

## Effect of Environmental Changes on Chemical and Electrochemical Parameters in Reinforced Concrete. The Case of a Tropical Marine Atmosphere

*P. Castro-Borges<sup>1,\*</sup>, L. Veleva<sup>1</sup>, M. Balancán-Zapata<sup>1</sup>, J. M. Mendoza-Rangel<sup>2</sup>, L. A. Juárez-Ruiz<sup>3</sup>*

<sup>1</sup> Centro de Investigación y de Estudios Avanzados del IPN Unidad Mérida, Antigua Carretera a Progreso Km. 6, Cordemex, C. P. 97310 Mérida, Yucatan, México

<sup>2</sup> Facultad de Ingeniería Civil de la Universidad Autónoma de Nuevo León, Pedro de Alba s/n, C. P. 66451 San Nicolás de los Garza, Nuevo León, Mexico.

<sup>3</sup> Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional del IPN Unidad Oaxaca, Hornos No. 1003, Col. Noche Buena, Municipio de Santa Cruz Xoxocotlán, C. P. 71230, Oaxaca de Juárez, Oaxaca, México.

\*E-mail: [pcastro@mda.cinvestav.mx](mailto:pcastro@mda.cinvestav.mx)

*Received: 22 February 2013 / Accepted: 30 March 2013 / Published: 1 May 2013*

---

Environmental parameters such as airborne salinity (chloride deposition rate, CDR), time of wetness (TOW) and pluvial precipitation (PP) affect chemical and electrochemical parameters related to steel corrosion in reinforced concrete. Understanding the relationship of these parameters to corrosion is challenging because steel embedded in concrete has a different corrosion mechanism from that of steel exposed directly to the atmosphere. A necessary first step is to determine how these environmental parameters influence concrete and their consequently indirect effects on steel reinforcing bars. A comparison was made of changes in environmental parameters to those of electrochemical parameters (corrosion current and potential) in steel reinforcing and to chloride penetration profiles in concrete at different exposure times. At low exposure times (0, 6 and 12 months), corrosion behavior depended on concrete parameters such as water/cement ratio (w/c) and time of curing (tc) under strong influence from changes in TOW, CDR and PP. Once the corrosion process began, changes in CDR or PP no longer had an effect.

---

**Keywords:** reinforced concrete, marine environment, chloride profile, time of wetness, pluvial precipitation.

### 1. INTRODUCTION

Chlorides and environmental pollutants heavily influence the corrosion of steel reinforcing embedded in concrete exposed to marine environments [1, 2]. Quantifying a direct correspondence

between these corrosive elements and corrosion of steel reinforcing can be challenging due to the protective layer of concrete. As a result, corrosion of steel embedded in concrete differs from corrosion of steel exposed to atmospheric conditions. Air-borne salinity immediately affects exposed steel bars, but chlorides must first pass through a concrete protective layer before coming into contact with steel reinforcing; transport through concrete can occur by absorption and/or diffusion [3, 4, 5]. The atmospheric variables time of wetness (TOW), temperature and pluvial precipitation (PP) also influence the corrosion mechanism in steel [6]. Again, this influence is not direct in embedded steel reinforcement. The extent to which these variables affect steel reinforcing depends on the specific structural characteristics of a concrete, such as water/cement ratio (w/c) and time of curing (tc), as well as the initial passive state of the embedded steel. For example, a long TOW can produce water concrete saturation. If the concrete is dense enough, this humidity will penetrate only superficially for long periods, but if it is not dense and atmospheric humidity and chlorides levels remain high, the steel/concrete interface will remain humid. Consequently, corrosion rates can vary between exposed and embedded steel, as well as between steel embedded in cements of different qualities [6]. Typical annual TOW for the materials surfaces exposed to the marine coastal tropical environments of Caribbean area is around 8,500 h (95% of the annual period of time), due to the high chloride contamination [7]. Besides, the larger percentage of TOW (64-73%) occurs in the 25 -30°C temperature range. This determines accelerated metal corrosion process in the tropical marine environment.

Considering the above, fully understanding the influence of environmental parameters on steel reinforcement requires first studying their effects on concrete and then analyzing their indirect effects on corrosion of the steel encased in that concrete. The present study objective was to quantify the influence of air-borne salinity, expressed as CDR, TOW and PP, on the chlorides concentration profile of concrete located in a marine environment. Based on these data, an estimate is made of the effect of chlorides and TOW on the corrosion potential ( $E_{\text{corr}}$ ) and corrosion rate ( $i_{\text{corr}}$ ) of steel reinforcing.

## 2. TESTING METHODOLOGY

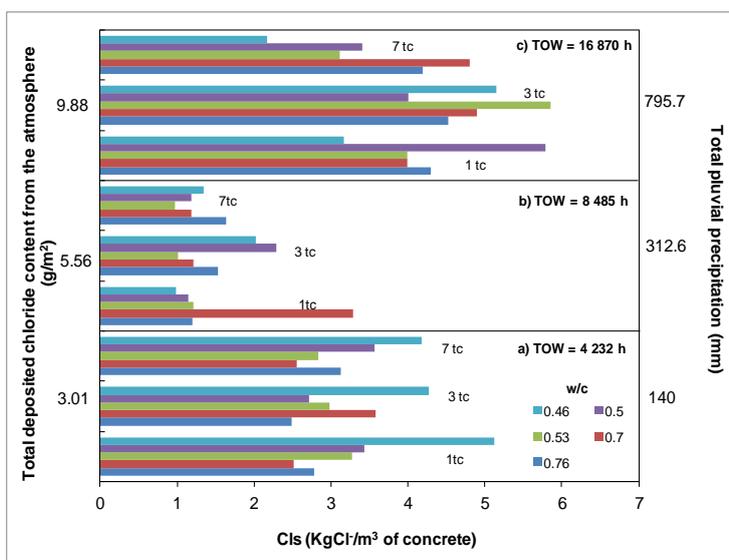
Sixty Portland cement concrete cylinders (7.5 cm diameter, 15 cm long) were exposed for 24 months at a test site located at Progreso, Yucatan, Mexico. The site fronts on the Gulf of Mexico (50 m from tideline), and is fully exposed to the tropical marine-coastal environment of the northern Yucatan Peninsula. Concrete for the cylinders was prepared using limestone aggregates. Half ( $n = 30$ ) of the cylinders contained 0.95 cm diameter steel bars (A #3, grade 42) embedded in the center, and activated titanium rods (ATR) as reference electrodes [8]. Any exposed portions of steel were covered with insulating tape and exposed concrete was coated with epoxy [9]. Five w/c ratios (0.46, 0.50, 0.53, 0.70 and 0.76) and three tc (1, 3 and 7 days) were tested. Two cylinders were assigned each treatment (i.e. w/c ratio and tc combination). The remaining 30 cylinders contained only concrete. Slices were taken of these periodically to generate chloride concentration profiles using an acid extraction method [10] and an ion-selective electrode. Surface chloride concentration (Cl<sub>s</sub>) was measured at 2 mm depth. Epoxy was applied to the ends of the plain concrete cylinders to prevent axial chloride penetration.

Electrochemical measurements were taken with a Potentiostat/Galvanostat/ZRA and included corrosion potential ( $E_{corr}$ ) and corrosion rate ( $i_{corr}$ ). The polarization resistance ( $R_p$ ) technique was used [11, 12]. Ohmic drop ( $R_s$ ) was measured with a resistance meter. Measurements of  $E_{corr}$ ,  $i_{corr}$  and  $R_s$  were taken every three months from the beginning of exposure of the reinforced concrete cylinders. Sections of the plain concrete cylinders were cut at 0, 6, 12 and 24 months. Monthly data were recorded for PP, and TOW calculated according to ISO 9223 [13] using temperature/relative humidity complex data from a meteorological station near the test site. The CDR was measured by the wet candle method according to ISO 9225 [14].

### 3. RESULTS AND DISCUSSION

#### 3.1 TOW, CDR and PP vs. surface chloride concentration (Cl<sub>s</sub>)

Total CDR and Cl<sub>s</sub> values, as well as cumulative TOW are shown in Figure 1: Figure 1a represents values for 6 months; 1b for 12 months; and 1c for 24 months. Within each time period are three groups of bars corresponding to the three tested tc, and within each group are five bars corresponding to the five w/c ratios. The data shown in Figure 1(a) were recorded at the end of the winter dry period (PP = 140 mm) when airborne salinity (CDR = 3.01g/m<sup>2</sup>) was significantly higher due to north winds blowing in off the Gulf of Mexico. During this period, Cl<sub>s</sub> values are primarily influenced by CDR and TOW, which is why Cl<sub>s</sub> are relatively high. Overall, the lowest w/c ratio corresponds to the highest Cl<sub>s</sub>, a correspondence clearly visible at 1 and 7 days tc. Concrete microstructural properties probably most affected this phenomenon since denser concrete slows chloride penetration, be it by absorption or diffusion.



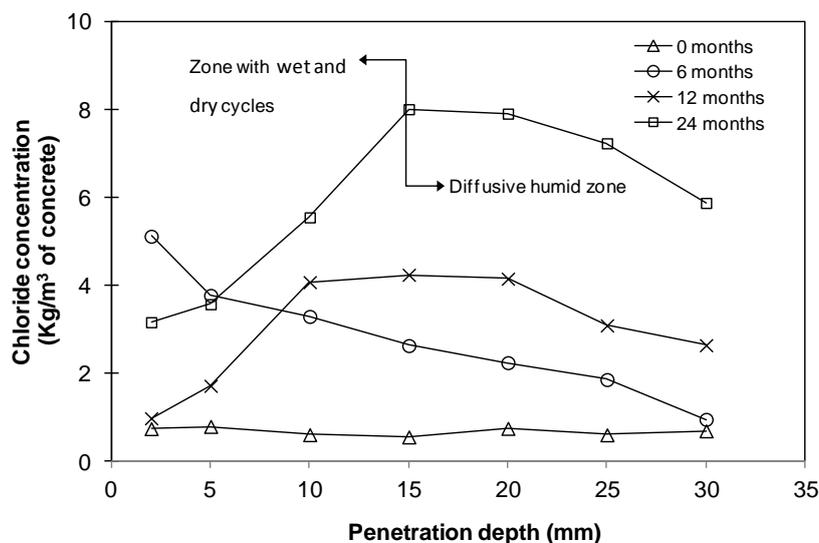
**Figure 1.** Surface chloride concentration (Cl<sub>s</sub>) in concrete probes as a function of pluvial precipitation, chloride deposition rate (CDR) from the atmosphere and time of wetness (TOW) for periods of (a) 6, (b) 12 and (c) 24 months exposure to a tropical marine environment.

At 12 months (Figure 1(b)), the rainy season was well underway, causing the washing away of a portion of the surface chlorides. As a result, Cls values clearly decrease in all cases, and w/c ratios differ from those in the 6-month period. Both TOW and CDR values are approximately twice those recorded at 6 months, suggesting that Cls was apparently influenced more by PP than by TOW or CDR at 12 months.

After 24 months (Figure 1(c)), the concrete had been exposed to additional dry and rainy seasons. TOW, PP and CDR are approximately twice those observed at 12 months (Figure 1(b)). The higher Cls values do not necessarily indicate an absence of effect by PP. The salient aspect of the 24-month data is that the higher TOW and CDR at this point allowed chloride content to increase inside the concrete. The actual mechanism by which chlorides penetrated the concrete is more complex due to the variations inherent in dry and rainy cycles. For example, a certain amount of surface chlorides wash away during the rainy period, while chlorides inside the concrete will tend to move towards the surface in response to changes in the chloride concentration gradient. No new trends in w/c ratios and Cls were observed at 24 months.

### 3.2 TOW, CDR and PP vs. chloride concentration profile

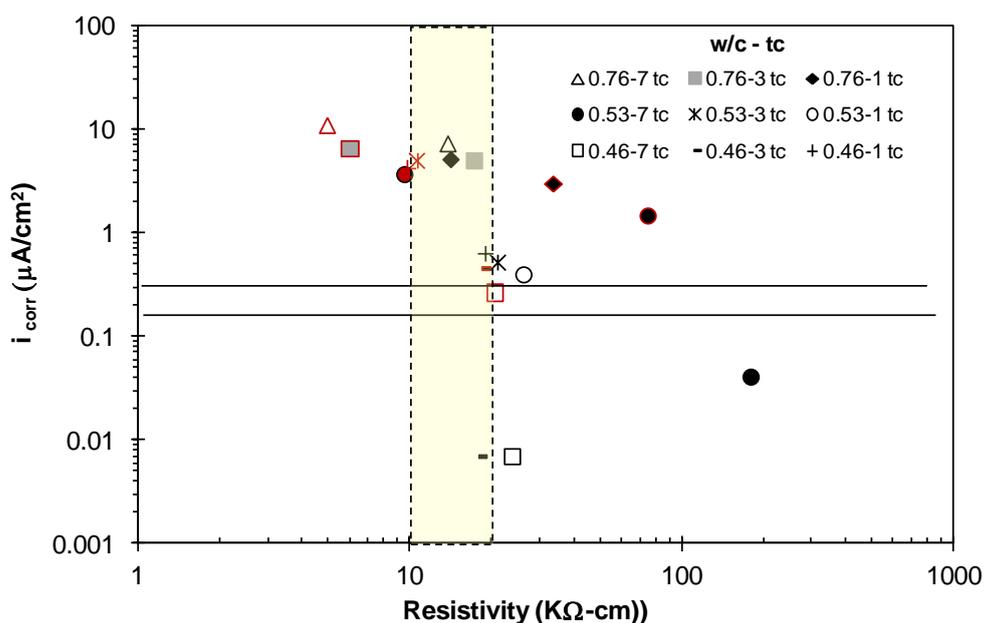
Chloride concentration profiles in concrete specimens (w/c=0.46,  $t_c = 1$ ), at 0, 6, 12 and 24 months confirmed that there was essentially no initial chloride profile inside the concrete at the beginning of exposure (Figure 2). At 6 months, the profile manifests the continuous chloride deposition on the concrete surface and almost constant TOW. This profile indicates that constant humidity inside the concrete allowed chloride penetration mainly by diffusion.



**Figure 2.** Chloride Concentration Profiles for concrete with a w/c = 0.46 and a  $t_c = 1$  day. Each point represents the average of two specimens.

After 12 months exposure, the profile changes form. During the dry winter period, the concrete dries to a depth of 10 mm, but from 10 to 30 mm the concrete remains wet and the profile conserves its

diffusive behavior. The concrete remains wet due to its internal humidity and chloride hygroscopicity [15], which is confirmed by concrete resistivity data, Figure 3 [16, 17]. Beginning at 10 mm, the profile reverses because of two parallel processes: surface chloride washing naturally decreases Cl<sub>s</sub>; and changes in the chloride gradient caused by washing cause the return of part of the interior chlorides to the surface [18]. After 24 months exposure, the chloride profile shape remains essentially the same, albeit with overall higher values and a more pronounced reverse profile starting at 15 mm depth. The profile shape responds to the same conditions present at 12 months, but the longer exposure time explains the higher chloride values.

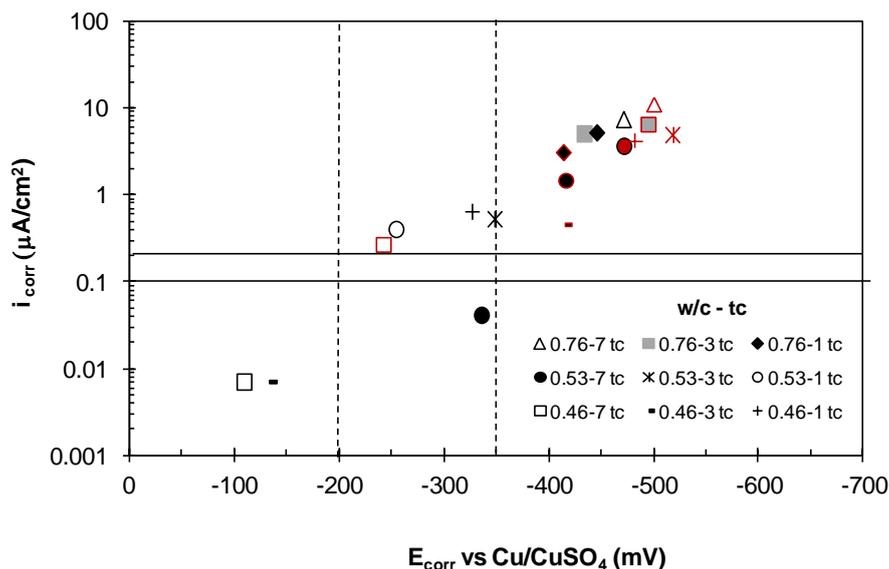


Note: Black symbols represent data for 12 months and red symbols data for 24 months exposure.

**Figure 3.**  $i_{corr}$  vs Resistivity for specimens exposed for 12 and 24 months to a tropical marine environment at Progreso, Yucatan.

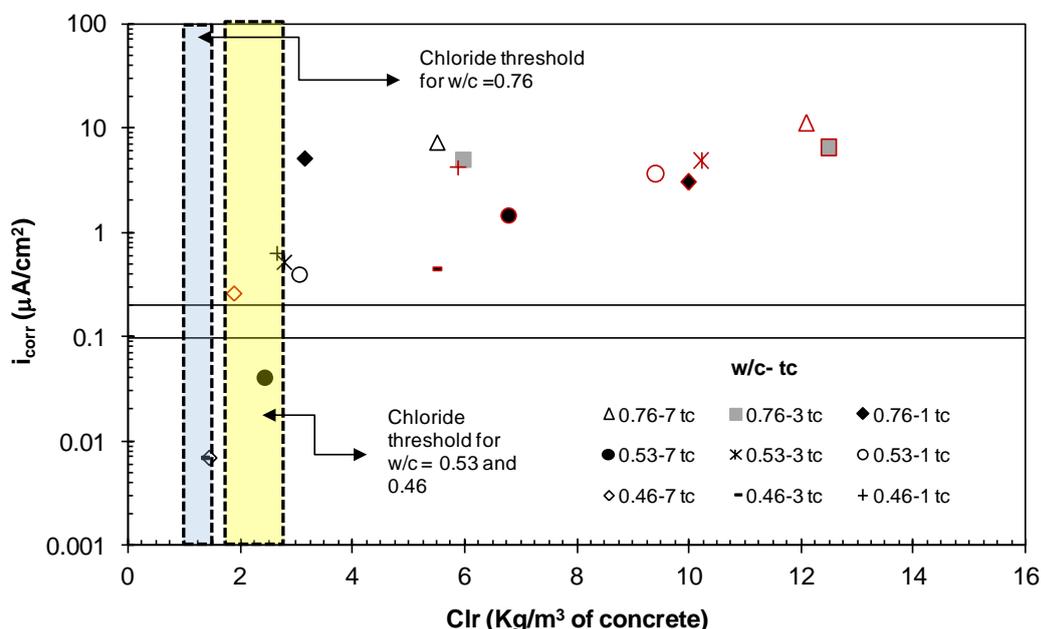
### 3.3 TOW, CDR and PP vs. electrochemical parameters ( $i_{corr}$ and $E_{corr}$ )

The high and constant TOW values sustained moisture levels in the concrete surrounding the steel rebar, a phenomenon facilitated by transit of chlorides to the area near the bar due to hygroscopicity. This was confirmed by a slow decline in concrete resistivity beginning at 3 months caused by higher conductivity in the presence of a greater chlorides concentration. A direct relationship is therefore caused between  $i_{corr}$  and  $E_{corr}$ . Constant increase in these parameters over time responds to a continuous increase in chlorides content and constant humidity near the steel rebar. This can be seen clearly in Fig. 4 (only three w/c ratios are shown for simplicity), where at 12 months the more negative  $E_{corr}$  values correspond to the highest  $i_{corr}$  values, and the higher  $i_{corr}$  and more negative  $E_{corr}$  values correspond to higher w/c ratios. At 24 months, this trend is not as clear because chlorides content has surpassed the critical chlorides threshold in most of the specimens.



Note: Black symbols represent data for 12 months and red symbols data for 24 months exposure.

**Figure 4.**  $i_{corr}$  vs.  $E_{corr}$  for specimens exposed for 12 and 24 months to a tropical marine environment at Progreso, Yucatan.



Note: Black symbols represent data for 12 months and red symbols data for 24 months exposure.

**Figure 5.**  $i_{corr}$  vs. Chloride content close to the steel rebar (Clr) in specimens exposed for 12 and 24 months to a marine environment at Progreso, Yucatan.

When chloride content close to the steel rebar (Clr) exceeds  $4 \text{ kg/m}^3$ ,  $i_{corr}$  stabilizes and becomes independent of the w/c ratio and tc (Figure 5). Once this process begins, TOW, CDR and PP have no direct influence on steel rebar corrosion because concrete microstructure becomes an additional determining parameter after exposure has begun. In other words, even if CDR and/or PP

cease to have an effect at any given moment corrosion of the reinforced concrete will continue since once it begins it will depend principally on TOW. The TOW is even more important during long dry periods.

#### 4. CONCLUSIONS

Surface chloride concentration and chloride penetration profiles in reinforced concrete are strongly influenced by TOW, CDR and PP. Therefore, at short exposure times the chloride profile and Cls values can be explained by changes in TOW, CDR and PP values.

Initial corrosion behavior of the steel rebar may be indirectly influenced by changes in CDR, TOW and PP that affect the concrete surrounding it. However, for the tested period, once the corrosion process begins changes in CDR or PP no longer have an effect.

The main factor controlling the progress of steel corrosion in concrete is the TOW, as a period with presence of aggressive electrolyte at the interface steel bar – concrete.

In the tested natural exposure environment, the  $i_{\text{corr}}$  becomes stable and independent of the w/c ratio and  $t_c$  when chloride content near the steel rebar (Clr) exceeds  $4 \text{ kg/m}^3$ .

#### ACKNOWLEDGMENTS

Various phases of the research reported herein were financed by the CINVESTAV-IPN and the CONACyT (National Mexican Council of Science and Technology) through several contracts. The opinions and findings reported here are those of the authors and not necessarily those of the supporting organizations.

#### References

1. H. Ye, N. Jin, X. Jin and, C. Fu, *Construction and Building Materials*, 36 (2012)259
2. E. Zitrou, J. Nikolaou, P.E. Tsakiridis and G.D. Papadimitriou, *Construction and Building Materials* 21 (2007) 1161.
3. M.A. Mustafa and K.M. Yusof, *Cement and Concrete Research* 24 (1994) 661
4. H.W. Song, C.H. Lee and K.Y. Ann, *Cement and Concrete Composites*, 30 (2008) 113.
5. T. Pérez López, G. Canto, V. M. Moo-Yam, J. Reyes, J. T. Pérez-Quiroz and J. Genescá, *International Journal of Electrochemical Science*, 7 (2012) 426.
6. L. Véleva, P. Castro, G. Hernández-Duque, M. Shorr, *Corrosion Reviews*, 16 (1998) 235
7. L. Veleval, G. Pérez G. and M. Acosta, *Atmospheric Environment*, 31 (1997) 773.
8. P. Castro, A. Sagües, E.I. Moreno, L. Maldonado and J. Genescá, *Corrosion* 52 (1996) 609.
9. A.A. Sagües, P. Castro, L. Maldonado, E.I. Moreno and J. Genescá, *Proceedings of the First Mexican Symposium on Metallic Corrosion*, Paper 64 (1994)
10. P. Castro and L. Maldonado, Initial Efforts to Evaluate the Corrosion Problems in the Infrastructure of Mexican Southeast Coastal Zones. In *Innovative Ideas for Controlling the Decaying Infrastructure*, V. Chaker, ed. (1995).
11. C. Andrade, M.C. Alonso and J.A. González, In: *Corrosion Rates of Steel in Concrete*, N.S. Berke, V. Chaker and D. Whiting, eds., ASTM STP 1065 (1990), 29.

12. C. Andrade , V. Castellote, C. Alonso and J.A González, In: *Corrosion Effect of Stray Currents and Techniques for Evaluating Corrosion of Rebars in Concrete*, V. Chaker, ed., ASTM STP 906, (1984) 43.
13. ISO Standard 9223-92. *Corrosion of metals and alloys. Corrosivity of atmospheres. Classification* (1992).
14. ISO Standard 9225-92. *Corrosion of metals and alloys. Corrosivity of atmospheres. Measurement of pollution* (1992).
15. W. López, J.A. González, *Cem. and Conc. Res.* 23(1993) 2, 368 - 376.
16. P. Castro, *Diffusion and Corrosión by Chloride Ions in Reinforced Concrete*, Ph. D. thesis, Universidad Autónoma de México, Facultad de Química, (1995) (In Spanish).
17. W. Morris, A. Vico and M. Vázquez, *Electrochimica Acta*, (2004) 4447
18. P.B. Bamforth and W.F. Price, *Factors influencing chloride ingress in to marine structures*. In: Dhir RK, Jones MR, editors. *Concrete 2000* (1993)