

an extreme condition and was performed to better discriminate the expected relative performance of the different mixtures under very severe exposure conditions.

Figures 4 and 5 show the results obtained for concrete mixtures made with Type I and Type III Portland cement respectively. As discussed in a previous section, the lower chloride ion permeabilities associated to the lower W/B ratios and the presence of silica fume are due to the refinement of the capillary pore network as well as the reduction of the total pore volume. The results reported in Figures 4 and 5 reveal that drying can increase significantly the chloride ion permeability. This behavior can be partially explained by the internal microcracking resulting from thermal and moisture gradients. But a good part of the difference is most probably due to an important modification of the capillary pore structure. The removal of water from capillary pores is believed to open the thin water-filled spaces which connect the larger capillary pores to one another (this is known as the "ink bottle effect") [15, 16]. Drying is thus expected to yield a coarser pore structure with more interconnected capillary voids. The opening of the pore structure facilitate the migration of gas, liquids and ions through the cementitious matrix by means of different transport mechanisms such as capillary suction, ponding, permeability, osmosis, and diffusion. Consequently, drying can be harmful to concrete durability in many different aspects such as deicer salt scaling, chemical attack, corrosion of steel reinforcement, etc.

Some important conclusions can be drawn from the Figures 4 and 5. First of all, concrete mixtures with smaller W/B ratio appear to be less affected by drying especially those made with Type III Portland cement. But even concretes with a 0.25 W/B ratio were affected by drying at 110°C when they do not contain silica fume. However, concretes containing silica fume and having a W/B ratio of 0.25 were not significantly affected by drying, even at 110°C. It is thus possible to make high-performance concretes which are extremely resistant to internal damage caused by drying providing that the mixtures have a very low W/B ratio (about 0.25) and contain silica fume. The beneficial effect of silica fume is probably due to the fact that its capillary volume is very finely divided (see Figure 2) which make him much less vulnerable to the opening of the pore structure.

#### RESISTANCE TO CHEMICAL ATTACK

The chemical attacks can be roughly divided in two categories: (1) the constituents of cement paste (such as calcium hydroxide) can chemically react with substances present in the surrounding solution to form new swelling hydration products (such as chloroaluminates), or (2) hydration products can be dissolved when exposed to an aggressive environment. Of course, both of these phenomenon can occur simultaneously. Although very few experimental data are available, HPC are expected to be much better resistant to the first type of chemical attack than normal strength concretes because their very low porosity constrain the intrusion of aggressive substances. The resistance of HPC to the second type of chemical attack has been investigated in our laboratory [15]. This resistance is particularly important for special applications such as the making of nuclear

waste containers where the very long term durability (after a few hundred years) is of a paramount importance.

In order to study the resistance of HPC to chemical attack, cement pastes were made with a Type III Portland cement, 6% of silica fume, and two W/B ratios (0.38 and 0.25). After six months of curing in a saturated lime solution, paste disks (70 mm in diameter and 4 mm in thickness) were soaked in three different pH controlled solutions for a period of up to 3 years. The three aggressive solutions were as following: 3% NaCl (by weight) maintained at a pH level of 8.5; 0% NaCl at 8.5 and 0% NaCl at 4.5. It must be remembered that capillary water have a pH value of about 13, and that even pure water (with a pH of about 7) is thus an aggressive, acid solution. At regular intervals, paste disks were removed from the solutions and submitted to scanning electron microscope examinations, X-ray energy dispersion analyses, and mercury intrusion porosimetry.

The results obtained from X-ray energy dispersion are particularly interesting. The concentration of calcium, chlorine, and aluminium were measured at 10  $\mu\text{m}$  intervals along imaginary lines extending from the external surface in contact with the aggressive solution towards the internal part of the disks. The results obtained are shown on Figure 6. The horizontal line drawn on each diagram represents the concentration of calcium in the calcium silicate hydrates (C-S-H). The concentrations above this line correspond to the calcium contained in the calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), and the concentrations below, to the calcium of deteriorated C-S-H.

As can be seen in Figure 6, after three months of exposure to aggressive solutions, the calcium content far from the external surface was found to be similar to that in the control specimens (i.e. specimens tested immediately after the 6 months curing period). Near the external surfaces, however, the calcium content was much lower. The lower calcium content near the surface can be explained by the fact that calcium hydroxide and C-S-H are unstable at a pH lower than about 13. The decalcified zone was more pronounced for the mixtures having a W/B ratio of 0.38, than for the 0.25 mixtures. For example, after three months of exposure, the calcium content for the mixtures in contact with chlorides was lower in a zone covering approximately the first 375  $\mu\text{m}$  for the 0.25 mixture, and 570  $\mu\text{m}$  for the 0.38 mixture. The results also shows that the pH level of the corrosive solution plays an important role on the decalcification process. The influence of the pH level of the corrosive solution confirms the results obtained from previous studies at pH levels of 13 and 11.5 [16, 17]. Mercury intrusion porosimetry measurements indicate that the leaching of calcium also increases the capillary porosity. The pores having a diameter ranging from about 90 to 600  $\text{\AA}$  seems to be the most affected by this mechanism.

The results clearly indicate that the pH level of the aggressive solution is the most important factor controlling the durability of cement pastes subjected to chemical attack. The W/B ratio does not affect the deterioration processes but only influence the kinetics of these processes. The use of a lower W/B ratio slow down the leaching of calcium.

Plé, R., Pigeon, M., Hébert, E., and Atten, P.C., 1992. *Chemical Attack on Low Water-Cement Ratio Pastes Containing Silica Fume*, ACI Special Publication 112, pp. 1471-1490.



## CONCLUSION

When compared to normal strength concretes, high-performance concrete does not only provides a higher compressive strength, but also an improved durability. The properties of HPC can thus be advantageously used for a large number of applications which required a high quality construction material. Nevertheless, the design of the mixture composition, as well as the batching, delivery, and placing of concrete is more touchy with an HPC than with a normal strength concrete. Consequently, although HPC can be easily and efficiently produced in concrete plants with commonly used equipments, it remains that its production requires a well qualified staff and a higher quality control.

This paper was dealing exclusively with high-performance concretes made with Portland cements and silica fume. But other supplementary cementitious materials, such as fly ashes or blast-furnace slags, can also be successfully used to produce HPC mixtures. Actually, little data are available on that topic although a number of major works have been reported recently [18, 19]. The use of mineral by-products in the making of HPC is expected to grow significantly in the next years. However, research is still needed to better understand the properties of these concretes, especially as regards with their durability.

## ACKNOWLEDGMENTS

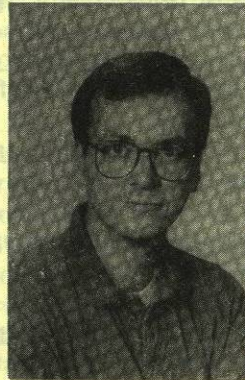
The authors are grateful to the Natural Science and Engineering Research Council of Canada for its financial support for this project which is part of the research program of the Network of Centers of Excellence on High-Performance Concrete. The authors also wish to thank Françoise Garnier, Caroline Verreault, Janicka Maltais, and Michel Lessard for their help in doing the laboratory experiments, and Ann Lamontagne for her help in preparing the manuscript.

## REFERENCES

- [1] Ipatti, A., 1991, A Bibliography on High-Strength Concrete 1930-1990, Imatran Voima Oy, Concrete and Soils Laboratory, Rajatorpantie 8, SF-01600 Vantaa, Finland, 70 p.
- [2] Aitcin, P.C., and Albinger, J.M., 1989, Les bétons à hautes performances: Expériences nord-américaine et française, Annales de l'Institut Technique du bâtiment et des travaux publics, No. 473, pp. 151-189.
- [3] American Concrete Institute, 1992, State of the Art Report on High-Strength Concrete, ACI Manual of Concrete Practice — Part I Materials and General Properties of Concrete, 48 p.
- [4] DeLarrard, F., and Malier, Y., 1992, Engineering Properties of Very High-Performance Concrete, High-Performance Concrete: From Material to Structure, E & SF Spon Editor, London, pp. 85-114.
- [5] Sarkar, S.L., and Aitcin, P.C., 1987, Comparative Study of the Microstructure of Normal and Very High-Strength Concrete, Cement, Concrete, and Aggregates, Vol. 9, No. 2, pp. 57-64.
- [6] Jolicoeur, C., Simard, M.A., Aitcin, P.C., Baalbaki, M., 1992, Cement-Superplasticizer Compatibility in High Performance Concrete: The Role of Sulfates, Proceedings of the ACI Symposium "Progress in Concrete", Montréal, Canada, 26 p.
- [7] Penttala, V., 1986, Compatibility of Binder and Superplasticizer in High-Strength Concrete, Nordic Concrete Research No. 5, pp. 117-128.
- [8] Pigeon, M., 1992, The Frost Durability of Concrete, Cement and Concrete Science & Technology, Vol. 1, Part II, ABI Books, S.N. Ghosh Editor, New Delhi, India, pp. 417-448.
- [9] American Concrete Institute, 1992, Guide to Durable Concrete, ACI Manual of Concrete Practice — Part I Materials and General Properties of Concrete, 37 p.
- [10] Powers, T.C., 1949, The Air Requirement of Frost Resistant Concrete, Proceedings of the Highway Research Board, Vol. 32, pp. 285-297.
- [11] Pigeon, M., 1989, La durabilité au gel du béton, Matériaux et Constructions/Materials and Structures, Vol. 22, No. 127, pp. 3-14.
- [12] Gagné, R., Aitcin, P.C., Pigeon, M., and Pleau, R., 1992, Frost Durability of High-Performance Concretes, High-Performance Concrete: From Material to Structure, E & SF Spon Editor, London, pp. 239-251.
- [13] Pigeon, M., Gagné, R., and Foy, C., Critical Air-Void Spacing Factor for Low Water-Cement Ratio Concretes With and Without Silica Fume, Cement and Concrete Research, Vol. 17, No. 6, pp. 896-906.
- [14] Pigeon, M., Garnier, F., Pleau, R., and Aitcin, P.C., 1993, Influence of Drying on the Chloride Ion Permeability of HPC, Concrete International, Vol. 15, No. 2, pp. 65-69.
- [15] Delagrave, A., Pigeon, M., and Révertégat, E., 1993, Durability of High Performance Cement Pastes Subjected to Chemical Attack, Bi-Annual Meeting of the Canadian Network of Centres of Excellence on High Performance Concrete, June 10, Québec, Canada, pp. 37-49.
- [16] Gagné, R., Pigeon, M., Révertégat, E., and Aitcin, P.C., 1992, Chloride-Ion Attack on Low Water-Cement Ratio Pastes Containing Silica Fume, ACI Special Publication SP-132, pp. 1471-1490.



- [17] Révertégat, E. Richet, C., and Gegout, P., 1992, Effect of pH on the Durability of Cement Pastes, Cement and Concrete Research, Vol. 22, Nos 2/3, pp. 259-272.
- [18] Bilodeau, A., and Malhotra, V.M., 1993, Concrete Incorporating High Volumes of ASTM Class F Fly Ashes: Mechanical Properties and Resistance to Deicer Salt Scaling and to Chloride-Ion Penetration, Forth International CANMET/ACI International Conference of Fly Ash, Silica Fume, Slag & Natural Pozzolans in Concrete, Vol. 1, Istanbul, Turkey, pp. 319-349.
- [19] Mukherjee, P.K., Loughborough, M.T., and Malhotra, V.M., 1982, Development of High-Strength Concrete Incorporating a Large Percentage of Fly Ash and Superplasticizers, Cement and Concrete Research, Vol. 4, No. 2, pp. 81-86.



**Richard Pleau**, School of Architecture,  
Laval University,  
Quebec, Canada, G1K 7P4

Table 1 - Volume of permeable pores obtained from ASTM C 642 water absorption test method.

|                     | W/B     | Type I cement |       |       | Type III cement |       |      |
|---------------------|---------|---------------|-------|-------|-----------------|-------|------|
|                     |         | 0.45          | 0.35  | 0.25  | 0.45            | 0.35  | 0.25 |
| without silica fume | 7 days  | 20.73         | 14.49 | 12.30 | 16.13           | 11.61 | 7.81 |
|                     | 28 days | 18.14         | 12.43 | 12.25 | 16.53           | 9.84  | 8.01 |
| with silica fume    | 7 days  | 16.19         | 13.35 | 10.07 | 14.99           | 12.63 | 8.09 |
|                     | 28 days | 14.93         | 12.03 | 8.78  | 14.79           | 9.83  | 8.28 |

Note: Each number represents the mean value obtained on two concrete specimens

Table 2 - Charge passing through concrete specimens as obtained from AASHTO T 227 rapid chloride ion permeability test method (Coulombs).

|                     | W/B     | Type I cement |       |       | Type III cement |       |      |
|---------------------|---------|---------------|-------|-------|-----------------|-------|------|
|                     |         | 0.45          | 0.35  | 0.25  | 0.45            | 0.35  | 0.25 |
| without silica fume | 7 days  | 11 326        | 6 225 | 3 283 | 3 579           | 2 077 | 662  |
|                     | 28 days | 5 045         | 2 737 | 1 809 | 424             | 276   | 164  |
| with silica fume    | 7 days  | 8 447         | 4 903 | 3 060 | 3 610           | 3 503 | 741  |
|                     | 28 days | 3 415         | 2 163 | 811   | 325             | 281   | 56   |

Note: Each number represents the mean value obtained on two concrete specimens



Table 3 - Composition and properties of concrete mixtures used for the comparative study on the influence of coarse aggregates on compressive strength of HPC.

| W/B                                   | 0.22        | 0.25        | 0.30        |
|---------------------------------------|-------------|-------------|-------------|
| Water (kg/m <sup>3</sup> )            | 109 – 112   | 127 – 129   | 126 – 129   |
| Cement (kg/m <sup>3</sup> )           | 550 – 570   | 540 – 550   | 445 – 455   |
| Fine aggregate (kg/m <sup>3</sup> )   | 690 – 720   | 710 – 730   | 840 – 860   |
| Coarse aggregate (kg/m <sup>3</sup> ) | 1100 – 1130 | 1050 – 1070 | 990 – 1010  |
| Superplasticizer (kg/m <sup>3</sup> ) | 14.0 – 18.1 | 10.0 – 10.2 | 7.0 – 7.1   |
| Slump (mm)                            | 170 – 220   | 205 – 230   | 170 – 195   |
| Unit Weight (kg/m <sup>3</sup> )      | 2475 – 2541 | 2437 – 2493 | 2405 – 2472 |
| Air content (%)                       | 2.2 – 3.8   | 2.7 – 3.3   | 3.4 – 4.0   |

Table 4 - Compressive strength of similar concretes made with different coarse aggregates (MPa).

| Age     | W/B  | Coarse aggregate |                         |                             |              |                 |               |
|---------|------|------------------|-------------------------|-----------------------------|--------------|-----------------|---------------|
|         |      | A<br>limestone   | B<br>granitic<br>gneiss | C<br>dolomitic<br>limestone | D<br>granite | E<br>peridotite | F<br>andesite |
| 48 hrs  | 0.22 | 66.6             | 53.8                    | 73.7                        | 61.2         | 60.2            | 62.6          |
|         | 0.25 | 62.1             | 50.6                    | 73.5                        | —            | —               | —             |
|         | 0.30 | 48.4             | 44.0                    | 56.0                        | —            | —               | —             |
| 28 days | 0.22 | 92.5             | 99.4                    | 111.6                       | 91.3         | 105.2           | 105.5         |
|         | 0.25 | 88.5             | 93.6                    | 106.2                       | —            | —               | —             |
|         | 0.30 | 83.8             | 87.1                    | 93.7                        | —            | —               | —             |

Note: Each number represents the mean value obtained on two concrete specimens.

Table 5 - Properties of concrete mixtures having exactly the same composition but made with different materials using different mixing techniques.

| Coarse aggregate    | Super-plasticizer admixture | Mixing sequence* | Dosage of super-plasticizer (L/m <sup>3</sup> ) | Slump (mm) | Air content (%) | 28 days compressive strength (MPa) |
|---------------------|-----------------------------|------------------|---|------------|-----------------|------------------------------------|
| dolomitic limestone | M<br>melamine               | A                | 6.5   | 90         | 2.1             | 59                                 |
|                     |                             | A                | 6.5   | 80         | 1.5             | 64                                 |
|                     |                             | B                | 6.5   | 50         | 2.4             | 64                                 |
|                     |                             | B                | 25.5  | 215        | 1.1             | 58                                 |
|                     | N1<br>naphtalene            | A                | 6.5   | 220        | 2.5             | 55                                 |
|                     |                             | A                | 6.5   | 220        | 2.1             | 59                                 |
|                     |                             | B                | 6.5   | 195        | 3.0             | 59                                 |
|                     |                             | B                | 13.6  | 205        | 2.1             | 62                                 |
|                     | N2<br>naphtalene            | A                | 6.5   | 220        | 1.8             | 44                                 |
|                     |                             | A                | 6.5   | 220        | 2.6             | 53                                 |
|                     |                             | B                | 6.5   | 155        | 3.3             | 59                                 |
|                     |                             | B                | 11.5  | 210        | 2.5             | 54                                 |
| granitic gneiss     | M<br>melamine               | A                | 6.5   | 165        | 2.3             | 61                                 |
|                     |                             | A                | 6.5   | 185        | 1.8             | 63                                 |
|                     |                             | B                | 6.5   | 60         | 1.5             | 63                                 |
|                     |                             | B                | 12.3  | 225        | 1.5             | 68                                 |
|                     | N1<br>naphtalene            | A                | 6.5   | 220        | 2.5             | 43                                 |
|                     |                             | A                | 6.5   | 215        | 2.8             | 43                                 |
|                     |                             | B                | 6.5   | 160        | 2.8             | 60                                 |
|                     |                             | B                | 11.0  | 220        | 2.5             | 61                                 |
|                     | N2<br>naphtalene            | A                | 6.5   | 235        | 2.4             | 41                                 |
|                     |                             | A                | 6.5   | 225        | 3.0             | 58                                 |
|                     |                             | B                | 6.5   | 165        | 2.8             | 60                                 |
|                     |                             | B                | 11.0  | 220        | 3.0             | 54                                 |

\* Mixing sequence : A : Cement, sand, water and superplasticizer were first mixed to obtain a homogeneous paste and the coarse aggregate were further added.

B : Cement, sand and coarse aggregates were first mixed to obtain a homogeneous mixture and the water and superplasticizer were further added.



Table 6 - Critical spacing factors obtained for different concrete mixtures subjected to 300 freezing and thawing cycles in air or in water ( $\mu\text{m}$ ).

| W/B   | Freezing and thawing cycles in water |   |   | Freezing and thawing cycles in air          |
|-------|--------------------------------------|---|---|---|
|       | Type I cement                        | Type I cement with silica fume <sup>#</sup> | Type III cement with silica fume <sup>#</sup> | Type I cement with silica fume <sup>#</sup> |
| 0.50  | 500                                  | 250   | —   | 400   |
| 0.50* | 500                                  | 200   | —   | 400   |
| 0.30* | 400                                  | 300   | > 800   | 450   |
| 0.25* | 750                                  | —   | > 800   | —   |

\* : These mixtures were made using a superplasticizer admixture.

#: Silica fume was used as a partial replacement for Portland cement (10% in weight).

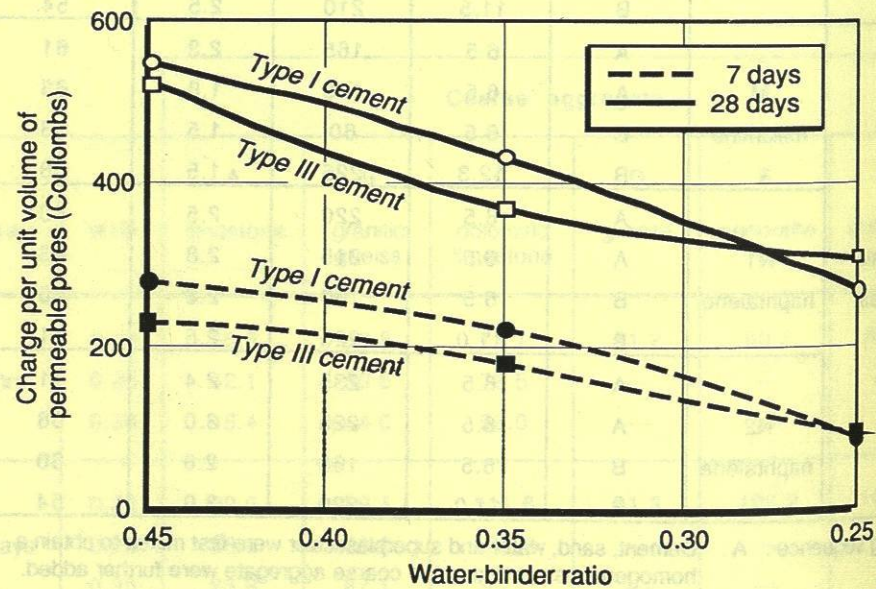


Figure 1 - Relationship between the charge passing through a unit volume of permeable pores and the water binder ratio for concretes not containing silica fume.

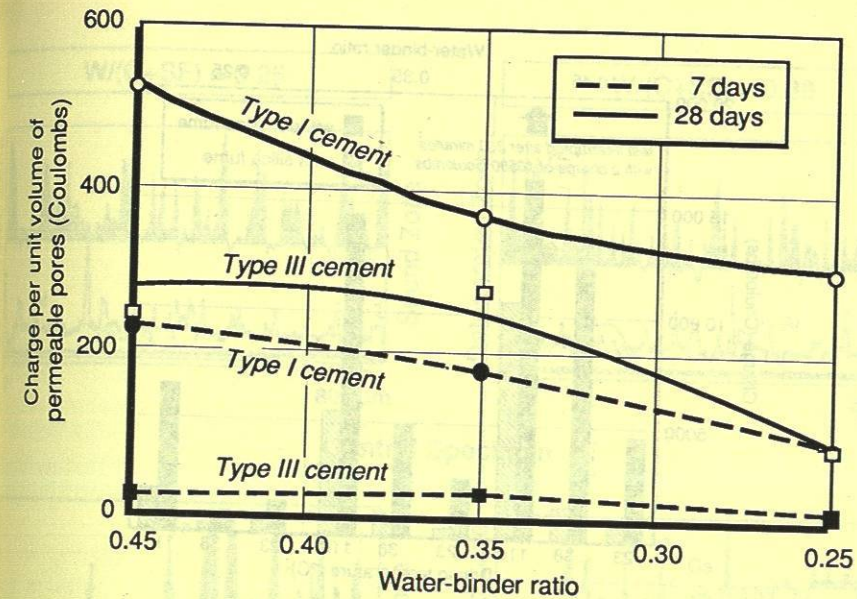


Figure 2 - Relationship between the charge passing through a unit volume of permeable pores and the water binder ratio for concretes containing silica fume.

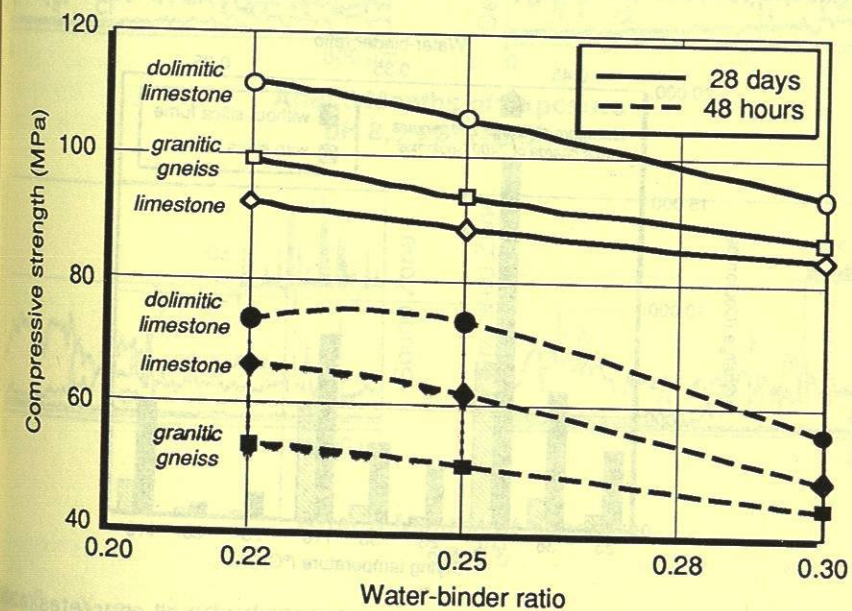


Figure 3 - Relationship between the compressive strength and the water-binder ratio for similar concretes made with three different coarse aggregates.



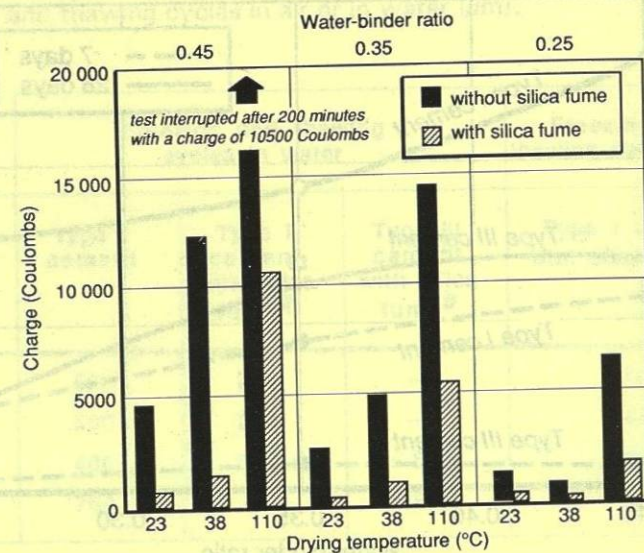


Figure 4 - Chloride ion permeability versus water binder ratio for all concretes made with Type I Portland cement (with and without silica fume) and dried for 90 days (at the temperature indicated) before the test.

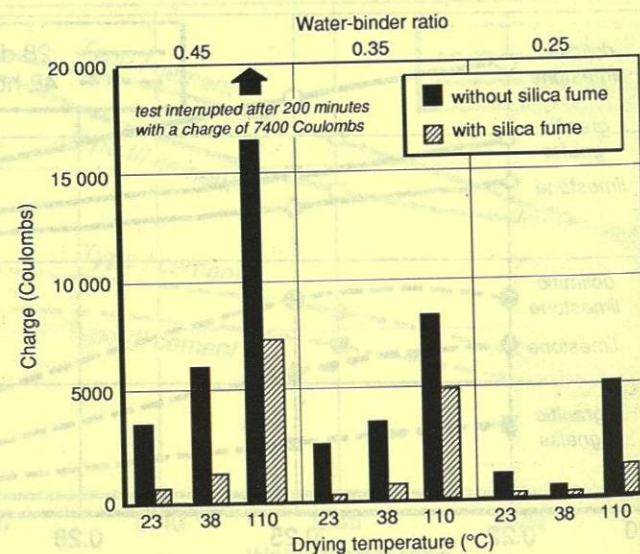


Figure 5 - Chloride ion permeability versus water binder ratio for all concretes made with Type III Portland cement (with and without silica fume) and dried for 90 days (at the temperature indicated) before the test.

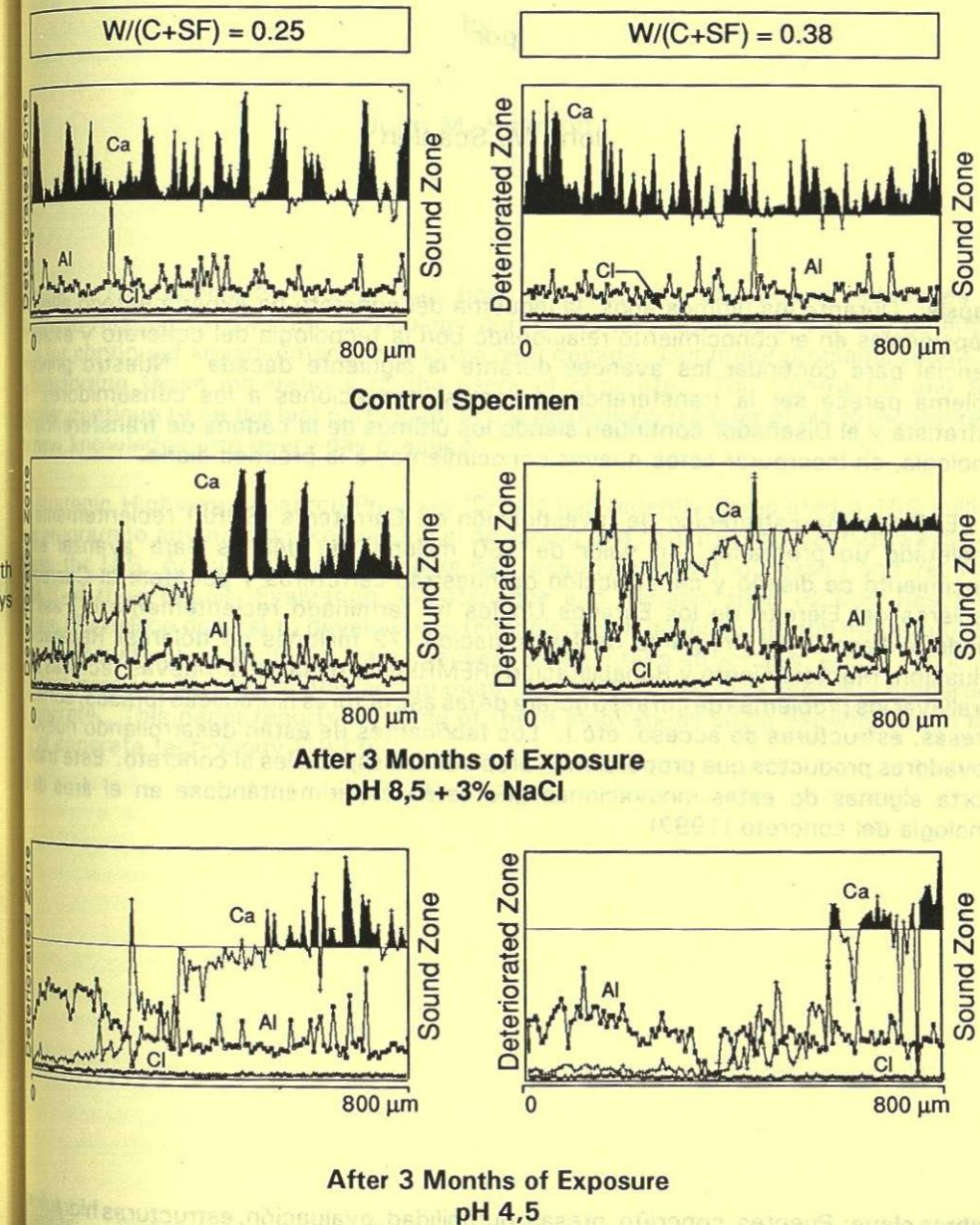


Figure 6 - X-ray energy dispersion measurements for cement pastes with low water-binder ratios (0.25 and 0.38) after three months of exposure to aggressive solutions (a pH of 8.5 with NaCl and a pH of 4.5).