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Effects of curing conditions on properties of concrete using slag replacement

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Abstract

The effects of curing conditions on properties of slag cement concrete were studied. Autoclaving (175°C, 0.5 MPa) and steam curing (80°C) were compared to normal curing (28 days, 20°C, and 100% RH). Four different concrete mix designs with the same mix proportions and different cement replacements were used: 0% slag (control), 25% slag, 50% slag, and 75% slag. The effects of slag replacement and curing conditions upon concrete properties were examined. The properties examined included mechanical properties (compressive and tensile strength), transport properties (chloride permeability and chloride penetration), and microstructural properties (pore structure and phase composition). There is little effect of slag replacement up to 50% upon strength, whereas higher replacement results in a drop in compressive strength. Steam curing reduces the compressive strength compared to the other curing types considered in this study. Chloride permeability and penetrability significantly decrease with increasing slag replacement except for autoclave curing, which is the least sensitive with respect to slag replacement compared to the other curing types considered in this study. The addition of slag reduces the continuous pore diameter, which correlates well with the initial current (IC) measured by the rapid chloride permeability test (RCPT). © 2000 Elsevier Science Inc. All rights reserved.

Keywords: Concrete; Curing; Chloride permeability; Granulated blast furnace slag; Pore size distribution

1. Introduction

Concrete is the most important element of the infrastructure and well-designed concrete can be a durable construction material. However, the environmental aspects of Portland cement are a growing concern, as cement manufacturing is responsible for about 2.5% of total worldwide emissions from industrial sources. One effective way to reduce the environmental impact is to use mineral admixtures, as a partial cement replacement. This strategy will have the potential to reduce costs, conserve energy, and reduce waste volumes. Mineral admixtures are silica-based materials, such as ground granulated blast furnace slag, fly ash, and silica fume, that react to form hydration products when introduced in Portland cement paste, so they can partially replace Portland cement. Mineral admixtures have been used more and more for concrete due to their benefits in terms of strength and durability. Slag-based blended cements are now marketable worldwide and slags have been incorporated in quantities up to 85% by weight in different mix designs [1].

There is a wealth of information in the literature related to the effect of different slag replacements on concrete properties. Detwiler et al. [2] reviewed the behavior of cement and concrete containing slag and optimization of cement performance. Many publications emphasize the beneficial effect of slag replacement on chloride penetration. Ozyildirim and Halstead [3] investigated the effect of 50% slag replacement on the chloride ion intrusion of concrete with water-to-cement ratios (*w/c*) ranging from 0.35 to 0.45 and concluded that concrete containing slag have strengths similar to the controls and lower chloride permeability. Sato et al. [4] compared the results of chloride ion penetration of 70% replacement slag concrete using different curing conditions: moist curing and natural environment conditions. They pointed

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out that slag addition reduces chloride ion permeability and that chloride permeability can be correlated to the volume of pores with diameters higher than 0.1 μm. Fukute et al. [5] studied chloride ion penetration into concrete containing 40% replacement slag using normal curing at 20°C and low pressure steam curing, using the so-called rapid chloride permeability test (RCPT) together with long term exposure test in sea water. A fairly good correlation was observed between the depth of chloride ion penetration and the RCPT results. Concrete containing slag exhibited higher resistance to chloride ion penetration than controls, while steam curing reduced the resistance to chloride ion ingress. Geiseler et al. [6] showed that the resistance of concrete to chloride penetration is markedly greater with a higher content of slag in the cement, which they attributed to the increased density of the cement paste. For plain Portland cement concrete, elevated curing temperatures result in a coarser pore structure and a corresponding decrease in the resistance to chloride ion diffusion [7]. The use of 30% slag replacement in concrete with water-to-binder ratio (*w*/*b*) of 0.40 and 0.50 is effective in reducing the chloride ion ingress probably due to a decrease in volume of large pores [8].

In the current study, slag was used as a replacement for Portland cement and the effect of slag replacement, ranging from 0% to 75% by weight, and curing conditions upon material properties were examined. Fast curing procedures, autoclave, and steam curing, were used to accelerate cement hydration, and then compared to normal curing. Compression test, RCPT, chloride penetration test, mercury intrusion porosimetry (MIP) measurements. and X-ray diffraction were used to determine the changes in material properties and microstructure for the materials and the curing conditions tested.

2. Experimental program

2.1. Mix proportions and curing

Table 1 presents the mix designs for four different concrete; corresponding pastes were also made. Table 2 gives the chemical analyses of the cementing materials. The fineness of the slag used in the present study (6000 cm^2/g) is almost twice that of Portland cement (3606 cm^2/g).

Table 1
Details of test series and mix proportions

	By weight			
Mix ingredients	M1 (0% slag)	M2 (25% slag)	M3 (50% slag)	M4 (75% slag)
Cement (type I)	1	0.75	0.50	0.25
Coarse aggregate (pea gravel, MSA = 10 mm)	2	2	2	2
Fine aggregate	2	2	2	2
Water added	0.42	0.42	0.42	0.42
Slag	0	0.25	0.50	0.75
w/*c* or *w*/*b*	0.42	0.42	0.42	0.42

Table 2
Composition of the cementing materials

Compound	Type I cement	Slag
SiO_2 (%)	21.17	37.31
Al_2O_3 (%)	5.34	8.36
Fe_2O_3 (%)	2.28	0.45
CaO (%)	63.92	38.85
MgO (%)	3.91	10.59
SO_3 (%)	2.32	2.85
Na_2O (%)	0.47	0.26
K_2O (%)	–	0.41
TiO_2 (%)	–	0.55
P_2O_5 (%)	–	0.01
Mn_2O_3 (%)	–	0.72
SiO (%)	–	0.05
ZnO (%)	–	0.01
Loss on ignition (LOI)	0.97	0.029
Blaine fineness (cm^2/g)	3606	6000
Grade		100

Autoclave and steam curing were compared to normal curing. For autoclave curing, the samples with the molds were put into the autoclave 6 h after casting, and the curing temperature was raised from room temperature (T = 20°C) to 175°C (350°F) and P = 0.5 MPa (75 psi) after 2 h. The temperature was maintained constant at 175°C for 15 h, and then cooled to room temperature in 2 h. Steam-cured samples were cast in molds for 6 h, and then presteamed in a water bath at room temperature (T = 20°C) for another 6 h. Then the temperature was raised from room temperature to 80°C over 2 h, maintained constant at 80°C for 15 h, and then cooled to room temperature in 2 h. For normal curing, the samples were demolded after 24 h and then stored in a controlled chamber, at 20°C and 100% RH until 28 days old. Concrete were cast in cylindrical molds with the following sizes: 100 × 200 mm (4 × 8 in.) for the RPCT, and 75 × 150 mm (3 × 6 in.) for the compression tests, split tension tests, and the chloride penetration tests. Paste samples were cast in 25 × 50-mm cylindrical molds. Material properties were measured immediately after ending each curing cycle.

2.2. Concrete properties

2.2.1. Strength

Concrete compressive strength was determined according to ASTM C 39-94 [9] for concrete samples. Two 75 × 150-mm (3 × 6-in.) samples which showed consistent results were tested in compression for each mix and curing condition. Concrete tensile strength was determined by split tension according to ASTM C 496-90 [10] using 75 × 75-mm (3 × 3-in.) sample.

2.2.2. Resistance to chloride ion penetration

The so-called RCPT is fully described in ASTM C 1202-94 [11]. Samples were prepared by cutting and discarding 25-mm slices from the top and bottom of 100 × 200-mm cylinders, and the remaining section cut into three 50-mm thick slices. The slices were then vacuum-saturated. Duplicate slices were tested. The test is referred to as a test of chloride "permeability," although it is rather a test of chloride penetrability. We refer to the RCPT as a test of resistance to chloride ion penetration. The amount of current transmitted during the test duration is a measure of the resistance to chloride ion penetration of concrete, and thus the quality of concrete can be assessed based on the total charge passed.

2.2.3. Chloride penetration test

Two 75 × 150-mm (3 × 6-in.) concrete cylinders were tested for chloride penetration after 10-month exposure to 5% by weight NaCl solution. Each cylinder was cut into two 75 × 75-mm (3 × 3-in.) pieces, which were then split diametrically either by sawing or using the split tension test according to ASTM C 496-90 [10]. Both sawn and fracture surfaces were sprayed with 0.1 N silver nitrate solution.

2.2.4. Characterization of pastes

X-ray diffraction (Rigaku D-max II diffractometer, Rigaku USA, Danvers, MA) was used to identify the crystalline hydrates. Patterns were obtained on finely ground samples using Cu Kα radiation and a scanning rate of 2° 2θ/min. Five scans were accumulated. MIP was used to determine pore size distribution for concrete and paste using pressures up to 50,000 psi (Autopore 9000, Micromasters, Norcross, GA). A contact angle of 140° was used to calculate pore diameter.

3. Discussion of results

3.1. Strength

3.1.1. Compressive strength

Fig. 1 shows that 25% slag replacement is optimal for strength for both normal and steam curing. Concretes with 50% slag replacement have compressive strength similar to control, which agrees with other results in the literature for slag with a comparable chemical composition and fineness [3]. Under autoclaving conditions adding slag up to 50% replacement has no effect on strength, whereas 75% slag replacement reduces the compressive strength no matter what curing type is used. Normal curing provides higher compressive strength compared to fast curing up to 50% slag replacement. This can be attributed to the increased volume of large mesopores [12]. Results obtained with autoclave curing are comparable to those obtained with normal curing for no slag and 50% slag replacement. Steam curing induces the greatest decrease in compressive strength for most of the materials tested. This is probably due to a less uniform distribution of the hydration products in the paste because of the rapid initial hydration, which is reflected in changes in the large capillary pore distribution [13].

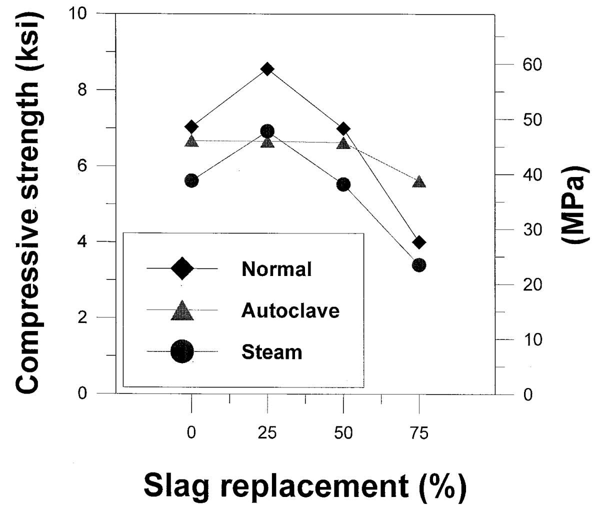

Fig. 1. Effect of slag replacement on compressive strength at the end of each curing cycle.

3.1.2. Split tension strength

The trend is comparable to that of compressive strength presented in Fig. 1. The 25% and 50% slag replacement have a beneficial effect compared to control, as tensile strength increases for all the curing types. The 50% slag replacement provides tensile strength slightly higher to no slag replacement, whereas the 75% slag replacement reduces the tensile strength regardless of the curing type used.

3.2. Resistance to chloride ion penetration

Prior studies have shown that there is a linear relationship between the total charge and the initial current (IC) measured during the test for resistance to chloride ion penetration both for normal strength concrete [14] and for high strength concrete with various mineral admixtures [5]. The total charge is the total current flow during the test duration, and the IC represents the value obtained 100 s after the application of voltage at the beginning of the test. Shane et al. [15] suggest a theoretical correlation between IC and total charge obtained for constant current, and conclude that this can be used to assess resistance to chloride ion penetration for concrete below the 4000-C threshold. Deviations from the theoretical line indicate that more charge is being conducted than is predicted by the IC, and this is easily explained by the increase in temperature associated with the Joule heating of the samples. Page [16] and McCarter [17] have shown a

Table 3
Material performance in terms of chloride penetrability according to ASTM C1202-94

Slag replacement (by weight of cement)	Curing type		
	Normal	Autoclave	Steam
0% slag (M1)	high	high	high
25% slag (M2)	high	high	high
50% slag (M3)	moderate	high	moderate
75% slag (M4)	very low	high	low

very strong dependence of the diffusion coefficient and electrical conductivity on temperature. Although both IC and total charge were measured, only IC results are presented, whereas the quality of the samples in terms of resistance to chloride ion penetration was assessed based on the total charge measured over the 6 h (Table 3). The measured total charge was higher than that from the theoretical correlation for most of the samples tested and the samples with "high" chloride penetrability (Table 3) boiled during the test.

From Fig. 2 and Table 3, it can be seen that slag replacement has beneficial effects, as it reduces drastically the chloride penetrability under all the curing regimes used. Samples without slag show "high" chloride penetrability no matter what curing type is used. According to Suprenant [18], the typical resistance to chloride ion penetration for concrete with a *w/c* ratio 0.4 is "moderate." The high results can be attributed to the small size of the coarse aggregate (10 mm) and thus the high amount of paste, which is more conductive than the aggregates. The 25% slag replacement reduces the chloride penetrability of the material (Fig. 2); but still, all the materials exhibit high chloride penetrability. Concrete with 50% and 75% slag replacement show the best performance in the test for resistance to chloride ion penetration, as reported by other researchers for 50% slag and the same *w/b* ratio [3]. Autoclaved concretes have systematically higher chloride penetrability values regardless of the level of slag replacement. This behavior is probably due to the increased macroporosity of the material due to autoclaving.

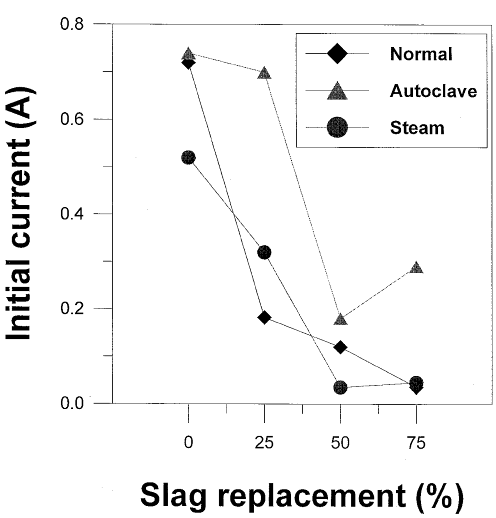

Fig. 2. Effect of slag replacement and curing conditions on the IC measured by the test for resistance to chloride ion penetration (ASTM C 1202-94).

3.3. Chloride penetration test

After spraying silver nitrate solution, the color of the sprayed surface changes due to the precipitation of white AgCl when the chloride ion is present. The depth of chloride penetration can be detected due to the lighter color compared to that of the unpenetrated material. This was measured as shown in Fig. 3a and expressed as a percentage of the diameter. Fig. 3b presents the effect of slag replacement and curing on depth of chloride penetration, each data point representing the average of six measurements, three on each side of the split sample.

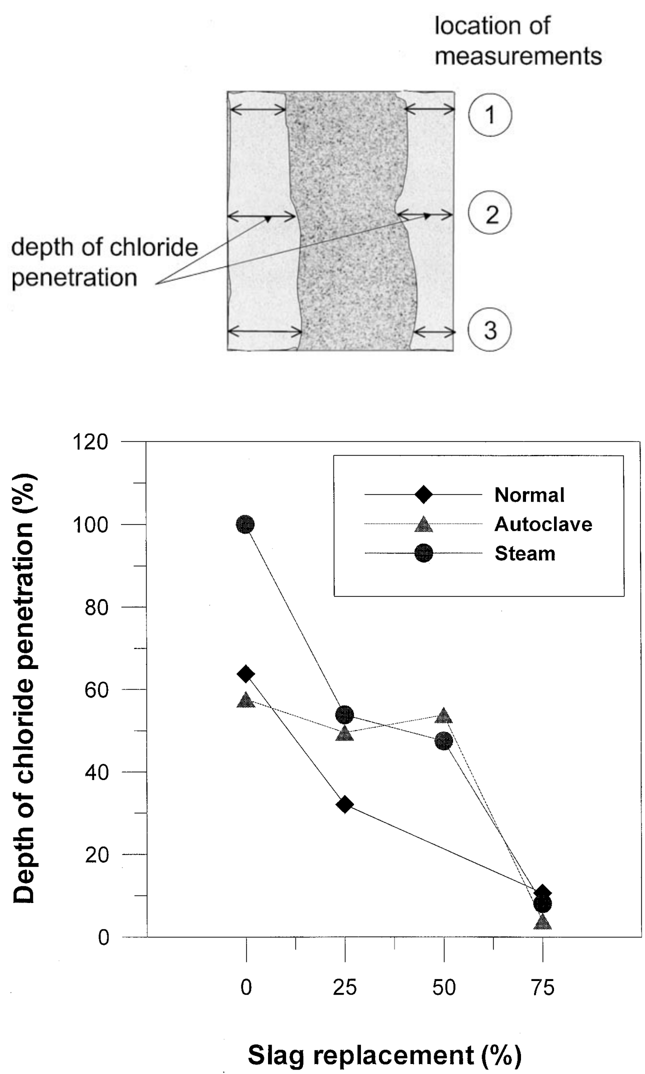

Fig. 3. Depth of chloride penetration. (a) Measurements made from both fracture surfaces. (b) Effect of slag replacement and curing conditions.

This confirms the beneficial effects of increasing slag replacement on the depth of chloride penetration, reducing it from 100% (fully penetrated sample) for steam-cured control concrete to less than 10% for 75% slag replacement, regardless of the curing cycle. Generally curing at higher temperatures was not beneficial. The results in Fig. 3b shows that steam curing reduced the resistance to chloride ion penetration compared to normal curing for slag replacements up to 50%, which is in good agreement with those presented by Fukute et al. [5]. Although the latter observed a fairly good correlation between the depth of chloride penetration and the resistance to chloride ion penetration results, a clear trend was not seen in this study.

3.4. X-ray diffraction of pastes

X-ray diffraction showed $Ca(OH)_2$ to be the major crystalline hydration product in all samples, indicating that this slag does not have high pozzolanic activity. However, there were no clear trends in the amount of $Ca(OH)_2$ formed; an anticipated reduction due to dilution by slag under similar hydration conditions was not clearly observed. Room temperature hydration showed the formation of ettringite, monosulfoaluminate, and sulfate-free Afm, which is probably partially carbonated. The presence of slag or higher hydration temperatures inhibited the formation of ettringite. Under steam curing conditions, ettringite breaks down to monosulfoaluminate and gypsum, while in the autoclave hydrogarnet is formed. The addition of slag does not alter these reactions significantly.

3.5. Porosity measurements

Most of the properties of hardened concrete are related to the quantity and the characteristics of pores in concrete. Strength, durability, permeability, ionic diffusion, which are investigated in this paper are directly influenced or controlled by the amounts, sizes and connectivity of pores. According to Young [12], two classifications of pores are commonly used.

1. The traditional classification of pores in concrete, that considers two classes: gel pores (<0.01 μm), which are associated with the formation of hydration products, and capillary pores (0.01 to 10 μm).
2. The classification used for other porous systems, that considers three classes: micropores (<0.0025 μm), mesopores (0.0025 to 0.05 μm) and macropores (0.05 to 10 μm).

The pore size distribution is strongly influenced by the curing temperature: high temperature increases the volume of mesopores [12], and thus fast curing used in the study is assumed to have increased this porosity. The pores exert their influence on different properties in various ways. For instance, strength is affected primarily by the total volume of pores, although according to Neville [19], the shape and pore size distribution must also be considered. Permeability and diffusivity are controlled by the volume, size, distribution, shape, tortuosity, and connectivity of pores. The pores relevant to permeability according to Neville [19] are capillary pores with a diameter at least 0.12 to 0.16 μm (macropores).

Fig. 4 present the MIP curves for companion paste samples. It can be seen that under the same curing regime 50% replacement leads to the highest proportion of coarser pores (>0.05 μm) and 75% to the lowest. The volume of coarse pores increases as the curing temperature increases, which agrees with published results.

There have been attempts to relate pore structure to permeability [4] and Nyame Illson [20] found a good correlation between the permeability coefficient and the continuous pore diameter (d_c) for cement paste. Fig. 5 shows the determination of d_c, which is correlated with the IC from the test for resistance to chloride ion penetration in Fig. 2, slag replacement and curing regime. Multiple regression [21] was used to estimate the relationship between the IC and the factors and covariates that might predict it, both in terms of quantifying the basic trends in those relationships and in terms of choosing which of those factors are truly important for predicting the IC. The following factors and covariates were considered:

- continuous pore diameter (CPD),
- slag replacement (SLAG),
- curing types:
  - autoclave curing (AUTO),
  - steam curing (STEAM),
- interaction between porosity and slag replacement (PS), where PS = CPD × SLAG.

Multiple regression models assess the extent to which the IC depends linearly upon these predictors. After several models were fit, AUTO was found to contribute little to the model, and so it was dropped. The final model fit is:

$$IC = -0.6871 + 30.7215 \times CPD + 1.2461 \times SLAG - 41.1788 \times PS - 0.2077 \times STEAM. \quad (1)$$

These coefficients possess signs and magnitudes that are in agreement with expected properties of the materials, and all the coefficients are significant at the 0.05 level. The regression factor (R^2) for the model [Eq. (1)] is 0.94. The dependence of IC on CPD alone is not really linear (R^2 = 0.64), but upon inclusion of the other variables the pattern of dependence can be captured much more accurately. Fig. 6 presents measured values compared to predicted values based on Eq. (1). The model shows that the factors considered cannot be separated, as they are all meaningful and

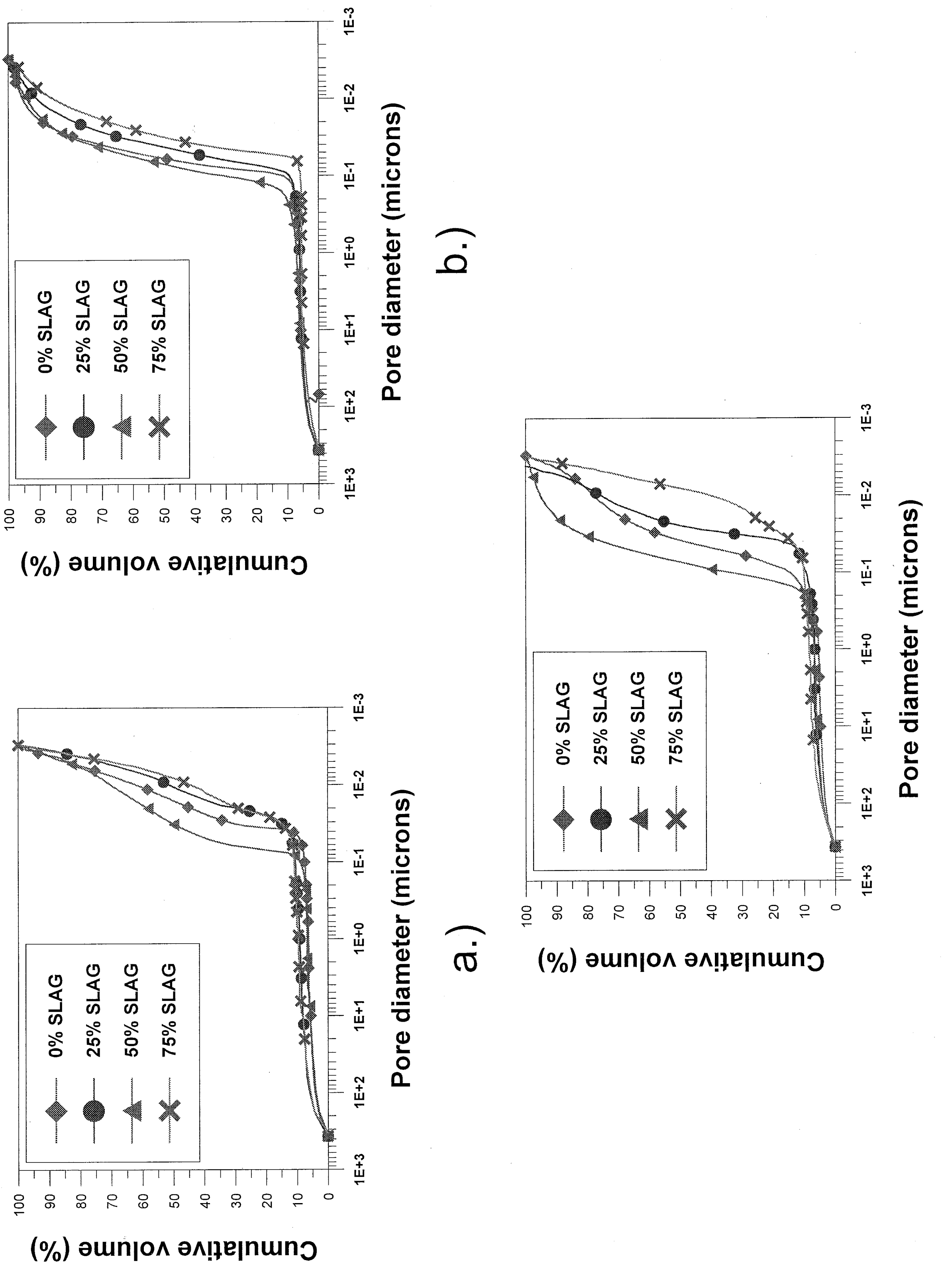

Fig. 4. Normalized intruded pore volume of pastes as a function of pore size. (a) Normal curing. (b) Autoclave curing. (c) Steam curing.

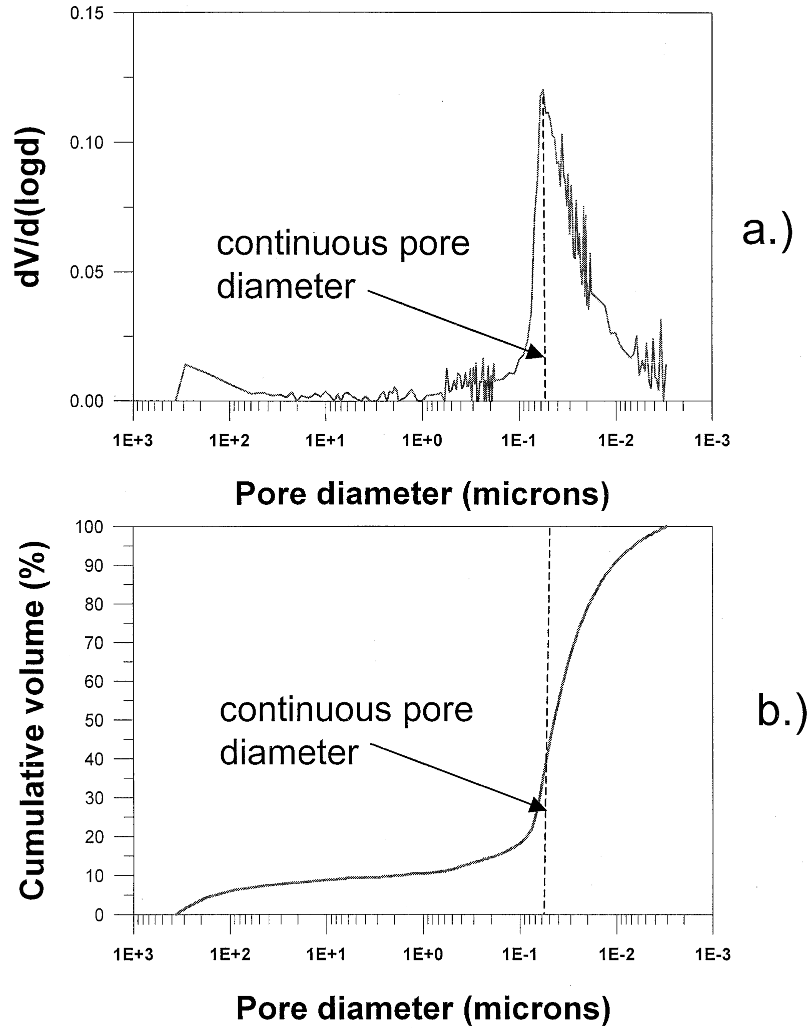

Fig. 5. Measurement of continuous pore diameter, d_c. Concrete with 25% slag, autoclave curing. (a) Differential intrusion. (b) Cumulative intrusion.

also that slag replacement reduces d_c for all the curing regimes and hence the IC. This suggests that pore structure may be related to chloride penetrability and thus the effect of slag replacement on chloride penetrability is due to a decrease in the pore size opening.

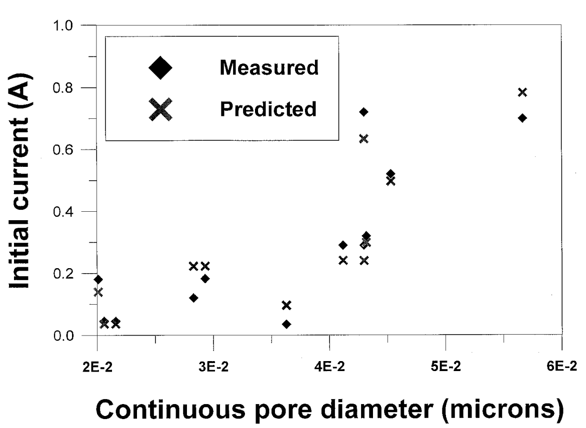

Fig. 6. Relationship between porosity and IC using multiple regression model.

4. Optimization of slag replacement

The data presented here emphasizes that a balance must be struck between strength and durability. To reduce chloride penetration a high slag content is desirable, while from a strength point of view, replacements greater than 25% are detrimental. Furthermore, the use of high temperature curing increases chloride penetration and should only be used when high early strength is essential. However, it is possible that subsequent moist curing at room temperature could improve the durability of these concretes. Therefore, when designing concretes with slag replacement targets for both strength and resistance to chloride penetration must be set and met simultaneously through adjustments to mix design. Replacement by 50% slag seems to give good resistance to chloride without sacrificing strength appreciably. With 75% replacement, unhydrated slag may help reduce the ingress of chloride, but does not contribute to strength.

5. Summary and conclusions

- The major improvement with increasing slag replacement consists in decreasing in chloride penetrability. Concretes with 50% slag replacement having strength similar to the control have lower chloride penetrability. Depending on the application, different percentages of replacement should be used to achieve either high strength or reduced chloride penetrability.
- For improved durability room temperature curing is the best, but steam curing is preferable to autoclave curing, if rapid strength development is required.
- The IC measured during the test for resistance to chloride ion penetration (ASTM C 1202-94) correlates well with the continuous pore diameter. The ability of slag replacement to reduce chloride penetrability depends on a refinement of the pore structure rather than any change in hydration chemistry.

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