Cement & Concrete Composites 25 (2003) 61–67

Cement & Concrete Composites

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Strength development of ternary blended cement with limestone filler and blast-furnace slag

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Received 26 November 2001; accepted 27 November 2001

Abstract

The benefits of limestone filler (LF) and granulated blast-furnace slag (BFS) as partial replacement of portland cement are well established. However, both supplementary materials have certain shortfalls. LF addition to portland cement causes an increase of hydration at early ages inducing a high early strength, but it can reduce the later strength due to the dilution effect. On the other hand, BFS contributes to hydration after seven days improving the strength at medium and later ages.

Mortar prisms in which portland cement was replaced by up to 20% LF and 35% BFS were tested at 1, 3, 7, 28 and 90 days. Results show that the contribution of LF to hydration degree of portland cement at 1 and 3 days increases the early strength of blended cements containing about 5–15% LF and 0–20% BFS. The later hydration of BFS is very effective in producing ternary blended cements with similar or higher compressive strength than portland cement at 28 and 90 days. Additionally, a statistical analysis is presented for the optimal strength estimation considering different proportions of LF and BFS at a given age. The use of ternary blended cements (PC–LF–BFS) provides economic and environmental advantages by reducing portland cement production and CO_2 emission, whilst also improving the early and the later compressive strength.

Keywords: Limestone filler; Blast-furnace slag; Mortar; Compressive strength; Hydration degree; Ternary blended cement

1. Introduction

Since 1970, considerable research effort has been spent on the use of supplementary materials as partial replacement of portland cement. These materials are natural resources (pozzolan, limestone, metakaolin) or by-products from other industries (fly ash, slag from different metallurgy processes, silica fume, rice husk ash, etc.).

Around the world, binary blended cements are standardised (e.g., ASTM C 595, EN 197, BS 146) such as portland slag cement, pozzolanic cements and limestone filler portland cements. Types of blended cement standardised depend on the available resources in the different countries and then several combinations can be found. The benefits of addition of active supplementary materials and fillers to portland cements are well documented [1,2].

During the 1990s, the use of cement made with portland cement and two supplementary materials, also called ternary or composite cements, has been increased because it presents more advantage than some binary cements [3–8]. Ternary blended cements containing the combinations of fly ash-silica fume or slag-silica fume are common in practice [9] and several studies have been published [3–7].

In Europe, the EN 197 standard identifies two types of portland composite cements according to replacement level of active supplementary materials (slag, silica fume, natural pozzolan, fly ash): type II/A-M containing 6–20% and type II/B-M containing 21–35%. These cements, as other types defined by this standard, can contain a proportion up to 5% of minor additional constituent and they are classified for different strength class according to the strength gain until 28 days.

Latin–American countries have also standardised composite cements. In Brazil, the EB-2138/91 standard

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PII: S0958-9465(01)00056-7

defines two types of portland composite cements: the type CPII-E contains slag to 34% plus a maximum of 10% of limestone filler and the type CPII-Z contains pozzolanic materials up to 14% and a maximum of 10% of limestone filler. In Argentine, portland composite cement was standardised in 1997 (IRAM 1730) and it can contain 0–35% of two or more additions (slag, pozzolan and calcareous materials). In Mexico, composite cement was recently standardised (NMX C-414-0/99).

Addition of limestone filler to clinker completes the fine fraction in the granulometric curve of cement without an increment on water demand, improves the cement packing and blocks the capillary pores. It interferes during hydration of C_3A forming carboaluminates and delays or impedes the ettringite-monosulfoaluminate transformation [10]. It also constitutes nucleation sites of calcium hydroxide crystals at early hydration ages [11,12] accelerating the hydration of clinker particles especially the C_3S [13,14]. Consequently, it improves the early strength, but it does not have pozzolanic properties and it does not produce C–S–H [15]. Finally, an associated effect of limestone addition is the reduction of potential cementing material, commonly called dilution, causing a reduction of later strength. For severely aggressive environments, more important durability problems reported in portland limestone cements are susceptible to sulphate attack (especially, thaumasite formation) and chloride-ion diffusion depending on the level of addition [16–18].

There is a general agreement that the principal hydration products formed when blast-furnace slag is mixed with portland cement and water is essentially C–S–H similar to the compound produced by the hydration of calcium silicates of portland cement [9]. The rate of hydration of blast-furnace slag is initially lower than that of portland cement. Thereafter, portland cement containing blast-furnace slag typically shows a reduction of strength at early ages (7–20 days) and similar or greater strength at later ages [9]. The addition of blast-furnace slag, regardless of composition and replacement level, reduces the permeability and the ionic diffusion of chloride in well-cured concrete [9]. Recently, addition of blast-furnace slag to reduce the damage caused by sulphate attack in concrete containing limestone aggregates has been investigated [19].

From the above description, it can be inferred that the combination of limestone filler and blast-furnace slag in a ternary blended cement can help to formulate a cement with adequate development of strength, because limestone filler contributes to the early strength and the blast-furnace slag increases the long-term strength. For a given portland cement, the problem to solve is the proportions of limestone filler and blast-furnace slag to obtain the optimal strength. The optimal results could differ when the materials are used as addition to portland cement or they are used in an intergrinding process because these materials have different grindabilities modifying the particle size distribution of the component.

The present paper is part of a wide research program, tending to determine the mechanical and durability performance of concrete containing ternary blended cement. The research reported herein provides information for the optimisation of the compressive strength in ternary blended cement containing limestone filler and blast furnace slag.

2. Experimental

A portland cement (PC) with a mineralogical composition (Bogue) of $C_3S = 58\%$, $C_2S = 18\%$, $C_3A = 2\%$ and $C_4AF = 13\%$ was used as reference in all mortars. Its low C_3A content is characteristic in portland clinkers produced in Argentine. Supplementary materials used were limestone filler (LF) obtained from a good limestone quarry containing 85% of $CaCO_3$ in calcite form without clay minerals and quartz as the main impurity and a ground blast-furnace slag (BFS) with a chemical modulus (C+M+A/S) of 1.8. Detailed chemical composition and physical characteristics of these materials are reported in Table 1.

Eleven blended cements were formulated varying the replacement of LF from 0% to 20% and the replacement of BFS from 0% to 35%. All replacements were made by mass. Table 2 shows the combination of blended cements studied in this experimental work.

For each blended cement, mortar was made using a well graded siliceous sand according to the ISO-RILEM guidelines and a cement to sand ratio of 1:3. The water to cementitious material ratio (w/cm) was 0.50. For the mixtures studied, results of flow tests (ASTM C 109) varied from 111% to 122% showing that both additions or their combinations did not affect negatively the water demand of mortar. Mixtures were cast into $40 \times 40 \times 160$ mm^3 prismatic moulds and mechanically compacted in two layers. After casting, moulds containing the specimens were covered with a plastic sheet and stored in the laboratory environment for 24 h. At this age, specimens were demoulded and immersed in lime saturated water until test time at 20 ± 1 °C.

At 1, 3, 7, 28 and 90 days, compressive strength was determined on pieces of prisms, according to ISO 679 standard, resulting from previous flexural strength test. Data reported represent the average values obtained on three specimens corresponding to six compressive strength values.

After test, fragments of mortar were ground and used to determine the amount of non-evaporable water

Table 1
Chemical composition and physical characteristics of materials used

	Portland cement	Limestone filler	Blast-furnace slag
Chemical composition (%)			
SiO_2	21.44	10.63	34.27
Al_2O_3	3.40	1.20	12.68
Fe_2O_3	4.20	0.78	0.84
CaO	63.45	47.16	40.58
MgO	0.57	0.39	9.75
K_2O	1.18	0.34	0.41
Na_2O	0.04	–	0.05
SO_3	2.91	0.16	0.41
Loss by ignition	1.82	37.50	0.11
Physical characteristics			
Specific gravity	3.15	2.73	2.80
Fineness (Blaine) (m^2/kg)	321	710	458
Retained on sieve (%)			
75 μm (#200)	3.9	5.0	0.0
45 μm (#325)	16.4	14.3	1.3
Position parameter x (μm)[a]	28.81	13.2	18.87
Homogeneity parameter, n[b]	0.93	0.61	1.05

[a] Characteristic diameter of particle size distribution obtained at a cumulative mass of 63.2%.
[b] Slope of particle size distribution curve representing the wide of distribution.

Table 2
Composition and compressive strength of blended cements used

Mortar	Portland cement	Limestone filler	Blast-furnace slag	Compressive strength (MPa)				
				1 d	3 d	7 d	28 d	90 d
PC	100			8.3	20.1	31.3	45.1	46.8
PC10LF	90	10		9.6	26.3	32.1	45.0	44.5
PC20LF	80	20		7.2	23.0	29.9	43.5	41.9
PC10S	90		10	7.5	25.1	32.5	40.8	44.3
PC20S	80		20	6.5	21.5	27.8	39.5	47.2
PC35S	65		35	5.4	17.7	26.0	40.9	50.9
PC10LF10S	80	10	10	9.7	22.1	33.1	42.4	47.3
PC10LF20S	70	10	20	9.6	21.0	32.1	42.2	44.2
PC10LF35S	55	10	35	8.8	21.2	31.0	42.6	47.9
PC20LF10S	70	20	10	6.4	18.2	30.0	38.1	42.7
PC20LF20S	60	20	20	5.9	16.3	27.8	43.4	50.6
PC20LF35S	45	20	35	4.3	13.4	24.1	38.8	42.2

according to the procedure proposed by Powers [20]. This value was used as a means to estimate the progress of hydration reactions assuming that the filler is a chemically non-active constituent and all grains of BFS added are reactive. Results provided by this method are not accurate, but they are sufficiently indicative of hydration reaction progress. The relative combined water was calculated as the ratio between combined water in the blended cement and the combined water in plain portland cement at the same test age.

3. Results and discussion

Table 2 reports the mean value of compressive strength for cements used at all ages. Fig. 1 illustrates the typical development of compressive strength for mortars containing portland cement (PC), 20% of LF (PC20LF), 20% of BFS (PC20S) and ternary blended cement containing 10% of LF plus 20% of BFS (PC10LF20S). It can be observed that differences of strength are not very significant. However, a general tendency can be showed for each type of blended cement. For filler blended cements, compressive strength is generally higher than the corresponding PC at early ages, comparable strength at 7 days and lower strength at later ages. In mortar containing 20% BFS, compressive strength is generally lower than PC mortar until 28 days and then it is greater. However, the compressive strength of ternary blended cement has strength values close to PC for all ages studied.

The problem to solve is which are the optimum percentages of blending BFS and LF simultaneously with the portland cements to obtain a given strength class of

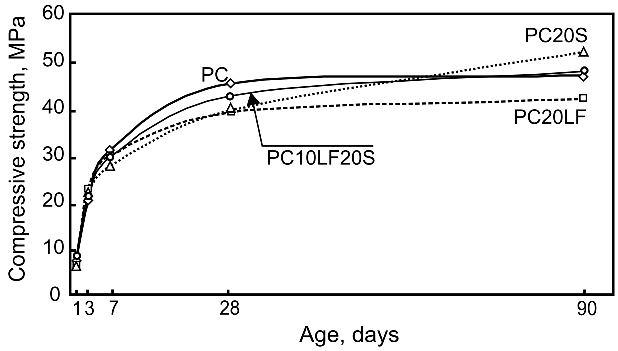

Fig. 1. Typical compressive strength gain on mortar made with various mixes.

ternary blend cement or the maximum strength for a given age. For this purpose, multivaried regression analyses were carried out and a model was developed at each age. This is based on the quadratic response surface model where the two experimental variables (the proportion of LF and BFS used as partial replacement of cement) have been used. The model is as follows:

$$f_{c(n)} = a + bx_1 + cx_2 + dx_1^2 + ex_2^2 + fx_1x_2,$$

where $f_{c(n)}$ is the compressive strength at n days, x_1 is the percentage of LF, x_2 is the percentage of BFS and a, b, c, d, e and f are the coefficients obtained after the best fit to models using the least squares method. The coefficients for the equation at 1, 3, 7, 28 and 90 days are shown in Table 3, where R^2 is the coefficient of determination.

Fig. 2 illustrates the isoresponse curves of compressive strength showing the interaction effect of LF and BFS for the domain studied in the ternary system. At one day (Fig. 2(a)), the stationary point corresponding to the maximum compressive strength is obtained by the replacement of 10% of LF and a very little content of BFS. The maximum is 16% higher than the strength of PC mortar. The isoresponse curves have a similar contour for three and seven days (Figs. 2(b) and (c)), while the zone of maximum strength is located around 10% of LF replacement and low level of BFS replacement (0–12%). However, the contour of isoresponse curves changes markedly at 28 days. Mortars have a similar compressive strength for mixtures containing up to 10% of BFS and any content of LF. As at earlier ages, the maximum strength is located at very low replacement of BFS and 10% of LF. At 90 days, the maximum compressive strength is obtained when the ternary blended cement contains the larger proportion of BFS (35%) and around 7.5% of LF. At this point, the strength was 7% higher than the corresponding PC mortar.

In summary, the point of maximum strengths is around 10% of LF and low BFS replacement level at the early ages (1, 3 and 7 days). After 28 days, this point moves toward the high level of BFS replacement and low LF content.

This behaviour can be attributed to the contribution of limestone filler to hydration acceleration at early ages, but this effect cannot compensate for the dilution of clinker grains when the replacement level for both supplementary materials is very large. Under these circumstances, there is a negative effect on mortar strength. At later ages, the BFS produces a cementing material (C–S–H) that improves the pore filling and enhances the strength when the BFS replacement increases. The dilution effect produced by filler addition is also present, and high replacement levels of limestone filler produce a decrease of strength. Additionally, the increase in w/c ratio should be computed in cements containing LF at all ages or in cements containing BFS at early ages due to the little or null contribution to produce cementing compound by both supplementary materials. For example, the w/c is 0.625 for mortars containing 20% of LF.

To corroborate this explanation for the strength developed in binary and ternary blended cements, the results of relative non-evaporable water (W_{ne}) are illustrated in Fig. 3. For cements containing only limestone filler addition (Fig. 3(a)), the relative W_{ne} increases when the filler content increases especially at early ages. At 3 days, the relative W_{ne} is 1.16 and 1.32 for 10% and 20% LF, respectively. It should be taken into account that clinker particles have the same particle size distribution. At later ages, the progress of portland cement hydration tends to minimise this advantage and it cannot compensate for the dilution. The fineness of limestone filler used has little influence on the compressive strength, because the effects of

Table 3
Coefficients model for compressive strength

Age (days)	Coefficients						R^2
	a	b	c	d	e	f	
1	7.83	33.76	3.49	−161.00	−34.75	−10.80	0.85
3	22.45	32.81	5.85	−149.25	−53.21	−86.67	0.87
7	31.02	34.33	9.29	−180.74	−72.90	−0.42	0.87
28	44.00	43.12	−35.71	−222.88	78.39	−20.36	0.85
90	44.69	39.96	12.97	−253.38	12.06	−75.06	0.83

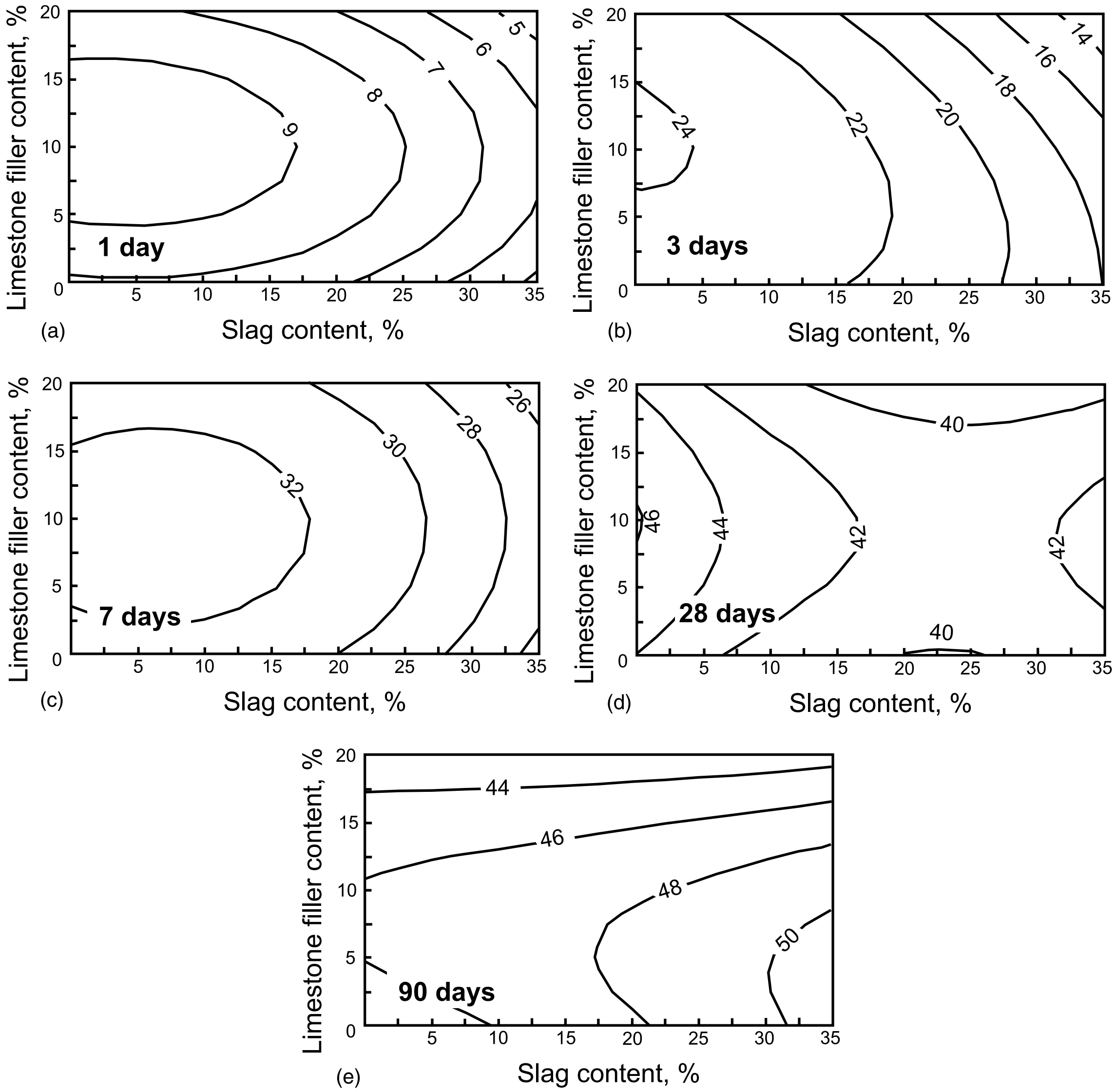

Fig. 2. Compressive strength (in MPa) isoresponse curves for the ternary system at different ages.

dispersion and the packing of cement grains are equivalent when LF particles are smaller than 75 μm [12,21].

Low percentage of BFS addition also produces a positive filler effect [22] causing an increase of relative W_{ne} as shown in Fig. 3(b) for mixtures containing 10% BFS at 3 days. Thereafter, the dilution effect of clinker grains is preponderant because the BFS does not react as indicated by the non-evaporable water. Consequently, the compressive strength decreases when the BFS content increases.

After seven days, the BFS reacts slowly forming calcium silicate hydrated that augment the relative W_{ne} attaining to similar or higher values at 90 days. At this age, BFS participates in the W_{ne} estimations and the dilution effect is absent.

For a given portland cement, the age at which the BFS contributes to hydration depends on the particle size of addition and its reactivity. BFS used in this work has only 7% of particles higher than 45 μm and 60% of particles higher than 10 μm. For this particle size, the contribution to strength will be expected beyond 21 days [23].

For ternary blended cements, the evolution of relative W_{ne} is shown in Figs. 3(c) and (d). The filler effect appears fundamentally during the first days of hydration and the contribution of BFS to the cementing compounds appears after seven days of hydration. At 90 days, the relative W_{ne} ranged from 1.07 to 1.10 for ternary blended cement containing 10% of LF and from 1.14 to 1.18 for ternary blended cement containing 20% of filler. Finally, ternary blended cements containing 10% of LF and up to 35% of BFS show low compressive

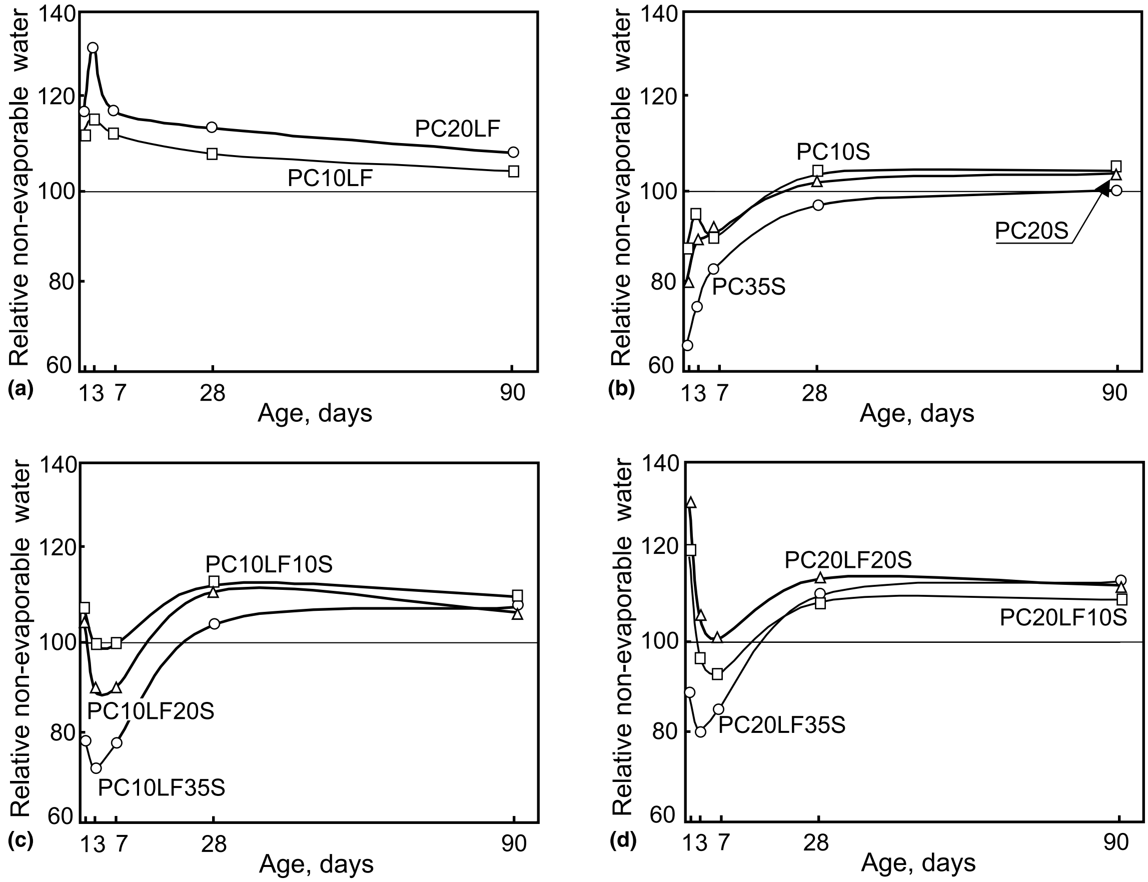

Fig. 3. Evolution of relative non-evaporable water of mortars.

strength at early ages when BFS content increases due to its slow rate of hydration. Up to seven days, the high hydration degree caused by LF can only compensate some part of the dilution effect. At later ages, the BFS contributes to enhance the strength.

Finally, the solution for the optimum proportions of ternary blended cement that satisfies the requirement of particular strength gain curve or the strength requirement of the standard (e.g., EN 197, EB-2138 or IRAM 1730) for given materials can be solved using the superposition of the contour curves. Briefly, the procedure steps are:

1. select the strength curve gain to obtain in the ternary blended cement,
2. for each age (Fig. 2), select the regions in graphic with higher strength than the limit proposed in step 1,
3. trace the limit line for the maximum percentages of supplementary materials established in the standard,
4. superpose all regions and determine the intersection area.

For example, if strength limits for the ternary blended cements are 8, 20, 30, 40 and 45 MPa at 1, 3, 7, 28 and 90 days, respectively, the superposition of regions that meet with these criteria are plotted in Fig. 4. Also, the limit line of maximum amount of both additions (35%) in the ternary blended cement proposed by standard is plotted in this figure. The zone resulting from the intersection of the strength regions and standard requirement are the solutions for the proportion of additions in ternary blended cement that meet the strength gain curve proposed. This procedure solves propor-

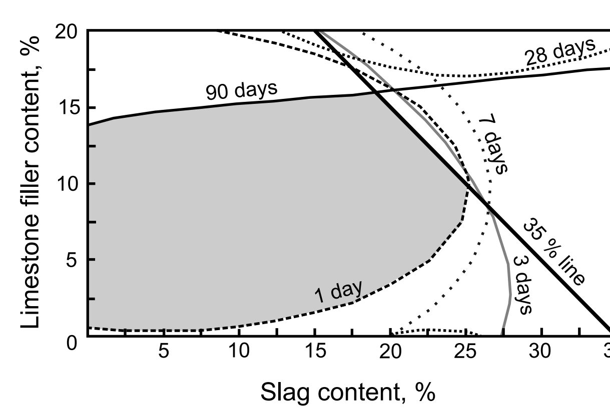

Fig. 4. Proportions of LF and BFS for strength desing.

tions of LF and BFS using a limited number of mixture combinations and it can be extended to other requirements. It can be observed that the zone is limited by the isoresponse curve of one-day's strength for the maximum content of BFS and the 90 days' compressive strength for the maximum content of limestone filler of cement. The maximum proportion proposed by the standard also limits this region for combinations.

4. Conclusions

For the limestone filler – blast-furnace slag – portland cement system containing up to 20% of LF and up to 35% of BFS, the following conclusion can be drawn:

- The combination of limestone filler and blast-furnace slag is complementary: the limestone filler improves the early strength of cement while the BFS improves the later strength by the cementing reaction that refines the pore systems. It is proved that the ternary cementitious blend of limestone filler offers advantage over the binary blended cements and plain portland cements.
- Using regression and other statistical methods, the isoresponse curves for a given property can help to define some possibilities of ternary combinations that meet with the imposed requirements and use more abundant or less expensive supplementary materials in each country or regions.
- The use of ternary cements containing an adequate combination of limestone filler and blast-furnace slag can lead to an efficient use of natural resources and by-products, saving energy consumption and reduce gaseous emissions without compromising the mechanical properties of cement.

Acknowledgements

The research on which this paper is based was carried out under PICT97 12-00000-01323 project supported by the Agencia Nacional de Promoción Científica y Técnica and the Secretaría de Ciencia y Técnica de la Universidad Nacional del Centro de la Provincia de Buenos Aires.

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