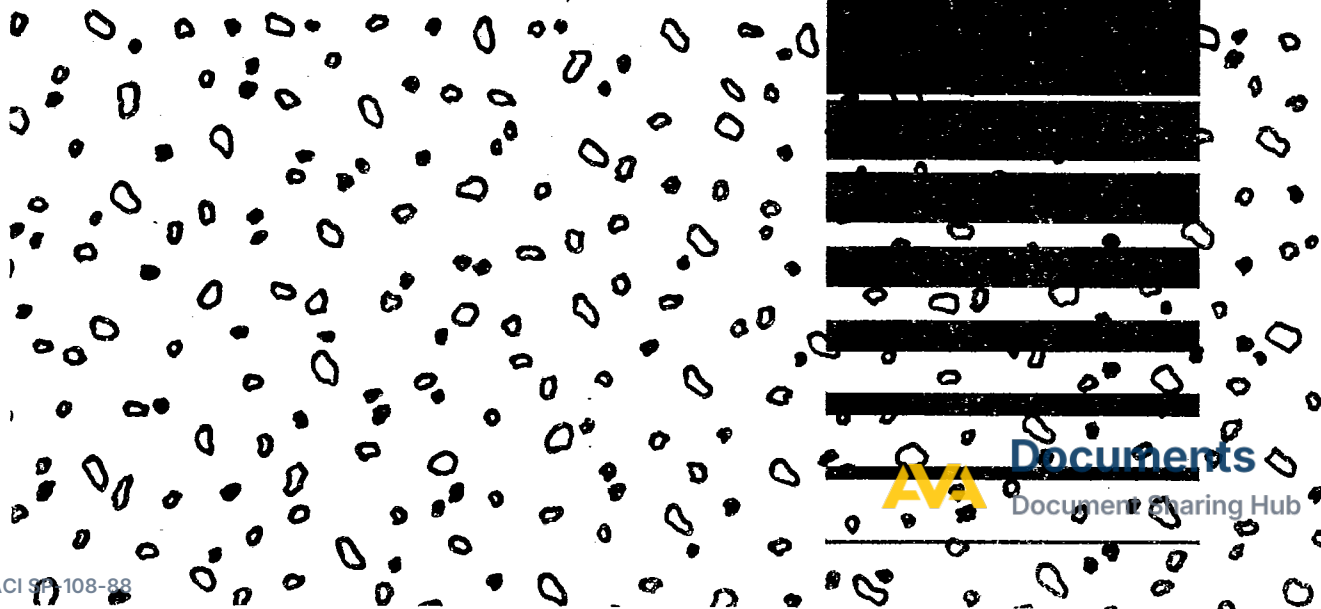


PERMEABILITY OF CONCRETE

David Whiting
Arthur Walitt
Editors

 SP-108

American Concrete Institute, Detroit



PREFACE

Concrete technologists throughout the world are becoming increasingly aware of the importance of permeability with regard to the durability and ultimate longevity of concrete structures. New materials for reducing permeability and techniques for its measurement are rapidly being developed. On November 12, 1987 two sessions on this subject were held at the ACI Fall Convention in Seattle, Washington. The eleven papers presented at these sessions form the subject matter of this volume.

These sessions on concrete permeability were sponsored by ACI Committee 201, Durability of Concrete, and ACI Committee 212, Chemical Admixtures for Concrete. We should like to thank the chairmen of these two committees, Mr. Paul Klieger and Mr. Edwin Decker, respectively, for their help and encouragement in development of this theme. Thanks are extended to all members of committees 201 and 212 who helped review manuscripts.

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A Review of the Pore Structure of Cement Paste and Concrete and its Influence on Permeability

by J.F. Young

Synopsis: The permeability of hardened cement paste is reviewed with particular reference to the influence of pore structure. Permeability is usually modelled by applying D'Arcy's Law, although permeability measurements and pore size distributions determinations reveals the strong influence of large capillary pores (macropores) on flow through cement paste. The macropores form a continuous flow path within the paste. The effects of curing temperature, drying and admixtures on permeability can be understood in terms of their influence on macropores. Paste containing fly ash show anomalous behavior which apparently arises from internal damage occurring during pore structure measurements. It appears that the presence of fly ash promotes the formation of a discontinuous macropore system which inhibits flow.

Keywords: admixtures; calcium chlorides; cement pastes; concretes; fly ash; hardened paste structure; permeability; porosity; slags; water-reducing agents

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INTRODUCTION

Permeability is an important property with regard to the durability of concrete. It represents the ease with which water (or other fluids) can move through concrete, thereby transporting aggressive agents. It is thus of critical importance for many types of distress experienced by concrete. For example:

- | | |
|-------------------------|--|
| sulfate attack | - movement of sulfate ions into concrete where adverse chemical reactions occur. |
| frost resistance | - flow of water to relieve stresses caused by ice formation. |
| alkali-aggregate attack | - movement of alkali ions to aggregates and water to swelling gels. |
| fire resistance | - escape of steam from heated layers causing spalling. |
| corrosion of steel | - movement of chloride ions to the surface of the steel. |

PORE STRUCTURE

Since fluid flow takes place in the pore system it is first necessary to examine the pore structure in concrete. Pores in normal-weight concrete are considered part of the paste fraction and cover a very large size range (Figure 1). The traditional classification, suggested by Powers and Brownyard [1], considers two classes of pores: gel pores are associated with the formation of the hydration products ("cement gel"), which is the intrinsic porosity, while capillary pores are considered to be the remnants of water-filled space. However, it is customary with other porous systems to use a different classification which depends on how water behaves in the pores. Micropores are considered to form the intrinsic porosity although there are good reasons to include also the smaller mesopores. Both meso and macropores make up the capillary pore system.

In cement paste these pores form a continuum which can be measured using mercury intrusion porosity (MIP) down to the largest of gel pores (small mesopores). Sorption techniques are required to investigate the finest mesopores and micropores. Both capillary pore volume and pore size decrease significantly as hydration proceeds, or as w/c ratio is reduced. MIP is the most useful method of measuring pores for permeability predictions, but it must be remembered that there are several important assumptions inherent in the calculations and we are not

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really measuring absolute values. This will become clearer in later discussion.

CAPILLARY FLOW

Flow in capillary pores can be described by D'Arcy's law for laminar flow through porous media:

$$dq/dt = KA(\Delta h/L) \quad (1)$$

where dq/dt is the rate of flow, A is the cross-sectional area of the specimen, and $\Delta h/L$ is the hydraulic gradient across the section. K is the measured proportionality constant which represents the ease with which water flows through the specimen. The permeability coefficient is a material constant independent of the fluid used:

$$K' = \frac{K\eta}{\rho g} \quad (2)$$

where η is the viscosity of the fluid, ρ is its density, and g is the gravitational constant. In practice the measured value K is usually reported as the permeability coefficient, rather than K' . The first comprehensive study of the factors affecting permeability of cement paste using this approach was made by Powers and his co-workers [2,3]. They quantitatively showed the effects of w/c ratio (Figure 2) and time of moist curing (Table 1). It was shown that well-cured pastes can attain very low permeabilities, characteristic of dense rocks, even though the total pore volumes of these pastes are high (Table 2). This was attributed to the fact that the continuous capillary pore system, through which water flows relatively easily, becomes cut off by the deposition of hydration products. The time at which this can occur is strongly dependant on the w/c ratio of the paste (Table 3).

In such discontinuous pore systems flow is limited by movement through the very fine gel pores (micropores), so that D'Arcy flow is greatly modified by the adsorption of water on the pore surfaces. Powers et al. [4] developed a theoretical approach to model this using Stokes Law applied to a concentrated suspension. Equation 3 was derived using a number of simplifying assumptions, which gave good agreement between observed and calculated values over the range 0-30°C.

$$K_1 = \frac{1.36 \times 10^{-12}}{\eta(\theta)} \frac{(1-c)^2}{c} \exp\left(-\frac{1242}{T}\right) + 0.7\left(\frac{c}{1-c}\right) \quad (3)$$

where $\eta(\theta)$ is the viscosity of the fluid as a function of temperature T , and c is the volume fraction of solid material. (The porosity of the paste is equal to $(1 - c) - 0.26$). However, since in practice permeation in concrete mostly involves capillary flow, we will not concern ourselves with the details of this approach.



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Hughes [5] used a different approach, considering Poiseuille flow in a 3-D random array of tortuous pores with circular cross-section. The flow equation thus obtained is:

$$dq/dt = \left(\frac{P}{32n^2\eta} \right) r^2 A (\Delta h/L) \quad (4)$$

where P is the porosity, n^2 is a tortuosity factor, and r is the pore radius.

INFLUENCE OF PORE STRUCTURE

Since the work of Powers, MIP has been developed commercially, so that pore size distributions can be measured routinely. Briefly, the method measures the volume of mercury forced into the pores under an applied pressure. Pore size is related to pressure by the Washburn equation, which assumes a circular cross section

$$P = - \frac{2\gamma \cos \theta}{r} \quad (5)$$

where γ is the surface tension of mercury and θ is the contact angle. In recent years there have been attempts to correlate pore structure with permeability. Parameters used and defined for this purpose are given in Figure 3. The pore diameters used to limit V_1 and V_2 are arbitrary and several values have been used: 135nm [6], 88nm [7], 75nm [8], and 50nm [5] for V_1 ; 30nm [6] and 15nm [5] for V_2 .

Using paste of different w/c ratios Mehta and Manmohan [6] obtained extensive data, part of which is summarized in Table 4, from which the Equation 6 was obtained by regression analysis

$$\ln K = 3.84V_1 + 0.20V_2 + 0.56 \times 10^{-6} d_t + 8.09V'_t - 2.53 \text{ m/s} \quad (6)$$

where V'_t is the total capillary porosity divided by the degree of hydration [i.e., $V'_t = (V_1 + V_2)/\alpha$]. This accounts for different amounts of hydration. Inspection of Equation 6 shows that V_1 and V'_t are the most important parameters and the pore-structure-permeability relationship can be approximated by:

$$\ln K = 4V_1 + 8V'_t - 2.5 \text{ m/s} \quad (7)$$

or by [8]:

$$\ln K = 10.9V'_t - 3.4 \quad (8)$$

Nyame and Illston [9], on the other hand, found a good correlation between $\ln K$ and $\ln r_\infty$ (Figure 4). This latter parameter was taken to represent the smallest radius for which there is a continuous capillary pore system through which D'Arcy flow can

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occur. A similar correlation with threshold diameter could be obtained [6] with a similar justification. In this way the complications of flow through micropores is eliminated from the analysis.

Hughes [5] used Equation 4 together with MIP data to obtain an experimental function for r^2 . A value of 2.5 was used for n^2 , which has been estimated for fluid flow through granular beds [10]. Hughes also recognized the restrictive nature of the gel pores, which were eliminated in the analysis by ignoring all pores with $r < 7.5\text{nm}$. He also assumed that he was considering only the continuous pore system (as suggested by Nyame and Illston) by using the second intrusion curve (Figure 5). The first intrusion is considered to fill all capillary pores, but only those pores without restricted entryways will empty during extrusion. Thus the second intrusion is a measure of the continuous pore system through which mercury flows readily, and presumably also water.

Effect of Curing Temperature

The pore size distribution is strongly influenced by the curing temperature: high temperatures increase the volume of large mesopores [8,11] (see, for example Figure 6). One might expect this change to be reflected by higher permeabilities, and this has indeed been found [8,12] when curing temperatures are varied (see control curves in Figure 7).

Effect of Drying

The early work at PCA showed that drying a well-cured paste increased the K value nearly 100-fold [2]. Recent studies have shown that drying changes the pore size distribution [13,14], being most graphically illustrated by observing freezing behavior [14] (see Figure 8).

Effect of Mineral Admixtures

Mineral admixtures, such as fly ashes and slags, are now accepted as valuable ingredients for durable concrete. Reductions in permeability are believed to be an important aspect of their beneficial effects. Several studies [7,15,16] have shown that for cement pastes containing reactive mineral admixtures, such as fly ash, silica fume, and rice husk ash, the total porosity is reduced compared to pastes of pure cement and a finer pore structure results (Figures 9 and 10). These changes correlate qualitatively with observed reductions in permeability. However, pastes containing fly ash show anomalous behavior. Such pastes have reduced permeabilities even though the much slower reactions of fly ash result in higher porosities and coarser pore structures even after 60 days curing (Figure 9).

It is clear that the pore structure-permeability relationships discussed above do not apply here. The pozzolanic



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reaction seems to be able to develop a discontinuous pore system more readily [17]. Recently Feldman [18] has concluded that pastes containing fly ash are more prone to damage when MIP is used to measure pore sizes. This can be seen by comparing the first and second intrusion curves (Figure 4). It appears that mercury under pressure breaks through rather fragile barriers that isolate large pores, whereas this does not happen in pure cement pastes. These results suggest that lack of adequate curing of concretes with fly ash could seriously affect its potential permeability. However, increased curing temperature greatly increases the rate of pozzolanic reaction and reduces water flow [12] (see Figure 7). In contrast the curing temperature had a much less effect on slag hydration.

The pronounced reduction in pore size in pastes containing silica fume is attributed [16] both to its high pozzolanic reactivity, and also to its very small particle size which allows it to pack efficiently between the cement grains, thereby subdividing the space. The permeability coefficients are thus greatly reduced [18], particularly at high w/c ratios (Table 5).

Effect of Chemical Admixtures

Chemical admixtures should also affect permeability if they change pore size distributions in cement pastes. Additions of calcium chloride increase the volume of fine capillary pores at the expense of large ones [15,20] and provide a less permeable paste [15]. The addition of water-reducing agents should reduce permeability if they are used to lower w/c ratios. However, like calcium chloride, water reducing agents often increase drying shrinkage, which has been correlated with finer pores. Thus, they may well reduce permeability even when the w/c is not changed. A more uniform dispersion of cement grains within a paste, which is a consequence of using a water reducing agent, is more likely to provide a more uniform pore structure with less coarse pores.

Mortars and Concretes

It is now well known that the cement-aggregate interface is more porous than the bulk paste, in all but very well-cured systems [21]. This has been demonstrated by SEM observations, but it is not so easy to quantify. Only a few comparative MIP measurements on paste and mortars have been made [22,23] see Figure 11. It seems likely that the interfacial zone will be a favorable pathway for water flow. This is even more likely if bond cracking occurs under local stresses caused by thermal mismatch between paste and aggregate, or restraint of paste shrinkage by the aggregate.

The permeability coefficients for concrete are generally about 100 times higher than for comparable pastes (Figure 12) while for mortars they are 3-10 times higher.

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CONCLUDING DISCUSSION

A link between pore structure and permeability has now been clearly established for cement pastes, although the exact quantitative relationships still need to be refined. It should be possible to meld the various approaches into a unified theory. Specific relationships need to be developed for pastes formed with blended cements, taking into account the anomalies inherent in the measurements. The role of the cement-aggregate interface needs to be further studied and quantified if the performance of field concrete is to be predicted with certainty.

Two cautionary notes should be mentioned which merit further consideration. Space does not permit detailed discussions; either topic could well be the subject of a separate paper. The first concern involves the assumptions inherent in the porosimetry measurements. Analysis involves idealized assumptions of geometry which are not realistic; the problem of restricted entryways to large pores is particularly troublesome. Furthermore, the paste or mortar must be strongly dried before mercury can be intruded. It is now recognized that drying significantly changes the pore structure (see Figure 8), particularly in pastes with a fine pore structure. Also, internal shrinkage stresses in mortars or concretes associated with differential shrinkage of paste and aggregate will undoubtedly lead to the formation of microcracks. It is uncertain the degree to which the apparent pore structure determined experimentally differs from the original material under study. Direct pore structure measurements on undried specimens would be most desirable.

The second concern is the degree to which the permeability coefficient for a given paste or mortar will differ for different chemical species, i.e., water, chloride ions, sulfate ions and mercury (in porosimetry). Until such relationships are known the prediction of field concrete durability from laboratory data cannot be successful. Accurate laboratory measurements of permeability coefficients require experiments of long duration with inherently large scatter. Current approaches to in situ permeability measurements need to be critically examined, and a continued search maintained for alternate methods.

ACKNOWLEDGMENTS

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TABLE 1

Effect of Curing Time of Cement Paste ($w/c = 0.51$) on
Its Permeability Coefficient (Based on Data from Ref. 2)

Time of Curing (Days)	Permeability Coefficient (m/s)
1	10^{-8}
3	10^{-9}
7	10^{-11}
14	10^{-12}
28	10^{-13}
90	10^{-16}

TABLE 2

Comparisons of Permeability and Capillary Porosity
between Well-Hydrated Cement Paste and Natural Rocks
(Data from Ref. 2)

Rock		Permeability Coefficient (m/s)	Cement Paste	
Type	Porosity (%)		Porosity (%)	w/c
Sandstone	4.3	1.7×10^{-11}	30	0.71
Limestone	3.1	8.0×10^{-13}	28	0.66
Fine-grained Marble	1.8	3.3×10^{-14}	15	0.48
Dense Trap	0.6	3.5×10^{-15}	6	0.38

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TABLE 3

Curing Time Required to Achieve a
Discontinuous Capillary Pore System [3]

w/c	Curing Time (days)
0.40	3
0.45	7
0.50	28
0.60	180
0.70	365

TABLE 4

Volumetric Characteristics of Hydrated Cement
Paste [6] (See text for definition of symbols)

w/c	V_1 (cm ³ /g)	V'_t (cm ³ /g)	d_t (nm)	$10^{12}K$ (m/s)
0.4	0	0.26	<100	0.1
0.5	0	0.33	100	0.3
0.6	0.19	0.47	220	2.3
0.7	0.28	0.54	460	22
0.8	0.38	0.63	780	96
0.9	0.44	0.77	1400	410

TABLE 5

Influence of Silica Fume Additions
on the Permeability of Concrete [19]

Cement Content (kg/m ³)	Silica Fume (wt. %)	w/s	Permeability Coefficient (10 ¹² m/s)
100	-	2.4	12,000
100	10	2.3	1,000
250	-	0.8	0.6
250	10	1.0	0.1
400	-	0.5	0.007
400	10	0.5	0.04

PORE CLASSIFICATION

POWERS

GEL	CAPILLARY	AIR VOIDS
2.5	50	10,000
10		
		PORE DIA. (nm)

IUPAC

MICRO	MESO	MACRO	AIR VOIDS
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Fig. 1--Pore size classifications for cement paste

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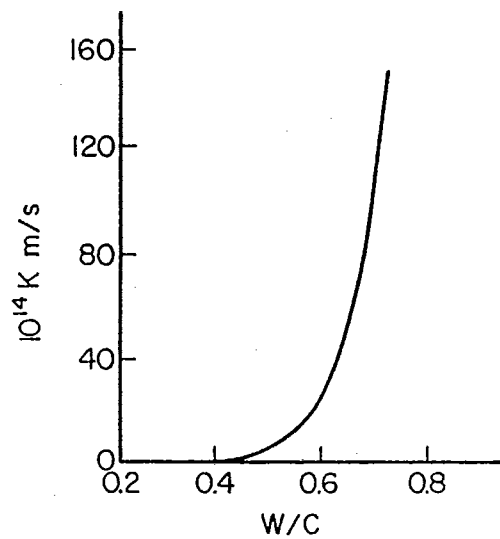


Fig. 2--Effect of w/c ratio on permeability (Reference 2)

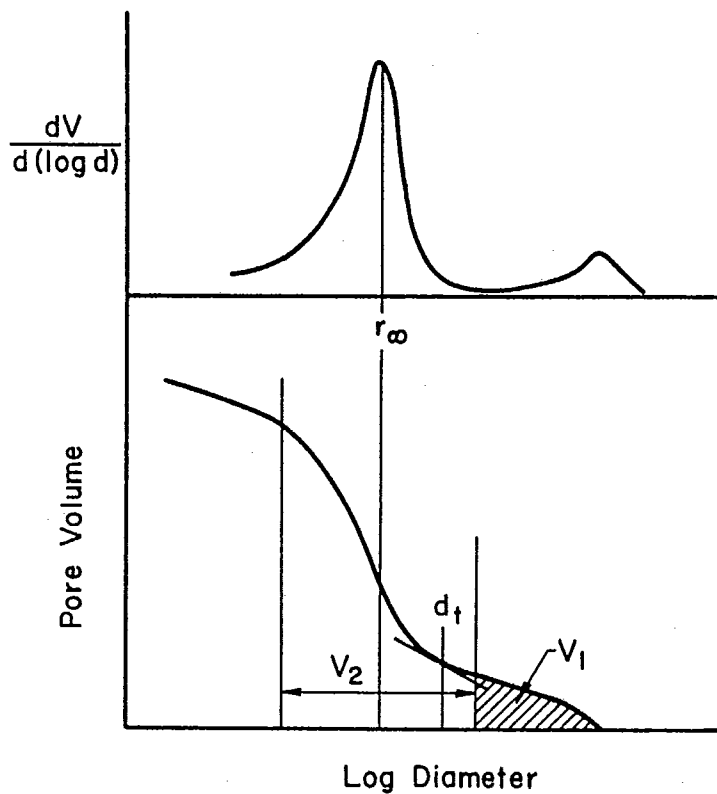


Fig. 3--Parameters defining MIP pore size distributions V_1 and V_2 are the pore volumes over the size ranges indicated, d_t the threshold diameter, and r_∞ the continuous pore diameter

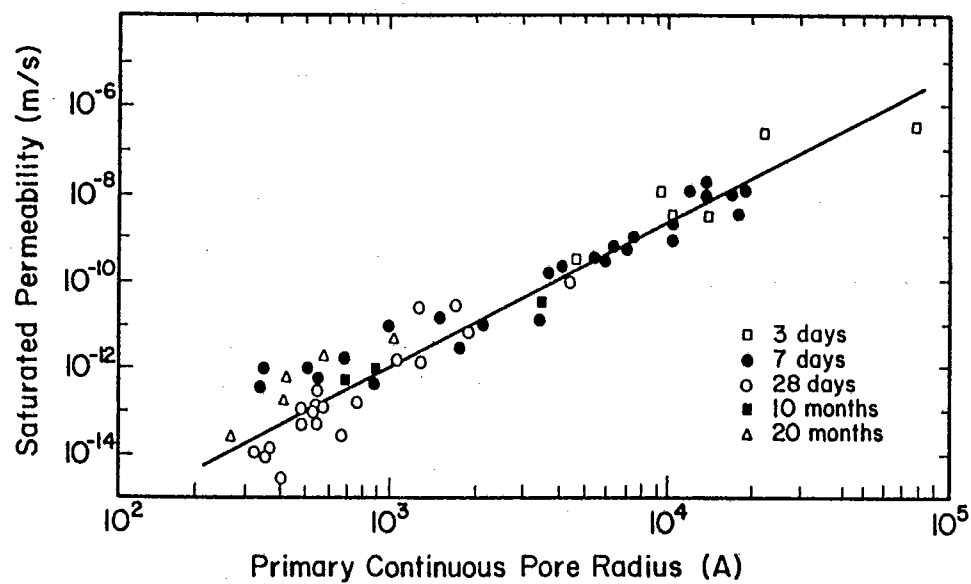


Fig. 4--Influence of continuous pore radius on permeability (Reference 9)

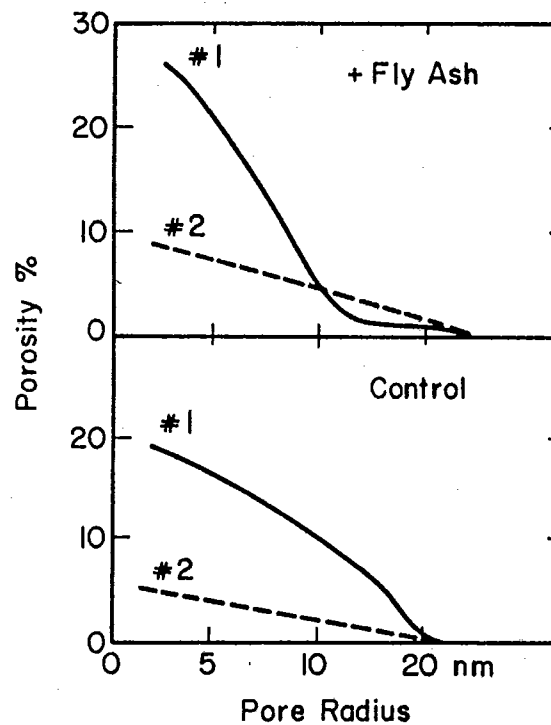


Fig. 5--Pore size distribution curves for cement pastes with and without fly ash (Reference 5)

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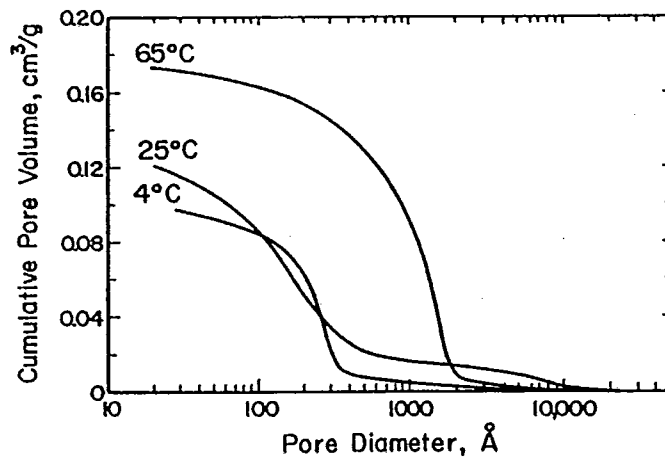


Fig. 6--Effect of curing temperature on pore size distribution
(data for C3S pastes from Reference 11 at equal hydration
[$\alpha = 0.87$])

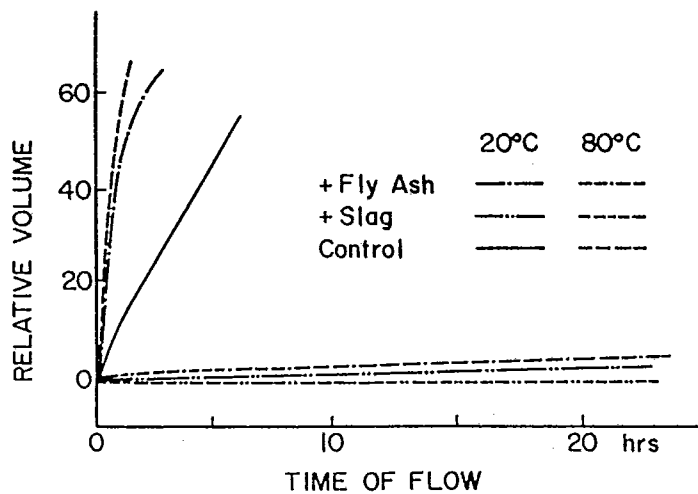


Fig. 7--Effect of curing temperature on water flow through pastes
made with or without mineral admixtures (Reference 12)

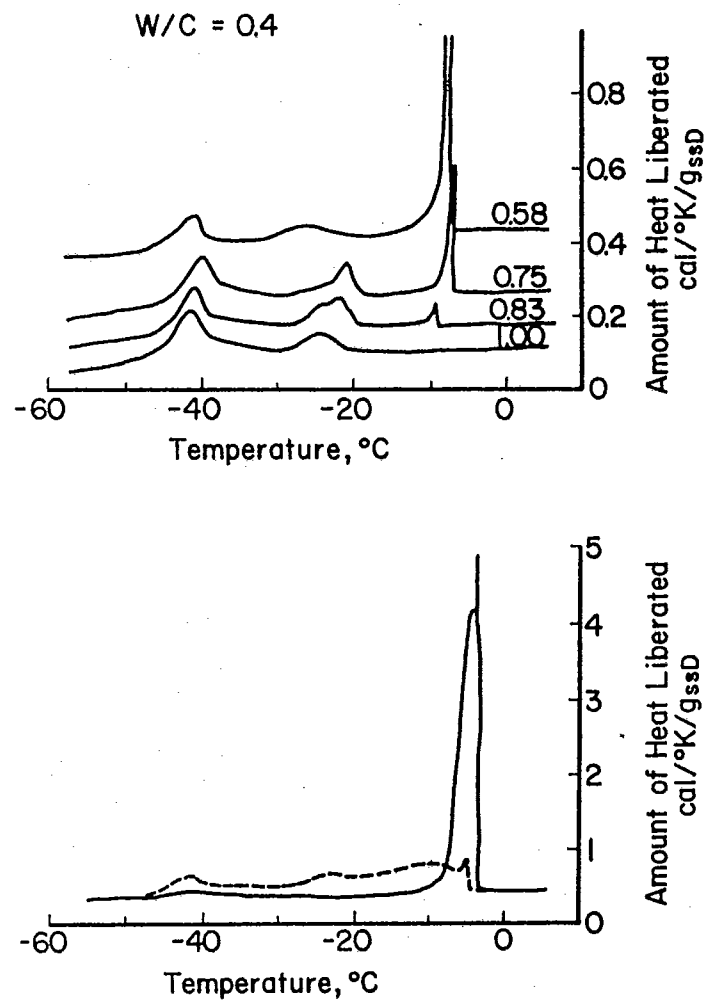


Fig. 8--Heat evolved during freezing of a cement paste; a) dried to the relative humidities indicated and resaturated, b) full line: virgin paste, dashed line dried to r.h. = 0.58 and resaturated

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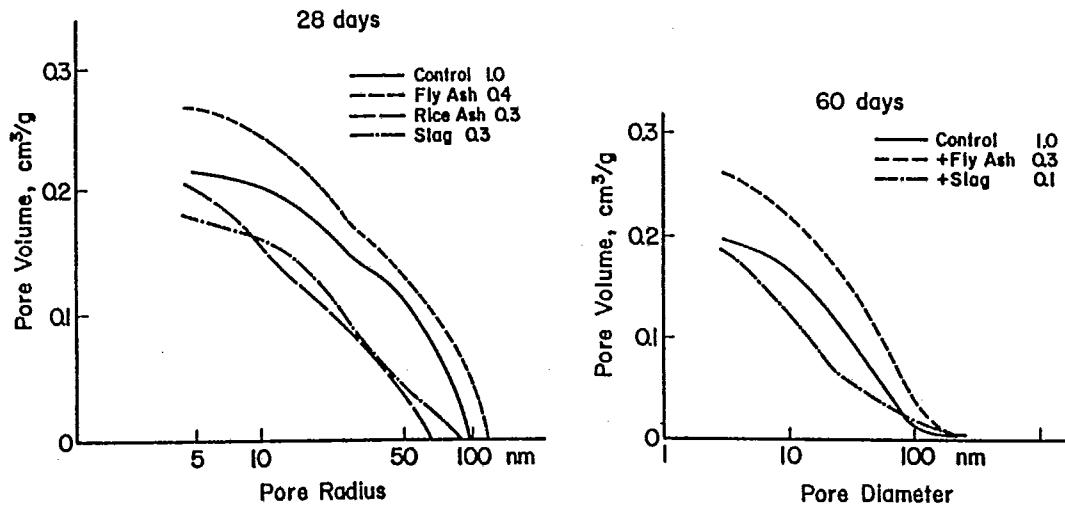


Fig. 9--Pore size distributions in cement pastes made with and without mineral admixtures — numbers beside legends represent relative permeability: control = 1.0 (Reference 15)

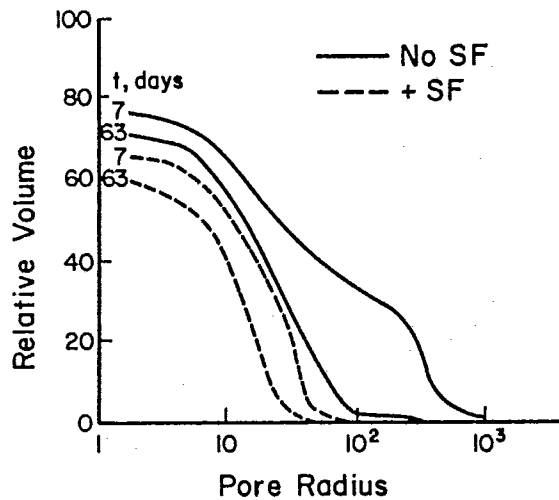


Fig. 10--Pore size distribution for paste made with and without silica fume (SF) (Reference 16)

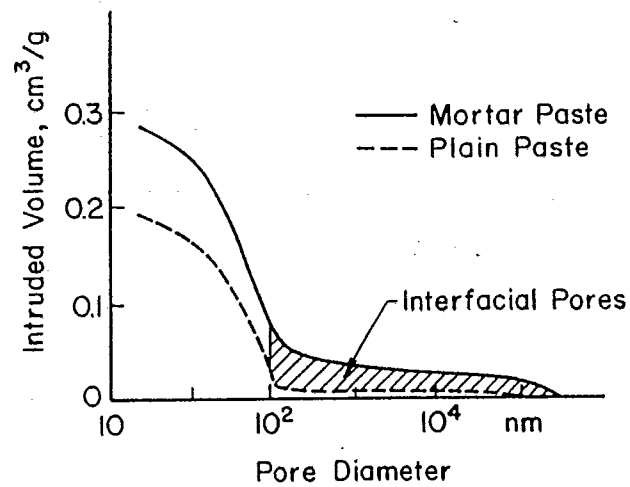


Fig. 11--Pore size distribution for plain paste and paste in mortar (Reference 23)

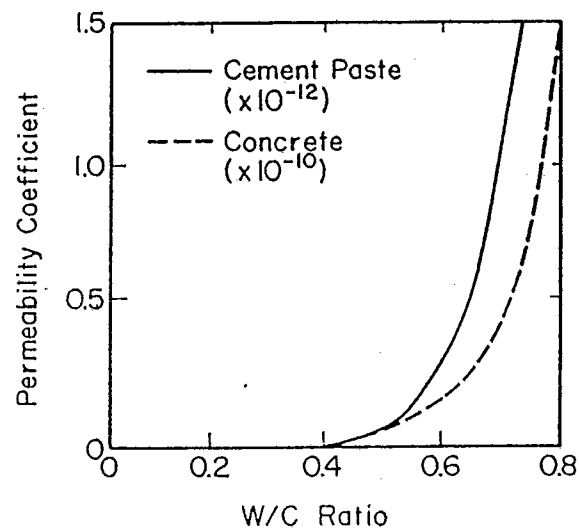


Fig. 12--Comparison of permeability for paste and concrete

SP 108-2

Influence of Superplasticizers, Polymer Admixtures, and Silica Fume in Concrete on Chloride Ion Permeability

by S.L. Marusin

Synopsis: This paper summarizes the results of permeability studies that have been undertaken at Wiss, Janney, Elstner Association, Inc. (WJE) since 1979. The research used a test procedure developed during the NCHRP Project 12-19A, "Concrete Sealers for Protection of Bridge Structures" which was reprinted in 1981 as NCHRP Report No. 244. This test method utilizes 10-cm-concrete cubes, and chloride ion penetration is determined at 4 depths after 21 days exposure to 15 percent NaCl solution. The test results show that lowering of w/c ratio in portland cement concrete or presence of superplasticizers, polymer admixtures, and silica fumes are able to significantly reduce concrete permeability.

Keywords: admixtures; chlorides; concretes; epoxy resins; latex; permeability; plasticizers; plastics, polymers, and resins; silica fume

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INTRODUCTION

Deterioration of concrete structures by the corrosion of reinforced steel due to the ingress of chloride ion is a serious and universal problem throughout the world. It is well known that the penetration of chloride ion into concrete depends on the quality of concrete and especially on its permeability. This paper summarizes the research that the author has undertaken since 1979 on the use of various chemical admixtures to minimize the chloride ion penetration from external sources into the concrete. The research used a test procedure developed by WJE during the National Cooperative Highway Research Program (NCHRP) Project 12-19A, "Concrete Sealers for Protection of Bridge Structures (1), conducted by the United States Transportation Research Board (TRB). The test results and recommendations for the methods are reported in NCHRP Report No. 244. This test method utilizes 10-cm-concrete cube specimens and the chloride ion content is measured on an entire half of each split cube after 21 days exposure to 15 percent NaCl solution. Subsequent studies determined the chloride ion content profile at four different depths. Following this research project, a research effort was undertaken to study chloride ion permeability of concretes made with various admixtures (2,3,4,5).

DESCRIPTION OF TEST PROGRAM

Materials

All tested concretes were made by using a Type I portland cement and a natural chloride-free river sand and gravel. Neutralized vinsol resin was used as an air-entraining agent.

Casting, Curing and Testing Procedure

All concretes were mixed and cast at room temperature at the WJE laboratories. The forms used for making the 10 cm cubes were constructed with a special resin-coated wood to preclude the need for any release agent which might chemically contaminate the concrete surfaces during casting. The forms were table-vibrated for each of two lifts of concrete. The top surfaces were then finished with a wooden float and covered with a polyethylene film for overnight curing at 23°C. The specimens were stripped at one day, lightly sandblasted and then placed within sealed heavy-duty plastic bags for 21 days of moist curing. They were then removed from the plastic bags and placed in the controlled

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climate room on steel racks for air drying at $23 \pm 3^\circ\text{C}$ and 50 ± 4 percent R. H. for 14 days before immersing in a 15 percent NaCl solution. After 21 days of soaking, the cubes were exposed to air of a controlled climate room for an additional 21 days. Following this final air-drying period, 6 mm holes were drilled through the center of each cube face on all six sides of the cube to obtain powder samples for chloride ion determination at four different depth intervals. The intervals were 0 to 12 mm, 12 to 25 mm, 25 to 37 mm and 37 to 50 mm. Acid soluble chloride ion content was determined using an acid digestion, potentiometric titration procedure. All tests were performed on duplicate specimens and average values are listed in tables and graphs.

Of particular importance in reviewing the measured chloride ion profiles through the concrete, is the assumption that the corrosion threshold level for acid-soluble chloride ion content in normal weight reinforced concrete is about 0.03 percent by weight of concrete.

TEST RESULTS AND DISCUSSION

Conventional Portland Cement Air-Entrained Concrete

Mix proportions and properties of four portland cement concretes having cement contents from 325 to 365 kg/m³ and with w/c ratio ranges from 0.35 to 0.55 are given in Table 1. Chloride ion contents at 4 depths are listed in Table 2 and graphically depicted in Fig. 1. The data in Table 2 show that the concrete of the depth interval from 0 to 12 mm has extremely high levels of chloride ranging from 0.38 to 0.45 percent by weight of concrete. These values are thus about 13 to 15 times the corrosion threshold level. No significant influence of decrease of w/c on concrete permeability was found in this depth. In the next depth interval, 12 to 25 mm, the chloride contents range from 0.09 to 0.26 percent and the influence of w/c is well pronounced. For the concrete having a w/c of 0.35, the chloride content is about 5 times lower than was found at the depth interval of 0 to 12 mm and for the concrete having w/c of 0.55 about 2 times lower. However, the measured chloride ion content is still 3 to 9 times the corrosion threshold level. At a depth from 25 to 37 mm, the chloride value is less than the corrosion threshold level for concrete with w/c of 0.35. The concretes having w/c of 0.50 and 0.55 did not show any differences in permeability at this depth. In both concretes the chloride value is about 2 times the corrosion threshold level of 0.03 percent. At a depth of 37 to 50 mm the chloride level of the concrete having w/c of 0.40 fell to the corrosion threshold level. Both concretes with w/c of 0.50 and 0.55 were above this level, and again the chloride ion contents were similar and not influenced by increasing the w/c from 0.50 to 0.55. The influence of w/c on chloride ion content at different depths is graphically shown in Fig. 2.

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Concretes Containing Superplasticizers and Polymer Admixtures

Mix proportions and properties of 5 concretes containing superplasticizers ("high-range water reducers", or HRWR) and polymer admixtures are given in Table 3. Chloride ion contents at 4 depths are listed in Table 4 and graphically depicted in Fig. 2.

The data in Table 3 show that the depth interval from 0 to 12 mm has high levels of chloride, ranging from 0.27 to 0.40 percent by weight of concrete. These values are lower than in conventional concrete, but still about 10 to 13 times the corrosion threshold level of 0.03 percent. Concretes A and B with HRWR contained 460 and 300 kg/m³ of cement and had w/c of 0.29 and 0.40, respectively. Concrete A was able to reduce the chloride ion content below the threshold level at the depth from 12 to 25 mm, and concrete B was able to do this at the next depth, 25 to 37 mm. Concretes C and D containing latexes reached the threshold level at the depth from 12 to 25 mm and reduced the chloride ion content below this level at the next depth of 25 to 37 mm. Concrete E with epoxy was able to reduce the chloride ion content below the threshold level at the depth of 25 to 37 mm. The influence of admixtures on chloride ion content is shown in Fig. 4.

Concrete containing Silica Fume (SF)

Mix proportions and properties of 9 concretes containing silica fume are given in Table 5. Chloride ion contents at 4 depths are listed in Table 6 and graphically depicted in Figs. 5 and 6.

Six concretes, identified as Mix No. SF1 through Mix No. SF6 and having cement contents from 340 to 370 kg/m³ and SF ranges from 2.5 to 15 percent by weight of cement were made. The other three concretes were made with about 300 kg/m³ of cement and their SF contents range from 6 to 30 percent.

As shown in Table 6, for all concretes, the depth interval from 0 to 12 mm has high levels of chloride, similar to concretes containing HRWR or polymer admixtures, ranging from 0.27 to 0.39 percent by weight of concrete. These values are about 10 to 13 times the corrosion threshold level of 0.03 percent.

In the next depth interval of 12 to 25 mm the chloride ion content is greatly reduced, to 0.03 and 0.06 percent by weight of concrete. Four concretes containing 6, 8 and 10 percent of SF were able to reach the corrosion threshold limit at this depth.

In the depth intervals of 25 to 37 mm and 37 to 50 mm all concretes exhibited chloride ion contents below the threshold level.

SUMMARY

A summary of test results is given in Table 7.

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The vast majority of the absorbed chloride ion was found within the first 12 mm of depth in all tested concretes. The shape of chloride ion distribution is generally influenced by w/c for the portland cement concretes. However, this statement does not seem to be true in the first 12 mm depth interval and is also not well pronounced if w/c is increased from 0.50 to 0.55. Only the portland cement concrete with w/c of 0.35 exhibited a chloride ion content below the corrosion threshold limit at a depth of 25 to 37 mm. The concrete with w/c = 0.40 fell to the corrosion threshold limit at a depth of 37 to 50 mm and the concretes with w/c equal and above 0.50 were well contaminated with chloride.

The presence of HRWR, polymer admixtures and SF greatly influenced and decreased the concrete permeability. The permeability for portland cement concrete of w/c = 0.35 and concretes containing HRWR, polymer admixtures and SF was found to be similar. All these concretes were able to reach the corrosion threshold chloride ion level of about 0.03 percent, or exhibited a chloride ion content below this value at the depth interval of 25 to 37 mm. The presence of HRWR, latex type admixtures and SF from 6 to 10 percent by weight of cement reduced concrete permeability in such a way that the corrosion threshold level was reached at the depth of 12 to 25 mm.

No direct relationship was found between increased amounts of SF in concrete and a decrease of concrete permeability. However, the concrete permeability is more influenced by the amount of SF in concrete than the w/c value. It is believed that the best permeability reduction could be obtained with a concrete containing 10 percent of SF by weight of cement.

Decrease of concrete permeability could be achieved by lowering w/c at conventional portland cement concrete, using admixtures (i.e., HRWR and polymers), and, of course, using properly consolidated and cured concrete.

Results of this limited study also showed the importance of deep cover over the embedded reinforcement.

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TABLE 1 - MIX DESIGN AND PROPERTIES OF FRESH AND HARDENED PORTLAND CEMENT CONCRETE

Mix No.	Mix proportions, kg/m ³		Properties of fresh concrete			w/c by weight	28-day compressive strength, MPa
	Portland cement	Sand	Gravel	Water	Air content (%)	Slump (cm)	
1	330	775	1175	115	6.0	5	46
2	365	639	1044	145	6.5	10	35
3	348	887	1012	175	6.0	15	35
4	325	721	1092	180	6.0	19	30

Conversion factors:

$1 \text{ N/mm}^2 = 1 \text{ MPa} = 145 \text{ psi}$
 $\text{kg/m}^3 = 1.7 \text{ lb/yd}^3$
 $1 \text{ cm} = 0.39 \text{ in.}$

TABLE 2 - ACID-SOLUBLE CHLORIDE ION CONTENT AT DIFFERENT DEPTHS OF PORTLAND CEMENT CONCRETE

Mix No.	W/C	Depth (mm)			
		0-12	12-25	25-37	37-50
1	0.35	0.427	0.085	0.014	0.012
2	0.40	0.384	0.100	0.037	0.031
3	0.50	0.442	0.200	0.052	0.035
4	0.55	0.451	0.263	0.052	0.036

TABLE 3 - MIX DESIGN AND PROPERTIES OF FRESH
AND HARDENED CONCRETES CONTAINING
SUPERPLASTICIZERS (HRWR) OR POLYMER ADMIXTURES

Mix No.	Concrete with admixtures	kg/m ³				Air content (%)	Slump (cm)	W/C by wt	28 day compressive strength (MPa)
		Portland cement	Sand	Gravel	Water*				
A	HRWR	462	870	878	168	2	13.5	0.29	53
B	HRWR	300	889	1000	119	58	14	0.40	42
C	A latex	392	726	1077	113	108	25	0.29	30
D	S-B latex	391	706	1055	132	105	25	0.34	36
E	Epoxy	390	738	1112	101	78	23.5	0.26	34

TABLE 4 - ACID-SOLUBLE CHLORIDE ION CONTENT

Mix No.	Type of concrete	W/C	Depth (mm)			
			0-12	12-25	25-37	37-50
A	HRWR	0.29	0.334	0.021	0.012	0.009
B	HRWR	0.40	0.399	0.046	0.026	0.016
C	A latex	0.29	0.273	0.032	0.018	0.008
D	S-B latex	0.34	0.296	0.028	0.012	0.007
E	Epoxy	0.26	0.343	0.115	0.027	0.017

TABLE 5 - MIX DESIGN AND PROPERTIES OF FRESH AND HARDENED CONCRETE CONTAINING SILICA FUME (SF)

Mix No.	Mix Properties (kg/m ³)				Properties of Fresh concrete			28-day compressive strength (MPa)
	Portland cement	Silica* Fume	Sand	Gravel	Water**	Air content (%)	Slump (cm)	W/C by weight
SF1	368	2.5	795	963	136	7.0	7	0.37
SF2	363	5.0	790	952	139	7.0	8	0.38
SF3	382	5.0	654	1064	157	5.6	7	0.41
SF4	367	10.0	803	970	127	6.5	9	0.35
SF5	354	10.0	633	1032	145	7.4	8	0.41
SF6	337	15.0	638	1039	138	7.0	13	0.41
SF7	304	6.0	989	989	126	6.3	12	0.42
SF8	300	8.0	989	973	120	6.3	12	0.40
SF9	283	30.0	638	1042	122	5.4	13	0.43

* Percent by weight of cement

** Including water in SF admixture

TABLE 6 - ACID-SOLUBLE CHLORIDE ION CONTENT
AT DIFFERENT DEPTHS OF CONCRETE
CONTAINING SILICA FUME

Mix No.	Amount of SF* (%)	Cement kg/m ³	Depth (mm)			
			0-12	12-25	25-37	37-50
SF1	2.5	368	0.390	0.057	0.021	0.020
SF2	5	363	0.370	0.041	0.024	0.020
SF3	5	382	0.363	0.056	0.023	0.019
SF4	10	367	0.271	0.030	0.019	0.016
SF5	10	354	0.338	0.033	0.020	0.019
SF6	15	337	0.348	0.035	0.027	0.020
SF7	6	304	0.280	0.025	0.016	0.009
SF8	8	300	0.270	0.028	0.019	0.012
SF9	30	283	0.365	0.039	0.027	0.020

* % by weight of cement

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TABLE 7 - SUMMARY OF TEST RESULTS

Type of concrete	Cement content (kg/m ³)	Admixtures type	kg/m ³ or % by wt** of cement	Chloride ion content at depth (mm)			
				0-12	12-25	25-37	37-50
Portland cement concrete	330	---	---	0.43	0.08	0.01	0.01
	365	---	---	0.38	0.10	0.04	0.03
	348	---	---	0.44	0.20	0.05	0.04
	325	---	---	0.45	0.26	0.05	0.04
Concrete with HRWR and polymers	462	HRWR	2	0.33	0.02	0.01	0.01
	300	HRWR	58	0.40	0.05	0.03	0.02
	392	A latex	108	0.27	0.03	0.02	<0.01
	391	S-B latex	105	0.30	0.03	0.01	<0.01
	390	Epoxy	78	0.34	0.12	0.03	0.02
Concrete with SF	368	SF	2.5	0.39	0.06	0.02	0.02
	363	SF	5.0	0.37	0.04	0.02	0.02
	382	SF	5.0	0.36	0.06	0.02	0.02
	367	SF	10.0	0.27	0.03	0.02	<0.02
	354	SF	10.0	0.34	0.03	0.02	0.02
	337	SF	15.0	0.35	0.04	0.03	0.02
	304	SF	6.0	0.28	0.03	0.02	<0.01
	300	SF	8.0	0.27	0.03	0.02	0.01
	283	SF	30.0	0.37	0.04	0.03	0.02

* kg/m³ for HRWR and polymers

** % by wt of cement for SF

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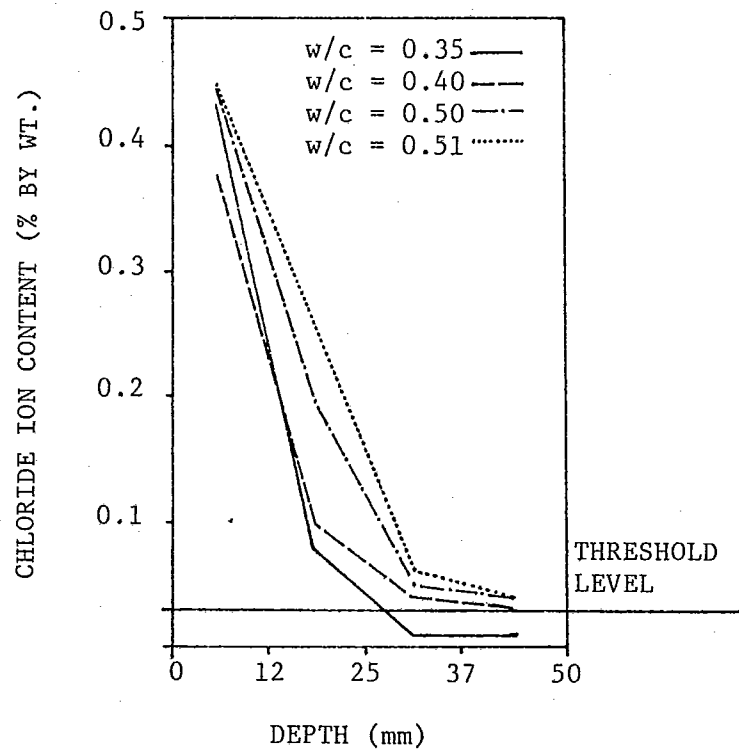


Fig. 1--Portland cement concretes — chloride ion content at 4 depths

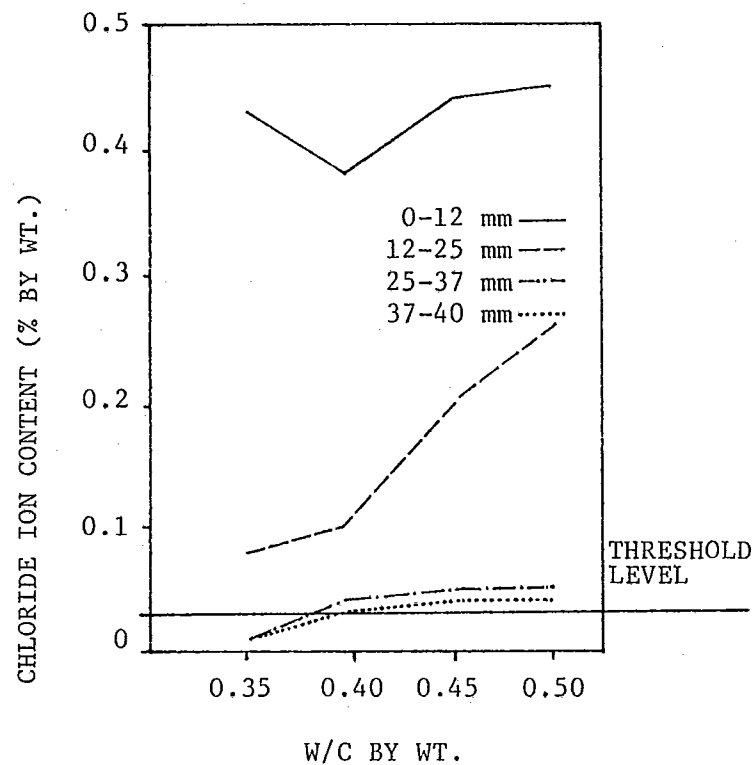


Fig. 2--Portland cement concretes — chloride ion content within 4 depths versus w/c ratio

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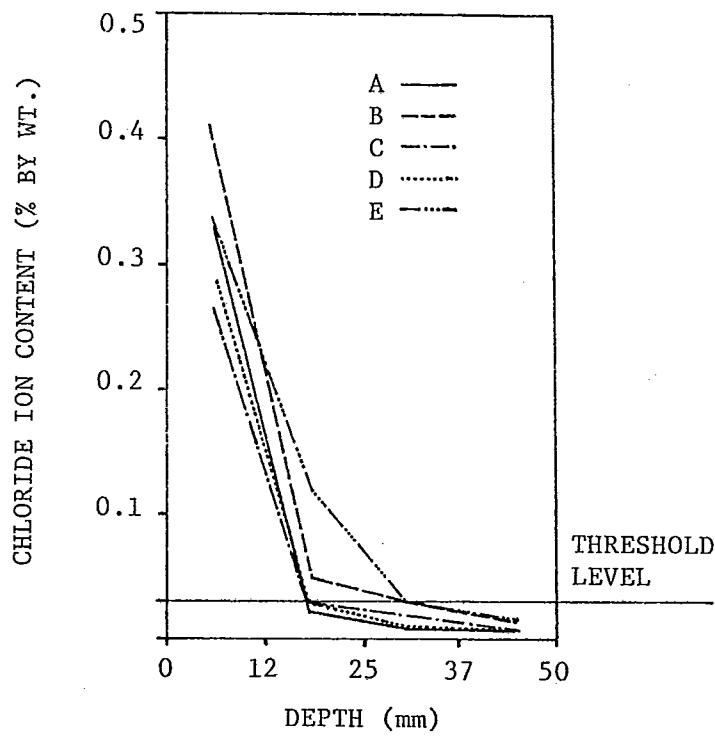


Fig. 3--Concretes containing HRWR and polymers — chloride ion content at 4 depths

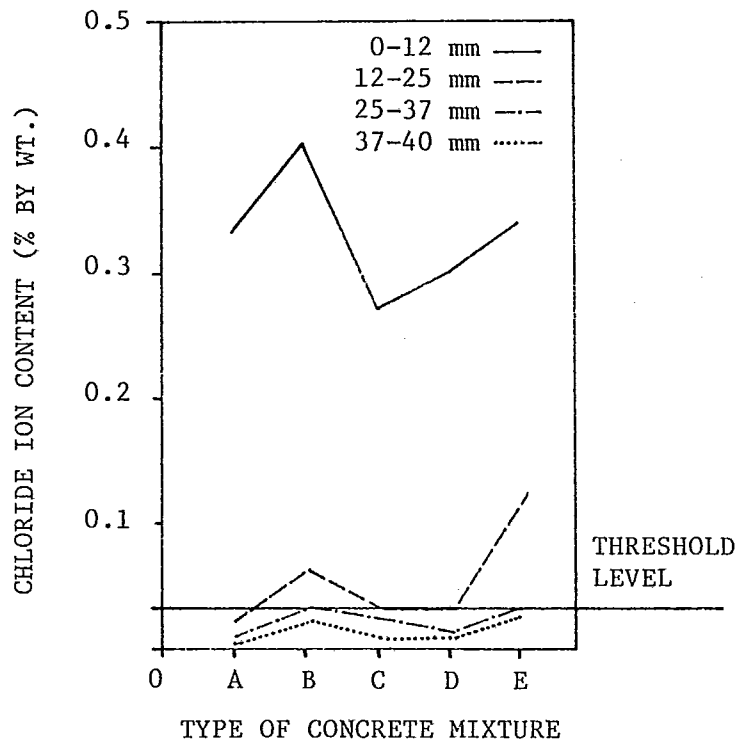


Fig. 4--Concrete containing HRWR and polymers — chloride ion content within 4 depths versus type of concrete admixtures

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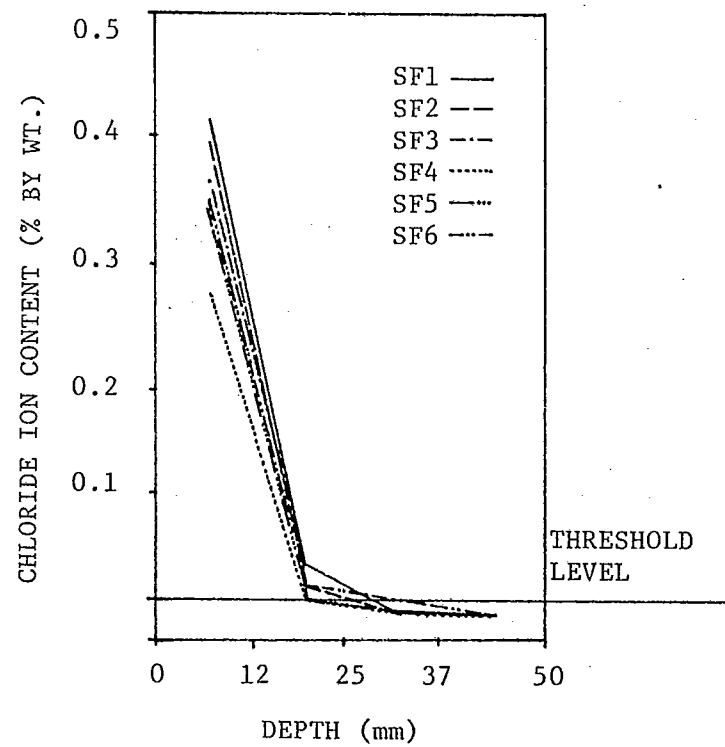


Fig. 5--Concretes containing SF (cement content 340-370 kg/m³) — chloride ion content at 4 depths

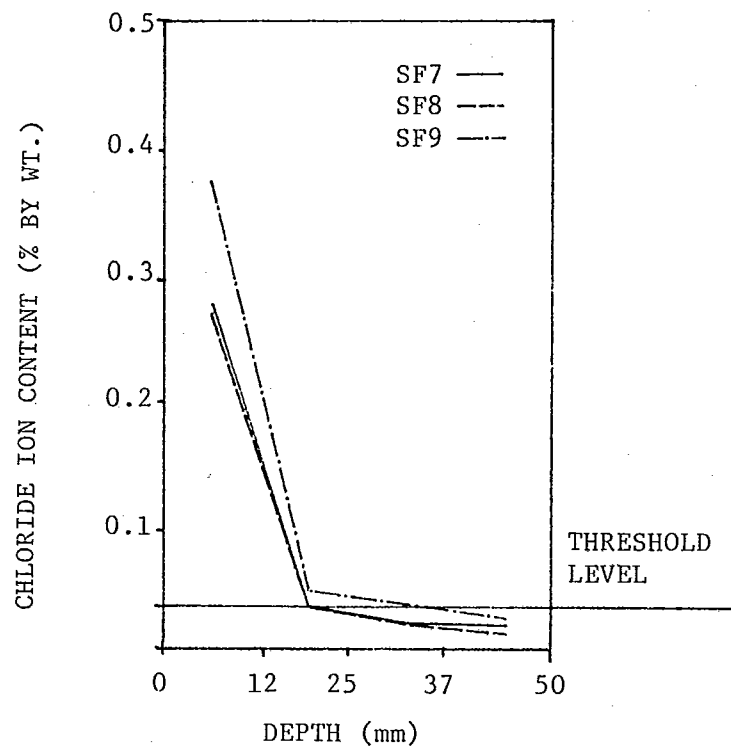


Fig. 6--Concrete containing SF (cement content ~ 300 kg/m³) — chloride ion content at 4 depths

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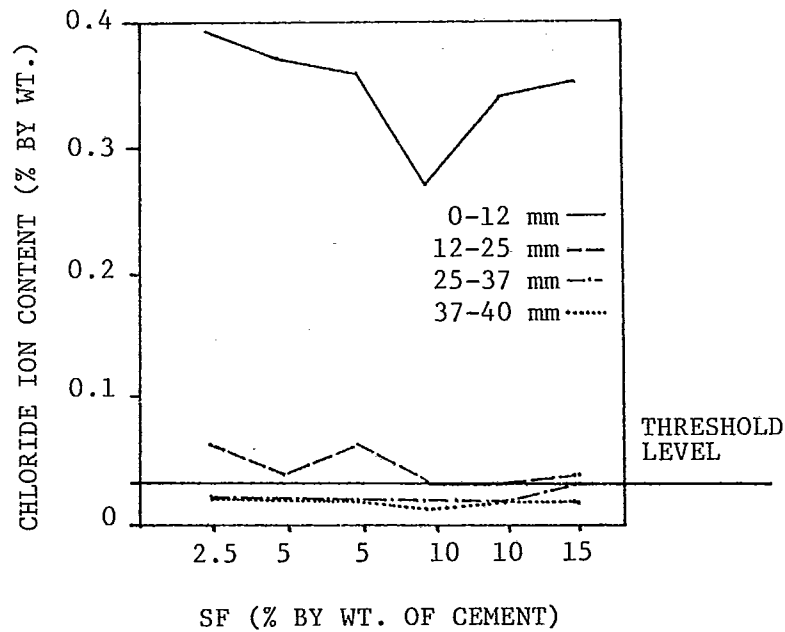


Fig. 7--Concretes containing SF (cement content 340-370 kg/m³) — chloride ion content within 4 depths versus amount of SF in concrete

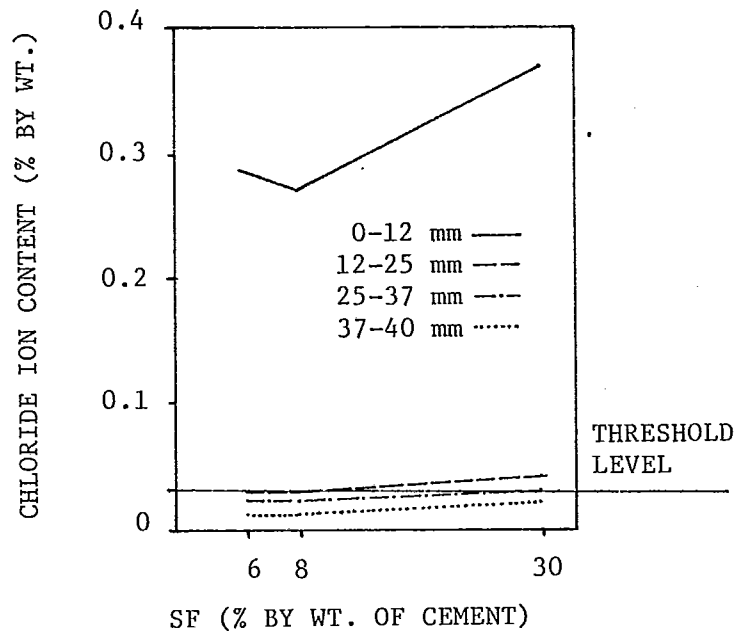


Fig. 8--Concrete containing SF (cement content ~ 300 kg/m³) — chloride ion content within 4 depths versus amount of SF in concrete

SP 108-3

Resistance to Chloride Ion Penetration of Concretes Containing Fly Ash, Silica Fume, or Slag

by C. Ozyildirim and W. Halstead

Synopsis: The effects of two pozzolanic admixtures, fly ash and silica fume, and a ground-granulated blast furnace slag on the chloride ion intrusion of concretes prepared with low water-to-cementitious material ratios (w/c) (0.35 to 0.45) were investigated.

Results of the rapid permeability test (AASHTO T 277) showed that the resistance of concrete to the penetration of chloride ions increases significantly as the w/c is decreased for the same proportions of solid ingredients. Usually, concretes with pozzolans or slag exhibited higher resistance to chloride ion penetration than the control concretes containing Portland cement as the cementitious material. Results of the 90-day ponding test (similar to AASHTO T 259), which was conducted with 0.40 w/c concretes only, indicated minimal chloride content at depths below 3/4 in (19 mm) for all the test concretes. Strength values for all concretes made with the pozzolans and slag at 90 days were in excess of 5,000 psi (34.5 MPa), which is satisfactory.

Keywords: blast furnace slag; chlorides; compressive strength; concretes; fly ash; permeability; pozzolans; silica fume

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INTRODUCTION

Significant damage to concrete results from the intrusion of corrosive solutions; for example, dissolved chlorides corrode reinforcing steel and cause spalling. Any treatment that effectively blocks the penetration of these solutions will eliminate or greatly reduce this damage and lead to increased durability with the consequent economic benefits.

Considerable research has been conducted on this problem, including the evaluation of special coatings, pore-blocking admixtures, and special concretes applied as overlays in the thickness range of 1-1/4 to 2 in (32 to 50 mm)(1,2). The overlay concretes include water-reducing admixtures and usually have a w/c of 0.40 or lower. One successful system for overlays at a minimum thickness of 1-1/4 in (32 mm) has been latex-modified concrete (LMC). In addition to the added cost of materials for such overlays, special expertise and equipment are needed for field applications; consequently, such concretes are considerably more expensive than commercially prepared ready-mixed concretes.

The study summarized in this paper was conducted to assess the potential usefulness of several supplemental cementitious materials for increasing the resistance of hydraulic-cement concretes to penetration of chloride ions. The materials evaluated were a fly ash conforming to ASTM Specification C 618 (Class F), a silica fume and ground granulated iron blast furnace slag. A latex-modified concrete was included in the study for comparison.

The amounts of each supplemental cementitious material used were recommended by promoters of the various materials or by previous laboratory studies at the Council.

1. 15% of the cement by mass was replaced with 1.2 times that mass by a Class F fly ash.
2. 25% of the cement by mass was replaced with 1.2 times that mass by a Class F fly ash.
3. 50% of the cement by mass was replaced with slag
4. 7% of the cement by mass was replaced with silica fume.

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Each combination of materials with C2, a Type II cement, was tested at w/c of 0.35, 0.40, and 0.45. Combinations with C1, a Type I cement, were tested at a w/c of 0.40. Also, specimens were prepared from control concretes and concretes with 15% fly ash, 50% slag, and 7% silica fume with Type II (C2) and Type III cements at 0.40 w/c to investigate the effect of curing temperatures of 40°F(4°C), 73°F(23°C), and 100°F(38°C). The material combinations, mixture proportions, and characteristics of the materials are given in the Appendix.

TESTS CONDUCTED AND MIXTURE PROPORTIONS

The concretes were mixed and specimens prepared in accordance with ASTM C 192. They all contained an air-entraining and a water-reducing admixture. The air-entraining admixture was a neutralized vinsol resin added at amounts adequate to give the desired air content, and the water-reducing admixture was an aqueous solution of complex organic compounds added at the recommended dosage. A high-range water-reducing admixture (HRWR) was used to achieve workable concretes at w/c of 0.35 and 0.40; it was an aqueous solution of a modified naphthalene sulfonate. At a w/c of 0.35, it was necessary to add HRWR in amounts approximately double the dosage recommended by the manufacturer. At the 0.40 w/c, the amounts of HRWR added were within the manufacturer's recommended dosages. At a w/c of 0.45, HRWR was added only to the concretes containing silica fume. It was needed in this case to aid in the dispersion of the very fine silica fume particles and to increase the workability of the concretes. The air content of the freshly mixed concrete was measured by the pressure method, (ASTM C 231). Slump was measured by ASTM C 143, and unit weight determined by ASTM C 138.

The hardened concretes were tested for resistance to chloride ion penetration and compressive strength using 4 in by 8 in (100 by 200 mm) cylinders. The resistance to chloride ion penetration was determined using AASHTO T 277 ("Rapid Determination of the Chloride Permeability of Concrete"). This test is based on a relationship between the electrical conductance and the resistance to chloride ion penetration. The cylinders used for the test were moist cured for 2 weeks after which the top 2 in (50 mm) was cut off and used as the test specimen. The sides of the specimens were coated with an epoxy resin to prevent lateral moisture loss, and they were set on a plastic sheet and kept in the ambient laboratory conditions until the time of the test. This procedure is believed to partially simulate the continued curing of concrete in service where only the top surface is exposed to the atmosphere. Each reported test value is an average of the results from two cylinders.

The resistance of concretes to chloride penetration was also evaluated by tests on two cylinders from each batch at a w/c of 0.40 using a ponding test similar to AASHTO T 259 (Resistance of Concrete to Chloride Ion Penetration). Cylinders measuring 4 in



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by 8 in were moist cured for 2 weeks and air dried for an additional 2 weeks. Then they were ponded with 3% NaCl for 90 days. Afterward, they were drilled with a 2-in diameter bit to obtain samples for a determination of chloride content at two depths: 1/4 to 3/4 in (6 to 19 mm) and 3/4 to 1 1/4 in (19 to 32 mm). Samples were pulverized and the chloride ion contents determined using AASHTO T 260.

Compressive strength was determined at 1, 7, 28, 90, and 365 days. Specimens were prepared and tested in accordance with AASHTO T 22 using neoprene pads in steel-end caps for capping. Each reported test value is an average of the results from three cylinders.

Samples prepared using Type II and Type III cements to study the effect of curing temperature were tested for permeability (AASHTO T 277) and strength at 28 days.

TEST RESULTS

The slump, air content, and unit weight of the freshly mixed concretes are summarized in Table A-3 of the Appendix. Air-entrained concretes with satisfactory workability can be obtained with the use of air-entraining and either regular or regular and high-range water-reducing admixtures, depending on the w/c.

The results of the tests made on the hardened concretes were generally consistent with the results reported by others(3,4,5,6). However, the quantitative evaluation of the effect of different variables will be useful as a basis for the selection of combinations of available cementitious materials that will provide good resistance to chloride ion penetration of concrete at economical cost.

Chloride Ion Penetration

Electrical Conductance Test -- Table 1 shows the results of the tests for electrical conductance as determined by AASHTO Method T 277. This test measures the quantity of electricity, expressed as coulombs, that passes through the test specimens in six hours. This quantity is designated as Q for the purposes of this report. In accordance with AASHTO T 277, the test results are used to rate the concretes with respect to chloride permeability as follows:

<u>Coulombs</u>		<u>Permeability</u>
>4,000	-	high
2000 - 4000	-	moderate
1000 - 2000	-	low
100 - 1000	-	very low
<100	-	negligible

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Figures 1 and 2 show the values of Q at 28 and 90 days for concrete made with the Type II cement (C2). The w/c significantly affected the test results in all cases: the value of Q decreased as the w/c decreased. At 28 days, the Q values for the controls and the concretes containing fly ash were in the moderate or high permeability zone in all cases. The concretes containing slag had Q values in the moderate permeability zone with a w/c of 0.40 and 0.45, and in the low zone with a w/c of 0.35. At a 0.45 w/c, the Q values for slag concretes were slightly higher, and with 0.35 and 0.40 w/c they were lower than the LMC (with a w/c of 0.37). The most significant effect on the chloride permeability test results was shown by the concretes containing silica fume. With silica fume, the values of Q at 28 days were below 1,000 coulombs except for one at 1,020. At 28 days, the Q values for the LMC regularly used as overlay material over bridge decks were in the moderate permeability range.

At 90 days, controls and concretes with fly ash exhibited Q values that decreased significantly as the w/c decreased. The results for the LMC and the concretes containing slag were generally within the low range for all w/c. The results for the concretes containing silica fume were all substantially less than 1,000 coulombs, indicating a very low permeability to chloride ion.

The trends with respect to the effects of w/c at 28 and 90 days were also shown by the tests on the 365-day specimens.

A comparison of results on 28-day specimens and 90-day specimens indicate that for most concretes the resistance to chloride ion intrusion increases during that period. With the exception of concrete made with Type I cement with a 0.45 w/c, all the Q values for 90-day specimens were lower than the Q value for the corresponding 28-day specimens, and in most cases the difference was significant. Changes for those concretes containing pozzolans or slag were proportionately greater than the changes for the controls. Q values measured on 365-day specimens are inconclusive as to whether further changes occur after 90 days. In a majority of the cases, the Q value for the 365-day specimens, was greater than that recorded for the corresponding 90-day specimens. However, the chloride ion permeability classification in accordance with AASHTO T 277 remained unchanged in most cases. A notable exception is the LMC made with both cements. The Q values at 365 days for these concretes were in the very low range.

While there are some indications of differences between concretes made with Type I cement and Type II cement, such differences are not great. This indicates the relatively small effect of the cement type in these experiments. The effect, if any, is that at 28 days, concretes made with Type I cements have lower Q values than concretes made with Type II cements. At later ages,

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differences caused by the cement type have diminished.

90-Day Ponding Tests

Table 2 summarizes the results of the tests for resistance of concrete with a w/c of 0.40 to chloride ion penetration using the 90-day ponding test. The results indicate that at a depth of 1/4 to 3/4 in (6 to 19 mm), all of the concretes except the one with silica fume and C1 had chloride content above 1.32 lb/yd³ (0.78 kg/m³), which is the threshold value for corrosion of the reinforcing steel reported by FHWA(7). The value for LMC with C1 was close to the threshold value. The concretes with Type I cement exhibited lower chloride content than those with Type II cement, except for the fly-ash concretes. The concretes with supplemental cementitious materials as well as LMC had a lower chloride content than the controls. Concretes with SF had the least amount of chloride penetration. At the lower depth of 3/4 to 1-1/4 in (10 to 32 mm) all the concretes had significantly lower values than the corrosion threshold value; the highest average value of any pair of two samples was 0.38 lb/yd³ (0.22 kg/m³). Thus, it appears that all the concretes with a low w/c in this study would have significant resistance to chloride ion penetration under actual service conditions. However, these results do not provide a measure of the length of service that may be expected from the concretes.

Relation of Rapid Permeability Test to 90-Day Ponding Test

The rapid chloride permeability test was developed by the Construction Technology Laboratories of the Portland Cement Association on a contract for the Federal Highway Administration(8). The development work showed a generally good correlation with the 90-day ponding test for chloride intrusion; but a large standard error for the test led the developer to conclude that the test was best utilized to rank concretes in order of expected permeability rather than to predict 90-day ponding results. It is also apparent that the condition of the test specimens and the characteristics of the materials being tested make it difficult to establish a relationship between the results of the 90-day ponding test and those from the rapid permeability test. Consequently, the extent to which differences in the Q values can be considered a measure of the differences in chloride permeability of the concrete under actual service conditions is uncertain.

Table 2 gives the Q value as an average of 2 specimens obtained for the same batch of concrete after the specimens had been aged for 28 and 90 days. The same table also gives the individual chloride content after the ponding test. There were large differences in the total salt found in the duplicate specimens. These differences make it impossible to establish a quantitative relationship between the Q values obtained in the rapid permeability test and the results of the ponding test.

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When the sum of the average of chlorides absorbed at $1/4$ to $3/4$ in (6 to 19 mm) and $3/4$ to $1-1/4$ in (19 to 32 mm) are plotted against the Q values for the 28-day specimens on a logarithmic scale as shown in Figure 3, considerable scatter of the points is evident. Much of this may be caused by the poor precision of both the ponding test and the rapid permeability test. The line of best fit shows a correlation coefficient of 0.625 and indicates a general relationship of lower salt content with lower values of Q . A similar relationship was obtained at 90 days with a correlation coefficient of 0.577.

Strength Development

Table 3 provides the test results for compressive strengths at various ages for each combination of materials. The results are depicted in Figure 4 in which bar graphs of the strengths at 0.35, 0.40, and 0.45 w/c are shown for each combination of materials using Type II cement at 28 days. Figure 5 shows the pattern of strength development with age for the various materials. The plotted results are those for a w/c of 0.40, but the relationships are essentially the same at the other w/c tested. As noted in Figure 5, the patterns vary depending on the supplemental cementitious material used.

The results are summarized in the following sections.

Effect of w/c

In all cases an increase in strength is attained by reducing the w/c for a given proportion of solid ingredients. It should be noted that workable concretes with the lower w/c were obtained only through use of high-range water-reducing admixtures under laboratory conditions. Ratios as low as 0.35 may not be practicable for field concretes using locally available materials. However, these results indicate that the lowest practicable w/c ratio should be used in conjunction with all the supplemental cementitious material tested and that potentially lower strengths for concretes containing pozzolanic admixtures such as fly ash can be counteracted with relatively minor reductions of the w/c.

Concretes Containing Fly Ash

Results for concretes containing fly ash are as would be expected from previous research(9). In each case the strengths at early ages were lower than the controls. Generally, the strengths of the fly ash concretes increased at a slightly greater rate than the controls, and the rate of increase accelerated during the 28 to 90 day period. At 90 and 365 days, the fly ash concretes generally had strengths comparable to or significantly greater than the controls.

The same general trends were indicated by both the 15 and 25% replacement series. The lowest values were those for the 25% re-

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placement specimens at the 0.45 w/c. They were 4,150 psi (28.6 MPa) at 28 days, 5,750 psi (39.6 MPa) at 90 days, and 6,620 psi (45.6 MPa) at 365 days, indicating satisfactory strength for bridge-deck concrete. This implies that the greater economy of replacing a larger proportion of the cement could be utilized with only minor adjustment in specifications and construction practices, and this would result in concretes with equal or higher strengths at later ages.

Concretes Containing Slag

The results show that an activation period is needed for strength development by the hydration of the slag components. One-day strengths are very low; they are approximately one half of the value of the control. But at seven days the slag concretes were stronger than the controls. There were further significant increases up to 28 days. After 28 days the slag concrete and control increased in strength at approximately the same rate.

Concretes Containing Silica Fume

The concretes containing silica fume developed strengths at approximately the same rate and amount as the control. Some differences are apparent for the different w/c, but this may be experimental error. The general indications are that the pozzolanic reactions with silica fume occur rapidly⁽¹⁰⁾. Long-term increases such as those observed for fly ash concretes, should not be expected, especially for the small percentages of silica fume used in this study.

Latex-Modified Concretes

The strength development curves for the LMC are essentially parallel to those for the controls, but consistently lower. These concretes were prepared at a w/c of 0.37, the value normally used for bridge deck overlays using this material.

Type I vs Type II Cement

In general, control concretes with Type II cement had lower strengths than those with Type I cement at early ages and about equal strengths at 28 and 90 days. For each supplemental cementitious materials, similar trends were observed, indicating relatively minor effects of the cement characteristics at later ages.

Relation of Strength to Chloride Permeability

For the same type and amount of supplemental cementitious material, Q values decrease as strength increases, indicating an inverse relationship between chloride permeability (AASHTO T 277) and strength. However, there is no specific

relation between the Q values and strength per se. For example, concretes containing silica fume had significantly lower Q values, indicating lower permeabilities than concretes containing slag; but their strengths were significantly lower.

Effects of Curing Temperature on Chloride Permeability and Strength

All of the specimens tested thus far in this study were cured under standard conditions in a moist room or air dried at 73°F (23°C). However, since it is known that moisture and temperature affect the rate of hydration or pozzolanic reactions, it was of interest to obtain some indication of the potential effects of curing temperatures on the results of the chloride permeability test and strength. It was also of interest to determine if Type II cements reacted significantly differently from Type III, especially with respect to the resistance to penetration of chloride ions as evaluated by the electrical conductance tests. Accordingly, additional specimens were made at a w/c of 0.40.

Control concretes and concretes containing 15% fly ash, 50% slag, and 7% silica fume with the same proportions given in the Appendix were prepared. For each variable, two batches of concrete, one with Type II and the other with Type III cement, were prepared. The concretes were tested at the fresh stage, and the characteristics are summarized in Table 4. Test specimens were prepared for chloride permeability and strength at room temperature, and within half an hour, they were placed in different curing environments at 40°F (4°C), 73°F (23°C), and 100°F (38°C) without removal of the molds. Molds were removed the following day and the specimens were returned to different temperature environments. Cylinders for the rapid chloride permeability test were kept moist for 2 weeks and air dried for 2 weeks. Those for the strength test were moist cured until the time of test.

Results at 28 days, summarized in Table 5, indicate that control concretes with either cement had comparable Q values when cured at 73°F (23°C) and 100°F (38°C); but concretes cured at 40°F (4°C) had significantly higher Q values except in one case. Strengths were comparable or significantly higher for the concretes containing Type III cement. With either cement the highest strengths were obtained when cured at 73°F (23°C) and the lowest when cured at 100°F (38°C). Of particular interest is the behavior of the concretes with fly ash with respect to the chloride permeability as indicated by the rapid permeability test. With either cement, the Q values of the specimens decreased significantly as the curing temperature increased. Specimens cured at 100°F (38°C) had Q values indicative of chloride permeabilities in or very close to the very low range. The results for specimens cured at 73°F (23°C) indicated high chloride permeabilities, and those for specimens cured at 40°F (4°C) indicated even higher permeabilities. Fly ash concretes with Type II cement had the lowest strength when cured at 40°F (4°C) and the

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highest strength when cured at 100°F(38°C). With Type III cement, fly ash specimens cured at 73°F developed the highest strength.

The Q values for concretes containing slag cured at 73°F(23°C) and 100°F(38°C) indicated comparable chloride permeabilities. For specimens cured at 40°F, the Q values for concretes with Type II cement were the same as those for specimens cured at 73°F(23°C) and 100°F(38°C), but specimens containing Type III cement had significantly larger Q values when cured at 40°F(4°C). Strength values for concretes containing slag were higher for the concretes cured at 73°F(23°C) and 100°F(38°C) (those with Type III cement exhibited higher values) and lower for those cured at 40°F(4°C).

The results for concretes with silica fume indicated the lowest permeability of 580 coulombs when combined with Type III cement and cured at 100°F(38°C). The Q values for concretes made with either cement and cured at 73°F(23°C) were approximately 1,000 coulombs, indicating a low chloride permeability. This was also true for those containing Type II cement cured at 100°F(38°C). Significantly higher Q values were obtained for concretes containing either cement when cured at 40°F(4°C). The highest strengths for concretes containing SF were obtained when specimens were cured at 73°F(23°C) for either cement.

In general, the test results indicate that the chloride permeabilities were comparable in concretes with Type II and Type III cements, except that considerable differences were obtained for slag and silica fume concretes at 40°F(4°C) both of which had higher Q values with Type III cement (this needs further investigation). Strengths were comparable or significantly higher for the concretes containing Type III cement.

SUMMARY OF RESULTS AND CONCLUSIONS

1. Concretes with different w/c and prepared with different supplemental cementitious materials varied in their resistance to chloride permeability (using AASHTO Test Method T 277). For each combination of materials, a reduction in the Q value in coulombs occurred as the w/c was decreased. Concretes with pozzolans, slag, or latex had lower Q values than the controls. Q values decreased as the age of the specimens increased from 28 to 90 days. The 365-day results were inconclusive as to whether changes in permeabilities occurred after 90 days.
2. Concretes with fly ash and slag had lower early strengths but generally higher ultimate strengths than the controls. For concretes containing silica fume, strengths were about the same or slightly higher at all ages. In all cases, a lower w/c resulted in higher strengths for concretes containing the same proportion of solid ingredients.

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3. Strengths of all the concretes at 90 days were in excess of 5,000 psi (34.5 MPa) and thus are satisfactory. In some concretes, early strengths were low. For the same type and amount of supplemental cementitious material, strength increased as Q values decreased. However, when concretes with different composition are considered, there is no specific relationship between strength and the results of the rapid test for chloride permeability (AASHTO T 277). Concretes with essentially equal strength but containing different supplemental cementitious material had significantly different Q values. For example, the test results indicated that concretes with pozzolans or slag having strengths similar to the controls generally had lower Q values.
4. Results of the 90-day ponding test on concretes with w/c of 0.40 and containing different supplemental cementitious material indicate differences in the chloride content at a depth of $1/4$ to $3/4$ in (6 to 19 mm). Concretes with pozzolans, slag, or latex had less chloride intrusion than the controls, but all the values were above the threshold value of 1.32 lb/yd³ (0.78 kg/m³) except for one batch of silica-fume concrete. At the deeper depth of $3/4$ to $1\ 1/4$ in (19 to 32 mm), the chloride intrusion for all the concretes was very low. The highest value was in a control concrete that had an average chloride content of 0.38 lb/yd³ (0.22 kg/m³). It appears likely that all the low w/c concretes in this study (0.40 or less) would have significant resistance to chloride ion penetration under actual service conditions. However, these values do not provide a measure of the length of service that may be expected from them.
5. When control, slag, and silica-fume concretes with Type II and Type III cements were cured at 73°F (23°C) and 100°F (38°C), there was little difference in the chloride permeabilities for the same concrete at each temperature. For concretes cured at 40°F (4°C), the chloride permeabilities were generally higher. However, fly ash concretes made with either cement showed a very significant reduction in Q values as the curing temperature increased. When the fly ash concrete was cured at 40°F (4°C) or 73°F (23°C), chloride permeabilities were in the high range, but when they were cured at 100°F (38°C), they were in or very close to the very low range. In general, the strengths of all concretes were highest when cured at 73°F (23°C). Concretes with Type III cement had strengths comparable to or significantly higher than those with Type II cement.

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APPENDIX A — TESTS CONDUCTED AND MIXTURE PROPORTIONS

TABLE A-1--MATERIAL COMBINATIONS AND BATCH PARAMETERS

Identification	Cementitious Material ^a	Percent Cement Replaced	Water-Cementitious Ratio ^b		
			0.45	0.40	0.35
C2 (Control)	C2	0	x	x	x
C1 (Control)	C1	0	x	x	x
C2F-15	F + C2	15 ^c	x	x	x
C1F-15	F + C1	15 ^c		x	
C2F-25	F + C2	25 ^c	x	x	x
C1F-25	F + C1	25 ^c		x	
C2S-50	S + C2	50	x	x	x
C1S-50	S + C1	50		x	
C2SF-7	SF + C2	7	x	x	x
C1SF-7	SF + C1	7		x	
C2L	L + C2			x ^d	
C1L	L + C1			x ^d	

- ^a C2 - Type II cement -- alkalis, 0.50%
 C1 - Type I cement -- alkalis, 0.78%
 F - Class F fly ash with good performance record
 S - Ground iron blast furnace slag with good performance record
 SF - Silica fume
 L - Latex

^b ratio of water to cement plus supplemental cementitious ingredient w/c.

^c The mass of fly ash added was 1.2 times the mass of cement replaced.

^d Water-cement ratio = 0.37.