SP 192–10

Durability of High-Performance Concretes with Pozzolanic and Composite Cements

by S. Collepardi, V. Corinaldesi, G. Moriconi, G. Bonora, and M. Collepardi

Synopsis: Pozzolanic cements with 50% fly ash, and composite cements with 25% fly ash and 25% ground granulated blastfurnace slag were produced to manufacture high performance concretes. These binders are in agreement with the European standard (EN 197/1) for cements type IV/B and V/A, respectively. Unground and ground fly ash was used for pozzolanic and composite cements. Ground slag was used for composite cements. Eight different blended cements were produced and characterized by strength measurements on standard mortar bars.

High performance concrete mixtures were all manufactured with a water-to cementitious material ratio as low as 0.32, a portland cement factor of 235 kg/m^3, and a fly ash or slag plus fly ash content of 235 kg/m^3. A naphthalene-based superplasticizer was used to produce flowing concretes with a slump in the range of 190-220 mm. A slightly higher dosage of superplasticizer was needed to compensate the slump reduction caused by the fineness increase of the blended cements.

Cube concrete specimens were cured at 5°C and 20°C. Compressive strength was measured at 3, 7, 28, and 90 days. The 28-day compressive strength at 20°C was in the range of 60-80 MPa. Early compressive strength (at 3 days) was as high as 30-40 MPa even at the lower curing temperature (5°C).

Carbonation and chloride penetration tests were carried out to assess the influence of the cement fineness on the durability behavior. In general, the durability of these concretes in terms of carbonation and chloride penetration is excellent. However, there is no significant improvement related to higher fineness of the cementitious materials.

Keywords: blended cements; carbonation; compressive strength; fineness; fly ash; slags

Silvia Collepardi is a research civil engineer of Enco, Spresiano, Italy. She is working in the field of superplasticized concrete mixtures and has published several papers in this area.

Valeria Corinaldesi is a civil engineer and a PhD student in Materials Engineering. She is working in the area of cement and concrete materials.

Giacomo Moriconi is Professor of Materials Science at the University of Ancona, Italy. He is Head of the Department of Materials and Earth Sciences. He is author or co-author of numerous papers in the field of cement chemistry, concrete technology and building materials.

Giuseppe Bonora is the managing director of the R&D Laboratory in Gruppo Cementi Rossi, Piacenza, Italy. His research interests include: analytical chemistry, environmental problems in cement industry, microcements and standard specifications for hydraulic binders.

Mario Collepardi is Professor of Materials Science and Technology at the Ancona University, Italy. He is author or co-author of numerous papers on concrete technology and cement chemistry. He is also the recipient of several awards for his contributions to the fundamental knowledge of superplasticizers and their use in concrete.

INTRODUCTION

High volume fly ash blended cements may be produced in Europe in agreement with the European Standard 197/1 as CEM IV/B pozzolanic cement with a fly ash content up to 55% (1). Composite cements, based on ternary blends of portland cement, fly ash, and ground granulated blast-furnace slag, may also be produced in agreement with the above standard with a slag + fly ash content up to 60% (CEM V/A) or 80% (CEM V/B). However, both pozzolanic cements (CEM IV/B) and composite cements (CEM V/A or CEM V/B) are not widely used in practice.

The main purpose of the present paper was to study the concrete mixtures manufactured by using fly ash-portland cement or fly ash-slag-portland cement both with a portland cement replacement of 50% by mass.

Another purpose of this research was to study the influence of the specific surface area of the cement ingredients on the workability, compressive strength, and durability of concrete mixtures, all manufactured with a water-cementitious material ratio (*w/cm*) as low as 0.32.

Previous works on high volume fly ash concrete characterized by high portland cement replacement (50-65% by mass) and low *w/cm* were carried out by V.M. Malhotra and coworkers (2-5). Ternary blends of cement, slag, and fly ash were studied by Berry (6), Swamy (7), Douglas and Pouskouleli (8), Nagataki (9), Dehuai and Zhaoyuan (10).

MATERIALS

Cementitious materials. The chemical analysis of the ingredients (portland cement, fly ash, and slag) used to manufacture blended cements are shown in Table 1.

Table 2 shows the composition of four pozzolanic cements (*A*, *B*, *C*, and *D*) all with 50% portland cement replaced by the same mass of fly ash, the main difference being the fineness of portland cement (about 400 or 500 m^2/g) and fly ash (about 350, 400 and 500 m^2/g). Cements *A* and *C* were manufactured by blending ground portland cements with fly ash as received (350 m^2/g). Cements *B* and *D* were manufactured by blending portland cements and fly ash both ground at about the same fineness (400 or 500 m^2/g). Table 3 shows Blaine fineness, setting time, and compressive strength of the four blended cements CEM IV/B according to the EN 197/1 standard. The strength class is 32.5 R for blended cements *A* and *C* both with unground fly ash, and 42.5 for blended cements *B* and *D* both with ground fly ash.

Table 4 shows the composition of four composite cements (*E*, *F*, *G*, and *H*) all with 50% portland cement replaced by 25% of fly ash and 25% of ground slag, the main difference being the fineness of the three ingredients. Cements *E* and *G* were manufactured by blending unground fly ash with ground portland cement and slag at the same fineness (about 400 or 500 m^2/g). Cements *F* and *H* were manufactured by blending ground fly ash with the other two ingredients at the same fineness (about 400 or 500 m^2/g). Table 5 shows Blaine fineness, setting time, and compressive strength of the four blended cements according to the EN 197/1 standard: all are composite cements CEM V/A belonging to the same strength class of 42.5, although compressive strengths at early and later ages increase by increasing the Blaine fineness.

Aggregates. Natural sand (fineness modulus of 3.09) and two coarse aggregates were used. For all concrete mixtures a combined aggregate was used with 25% of sand, 40% of gravel (4-16 mm), and 35% of coarse aggregate (10-25 mm).

Superplasticizer. A 40% aqueous solution of naphthalene-based superplasticizer was used in all concrete mixtures.

Concrete mixtures. Table 6 shows the composition of concrete mixtures all at a *w/cm* of 0.32. The superplasticizer dosage (in the range of 1-1.25% by mass of cementitious material) was adjusted to obtain approximately the same slump level (190-220 mm).

The content of the cementitious material (including fly ash and/or slag) was about 470 kg/m^3 which corresponds to a content of portland cement of about 235 kg/m^3.

METHODS

Besides the slump measurements of fresh mixtures the following properties were determined:

- compressive strength of concrete specimens cured at 5°C or 20°C;
- depth of carbonation as measured by the phenolphthalein test (RILEM CPC – 18) of concrete specimen exposed to air after demoulding at 1 day;
- chloride penetration through the $AgNO_3$ and fluorescein test (11) of concrete specimens exposed to a 10% NaCl aqueous solution after a wet curing of 1 week and an air curing of 3 weeks.

RESULTS

Workability. The amount of superplasticizer required to obtain the same slump level at a given *w/cm* (0.32) depends on the fineness of the fly ash as well as that of the cement (Table 6). In concretes with ground fly ash – particularly that at higher fineness (482 m^2/g) – a higher dosage of superplasticizer is needed with respect to those with unground fly ash: for instance the dosage of superplasticizer changes from 1.05% to 1.25% by using 50% of ground fly ash (cement *D* in Mixture No. 4) instead of the same amount of unground fly ash (cement *C* in Mixture No. 3). This effect is related to the lost of coarse spherical particles produced by the grinding action (Fig. 1). The increase in the superplasticizer dosage is higher in concrete with pozzolanic cements where a higher amount of fly ash (50%) is used; in concretes with composite cements, with a lower amount of fly ash (25%), a lower increase in the superplasticizer dosage is needed to compensate the partial lost of spherical particles: for instance the change in the superplasticizer dosage is negligible (from 1.05% to 1.10%) by using 25% of ground fly ash (cement *H* in mixture No. 8) instead of the same amount of unground fly ash (cement *G* in mixture No. 7).

Compressive strength. Figures 2-5 show the compressive strength results of concrete mixtures cured at 5°C and 20°C at R.H. of 95%. In general, the compressive strength at 20°C is higher than that at 5°C at both early and later ages. However, even concrete specimens cured at lower temperature (5°C) reach strength levels as high as 30-40 MPa within 3 days. Although the portland cement content is as low a 235 kg/m^3, the strength level of all these concretes is relatively high at longer ages: 50-70 MPa at 28 days and 60-90 MPa at 90 days. This performance is related to the action of the cementitious activity of fly ash and/or slag combined with a *w/cm* as low as 0.32 due to the presence of superplasticizer. These data agree very well with those obtained by Malhotra et al. (2-5).

Figure 2 shows the effect of the fly ash fineness on the compressive strength of concrete mixtures with cement *A* and *B*, both containing portland cement with a Blaine fineness of about 400 m^2/g. The change from unground (350 m^2/g) to ground fly ash (395 m^2/g) produces a slight strength increase.

When using a finer portland cement (about 500 m^2/g), again the compressive strength is increased (Fig. 3) by using ground fly ash (482 m^2/g) instead of unground fly ash (351 m^2/g).

The combined use of ground slag (25%) and unground or ground fly ash (25%) appears to be still more effective (Fig. 4 and 5) than fly ash alone (50%). For instance cement *F*, with 25% ground fly ash and 25% ground slag (both at a fineness of about 400 m^2/g), performs better in concrete Mixture No. 6 than the corresponding cement *B* (with 50% fly ash) in concrete Mixture No. 2 (Fig. 4 vs. Fig. 2). Moreover, the workability behavior of the Mixture No. 6 with the composite cement *F* is better than that of the corresponding concrete Mixture No. 2 with pozzolanic cement *B* (Table 6): the slump level is higher (220 mm vs. 190 mm) even with a slightly lower superplasticizer dosage (1.00% vs. 1.05%).

Carbonation. Figure 6 shows the carbonation depth (x) as a function of time (t). After some months of exposure to air, the carbonation depth is un-detectable or negligible in all the eight studied concretes. However, due to the linear relationship between the CO_2 penetration depth and the square root of time ($x = k\sqrt{t}$), the extrapolated value of x after some years is less than 1 mm and even smaller than that found by Malhotra and coworkers (2): 2 mm after 2.5 years of exposure to air (Fig. 6). Then, it is confirmed (2) that carbonation does not pose problems for corrosion of the metallic reinforcements due to very low permeability of these concretes containing high volumes of fly ash and/or ground slag.

Chloride penetration. Figures 7 and 8 show the chloride penetration depth with time for the mixtures with pozzolanic and composite cements respectively. For comparative purposes, chloride penetration results of portland cement concretes with water-cement ratio of 0.32 (12) are also shown in Fig. 7 and 8. The chloride penetration rate in concrete mixtures with high volume fly ash blended cements (Fig. 7) or high volume fly ash and ground slag blended cements (Fig. 8) is lower than that in portland cement concrete mixtures with a water-cement ratio 0.32.

Chloride penetration does not seem to depend on the fineness of the cementitious material or the type (pozzolanic versus composite) of the blended cement.

CONCLUSIONS

High-volume fly ash blended cements (CEM IV/B pozzolanic cements) or high-volume fly ash and ground slag blended cements (CEM V/A composite cements) perform very well in concrete mixtures in terms of good workability (190-220 mm), high compressive strength (60-70 MPa at 28 days), and excellent durability behavior (negligible carbonation and very low chloride penetration).

The concrete performance in terms of workability and compressive strength is better when portland cement is replaced by fly ash (25%) and ground slag (25%) rather than by fly ash alone (50%).

The compressive strength is increased slightly by the grinding action of both fly ash and slag.

The durability behavior does not seem to be improved by increasing the fineness of the cementitious materials.

REFERENCES

1. European Standard EN 197-1, "Cement Composition, Specification and Conformity Criteria", Part 1, Common Cements, 1992.
2. Sivasundaram, V., Carette, G.C., and Malhotra, V.M., "Long-Term Strength Development of High Volume Fly Ash Concrete", *Cement and Concrete Composites*, V. 12, pp. 263-270, 1990.
3. Sivasundaram, V., Carette, G.C., and Malhotra, V.M., "Mechanical Properties, Creep, and Resistance to Diffusion of Chloride Ions of Concrete Incorporating High Volumes of ASTM Class F Fly Ashes from Seven Different Sources", *ACI Materials Journal*, V. 88, No. 4, pp. 407-416, 1991.
4. Bouzoubaâ, N., Zhang, M.H., Bilodeau, A., and Malhotra, V.M., "Laboratory-Produced High-Volume Fly Ash Blended Cements: Physical Properties and Compressive Strength of Mortars", *Cement and Concrete Research*, V. 28, pp. 1555-1569, 1998.
5. Bouzoubaâ, N., Zhang, M.H., and Malhotra, V.M., "Effects of Grinding on Physical and Mechanical Properties of High-Volume Fly Ash Blended Cements", *World Cement Research*, pp. 98-101, November 1998.
6. Berry, E.E., "Strength Development of Some Blended-Cement Mortars", *Cement and Concrete Research*, V. 10, pp. 1-11, 1980.
7. Swamy, R.N., "Cement Replacement Materials", Surrey University Press, 1986.
8. Douglas, E., and Pouskouleli, G., "Prediction of Compressive Strength of Mortars Made with Portland Cement–Blast Furnace Slag-Fly Ash Blends", *Cement and Concrete Research*, V. 21, pp. 523-534, 1991.

9. Nagataki, S., "Mineral Admixtures in Concrete: State of the Art and Trends", ACI SP-144, pp. 473-484, 1994.
10. Dehuai, W., and Zhaouyan, C., "On Predicting Compressive Strength of Mortars with Ternary Blends of Cement, GGBFS and Fly Ash", *Cement and Concrete Research*, V. 27, pp. 487-493, 1997.
11. Collepardi, M., Marcialis, A., and Turriziani, R., "Penetration of Chloride Ions into Cement Pastes and Concretes", *Journal of American Ceramic Society*, V. 53, pp. 534-535, 1972.
12. Monosi, S., Moriconi, G., Alverà, I., and Collepardi, M., "Effect of Water-Cement Ratio and Curing Time on Chloride Penetration into Concrete", *Materials Engineering*, V. 1, pp. 483-489, 1989.

Table 1 – Chemical composition of portland cement, fly ash, and slag used to produce blended cements.

Oxyde (%)	Portland cement	Fly Ash	Slag
SiO_2	21.25	59.94	36.50
Al_2O_3	4.33	22.87	11.67
Fe_2O_3	1.85	4.67	1.01*
TiO_2	0.13	0.94	0.20
CaO	64.30	3.08	38.95
MgO	1.81	1.55	8.08
SO_3	3.70	0.35	1.00**
K_2O	0.71	2.19	0.42
Na_2O	0.17	0.62	0.34
l.o.i.	1.50	3.34	1.28

*as FeO **as S

Table 2 - Composition and Blaine fineness of pozzolanic cements (CEM IV/B).

Blended Cement	Portland cement		Fly Ash		
	Fineness: 395 m^2/g	Fineness: 504 m^2/g	Unground. Fineness: 351 m^2/g	Ground. Fineness: 395 m^2/g	Ground. Fineness: 482 m^2/g
A	50	-	50	-	-
B	50	-	-	50	-
C	-	50	50	-	-
D	-	50	-	-	50

Table 3 – Performance of pozzolanic cements according to EN 197/1.

Blended Cement	Blaine fineness m^2/g	Setting time (hr:min)		Compressive strength (MPa) at:			Strength Class
		Initial	Final	2 days	7 days	28 days	
A	368	2:45	4:45	14.5	22.5	38.2	32.5R
B	388	2:35	4:10	15.2	26.0	42.9	42.5
C	415	2:15	3:30	16.0	26.3	42.0	32.5R
D	487	2:05	3:20	16.8	28.2	44.6	42.5

Table 4 - Composition and Blaine fineness of composite cements CEM V/A

Blended Cement	Portland cement Fineness (m²/g)		Fly Ash Unground	Fly Ash Ground	Fly Ash Ground	Ground Slag Fineness (m²/g)	
			Fineness (m²/g)				
	395	504	351	395	482	412	517
E	50	-	25	-	-	25	-
F	50	-	-	25	-	25	-
G	-	50	25	-	-	-	25
H	-	50	-	-	25	-	25

Table 5 – Performance of composite cements according to EN 197/1.

Blended Cement	Blaine fineness (m²/g)	Setting time (hr:min) Initial	Setting time (hr:min) Final	Compressive strength (MPa) at 2 days	7 days	28 days	Strength Class
E	384	2:30	3:40	15.1	28.8	45.1	42.5
F	392	2:15	3:25	17.7	31.2	51.6	42.5
G	472	2:00	3:00	19.7	35.4	56.9	42.5
H	499	1:55	2:50	19.9	38.0	58.3	42.5

Table 6 – Composition of concrete mixtures.

Mix No.	Cement Type	Cement (kg/m³)	Gravel 10-25 mm (kg/m³)	Gravel 4-16 mm (kg/m³)	Sand 0-4 mm (kg/m³)	Water (kg/m³)	Super-plasticizer (% by cem)	w/cm	Slump (mm)
1	A	463	453	729	641	148	1.00	0.32	200
2	B	465	455	732	643	145	1.05	0.32	190
3	C	463	453	729	641	148	1.05	0.32	190
4	D	465	455	732	643	145	1.25	0.32	190
5	E	469	459	738	648	150	1.00	0.32	220
6	F	471	461	741	651	150	1.00	0.32	220
7	G	467	457	735	646	149	1.05	0.32	200
8	H	472	462	744	653	151	1.10	0.32	200

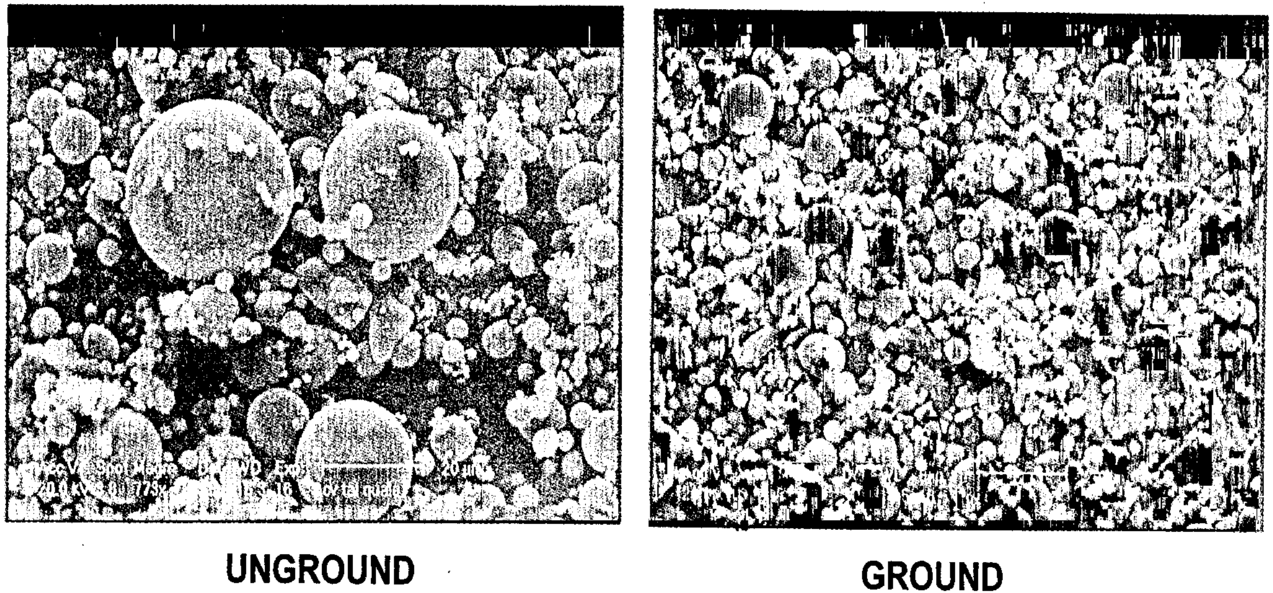

Fig. 1 - Scanning electron micrograph of unground (351 m^2/g) and ground fly ash (482 m^2/g).

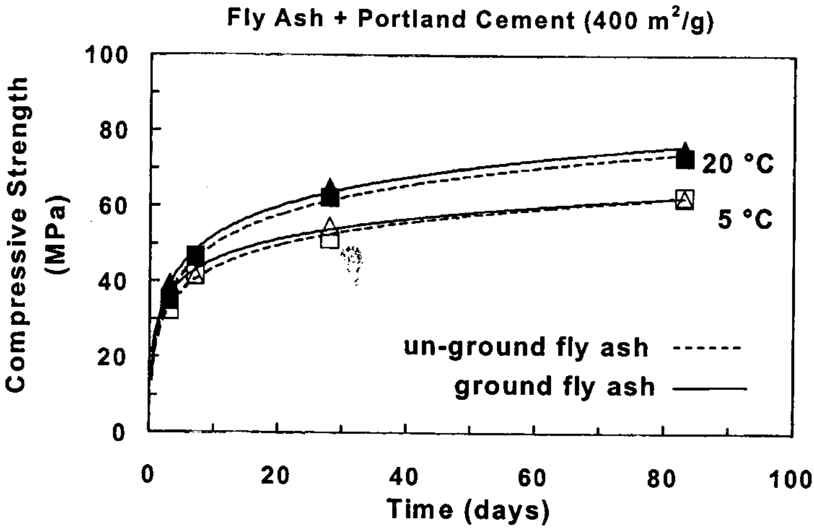

Fig. 2 - Compressive strength of concrete mixtures with blended pozzolanic cements *A* and *B* containing 50% of unground (351 m^2/g) or ground (395 m^2/g) fly ash respectively.

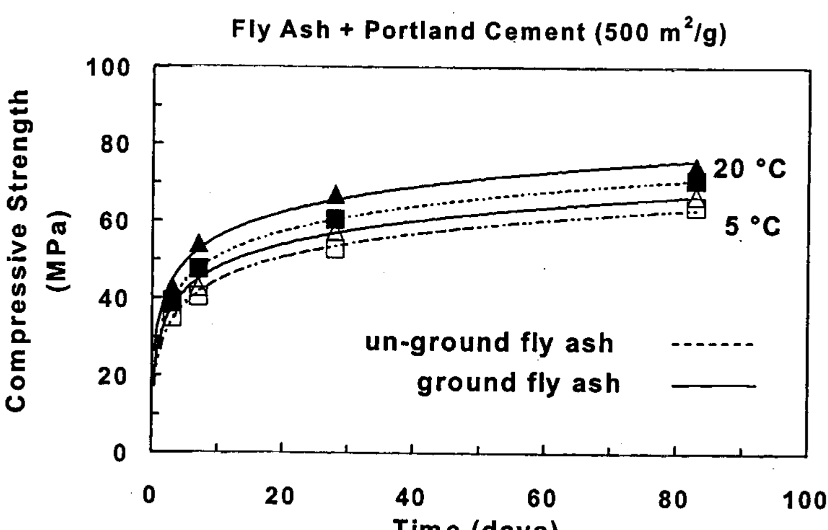

Fig. 3 - Compressive strength of concrete mixtures with blended pozzolanic cements *C* and *D* containing 50% of unground (351 m^2/g) or ground (482 m^2/g) fly ash respectively.

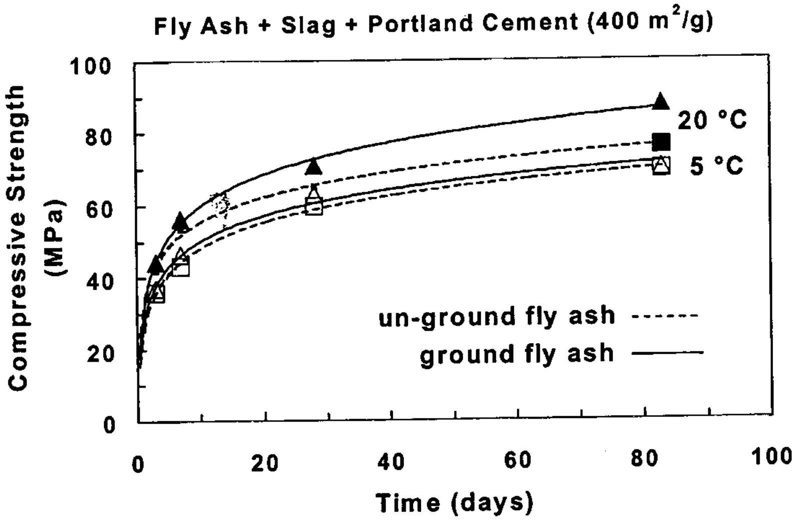

Fig. 4 - Compressive strength of concrete mixtures with composite cements *E* and *F* containing ground slag (412 m^2/g) and unground (351 m^2/g) or ground (395 m^2/g) fly ash respectively.

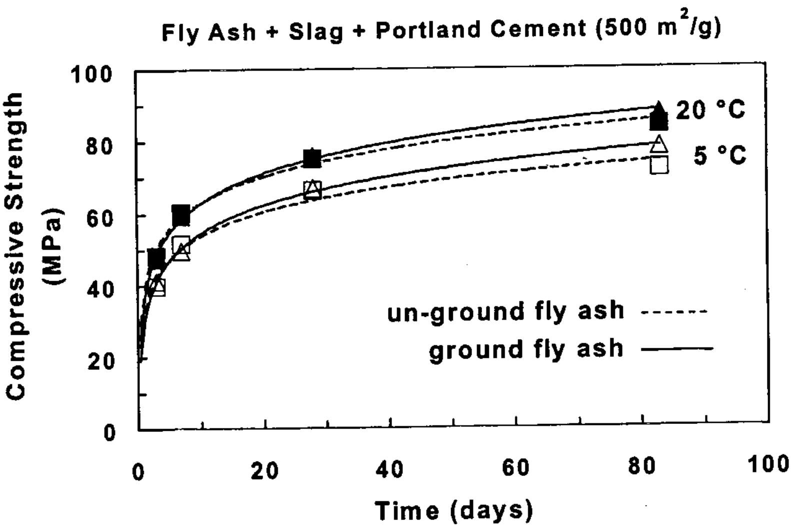

Fig. 5 - Compressive strength of concrete mixtures with composite cements *G* and *H* containing ground slag (517 m^2/g) and unground (351 m^2/g) or ground (482 m^2/g) fly ash respectively.

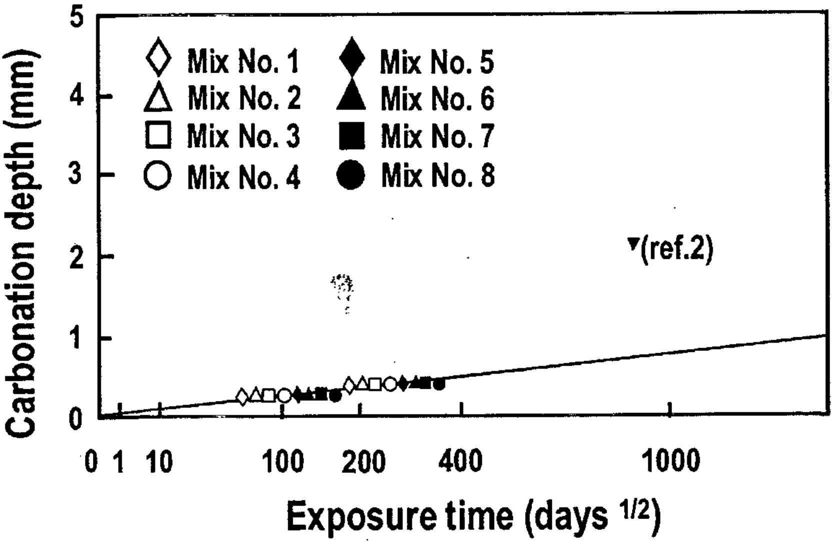

Fig. 6 – Carbonation depth as a function of time of exposure to air.

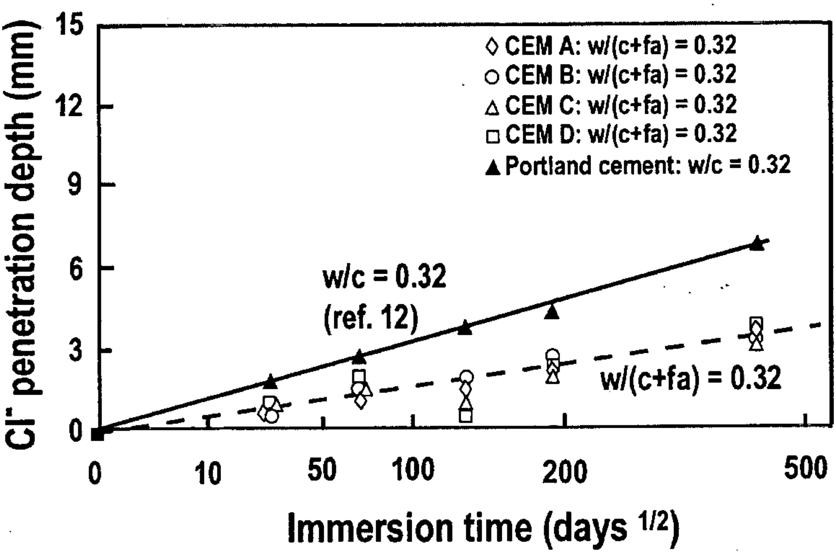

Fig. 7 – Chloride penetration in concrete mixtures with fly ash (fa) cements versus portland cement.

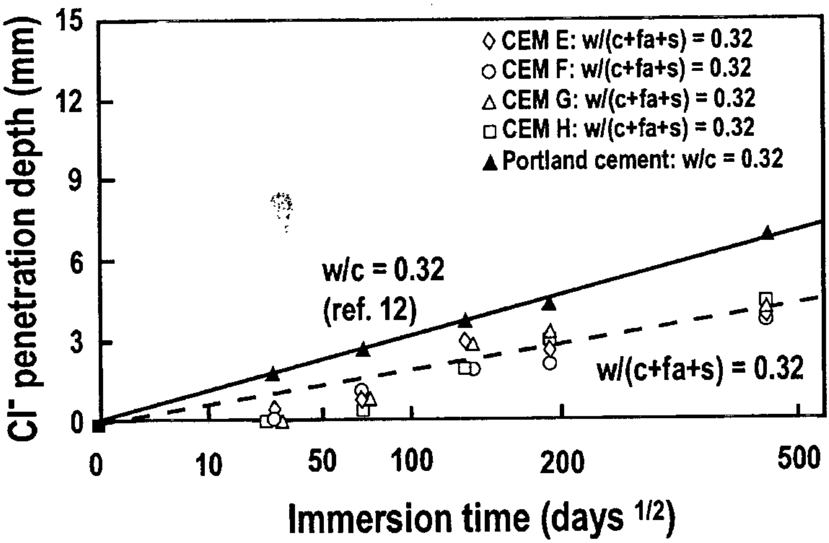

Fig. 8 – Chloride penetration in concrete mixtures with fly ash (fa) and slag (s) cements versus portland cement.