Res. 21 (5) (1991) 819–834.

[12] A. Macias, C. Andrade, Accuracy of different electrochemical laboratory techniques for evaluating corrosion rates of galvanized reinforcement, Proceedings of the 4th International Conference on Durability of Building Materials and Components, Singapore, 1987, pp. 516–522.

[13] B.B. Hope, A.K.C. Ip, Corrosion of steel in concrete made with slag cement, ACI Mater. J. (1987 November–December) 525–531.

[14] H.T. Cao, V. Sirivivatnanon, Corrosion of steel in concrete with and without silica fume, Cem. Concr. Res. 21 (2) (1991) 316–324.

[15] C. Andrade, M.C. Alonso, Values of corrosion rate of steel in concrete to predict service life of concrete, in: G. Cragnolino, N. Sridhar (Eds.), Application of Accelerated Corrosion Tests to Service Life Prediction of Materials, ASTM Special Technical Publication, vol. 1194, American Society for Testing and Materials, Philadelphia, PA, 1994, pp. 282–295.

[16] M.G. Stewart, D.V. Rosowsky, Structural safety and serviceability of concrete bridges subjected to corrosion, J. Infrastruct. Syst. 4 (4) (1998) 146–154.

[17] R.B. Polder, The influence of blast furnace slag, fly ash and silica fume on corrosion of reinforced concrete in a marine environment, Heron 41 (4) (1996) 287–300.

[18] C. Andrade, C. Alonso, Progress on design and residual life calcula-

tion with regards to rebar corrosion of reinforced concrete, in: N.S. Berke, E. Escalante, C.K. Nmai, D. Whiting (Eds.), Technique to Assess the Corrosion Activity of Steel Reinforced Concrete Structures, ASTM Special Technical Publication, vol. 1276, American Society for Testing and Materials, Philadelphia, PA, 1996, pp. 23–40.

[19] K. Tutti, Corrosion of Steel in Concrete, Swedish Cement and Concrete Institute (CIB), Report No. 4-82, 1982.

[20] A.H.J. Al–Tayyib, M.S. Khan, Corrosion rate measurement of reinforcing steel in concr\ete by electrochemical techniques, ACI Mater. J., (1988 May–June) 172–177.