SP 178-15

Influence of Unburnt Carbon in the Performance of Concrete Mixtures

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Synopsis: In many standard specifications there is a limit for the maximum amount of unburnt carbon of fly ashes often referred to as LOI. In particular, according to the European norm EN 450, this limit is 5% on the continental basis of the European Unity, or 7% on the domestic national basis. Therefore, fly ashes with LOI over 7% should be rejected as a supplementary cementitious material in concrete mixtures.

Four fly ashes from coal-fired electric generating plants, with LOI content of about 4, 7, 9, and 11%, were used to manufacture concrete mixtures. They had the water-cement (*w/c*) ratio of 0.68, corresponding to a water-binder ratio of 0.48 and a fly ash/binder ratio of 0.30. A small amount of superplasticizer (0.3-0.4% by cement mass) was required to compensate the slump decrease caused by fly ash with higher LOI ($\geq$ 7%). Two reference concrete mixtures, without fly ash, were also produced with a *w/c* of 0.68 and 0.48. The performance of all these concrete mixtures was assessed in terms of compressive strength at early and later ages (1-180 days), water-permeability, chloride diffusion, and carbonation rate.

There was no evidence available which indicated that the LOI content of the fly ash affected negatively any of the properties studied. In particular, due perhaps to its peculiar pozzolanic activity, the fly ash with the highest LOI content (11.30%) performed better than that with the smallest amount of LOI material (4.19%). This occurred in terms of higher compressive strength, lower water-permeability, slower chloride diffusion, and decreased carbonation rate in the corresponding concretes. Therefore, the conformity criteria adopted by some standard specifications in rejecting fly ashes only on the basis of the relatively high LOI content, without determining the corresponding concrete performance in terms of strength and durability, appear to be technologically inadequate and

Keywords: carbon; cementitious material; compressive strength; concrete; fly ash; slump; superplasticizer.

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INTRODUCTION

According to the European norm EN 450 (1), among the technical requirements for fly ash to be used as mineral additive in concrete mixtures, there is a limit in the LOI. This is 5% by mass for materials acceptable on a continental basis (European Union) and 7% for those acceptable on a national basis provided that available domestic norms give locally adequate regulations on the use of the fly ash in concrete mixtures. Therefore, fly ashes with an unburnt level higher than 7% cannot be used either in the European Union or in a local European nation. However, in many other countries (such as Canada, India, Korea, etc.) the limit for the LOI content of fly ash is as high as 12%.

The primary purpose of the present investigation was to study the influence of the LOI level in fly ash on the concrete performance in terms of slump, compressive strength, water penetration, and durability. Another important purpose of this work was to investigate whether the water-cement ratio (*w/c*) or the water-binder[*] ratio (*w/b*) is the effective factor in determining the durability performance of concrete mixtures exposed to aggressive environments. According to the European norms ENV 206 (2), the *w/c*, which should be adopted for durable concretes as a function of the *exposure class* (environmental aggression level), should not take into account the amount of pozzolanic or hydraulic admixtures - such as fly ash or ground granulated blastfurnace slag - when these products are used as separate mineral additives to replace part of cement in concrete mixtures.

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[*] *the term "binder is herewith used to indicate portland cement plus fly ash*

MATERIALS AND METHODS

Materials. *Portland cement* (Type CE I 42.5R according to the European norm EN 197/1) was used. Table 1 shows chemical, physical, and mechanical characteristics of this cement.

Four individual *aggregates* (specific gravity = 2.71 g/ml), with the particle size distribution shown in Fig. 1, were used. The following percentages (by mass) for each of the four aggregates were adopted:

- sand (0.125-4 mm) = 33.3 %
- gravel (2-8 mm) = 21.4 %
- gravel (4-10 mm) = 16.0 %
- gravel (8-20 mm) = 29.3 %

The particle size distribution of the combined aggregate is shown in Fig. 1.

Four *fly ashes* (*A*, *B*, *C*, and *D*), characterized by a different LOI content (in the range of 4-11%), were used. Fly ash *A* and *D* came from two different coal-fired electric generating plants, whereas fly ash *B* and *C* were produced by mixing the other two materials. Table 2 shows the chemical composition of the four fly ash samples. The main difference between these products is the LOI level which changes from a minimum level of 4.19% for the fly ash *A* up to a maximum content of 11.3% for the fly ash *D*. The increase in the LOI level was accompanied by a decrease in the bulk gravity which changed from 0.68 kg/l for the fly ash *D* to 0.88 kg/l for the fly ash *A*. No significant differences were recorded in the particle size distribution carried out by the laser-granulometer (Fig. 2).

A naphthalene-based *superplasticizer* (40% aqueous solution) was used in concretes containing fly ash *B*, *C*, and *D* in order to obtain approximately the same slump level (180-200 mm) in all concrete mixtures.The compositions of the *concrete mixtures*, as well as the properties of fresh concretes, are shown in Table 3. Two types of concretes were manufactured: reference mixtures and fly ash concretes.

Two *reference mixtures*, without fly ash, were produced with the same amount of mixing water (200 kg/m^3) and different cement factors: 417 kg/m^3 and 294 kg/m^3 for the reference concretes R_1 and R_2, respectively. Therefore, the adopted *w/c* was 0.48 and 0.68 for the reference mixtures R_1 and R_2, respectively. Due to a lower *w/c*, the reference mixture R_1 is potentially more durable than the reference concrete R_2. In particular, according to the European norm ENV 206 (2), the concrete R_1 is water-impermeable and resistant to the penetration of CO_2 in humid air (*exposure class: 2a*) and Cl^- ions in a sea water environment (*exposure class: 4a*). In fact, according to this European norm, the *w/c* should be not higher than 0.55 for the watertightness requirement, and 0.60 or 0.55 for the durability requirements in exposure class *2a* or *4a*, respectively. Consequently, the reference concrete R_2, with a *w/c* of 0.68, is definitely water-permeable and not durable with respect to the CO_2 and Cl^- penetration.

Four *fly ash concrete mixtures* were manufactured by substituting fly ash for 30% by mass of the cement content in the reference concrete R_1. Therefore, the amount of the binder in the fly ash concrete mixtures (about 420 kg/m^3) is the same as the cement content in the reference concrete R_1. On the other hand, the cement content of the fly ash concrete mixtures (about 294 kg/m^3) is the same as that of the other reference concrete R_2. The same amount of mixing water was used in the fly ash concretes (about 200 kg/m^3) as that in the reference mixtures (R_1 and R_2). However, with fly ashes at higher LOI content (*B*, *C*, and *D*), a superplasticizer (0.3-0.4% by cement mass) had to be used to attain to the same initial workability (slump = 190-200 mm) as that of the reference concretes at the given amount of mixing water (200 kg/m^3).

The *w/c* in the fly-ash-concretes (0.68) is the same as that of the reference mixture R_2 and higher than that of the reference mixture R_1 (0.48). However, by taking into account the amount of fly ash in the binder content, the *w/b* value in the fly ash mixtures was the same as that of the *w/c* (0.48) of the reference concrete R_1 and lower than that of the *w/c* (0.68) of the reference mixture R_2.

Methods. *Compressive strength* measurements were carried out by crushing cube specimens (100 mm) cured at 20°C (R.H = 95%) from 1 day to 6 months.

Water permeability tests (according to the ISO 7031 method) were carried out on 28- or 90-day wet cured specimens by measuring the penetration of water through concrete after increasing the water pressure from 1 bar up to 7 bar in four days (3). Concrete structures are considered by ENV 206 (2) to be impermeable in service when the water penetration depth in the corresponding 28-day cured specimens is not higher than 20 mm according to the ISO 7031 method (3).

Chloride penetration was measured according to the Italian UNI 7928 method (4) by using a fluorescein-silver nitrate aqueous solution to detect the pink-colored concrete portion penetrated by Cl^- ions in specimens demolded at 7 days, wet cured up to 28 days, and then permanently exposed to a 10% NaCl aqueous solution.

Carbon dioxide penetration was measured according to the Italian UNI 9944 method (5) by using a hydro-alcoholic phenolphthalein solution as chromatic indicator to detect the carbonation depth through concrete specimens demolded at 7 days and then immediately exposed to a CO_2-enriched air (30%) with 65% R.H. No additional wet curing was carried out since carbonation occurs in real concrete structures exposed to air just after removing forms.

RESULTS

Figure 3 shows the influence of the fly ash type on the compressive strength development (from 1 day to 180 days) with respect to the two reference mixtures R_1 and R_2.

The compressive strength of the reference concrete R_1 was always higher than that of the reference mixture R_2 at early and longer ages. This was due, of course, to the difference in the *w/c* ratio (0.48 vs. 0.68).

The compressive strengths of the fly ash mixtures were always lower than that of the reference concrete R_1 and higher than that of the reference concrete R_2. These results agree very well with the expected strength trend related to the *w/c* (0.68) and the *w/b* (0.48) of the fly ash concrete mixtures. At longer ages (> 7 days), the rate of strength increase in the fly-ash mixtures was higher than that of the reference concretes. Again, these results agree very well with the expected role played by fly ash which acts as cementitious binder only at later ages, when calcium hydroxide coming from portland cement hydration is available, and then the pozzolanic reaction occurs. However, it was surprising to record that there was no relationship between the fly ash LOI content, and the concrete compressive strength development. As a matter of fact, the fly ash *D*, with the highest LOI content (11.30%), performed significantly better than the fly ash *A* with the lowest LOI content (4.19%). This does not necessarily means that the higher the LOI content, the better is the concrete performance in terms of compressive strength. This simply means that a discrimination based on the LOI content over 5% or 7% - as in the European norm EN 450 - may not be an adequate criterion to assess whether or not a given fly ash is acceptable as a concrete ingredient. On the other hand, it is noteworthy that fly ash *B*, *C* and in particular *D* - all with higher LOI content - performed better than fly ash *A* in terms of strength, provided that a small amount of superplasticizer (0.3-0.4% by cement mass) was used to adjust the slump at the same level as that of the reference concretes or the concrete with fly ash *A* (Table 3). Preliminary tests, not reported in the present paper, indicated that, in the absence of superplasticizer, a small reduction in the strength was measured in concrete mixtures at equal slump when fly ash with large LOI content were used. This was due to the small increase in the mixing water, at a given slump, caused by the excessive unburnt material in fly ash.

Figure 4 shows the results of the water penetration test carried out after 28 and 90 days of curing. The reference concrete R_1 was "impermeable" at 28 and 90 days since the water penetration was significantly lower than the maximum depth (20 mm) required by the European norm (2). This was due to the *w/c* (0.48) which was much lower than the maximum value (0.55) recommended for manufacture of impermeable concrete according to ENV 206 (2). On the other hand, the reference mixture R_2 was water-permeable since the penetration of water (60 mm at 28 days, and 50 mm at 90 days) was significantly over the limit of 20 mm. This was due to the *w/c* (0.68) which was much higher than the recommended maximum value (0.55), per ENV 206 (2).

The penetration of water through concrete specimens with fly ash was in agreement with the expected behavior of pozzolanic materials: at both 28-day and 90-day curing times, the penetration of water was lower than that of the reference concrete R_2 (at equal $w/c = 0.68$) and higher than that of the reference concrete R_1 (at equal $w/b = 0.48$). However, due to the pozzolanic reaction at later ages, the fly-ash-concrete mixtures at the 90-day curing time become water impermeable (penetration of water under the 20 mm limit), and very close to the watertightness performance of the reference concrete R_1. This trend is similar to that recorded for the compressive strength development (Fig. 3). Again, no negative role was played by the LOI content of the fly ashes on the penetration of water through the concrete specimens, provided that all the mixtures were manufactured at a given slump with equal w/c (Table 2). The concrete with the fly ash *D*, characterized by the highest LOI content (11.30%), performed a little better than the concrete mixture with the fly ash *A* containing unburnt material at as low amount as 4.19%. Therefore, within the LOI content range of 4-11% examined in this investigation, it seems that, the quality of the cementitious matrix enveloping the unburnt carbon particles played a more important role than the amount itself of the unburnt carbon in determining the concrete performance in terms of strength (Fig. 3) and watertightness (Fig. 4). It may be that, for some not yet known reasons related to the pozzolanic characteristics, the fly ash *D*, in spite of its higher LOI content, improved the quality of the cementitious matrix more than the fly ash *A*.

Figure 5 shows the chloride penetration in concrete specimens wet cured for 28 days and then immersed in a 10% NaCl aqueous solution. A square root scale was used for the time of immersion, since there was a quite good linear relationship between the Cl^- penetration depth ($\mathbf{x}$) and $\sqrt{\mathbf{t}}$:

$$\mathbf{x} = \mathbf{k}\,\sqrt{\mathbf{t}} \qquad [1]$$

where $\mathbf{t}$ is the time of immersion in the chloride solution. This indicates that chloride penetration through concrete specimens occurs in agreement with a diffusion process determined by the Fick's second law (6) and that the diffusion coefficient ($\mathbf{D}$) can be approximately calculated from the $\mathbf{k}$ value related to the slope curves (7):

$$\mathbf{D} = \mathbf{k}^2/16 \qquad [2]$$

From the slope of the curves in Fig. 5 ($\mathbf{k}$ values) and by using equation [2] the following diffusion coefficients were determined

- reference concrete R_2 ($w/c = 0.68$) : $\mathbf{D} = 6.3 \cdot 10^{-6}$ mm · sec^{-1}
- reference concrete R_1 ($w/c = 0.48$) : $\mathbf{D} = 3.2 \cdot 10^{-6}$ mm · sec^{-1}
- concretes with fly ashes *A,B,C* ($w/b = 0.48$) : $\mathbf{D} = 1.8 \cdot 10^{-6}$ mm · sec^{-1}
- concrete with fly ash *D* ($w/b = 0.68$) : $\mathbf{D} = 1.6 \cdot 10^{-6}$ mm · sec^{-1}

These data indicate that the chloride diffusion coefficient (**D**) is lower in concretes with fly ash with respect to that of the corresponding reference concretes R_1 and R_2. This is in agreement with the consolidated literature data on chloride diffusion through portland cement and pozzolan-portland cement concrete mixtures at equal w/b ratio, and it has been ascribed to the interaction between the Cl^- ions, diffusing through the water-filled concrete pores, and the surface area of pozzolan and/or lime-pozzolan products which are capable to adsorb Cl^- ions and retard their diffusion process (6). Of course, fly ash concretes performed much better than the reference concrete R_2 not only for the presence of pozzolanic material, which retards the Cl^- diffusion, but even for the lower w/b (0.48 versus 0.68).

Again, there was no increase in the Cl^- diffusion rate by increasing the amount of the LOI material in fly ashes (Fig. 5). The fly ash *D*, with the highest unburnt content (11.30%), performed better - in terms of lower chloride penetration - than other fly ashes and in particular than the fly ash *A* with the lowest LOI content (4.19%).

Figure 6 shows the carbonation rate of concrete specimens exposed to a CO_2-enriched air (30%). In general the CO_2 penetration in this accelerated test was about 100 times faster than that which occurs in normal natural air. For comparative purposes the carbonation of different concrete specimens can be assessed in few months by using this accelerated test. The carbonation rate of the fly ash concrete mixtures was lower than that of the reference concrete R_2 at equal w/c (0.68) and higher than that of the reference concrete R_1 at equal w/b (0.48). The carbonation process is not a mere diffusion of CO_2 through the open concrete pores, but it is the result of two distinct phenomena:

- diffusion of CO_2 through the porous system of the cementitious matrix: the more porous is this system, the faster is the CO_2 diffusion;
- combination of CO_2 with $Ca(OH)_2$ produced by cement hydration: the larger is the amount of free lime produced by portland cement hydration, the slower is the neutralization process.

What is measured through the phenolphtalein test is the depth of the neutralized portion of concrete after the consumption of free lime. Therefore, with respect to the fly ash concrete mixtures, the carbonation process in the reference concrete R_2, at equal w/c ratio (0.68), was higher (Fig. 6) because of the higher porosity which predominated over the higher amount of available $Ca(OH)_2$. On the other hand, the carbonation rate was lower in the reference concrete R_1 than in each fly ash concrete mixture since the former contained more free lime than the latter, and moreover the cement matrix was less porous - as indicated by water-penetration test (Fig. 4) - due to the lower w/c.

All the above data agree very well with other results published by the in 1990 concerning the influence of pozzolan additions on the carbonation process (8). What is new in the present work is the absence of any relationship between the LOI content in fly ashes and the carbonation rate of the corresponding concrete mixture. Again, the concrete with the fly ash *D*, characterized by the highest unburnt content (11.30%), performed better, in terms of lower carbonation rate (Fig. 6), than concrete with the fly ash *A* having the lowest amount of LOI material (4.10%).

CONCLUSIONS

The results of the present investigation indicate that fly ashes with a smaller LOI content did not necessarily perform better than those with a higher amount of LOI material. These results disagree with the conformity criteria of the European standard EN 450 (1) which rejects the use of fly ashes, as supplementary cementitious materials in concrete, when the LOI content is over the 5% limit (on a continental European level) or the 7% limit (on a domestic national level).

Indeed, the results of the present study indicated that, at equal slump and *w/c* ratio of the mixtures, there is no relationship between the fly ash LOI content (4-11%) and the concrete performance in terms of compressive strength, water penetration, chloride diffusion, and carbonation process.

Surprisingly, the fly ash *D*, with the largest LOI content (11.30%), performed always better than fly ash *A* with the smallest amount of LOI material (4.19%). This could be ascribed to the specific composition of the fly ash *D* which acted as a better pozzolan in spite of the higher amount of the LOI material.

However, since the increase in the LOI content of the fly ash was accompanied by an increase in the mixing water needed at a given slump, small amount of superplasticizer (0.3-0.4% by cement mass or 0.6-1% by fly ash mass) was required to compensate this effect and keep constant the w/c. In terms of cost, the superplasticizer, based on the unit cost of the naphthalene superplasticizer available in Italy (0.60 $ US/kg), corresponds to about 0.3-0.5 cents (US $) per kg of fly ash.

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TABLE 1—CHEMICAL, PHYSICAL AND MECHANICAL PROPERTIES OF PORTLAND CEMENT [CE I 42.5 R ACCORDING TO EN 197/1]

Chemical composition		**Physical and mechanical properties:**	
SiO_2	19.82%	Specific gravity	3.06 g/ml
Al_2O_3	5.10%		
Fe_2O_3	3.45%	Initial setting time	2:10 (hr:min)
CaO	62.42%		
MgO	1.70%	Blaine fineness	330 m^2/kg
SO_3	2.50%		
Na_2O	0.30%	2-day compressive strength	27.0 MPa
K2O	0.62%		
Cl^-	0.03%	28-day compressive strength	49.0 MPa
Loss on ignition	0.92%		

TABLE 2—CHEMICAL ANALYSIS AND BULK GRAVITY OF FLY ASHES

Chemical composition (%):	**Fly Ash:**			
	A	**B**	**C**	**D**
SiO_2	58.45	57.01	55.56	54.12
Al_2O_3	24.60	23.93	23.25	22.58
Fe_2O_3	2.65	2.70	2.74	2.78
CaO	0.96	1.02	1.07	1.13
MgO	0.35	0.48	0.61	0.74
Na_2O	0.40	0.41	0.42	0.43
K_2O	3.39	2.97	2.56	2.14
Li_2O	0.02	0.02	0.03	0.03
SrO	0.23	0.32	0.40	0.48
BaO	0.18	0.14	0.11	0.08
SO_3	0.22	0.27	0.32	0.37
Cl^-	0.06	0.08	0.09	0.11
P_2O_5	0.01	0.13	0.24	0.36
LOI	4.19	6.56	8.93	11.30
Bulk gravity (kg/l)	0.88	0.81	0.75	0.68

TABLE 3—MIXTURE PROPORTIONS AND PROPERTIES OF FRESH CONCRETES

Composition/Properties	Reference Concrete:		Concrete with fly ash:			
	R_1	R_2	A	B	C	D
cement (kg/m^3)	417	294	294	294	291	293
aggregate (kg/m^3)	1744	1879	1720	1720	1716	1717
water (kg/m^3)	200	200	200	200	198	199
superplasticizer (kg/m^3)	-	-	-	0.8	1.1	1.3
fly ash (kg/m^3)	-	-	126	126	124	125
fly ash/(fly ash+cement)	-	-	0.30	0.30	0.30	0.30
w/c	0.48	0.68	0.68	0.68	0.68	0.68
w/b	0.48	0.68	0.48	0.48	0.48	0.48
slump (mm)	190	200	200	190	190	190
air content (%)	2.1	1.1	1.2	1.2	1.5	1.4
specific gravity (kg/m^3)	2361	2373	2340	2341	2330	2335

Fig. 1—Particle size distribution for individual and combined aggregates

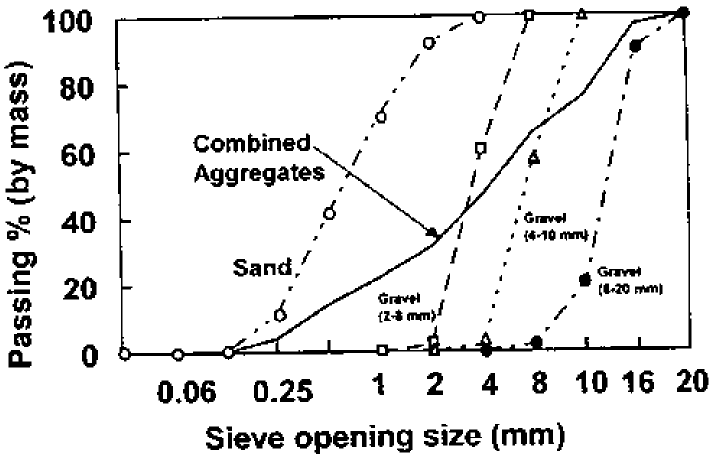

Fig. 2—Particle size distribution for fly ash, A, B, C, and D

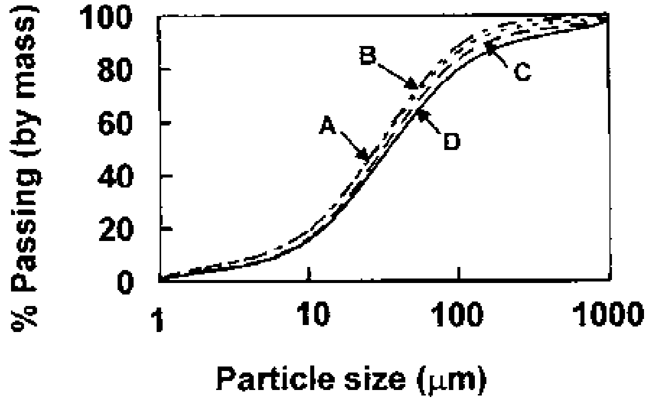

Fig. 3—Compressive strength development for references mixtures and fly ash concretes

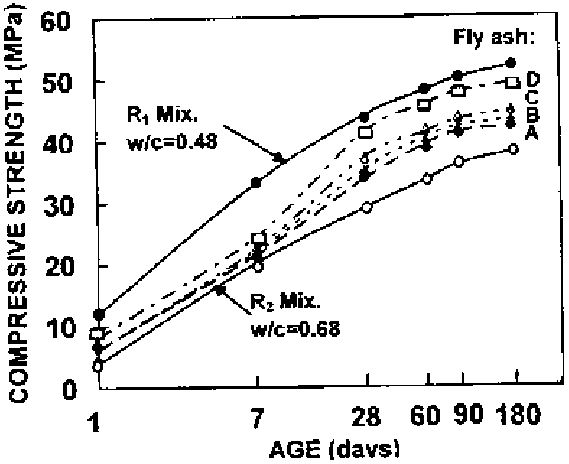

Fig. 4—Influence of fly ash (A,B,C,D) on the water penetration with respect to reference mixtures (R_1 and R_2). The horizontal dashed line at 20 mm indicates the border between permeable and impermeable concretes

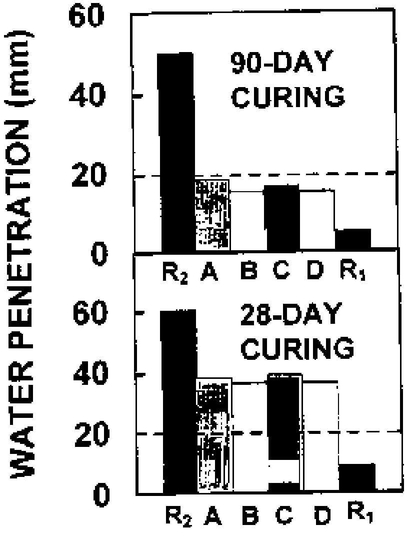

Fig. 5—Chloride penetration for 28 day cured concrete specimens as a function of exposure time to 10% NaCl aqueous solution

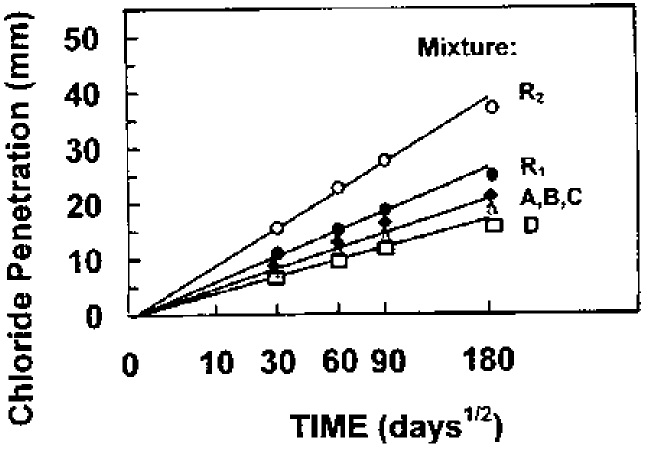

Fig. 6—Penetration of CO_2 in concrete specimens exposed to CO_2-enriched air (30%) Reference concretes R_1 and R_2; fly ash concrete mixtures: A,B,C, and D