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Use of Fly Ash in Concrete: Efficiency Factors of the Supplementary Cementing Material

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ABSTRACT

The use of the pozzolanic activity index characterises the efficiency of fly ash. Although the factor of efficiency can be defined for any concrete property, this study will refer specifically the compressive strength and the permeability to chlorides. The use of laboratory tests on concrete enables this study to verify the relationship between the efficiency factor and the following parameters: cement content, fly ash content and age of concrete.

INTRODUCTION

Fly ash is a by-product of coal combustion in thermal power plants. It is removed from the flue gas by electrostatic precipitators. The chemical composition is mainly SiO_2, Al_2O_3, Fe_2O_3, CaO. The ASTM C618 standard categorizes fly ashes in two groups: Class C and Class F. The first one contains high amount of calcium, therefore is an independent binder. The second one contains low amount of calcium and has no binding properties, however, due to the glassy structure of its silica particles it has pozzolanic properties.

$$Ca(OH)_2 + PFA + H_2O = C - S - H \quad (1)$$

Pozzolanic reaction, qualitatively described in (1), allows Class F fly ash to react with $Ca(OH)_2$, forming the same C – S – H fibres that are produced by the direct hydration of cement. Seeing as $Ca(OH)_2$ is a by-product of the hydration of cement, fly ash can react with it. This creates new C – S – H fibres that will improve strength and durability of the concrete. The pozzolanic activity of a fly ash is measured with reaction tests with CaO and depends on the silica content and the fineness. It is easier and more helpful to measure pozzolanic activity with the parameter k, known as factor of efficiency. This parameter is in relation to the most important hardened concrete property, known as the compressive strength. However, it can be in relation to other properties, such as the chloride penetration (Papadakis V.G. et al., 2002). The aim of this study is the experimental determination of efficiency factors of Italian Class F fly ash in relation to compressive strength and chloride permeability: the first property is important when referred to structural matters, the second to durability.

EQUIVALENT CEMENT AND EFFICENCY FACTOR

Considering a concrete mix with a "P" quantity of fly ash and a "c" quantity of cement, "c_{tot}" is the cement that would be needed to have the same compressive strength without fly ash. The difference between "c_{tot}" and "c" is called "equivalent cement" "c_{eq}". The ratio between "c_{eq}" and "P" is the *factor of efficiency* in relation to compressive strength, "k_s".

$$c_{tot} = c + c_{eq} = c + k_s \cdot P \qquad (2_A)$$

The European standard EN 206-1, "c_{tot}" is used to calculate the water – cement ratio and the minimum content of cement in concrete. According to EN 206-1 k_S can be either 0.2 or 0.4. These rates depend on type of cement. The experimental data found in this study show that these rates are lower limits, especially when referred to 56-90 days aged concrete.

Compressive strength

The compressive strength depends on many factors, therefore it is very difficult to describe with a mathematical model. However, the main factors are the water–cement ratio and the hydration rate α. The determination of α is very difficult, so it is commonly replaced with the time of hydration *t*. Under the hypothesis of steady temperature during the hydration of cement, no chemicals modifying the hydration's kinetic and standard curing conditions, compressive strength can be modelled as follows:

$$R_C = A_1 \left(\frac{w}{c} \right)^{A_2} \qquad (3)$$

Where "w" is water content, "c" is cement content, A_1 and A_2 are parameters depending on time of hydration and type of cement. When fly ash is used in concrete, (3) it can be written as follows:

$$R_C = A_1 \left(\frac{w}{c + k_S \cdot P} \right)^{A_2} \qquad (4)$$

Where "k_s" is the efficiency factor relative to compressive strength and P is fly ash content.

Chloride penetration

Chloride penetration in concrete can be modelled by the second Fick's law:

$$\frac{\partial c}{\partial t} = -D \cdot \frac{\partial^2 c}{\partial x^2} \qquad (5)$$

Where "D" is the diffusion coefficient. This coefficient depends on the factors in relation to concrete porosity (w/c ratio, hydration rate) and with the capability of the cement hydration products to react with chlorides (binders type). The efficiency factor related to chloride penetration, "k_{Cl}" can be defined as the efficiency factor related to compressive strength. Considering a concrete mix with a "P" quantity of fly ash and a "c" quantity of cement, "c_{tot}" is the cement that would be needed to have the same D value without fly ash. The quantity "c_{eq}" is the difference between "c_{tot}" and "c". The ratio between "c_{eq}" and P is the *factor of efficiency* in relation to chloride penetration "k_{Cl}".

$$c_{tot} = c + c_{eq} = c + k_{Cl} \cdot P \qquad (2_B)$$

After calculating D for a given number of concretes without fly ash it is possible to find a function “*f*” such as:

$$D = f\left(\frac{w}{c}\right) \qquad (6)$$

All the parameters that can modify D have been considered steady in all tests. When using fly ash in concrete it is possible to write (6) as follows:

$$D = f\left(\frac{w}{c + k_{Cl} \cdot P}\right) \qquad (7)$$

“k_s“ and “k_{Cl}“ are not constant values as they depend on many variables. The aim of this study is to show how they depend on cement content, fly ash content, age of concrete.

$$k = k\left(c, P, t\right) \qquad (8)$$

EXPERIMENTAL WORK

Materials

All concrete mixtures were made using Portland cement type CEM I 42.5R (EN 197-1 standard), a sand 0 - 4 mm with fineness modulus M_f = 3.04, two different types of gravels, 8-16 mm and 16-31.5 mm. An acrylic superplasticizer admixture was used. Therefore the same workability (Slump with Abrams test, according to EN 12350-2) was obtained with the same amount of water and different admixture dosages. The fly ash was italian, responding to UNI EN 450-1 standards. According to that standard the pozzolanic activity indices were calculated. The result was 85% at 7 days and 98% at 28 days. The chemical analysis results are shown in Table 1. The fly ash could be classified as Class F (ASTM C618).

Table 1. Main components of fly ash used

Chemical element	(%)
SiO_2	50.27
Al_2O_3	26.57
Fe_2O_3	5.82
CaO	5.27
Other components	6.96
l.o.i.	5.11

Mixture proportion, specimen preparation and curing

Twenty-four different concrete mixtures were made. Four of them were made without fly ash, with different w/c ratio. The remaining twenty were made with four different cement dosages, and with increasing amounts of fly ash. For all concrete mixtures several cubic (150 mm) specimens were made, in order to measure compressive strength and chloride penetrations at different ages. All of them were prepared and cured according to the UNI EN 12390-2 standard. In Table 2 mix designs and workabilities are shown.

Table 2. Concrete mix proportion

Concrete	Cement [kg/m^3]	Fly ash [kg/m^3]	Water [kg/m^3]	Superplasticizer admixture [%]	Slump [cm]
1	260	0	160	0.50	19
2	320	0	160	0.50	21
3	360	0	160	0.50	23
4	400	0	160	0.50	22
5	220	20	160	0.50	21
6	220	40	160	0.50	21
7	220	60	160	0.50	22
8	220	80	160	0.50	22
9	220	120	160	0.50	21
10	270	30	160	0.50	21
11	270	50	160	0.50	23
12	270	80	160	0.50	23
13	270	110	160	0.50	21
14	270	140	160	0.60	22
15	300	40	160	0.50	21
16	300	60	160	0.50	22
17	300	100	160	0.60	20
18	300	130	160	0.60	22
19	300	160	160	0.70	22
20	320	50	160	0.50	19
21	320	80	160	0.50	20
22	320	120	160	0.60	20
23	320	145	160	0.65	21
24	320	170	160	0.70	21

Results

The compressive strength was evaluated at different ages, according to UNI EN 12390-3 standard. The diffusion coefficient was evaluated at 90 days age. The specimens were tested for chloride content, then drowned for 20 days in a 3,5% NaCl solution, according to UNI 9944 standard. The diffusion coefficient was calculated using the following equation (Cranck's solution of second Fick's law):

$$C(x,t) - C_i = (C_S - C_i)\left[1 - erf\left(\frac{x}{2\sqrt{D \cdot t}}\right)\right] \quad (9)$$

Where “C(x)” is NaCl concentration in concrete at depth “x”, “C_S“ is NaCl concentration in the solution, “C_i“ is NaCl concentration in concrete evaluated before the test and “*erf*” is error function. On Table 3 the compressive strengths at different ages and the chloride diffusion coefficient at 90 days age are shown.

Table 3. Compressive strength and chloride diffusivity factor of tested concretes

Concrete	Compressive strength [N/mm^2]						Chloride diffusion factor D [m^2/s]
	2 days	7 days	14 days	28 days	56 days	90 days	
1	20.22	30.31	32.53	36.49	40.12	43.64	$1.65 \cdot 10^{-12}$
2	31.10	41.39	43.25	44.02	48.17	56.24	$1.59 \cdot 10^{-12}$
3	37.42	48.35	52.25	54.95	58.16	62.87	$1.48 \cdot 10^{-12}$
4	45.14	53.12	55.90	60.96	65.12	72.36	$1.44 \cdot 10^{-12}$
5	14.42	25.12	29.58	30.90	34.02	37.16	$1.68 \cdot 10^{-12}$
6	15.71	26.02	30.11	32.49	35.17	43.76	$1.56 \cdot 10^{-12}$
7	16.57	26.39	31.14	36.97	42.11	46.13	$1.48 \cdot 10^{-12}$
8	17.30	26.96	32.13	36.62	43.63	47.51	$1.42 \cdot 10^{-12}$
9	17.55	27.52	33.95	39.93	46.19	50.82	$1.36 \cdot 10^{-12}$
10	23.20	34.37	38.37	39.60	44.73	50.62	$1.56 \cdot 10^{-12}$
11	24.56	35.97	39.78	42.13	47.19	55.29	$1.50 \cdot 10^{-12}$
12	25.05	38.47	42.47	47.38	52.74	58.69	$1.41 \cdot 10^{-12}$
13	25.51	38.91	43.35	50.12	55.97	62.80	$1.36 \cdot 10^{-12}$
14	26.64	41.04	46.68	53.08	59.34	64.94	$1.33 \cdot 10^{-12}$
15	28.86	43.05	45.23	51.71	56.28	60.98	$1.49 \cdot 10^{-12}$
16	30.26	43.77	47.17	52.73	57.84	65.94	$1.45 \cdot 10^{-12}$
17	31.51	44.95	50.11	55.23	61.02	69.04	$1.35 \cdot 10^{-12}$
18	32.46	46.38	52.78	58.34	63.97	72.27	$1.31 \cdot 10^{-12}$
19	33.96	47.80	55.86	61.61	66.93	74.29	$1.28 \cdot 10^{-12}$
20	34.55	47.30	54.45	56.73	62.19	71.62	$1.46 \cdot 10^{-12}$
21	36.33	49.69	56.53	62.12	65.47	73.29	$1.35 \cdot 10^{-12}$
22	38.81	53.78	57.92	65.07	69.85	77.16	$1.31 \cdot 10^{-12}$
23	39.98	54.27	58.97	66.45	71.12	79.33	$1.28 \cdot 10^{-12}$
24	40.29	55.40	61.08	68.14	74.75	85.62	$1.28 \cdot 10^{-12}$

The compressive strength vs. w/c ratio correlation curves were drawn for any considered age using the no-fly ash concrete’s compressive strengths. Then, using eq. (4) the equivalent cement (related to compressive strength) values was calculated for each concrete at any age. The curve (6) was drawn using the no-fly ash concretes coefficients D. Then, using eq. (7) c_{eq} (related to chloride penetration) values were calculated for each concrete at 90 days age. The results in Table 4 show that, at a given cement dosage, to increase the fly ash content means to increase the equivalent cement. Therefore, as the water content was steady in the twenty-four tests, it means to decrease the w/c ratio, and to increase compressive strength. According to Table 4, the equivalent cement values related to compressive strength can be well modelled with the following logarithmic law:

$$\left(c_{eq}\right)_{S} = A_3 \cdot \ln\left(\;\right) + A_4 \qquad (10)$$

Where A_3 and A_4 are constant values depending on cement content.

Figure 1 shows "c_{tot}" related to compressive strength vs "P" trendlines at 28 and 90 days age. Same trends were found at different ages. For every concrete "c_{tot}" increases with time, because the efficiency factor k_S increases with time.

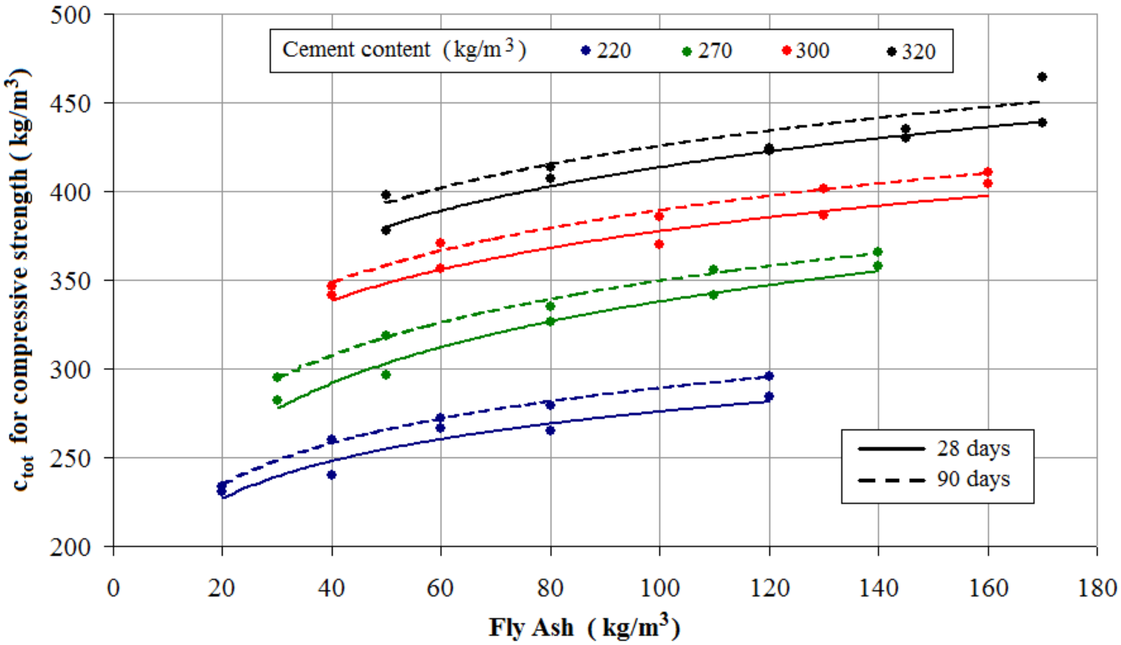

Figure 1. Total cement vs fly ash content for compressive strength

Table 4. Equivalent cement for compressive strength

Concrete	Equivalent cement for compressive strength [kg/m^3]					
	2 days	7 days	14 days	28 days	56 days	90 days
5	-	3	20	11	8	14
6	5	9	23	20	27	40
7	12	11	29	47	55	52
8	17	15	35	45	64	59
9	19	19	46	64	78	76
10	8	12	23	12	20	25
11	16	22	31	27	34	48
12	19	38	46	56	65	65
13	22	40	51	72	83	85
14	29	53	70	88	101	96
15	12	35	32	42	54	46
16	20	39	43	56	63	71
17	28	46	59	70	80	86
18	33	54	74	87	96	101
19	41	62	90	104	112	111
20	24	40	63	58	67	78
21	34	53	74	87	84	93
22	46	76	81	103	108	105
23	52	79	87	110	115	115
24	54	85	98	119	134	145

Table 5. Efficiency factor for compressive strength

Concrete	Efficiency factor for compressive strength					
	2 days	7 days	14 days	28 days	56 days	90 days
5	-	0.15	0.98	0.53	0.42	0.68
6	0.13	0.22	0.57	0.50	0.67	1.00
7	0.20	0.19	0.49	0.78	0.92	0.87
8	0.22	0.19	0.44	0.56	0.80	0.74
9	0.16	0.16	0.39	0.53	0.65	0.63
10	0.26	0.42	0.75	0.40	0.67	0.83
11	0.33	0.45	0.62	0.53	0.68	0.97
12	0.24	0.47	0.58	0.71	0.81	0.82
13	0.20	0.37	0.47	0.65	0.75	0.78
14	0.21	0.38	0.50	0.63	0.72	0.68
15	0.31	0.87	0.80	1.04	1.36	1.16
16	0.34	0.65	0.71	0.94	1.05	1.18
17	0.28	0.46	0.59	0.70	0.80	0.86
18	0.25	0.42	0.57	0.67	0.74	0.78
19	0.26	0.39	0.56	0.65	0.70	0.69
20	0.48	0.79	1.26	1.17	1.33	1.56
21	0.42	0.66	0.92	1.09	1.06	1.17
22	0.39	0.63	0.68	0.86	0.90	0.87
23	0.36	0.54	0.60	0.76	0.79	0.79
24	0.32	0.50	0.58	0.70	0.79	0.85

Table 6. Equivalent cement and efficiency factor for chloride penetration

Concrete	Equivalent cement [kg/m^3]	Efficiency factor
5	33	1.64
6	88	2.21
7	155	2.58
8	215	2.68
9	325	2.71
10	42	1.39
11	42	1.66
12	189	2.36
13	281	2.55
14	349	2.49
15	60	1.51
16	99	1.66
17	261	2.61
18	385	2.96
19	494	3.09
20	67	1.34
21	243	3.03
22	379	3.16
23	473	3.26
24	473	2.78

Figure 2 and 3 shows k_S vs "P" trendlines at 28 and 90 days age, compatible with (10).

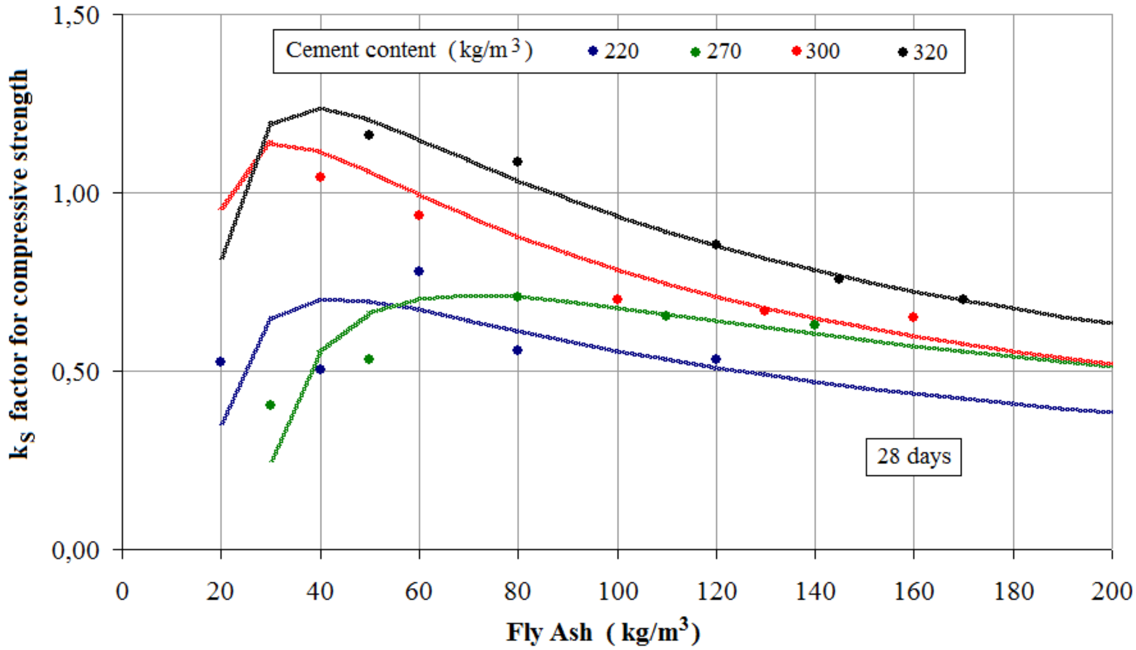

Figure 2. Efficiency factors k_S vs fly ash content for compressive strength at 28 days curing.

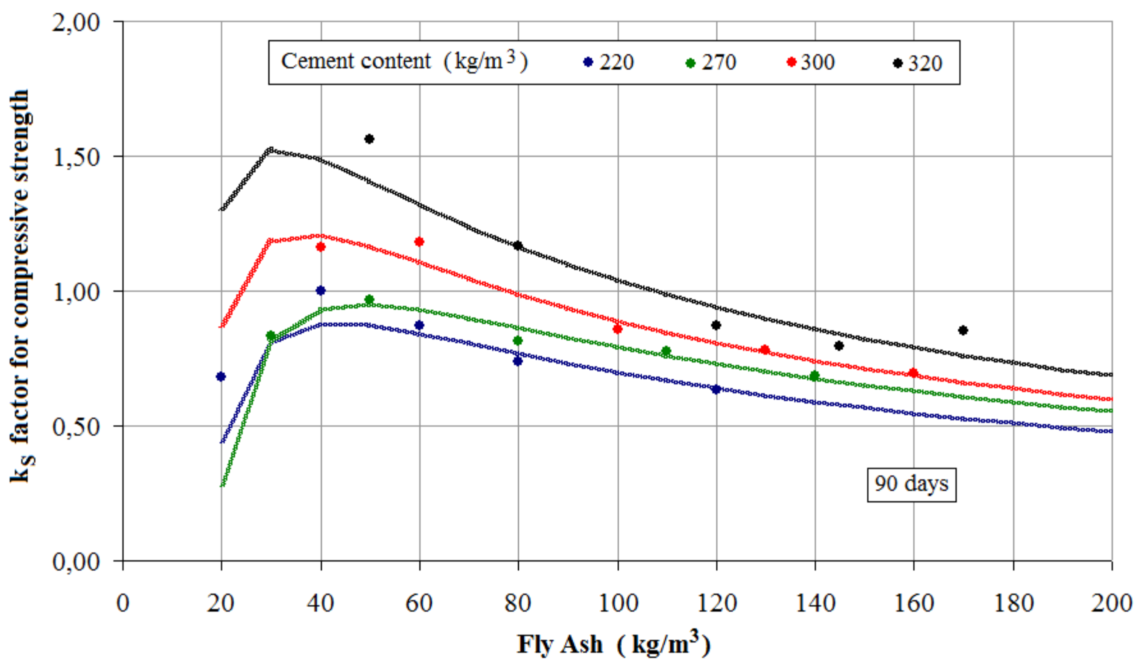

Figure 3. Efficiency factor k_S vs fly ash content for compressive strength at 90 days curing

Increasing the cement content at a given age and fly ash content, the efficiency factor k_S increases. Increasing the fly ash content at a given cement content, the efficiency factor k_S

increases to a peak, then decreases (A. Oner et al., 2004). The experimental data are much bigger than the values suggested by the standards. These values have been reached after only two days. After 28 days k_S was between 0.40 and 1.17 , and after 90 days k_S was between 0.63 and 1.56 . This depends on cement and fly ash content. According to Table 6, for all of the twenty-four concretes, at a given cement content if the fly ash content increases, then also $(C_{eq})_{Cl}$ increases. According to Table 6, the equivalent cement values related to chloride penetration can be well modelled with the following law:

$$(C_{eq})_{Cl} = A_5 \cdot P^{A_6} \qquad (11)$$

With A_5 , A_6 constant values depending on cement content.

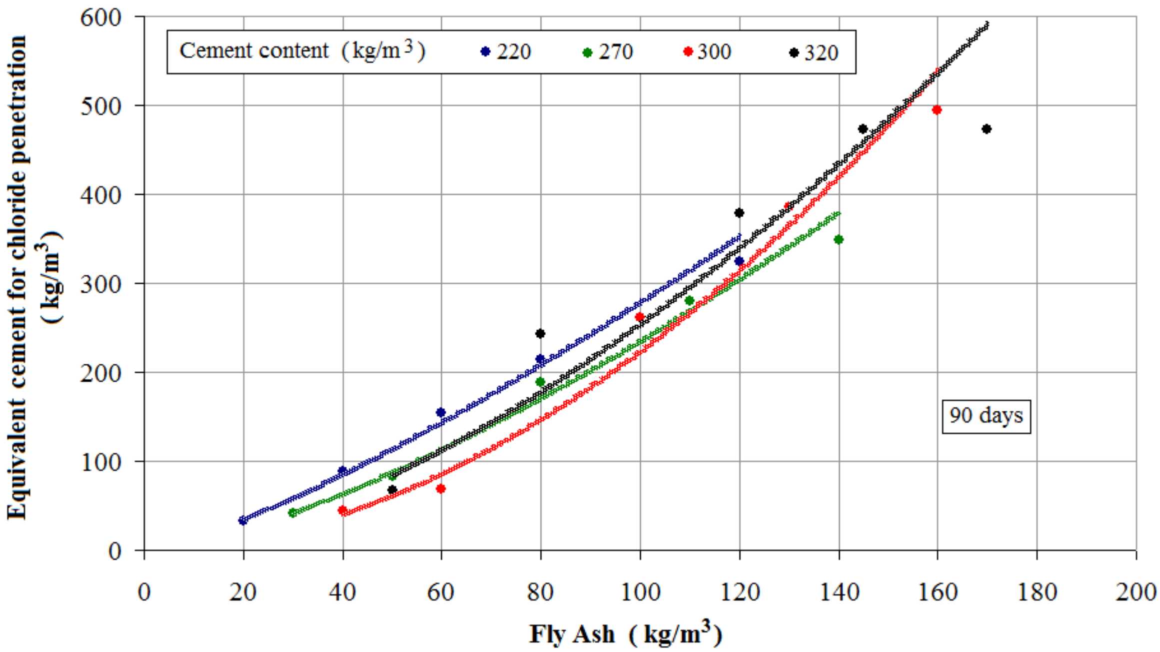

Figure 4. Equivalent cement vs fly ash content for chloride penetration at 90 days curing.

Assuming the (2_B), the k_{Cl} vs "P" curve can be well modelled with the following law:

$$k_{Cl} = A_5 \cdot P^{(A_6 - 1)} \qquad (12)$$

Figure 5 shows, for any cement content, the k_{Cl} – P trendlines, compatible with (12). Differently from k_S, the efficiency factor k_{Cl} doesn't increase when the fly ash content "P" increases.

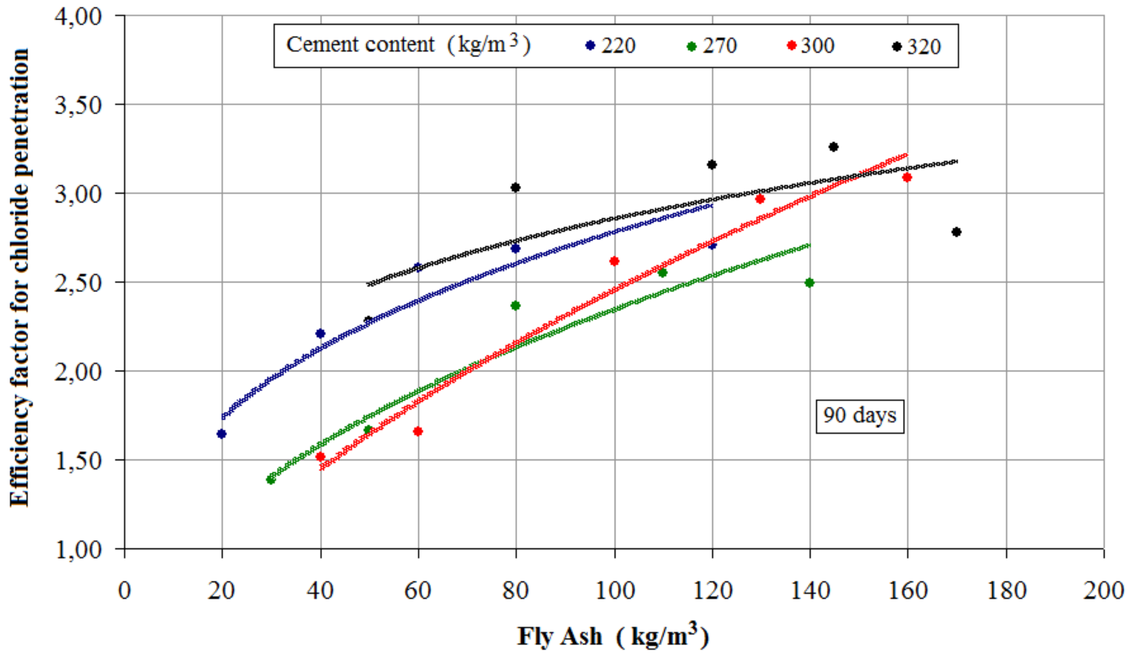

Figure 5. Efficiency factor vs fly ash content for chloride penetration at 90 days curing

After 90 days k_{Cl} was between 1.34 and 3.26 , depending on cement and fly ash content.

CONCLUSIONS

The effects of fly ash on the concrete's properties was described using the efficiency factor. In this study the fly ash efficiency factor was referred to two very important concrete properties: compressive strength and permeability to chlorides. The variability of aforesaid efficiency factors depends on cement content, fly ash content and age of concrete. The experimental data obtained in this study show that the efficiency factors suggested by European standards are much lower, especially when referred to 56-90 days aged concrete.

REFERENCES

Oner, A., Akyuz S. , Yildiz R. (2004) "*An experimental study on strength development of concrete containing fly ash and optimum usage of fly ash in concrete",* Cement and Concrete Research 35 (2005) 1165-1171.

Papadakis V.G. , Tsimas S. (2002) "*Supplementary cementing materials in concrete Part I: efficiency and design"*, Cement and Concrete Research 32 (2002) 1525-1532.

Papadakis V.G. , Antiohos S. , Tsimas S. (2002) "*Supplementary cementing materials in concrete Part II: A fundamental estimation of the efficiency factor"*, Cement and Concrete Research 32 (2002) 1533-1538.