

## **Sustainable Concrete in a Marine Environment**

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### **ABSTRACT**

This paper presents data from 25-year-old concrete specimens retrieved from the tidal zone of the Marine Exposure Station on Treat Island, Maine. The data indicate the importance of w/cm and binder type, with regards to the type and amount of supplementary cementing materials (SCM), in determining the performance of the concrete in marine conditions. Resistance to chloride ion penetration increases with the level of SCM at all levels or replacement studied. However, use of very high levels of these materials may render the concrete more susceptible to surface scaling in the tidal zone when subjected to freezing conditions. Thus, it is necessary to optimize the level of SCM for a given climate. The paper also compares output from two service-life models, ConcreteWorks and Life-365, with the experimental data. In general, the models are able to closely predict the rate of chloride ingress in concrete with and without SCM.

### **INTRODUCTION**

One of the many areas in which Professor Theodore Bremner has made a substantial contribution is in the study of the performance of concrete in a marine environment. Dr. Bremner has been closely involved with the operation of the Treat Island Marine Exposure Site at Treat Island, Maine, for over 30 years, conducting his own research studies and supervising data collection and maintenance on behalf of the USA Corps of Engineers (USACE) who own and operate the facility. In 1978, Malhotra and Bremner [1996] commenced an extensive investigation into the durability of concrete containing supplementary cementitious materials (SCM) in a marine environment with the placement of the first series of concrete blocks (305 x 305 x 915 mm) at the mid-tide level at Treat Island. Between 1978 and 1994 a total of 14 different series of mixes with w/cm ranging from 0.4 to 0.6 and containing various levels of slag, fly ash and silica fume were placed at Treat Island and a summary of concrete materials used is given in Table 1 [Malhorta and Bremner, 1996]. While at Treat Island the samples were monitored yearly to provide a record of performance based on visual assessment, pulse velocity and resonance frequency. In 2003, as the first of the concrete mixtures reached an age of 25 years, a program was initiated to retrieve one block from each mix for testing at the University of New Brunswick (UNB). The testing has included establishing existing chloride profiles following 25 years in seawater and extracting cores to determine chloride diffusion coefficients and electrical conductivity; mechanical properties (compressive and tensile splitting strength, modulus of elasticity) were also determined for some mixtures. To date, specimens from the first five phases have been tested

as the concrete reached an age 25 years (see Table 1) and it is planned to continue this program until specimens have been retrieved from all 14 phases.

This paper presents a summary of the data obtained by testing concrete from the first five phases. A detailed description of the testing of the blocks from Phase I has been published elsewhere [Thomas et al. 2008].

Table 1. Concrete Mixes Prepared at UNB [Malhotra and Bremner, 1996]

Phase	Year	W/CM	SCM	Other details
I(A)	1978	0.4 - 0.6	0, 25, 45, 65 SG	
I(B)	1978	0.50	None	AE & non-AE
II	1979	0.4 - 0.6	0, 25FA, 20/40 & 20/60 FA/SG	
III	1980	0.4 - 0.6	0, 25, 45, 65 SG	LWA
IV	1981	0.4 - 0.6	0, 25FA	
V(A)	1982	0.4 - 0.6	0, 80SG	
V(B)	1982	0.6	0, 10, 15, 20 SF	AE & non-AE
VI	1985	0.4 - 0.6	0, 6.5SF, 13.5FA	Steel fibres
VII	1986	0.26, 0.33	6, 7.5 SF	Ready-mix concrete
VIII	1987	0.40 - 0.45 0.31 - 0.35	Control (no SCM) 56FA	
IX	1987	0.50	0, 10SF, 25FA, 50SG	Steel rebar with 20 - 70 mm cover
X	1988	0.36, 0.40	7SF	LWA
XI	1990	0.38	56FA	LWA
XII	1991	0.45, 0.60	None	Epoxy-coated and plain steel rebar
XIII	1992	0.33	56FA	
XIV	1994	0.40	0, 10SF, 20 & 30FA	Reactive aggregate

LWA – lightweight aggregate

AE – air-entrained

Slag (SG), Fly Ash (FA), Silica Fume (SF)

## TREAT ISLAND MARINE EXPOSURE SITE

Treat Island lies in Passamaquoddy Bay, part of the Bay of Fundy, near the town of Eastport in Maine. The exposure site was established in 1936 to study concrete durability as there was interest at the time in constructing a tidal electrical generating system in Passamaquoddy Bay. Although the power project was never realized, studies on concrete durability continued at Treat Island to support the construction of concrete structures in the North Atlantic. Currently data are still being collected from a variety of concrete specimens from more than 40 different research programs some of which are more than 50 years old.

The exposure conditions in the Bay of Fundy are extremely aggressive for concrete with tides in excess of 6 metres and an average of 100 freeze-thaw cycles per year.

### CHLORIDE INGRESS

Figure 1 shows chloride profiles for 25-year-old concrete specimens from Phase II (binary mixes with portland cement + fly ash and ternary mixes with portland cement + fly ash + slag). The trend of decreasing chloride ingress with increasing SCM content was observed for the concrete for all 5 phases retrieved to date. Figure 2 shows the chloride content at depth (in the 60-70 mm depth increment) for all of the concretes tested to date. This depth interval was selected as it is consistent with the requirements in Canada where the minimum cover for reinforced concrete exposed to chlorides is 60 mm. The presence of SCM has a profound impact on the chloride profile, significantly increasing the resistance of the concrete to chloride ion penetration. Although reducing w/cm also increases the resistance to chlorides, the effect is small compared to the presence of SCM. Although there is no single value that represents the chloride threshold content required to initiate corrosion, values in the range of 0.05 to 0.10% are typically used. The data in Figure 2 indicate that the chloride content in the 60-70 mm depth increment in all of the control mixes without SCM is above that range after 25 years regardless of the w/cm. For concrete containing SCM, the chloride content at that depth is less than the threshold range for all replacement levels provided the w/cm = 0.40. At higher w/cm, higher SCM replacement levels are needed to keep the chloride content below the threshold level at 60-70 mm.

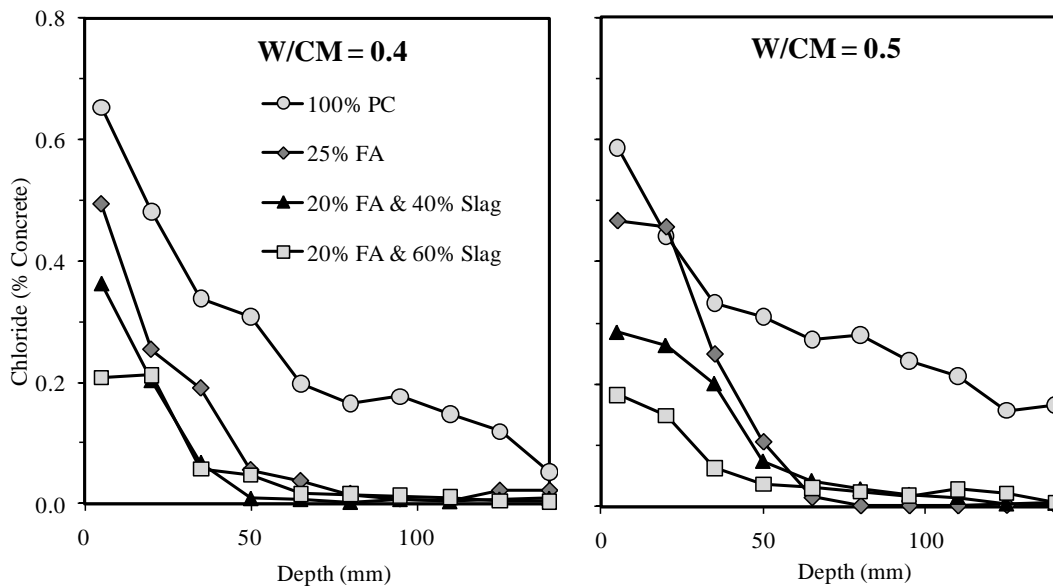


Fig. 1. Existing Chloride Profiles in Concretes after 25 Years Exposure in the Marine Tidal Zone (W/CM = 0.40 left and W/CM = 0.50 right)

### CONCRETEWORKS PREDICTIONS

The data for the concrete mixtures with W/CM = 0.40 were compared to predicted output from the service-life models, Life-365 [Ehlen et al. 2009] and ConcreteWorks [Riding, 2007]. Examples are shown here for ConcreteWorks. This model accounts for the time-dependent reduction in the diffusion coefficient of concrete by using Equation 1.

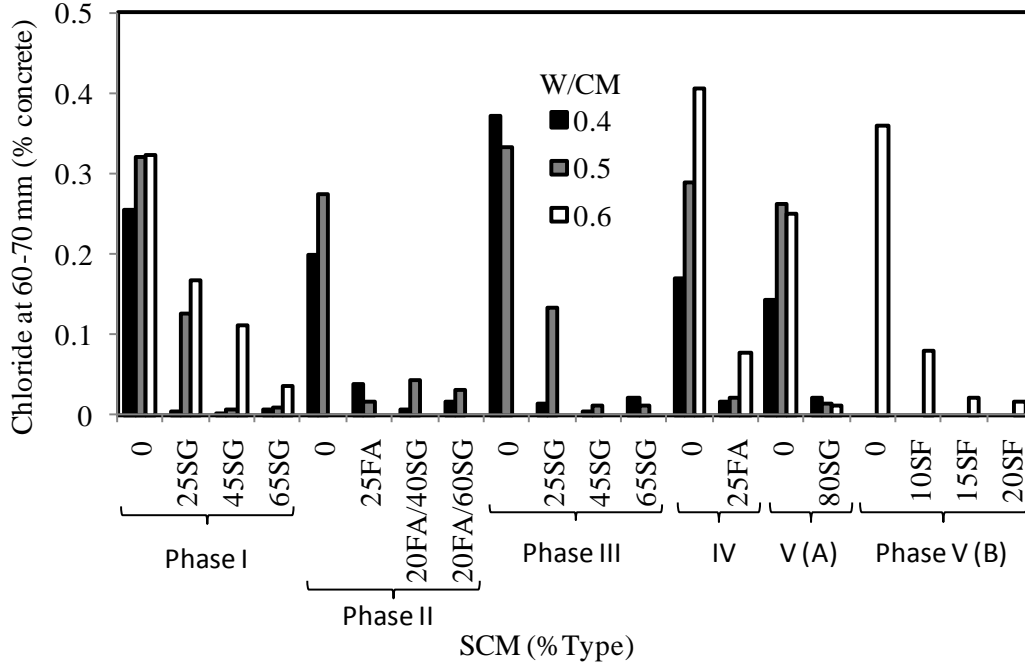


Fig. 2. Chloride Content at a Depth of 60-70 mm for all of the Concrete Samples Retrieved from Phases I to V

$$D_t = D_{28} \left( \frac{28}{t} \right)^m + D_{ult} \left( 1 - \left( \frac{28}{t} \right)^m \right) \quad \text{Eqn. 1}$$

where  $D_t$  and  $D_{28}$  are the diffusion coefficients at time  $t$  and 28 days, respectively, and  $D_{ult}$  represents the ultimate diffusion coefficient (at complete hydration).  $D_t$  is also corrected for temperature using the Arrhenius equation. Values for  $D_{28}$  and  $m$  are estimated by the model based on the mixture proportions (w/cm and quantity of pozzolans or slag). Concrete with w/cm = 0.40 is assigned a 28-day diffusion coefficient of  $D_{28} = 9.1 \times 10^{-12} \text{ m}^2/\text{s}$ . Silica fume reduces the diffusion coefficient according to the following equation:

$$\frac{D_{SF}}{D_{PC}} = 0.206 + 0.794e^{-\left( \frac{SF}{2.51} \right)} \quad \text{Eqn. 2}$$

where  $D_{SF}$  is the diffusion coefficient of concrete containing silica fume at a replacement level of  $SF$  % and  $D_{PC}$  is the diffusion coefficient of portland cement concrete of the same w/cm. Slag and fly ash do not affect the early-age diffusion coefficient,  $D_{28}$ . However, the value of  $m$  is influenced by the slag and fly ash content according to Equation 3:

$$m = 0.26 + 0.4 \left( \frac{FA}{50} + \frac{SG}{70} \right) \quad \text{Eqn. 3}$$

Figure 3 shows the chloride profiles predicted using ConcreteWorks for concrete with  $w/cm = 0.40$  and with 0, 25, 45 and 65% slag after 25 years in the tidal zone at Eastport, Maine, compared with the actual chloride profiles measured on concrete specimens from Phase I.

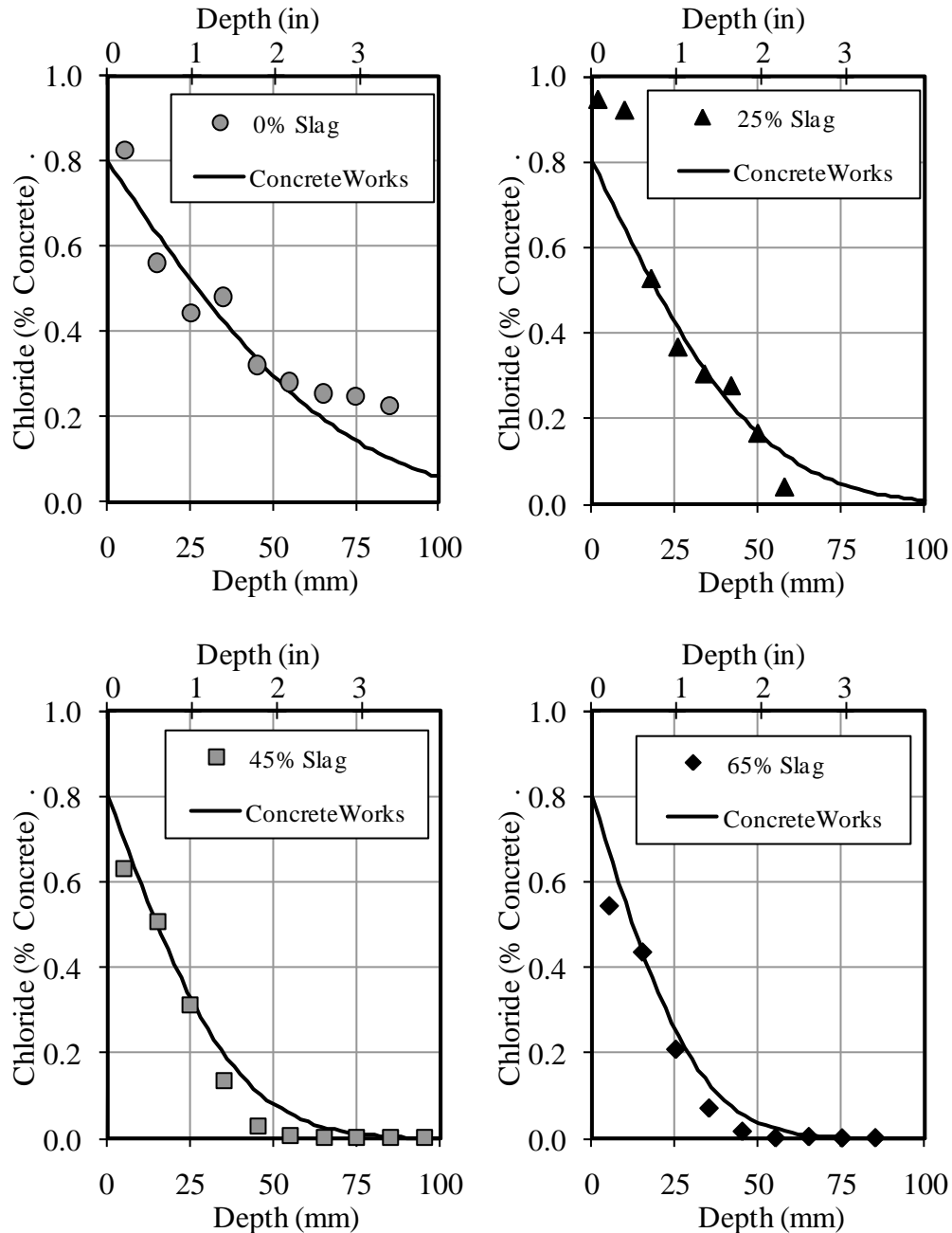


Fig. 3. Comparisons of Predictions from Life-365 Model and Experimental Data

The blocks at Treat Island provide an invaluable opportunity to validate service-life prediction models with long-term experimental data. The predictions from ConcreteWorks and Life-365 (which was also used in this study) are reasonably consistent with the experimental data collected so far for concrete with  $w/cm = 0.40$ . At higher  $w/cm$ , the

predictions are not as reliable because the actual surface chloride concentrations,  $C_0$ , are lower than those predicted by the models,  $C_0 = 0.80\%$  (by mass of concrete). This is thought to be due to the reduced paste content (lower cement content) with decreasing w/cm for the blocks. In a given phase, blocks were cast with similar water content and the w/cm was adjusted by changing the cementitious material content. Thus concrete with higher w/cm had lower paste content and a reduced capacity to accommodate chlorides. When the surface concentration used in the models is adjusted to match the experimental programs, the models successfully predict the remainder of the profile with a reasonable degree of accuracy.

## MEASURED CHLORIDE DIFFUSION COEFFICIENTS

The chloride diffusion coefficients for the 25-year-old concrete specimens were determined on concrete discs (100-mm diameter x 50-mm thick) cut from cores and tested following the procedure of ASTM C 1556. By cutting the discs from as close to the centre of the original block as possible, the possibility of “contamination” by existing chlorides (resulting from the 25-year exposure to seawater) was minimized, however, test specimens from control samples (without SCM) still had significant chloride present at the start of the test and this had to be corrected for by adjusting the background concentration in the equation below. After 91 days exposure to NaCl solution the disc samples were ground and analyzed to produce a chloride profile, and the diffusion coefficient,  $D_a$ , and the surface concentration,  $C_0$ , were found by fitting Equation 4 to the profile using the method of least squares.

$$\frac{C_x - C_b}{C_0 - C_b} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D_a t}}\right) \quad \text{Eqn. 4}$$

where  $D_a$  is the apparent diffusion coefficient ( $\text{m}^2/\text{s}$ ),  $C_x$  is the chloride concentration (%) at depth  $x$  (m) and time  $t$  (seconds),  $C_0$  is the surface chloride concentration (%), and  $C_b$  is the background chloride concentration (%).

An example of the profiles obtained for the concrete specimens with w/cm = 0.40 from Phase III after immersion in NaCl solution (165 g/l) for 91 days is shown in Figure 4. The results from the bulk diffusion test conducted on specimens from all concrete mixes from Phase I to IV are presented in Figure 5. In all cases the incorporation of SCM had a very significant impact on the penetration of chlorides during the relatively short exposure period (91 days) of the ASTM C 1556 “bulk diffusion” test and consequently on the calculated diffusion coefficient (using Eqn. 4), which is as much as 20 times lower in concretes with SCM as compared with the control mix (without SCM) of the same w/cm from the same test phase. The w/cm also influenced the diffusion coefficient measured at 25 years, but the effect was not as significant as the incorporation of SCM. For example reducing the w/cm from 0.50 to 0.40 generally reduced the diffusion coefficient by 2 to 3 times.

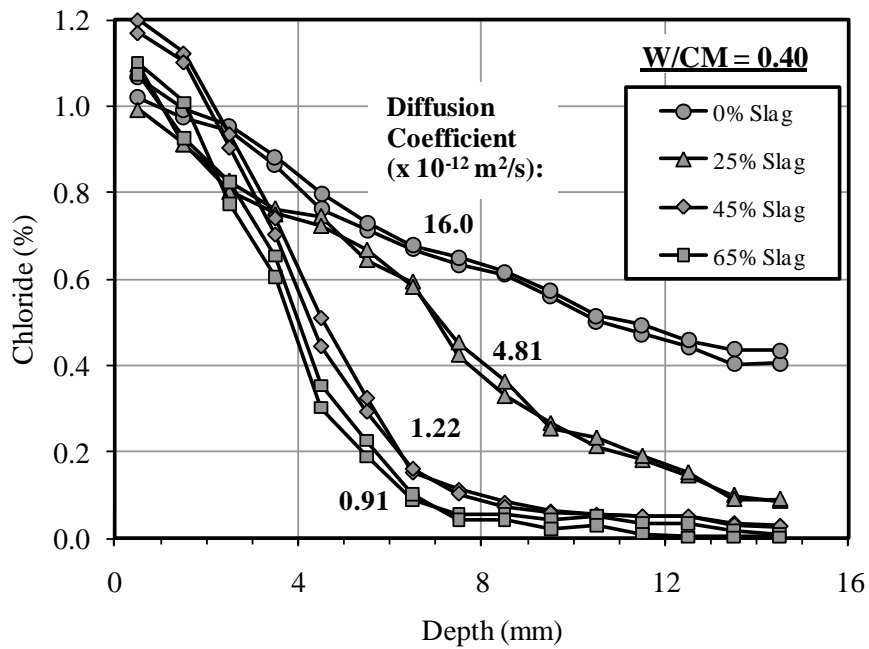


Fig. 4. Chloride Profiles in Test Specimens after 91 Days Immersion in NaCl Solution [ASTM C 1556] for Phase III Concrete with Lightweight Aggregate

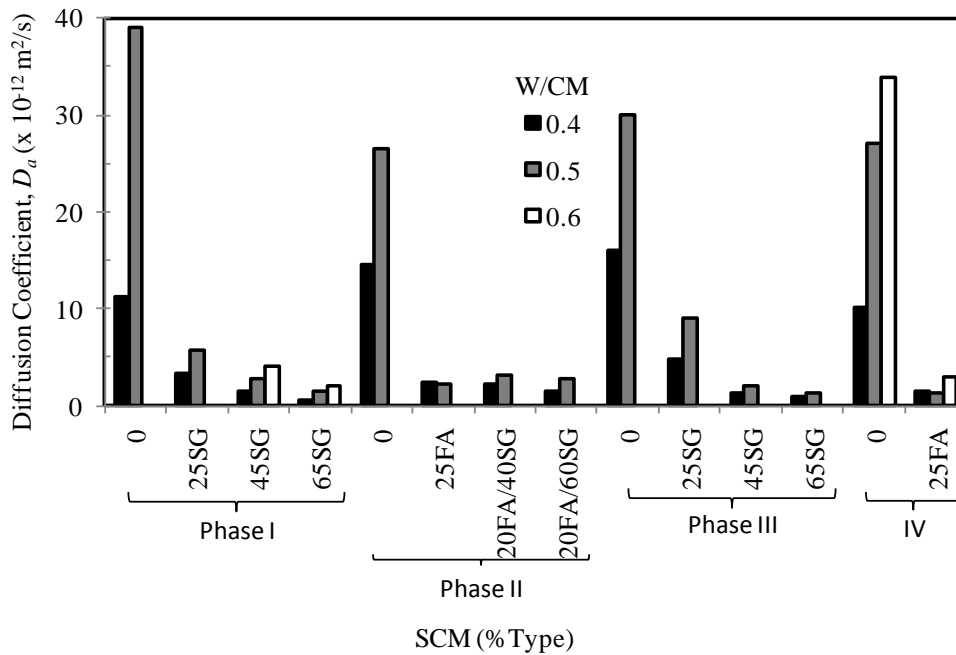


Figure 5 Calculated Diffusion Coefficients for Profiles from Bulk Diffusion Tests

## ELECTRICAL CONDUCTIVITY

The electrical conductivity (ASTM C 1202) was also measured on disc samples cut from cores using discs located as close as possible to the centre of the blocks to minimize the effect of “chloride contamination.” The results are shown in Figure 6.

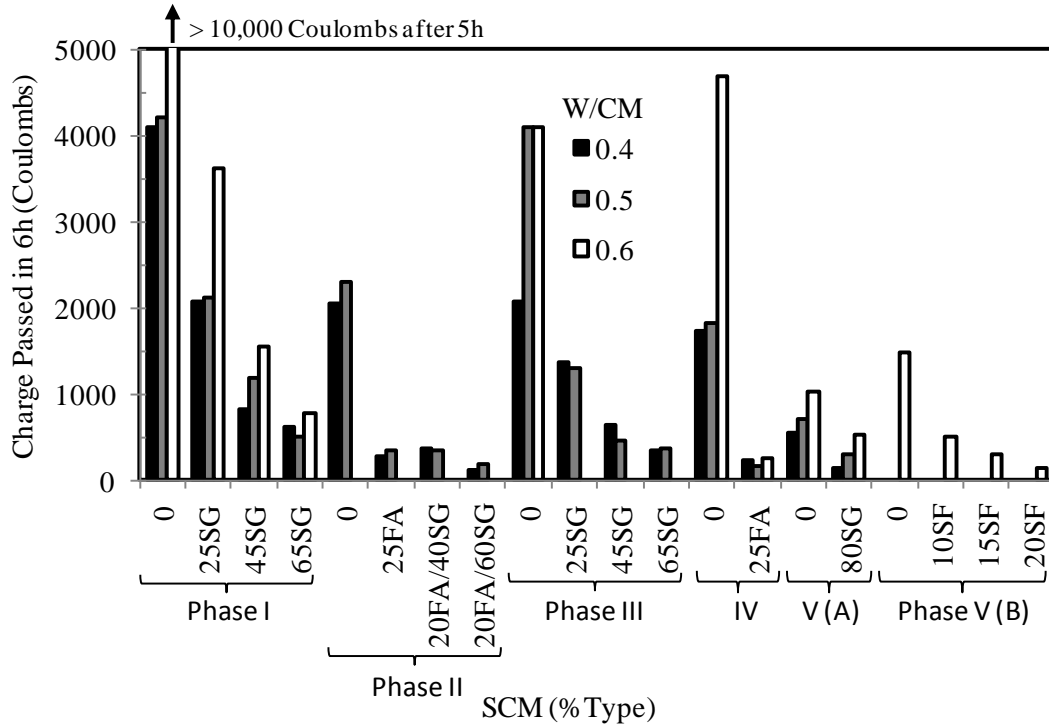


Fig. 6. Results of Electrical Conductivity Tests (ASTM C 1202) for all 25-Year-Old Concretes from Phase I to V

In all cases the electrical conductivity of the concrete, as measured by ASTM C 1202 (commonly referred to as the “rapid chloride permeability test”), was significantly reduced as the w/cm decreased and as the level of SCM increased. As observed for the 25-year chloride profiles and the calculated diffusion coefficients, the impact of SCM appears to be greater than that of w/cm. For example, the results within a given phase indicate that the conductivity of concrete with SCM and w/cm = 0.60 was less than the control concrete with w/cm = 0.40. The conductivity of the control samples in Phase V are significantly lower than that of the control samples in Phases I to IV. The reason for this is not known.

## SURFACE DETERIORATION

The visual appearance of the concrete blocks after 25 years exposure varied widely from little signs of surface deterioration to significant loss of the surface such that coarse aggregate particles were exposed over slightly more than half their perimeter to some level of disintegration such that the block was no longer intact or had suffered more than 20% volume.



In general, concretes produced with  $w/cm = 0.40$  performed well, with little or no significant surface loss and with any such surface loss being confined to the corners and edges of the specimens. The differences between control concretes (without SCM) and concrete with moderate levels of SCM were not significant, but concrete with higher levels of SCM (e.g.  $\geq 45\%$ ) did show a slight but noticeable increase in the loss of material at the corners and edges.

For concrete with  $w/cm = 0.50$ , the amount of surface loss was increased. The increase was slight for the control blocks, but the surface loss significantly as the level of SCM increased. Blocks with higher levels of SCM generally showed excessive surface loss with coarse aggregates being exposed over the whole surface.

For concrete with  $w/cm = 0.60$ , there was again a small increase in the surface loss of the control blocks (compared with  $w/cm = 0.60$ ), but all of the concretes with SCM, especially at higher replacement levels, showed severe surface scaling and, in some cases, partial disintegration (block no longer in one piece or showing more than 20% mass loss). Severely deteriorated blocks were not retrieved from Treat Island for analysis at UNB. An example of the surface condition of concrete with  $w/cm = 0.60$  is shown in Figure 7.

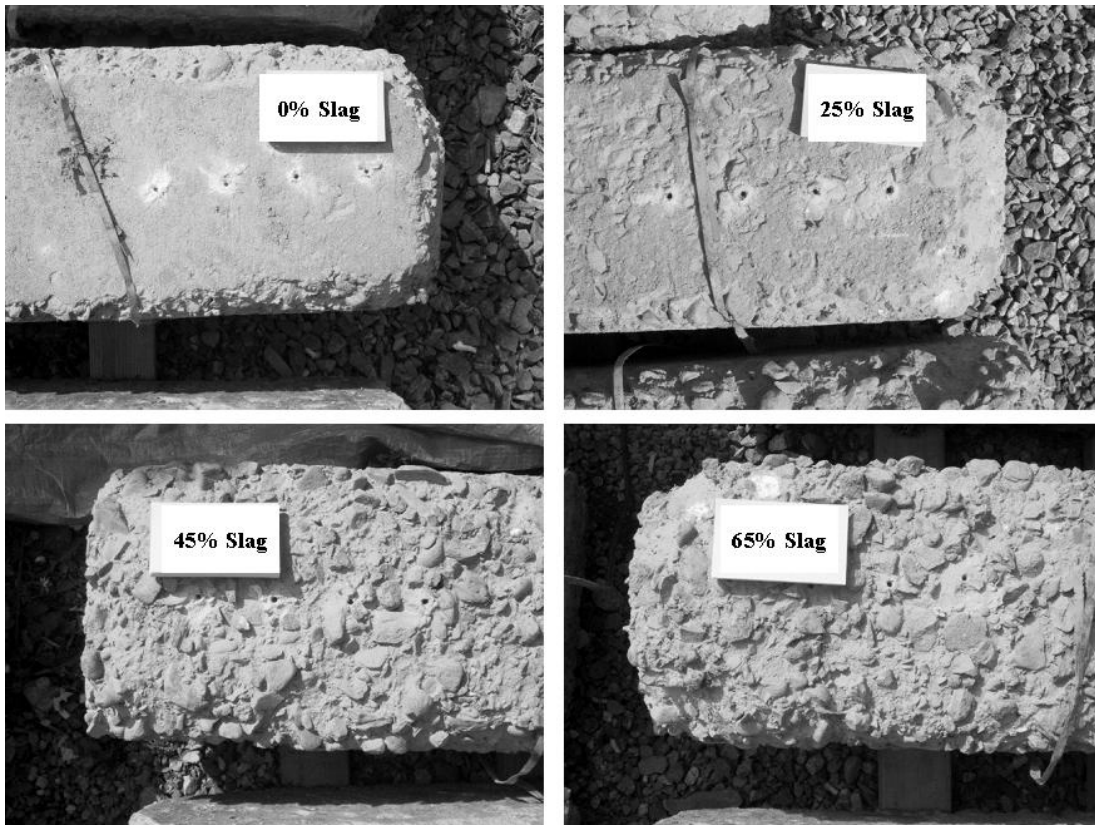


Figure 7 Concrete Blocks with  $w/cm = 0.60$  from Phase I after 25 Years

All of the concrete mixes from Phase I(B) and Phase V(B) produced without air-entrainment deteriorated rapidly at Treat Island and were not retrieved for testing at UNB.

## SUMMARY

The program initiated by Malhotra and Bremner [1996] at Treat Island provides very valuable long-term data regarding the performance of concrete with and without SCM in very aggressive marine exposure conditions. In all cases, the incorporation of fly ash, slag or silica fume leads to a substantial increase in the resistance to chloride ion penetration and the effect seems to increase as the SCM level increases at least in the range of replacement levels included in the first five phases of this study (up to 25% fly ash, 80% slag or combinations of fly ash and slag, and 20% silica fume). Concretes with higher levels of fly ash (up to 56%) were placed at Treat Island in some of the later test phases and these specimens will be examined at a later date.

From the perspective of producing sustainable concrete, the use of high levels of SCM should be encouraged for marine environments as the CO<sub>2</sub> footprint associated with the concrete decreases as the portland cement content decreases and the service-life increases as the level of SCM increases.

However, the results of the study also indicate that the use of SCM is not without problems and it is not prudent to increase the level of SCM without consideration of other factors. The increased surface loss observed with increasing SCM levels is of some concern and concrete with high levels of SCM may not be suitable for exposure to a marine environment with multiple cycles of freezing and thawing unless the water-to-cementing materials ratio is limited to  $w/cm \leq 0.40$ . Even at this  $w/cm$ , very high levels of SCM should be used judiciously in this very aggressive environment, and limiting the level of SCM to a more moderate level may be warranted in some cases.

Of course, selecting the appropriate level of SCM requires more than a consideration of the long-term durability issues (chloride ingress and scaling in this case) as other factors such as early-age strength, stripping times, or tendon-release times, may govern in some projects and possibly place practical restraints on the level of SCM that can be used.

The results of this study are further evidence of the need to optimize the level of SCM used based on a consideration of the environment and all of the performance requirements. A fuller discussion of optimizing the replacement level for fly ash concrete is provided in another paper at this conference (Thomas, 2010).

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