Pergamon

Cement and Concrete Research, Vol. 26, No. 6, pp. 883-893, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00071-3

OPTIMIZATION OF HIGH STRENGTH LIMESTONE FILLER CEMENT MORTARS

Moncef Nehdi, Sidney Mindess
Department of Civil Engineering, University of British Columbia
2324 Main Mall, Vancouver, B.C., Canada, V6T 1Z4

Pierre-Claude Aïtcin
Département de Génie Civil, Université de Sherbrooke, P.Q., Canada, J1K 2R1

(Refereed)
(Received December 4, 1995; in final form April 9, 1996)

ABSTRACT

The effect of limestone microfiller replacement of cement on the mechanical performance and cost effectiveness of low w/c ratio superplasticized portland cement mortars was investigated. The experiments were designed based on a so-called uniform-precision factorial plan. Cement pastes of different w/b ratios and incorporating various proportions of limestone powder and/or silica fume were designed to have a constant flow time. Mortars corresponding to the different cement pastes were made, their 1, 3, 7, 28 and 91 day compressive strengths were measured, and their cost effectiveness was analyzed. The statistical approach used permitted the calculation of the isoresponse curves for the parameters under study over the experimental domain and the optimization of their effect.

Introduction

Considerable research has been carried out within the last 15 years on the use of ground limestone in ordinary concrete. The main concerns were to improve the cost effectiveness of cement, to substitute limestone for gypsum as a set regulator, to improve the workability and stability of fresh concrete, and in some instances to improve durability [1]. In recent years, the emergence of high strength cement based materials has catalyzed a new interest in microfillers. Coupled with the effect of superplasticizers, these ultrafine powders improve the particle packing of the cementitious system, its rheological properties in the fresh state and its mechanical properties and durability. The most successful of these microfillers, silica fume, has seen its cost steadily increasing and its availability decreasing. This has stimulated the search for other substitutes. Various materials having pozzolanic properties have been successfully used in concrete, such as rice husk ash [2] and zeolite [3].

It has been observed that silica fume does not enhance the mechanical properties of cement paste as it does for concrete. This has led to some controversy as to the fundamental mechanisms by which improvements of concrete properties due to silica fume additions come about [4]. Recent research has shown that the physical filler effect imparted by silica fume due to the densification of the paste-aggregate transition zone and the refinement of the hydration products via a so-called nucleation mechanism can be at least as important as, and perhaps even more significant than, the pozzolanic effect [5,6]. This has given rise to the idea that inert and semi-reactive microfillers can probably play a similar physical role to silica fume, provided that they have the same fineness and particle shape, can be dispersed efficiently, and do not compromise the water demand. Some success in this direction has been achieved using carbon black [5,6], rutile [7], ground mill materials [8] and combinations of pozzolanic and ground mill products [9,10].

For high strength concrete (HSC), a significant part even of the cement acts as a filler due to the low w/c ratio and hence incomplete hydration. With the expected increase in cement production to meet the needs of a steadily growing world population, and with the urgent need to reduce the amount of energy consumed and CO_2 released in the air (the production of 1 ton of cement releases approximately 1 ton of CO_2), there will be an increasing pressure to reduce cement consumption. For HSC to be competitive in the future depends to some extent on the ability to use microfillers such as industrial byproducts and unprocessed materials as cement replacements, without compromising the fundamental characteristics of the HSC. This can be achieved by making better use of the hydraulic potential activity of the clinker when it is ground finer and by adding microfillers.

Since limestone is available at all cement plants (not all limestones are used for filler cements) and often has no additional transportation costs though, of course, associated with its possible use as a filler in cement, it is the focus of this work. Although the effect of using limestone powder in normal concrete has been extensively studied, the effect of adding limestone microfillers in low w/c ratio superplasticized concrete is not fully understood. This paper describes the effect of a limestone microfiller on the compressive strength and cost effectiveness of low w/c ratio mortars. Subsequent work will investigate similar effects in concrete.

Materials

Ordinary ASTM Type I cement (OPC), high purity limestone microfiller (LF) having a 3 μm mean particle size, and condensed silica fume (SF) were used. Their chemical and physical properties are summarized in Table 1. The particle size distributions for the cement and the limestone powder are illustrated in Fig. 1. A naphthalene sulfonate superplasticizer (HRWR) and tap water were employed for the mixing. The different mortars were all made with standard Ottawa sand.

Experimental Procedures

Cement pastes were mixed using a grout mixer equipped with a helix rotating at 3500 rpm. The mixing procedure was identical for all the cement pastes. First, the superplasticizer was added to the mixing water which was at a constant temperature of 17 ± 1 °C. Then the binder was added over a period of 1 min while mixing the grout at a constant speed of 3500 rpm for 3 min. A rest period of 1 min followed during which the inner sides of the mixer pan were scraped down. Finally, the grout was mixed at the same speed for 1 additional min.

The flow time was measured just after the mixing using a modified Marsh cone with a 5 mm outlet. A volume of 1.1 L of grout was placed in the cone while locking the outlet with the index.

TABLE 1
Chemical and Physical Properties of the Three Binders

Chemical composition [%]				Physical tests	OPC	SF	LF
Component	OPC	SF	LF				
SiO_2	21.5	93.6	≤0.25	Init. set. time [min]	125		
Al_2O_3	4.6	0.3		Final set. time [min]	230		
Fe_2O_3	3.2	0.5		Aut. expansion [%]	0.04		
CaO (total)	63.2	0.3		Air cont. of mortar [%]	7		
CaO (free)	0.6			Comp. strength at 3d [MPa]	24.6		
SO_3	2.7			7d [MPa]	30.0		
MgO	3.0	0.5		28d [MPa]	38.5		
$Na_2O + K_2O$	0.84	1.4		Passing 45 μm sieve (%)	87.8	100	100
Loss of ignition	0.7	2.8		Specific surface (Blaine) [m^2/kg]	346		
Insol. residue	0.2		0.35	Specific surface B.E.T. [m^2/kg]		17490	2300
C		1.9		Particle size range (sedigraph) [μm]		.04 -.28	0.2-12
$CaCO_3$			98.2	Mean particle size [μm]	14	0.18	3
$MgCO_3$			1.2	Residue on 325 mesh [%]		≤0.005	
				Specific gravity	3.16	2.23	2.71
Potential composition of the cement [%]				C_3A : 7	C_4AF : 10	C_3S : 51	C_2S : 23

A chronometer was switched on while removing the index and the time was measured for each 100 mL flow of grout up to 1 L. The superplasticizer dosage was varied for each cement paste until achieving a flow time of 110 ± 10 sec at 5 min. A flow time of 110 sec was selected because shorter flow times for the lower w/b ratio cement pastes were not achievable even at the HRWR saturation dosage.

A mortar corresponding to each grout was made using standard Ottawa sand. A proportion of sand of 2.3 times the mass of the binder was generally found suitable to achieve a flow of 100 ± 10% on a flow table for the designed mortars. The mixing procedure for the mortars was according to ASTM C 305 - 94 (Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency). Fifty mm standard cubes were cast and cured in the laboratory at 23 °C for 24 h then demoulded and cured in lime saturated water at room temperature till testing. The compressive strengths presented represent the average values obtained on 3 specimens.

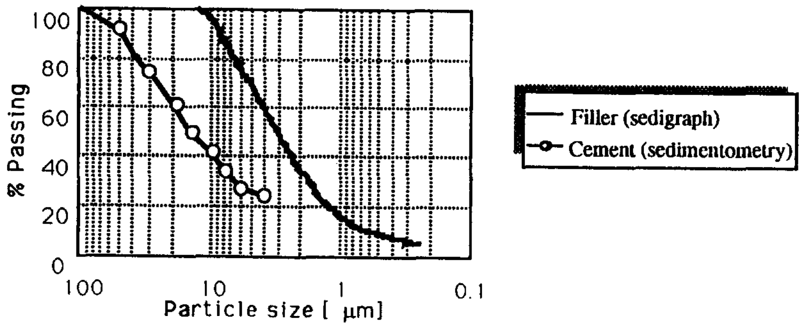


FIG. 1.
Particle size distributions of the cement and the limestone filler.

Experimental Plan

The experiments were designed according to a 2-level uniform-precision plan as shown in Fig. 2. This approach was selected to limit the number of mortars to be investigated, while first and second order models could be used to fit the data. In addition, this method highlights the significance of the effect of the experimental variables and their interactions, and has a predictive capability for the response of other experimental points located within the experimental domain.

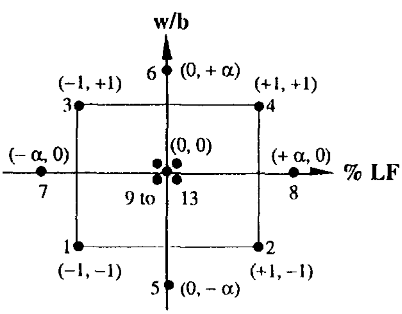
The experimental plan consisted of a 2-level factorial plan corresponding to mixes 1, 2, 3, and 4 in Fig. 2 (coded ± 1), augmented by 4 axial points corresponding to mixes 5, 6, 7 and 8 in Fig. 2 (coded ± α). The first set of experiments was used to fit a first-order model, whilst the second set allowed for a second-order model. Since a 2-level factorial plan does not allow for an estimate of the experimental error unless some runs are repeated, it is a common practice to augment the design with observations at the center of the experimental domain. Five central points are required for this uniform-precision plan, which affords more protection against bias in the regression coefficients as compared to the most widely used design to fit a second-order model; the centered-composite plan [11]. The sequence in which the experimental points were investigated was randomized to avoid any statistical significance of a blocking effect.

The two experimental variables were the water/binder ratio (w/b) and the proportion of limestone replacement by volume of cement (%LF). All other controllable parameters were kept constant. The same experimental plan was carried out on an OPC and an OPC with 10% silica fume replacement of cement. In addition, reference experimental points where the only variable was the w/b ratio, corresponding to an OPC and an OPC with 10% silica fume replacement of cement, were investigated. The responses of the designed experiments were the 1, 3, 7, 28 and 91d compressive strengths, and the cost effectiveness of the cementitious binder.

Results and Discussion

The data corresponding to the responses which resulted from the designed experimental program were analyzed and plotted using a statistics software package [12].

Effect on Mortar Compressive Strength. Fig. 3 illustrates the isoresponse curves corresponding to the compressive strength data over the experimental domain under investigation. The 1d



Quadratic model for the experimental plan:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 + a_{11}X_1^2 + a_{22}X_2^2$$

Where: X_1 and X_2: experimental variables
Y: response of the experiment
a_i, a_{ij}: coefficients of the model

FIG. 2.
Illustration of the uniform-precision experimental plan.

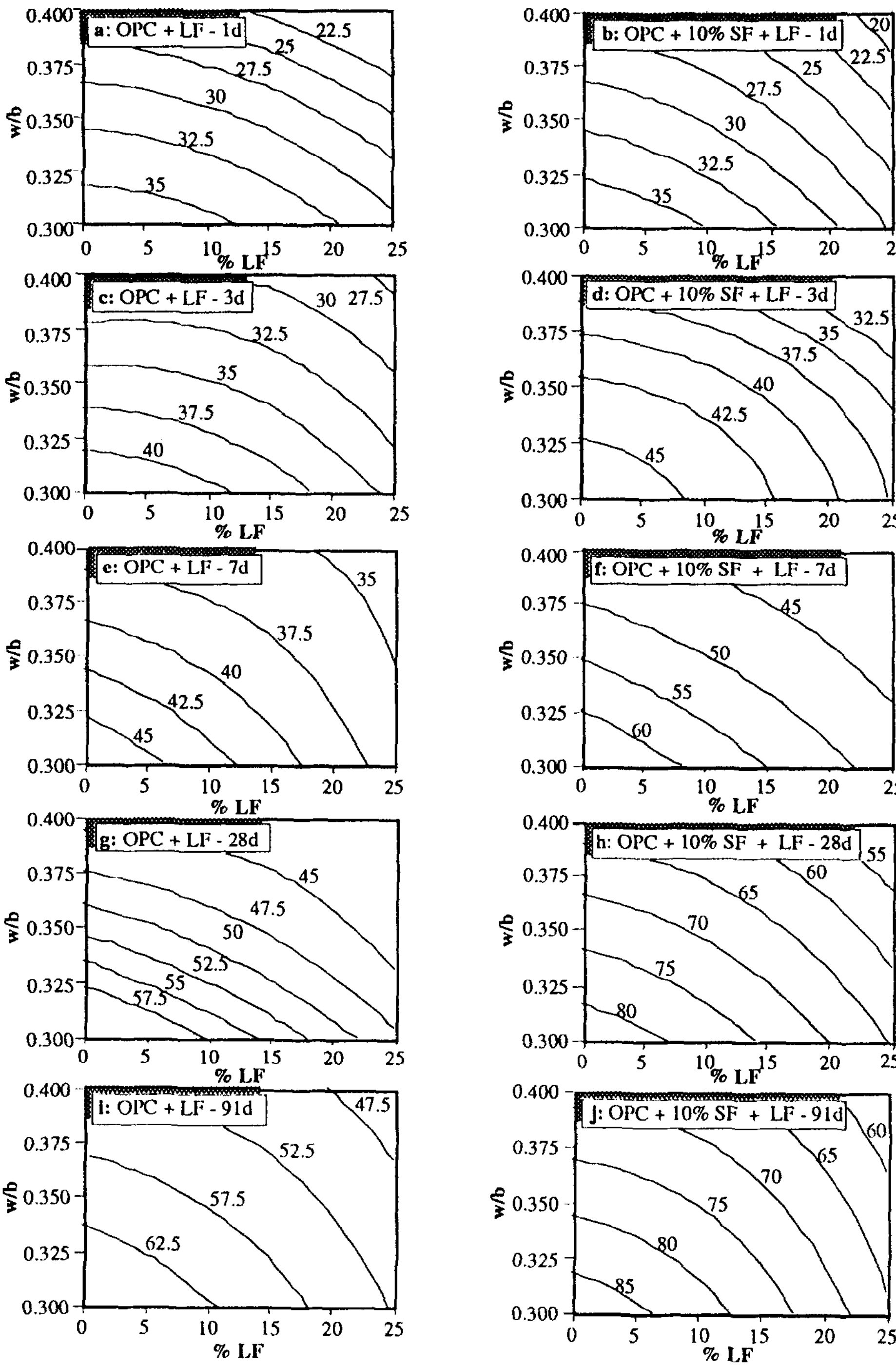


FIG. 3.

Isoresponse curves for the compressive strength of the mortars at various ages [MPa].

compressive strength decreased with increased w/b ratio. It seemed not to be drastically affected by the LF replacement of cement up to about 10 to 15%; then, the response curves became steeper, indicating a significant loss of strength at the higher levels of LF, with the SF mortars being somewhat more sensitive to this latter effect (Fig. 3-a and 3-b). For example, at a w/b ratio of 0.30, 1d compressive strengths of 35 and 32.5 MPa can be achieved with mortars having 12 and 21% LF, respectively, while in the presence of 10% SF, the same strengths can be achieved only with 10% and 15% LF, respectively.

At the age of 3d, the compressive strength was also not significantly affected by the LF replacement of cement up to about 10 to 15%. Then, the response curves again became steeper, and the strength decreased significantly with higher levels of LF replacement (Fig. 3-c and 3-d). The SF mixes started to outperform the non SF mixes at this age. A 3d compressive strength of 40 MPa can be achieved at a w/b ratio of 0.30 using 12% LF replacement of cement (Fig. 3-c), or using 10% SF and 21% LF replacement of cement (Fig. 3-d).

At 7d and later ages, the response curves became somewhat steeper towards the vertical axis, indicating that some early age effects due to the presence of LF are no longer as significant as they were at early ages. The differences in compressive strength between the SF and the non SF mixes became much larger (Fig. 3-e to 3-j).

The good performance of the LF cement at early ages can be mainly attributed to two factors. First, it is believed that $CaCO_3$ accelerates the C_3S hydration, particularly as the $CaCO_3$ becomes finer and its addition rate is increased [13]. $CaCO_3$ also enhances the formation of calcium hydroxide, probably because it provides nucleation sites for its growth [14,15]. Second, $CaCO_3$ is believed to react with C_3A in the presence of water to form calcium carboaluminates ($C_3A.CaCO_3.11H_2O$) [16,17]. The carboaluminates probably behave similarly to the sulfoaluminates in enhancing the early age strength. It was further observed that ettringite formation and its conversion to monosulfoaluminate were accelerated in the presence of $CaCO_3$ [18]. A reaction zone enriched in silica has been observed around calcite grains in filler cements, which may suggest that carboaluminates are not the sole contributors to the early strength. The C-S-H phase is also morphologically different in LF cements from that in OPC [13,19].

One interesting aspect of the above results is the positive effect of replacing some of the cement by a combination of LF and SF. Fig. 4 shows the compressive strength at w/b = 0.33

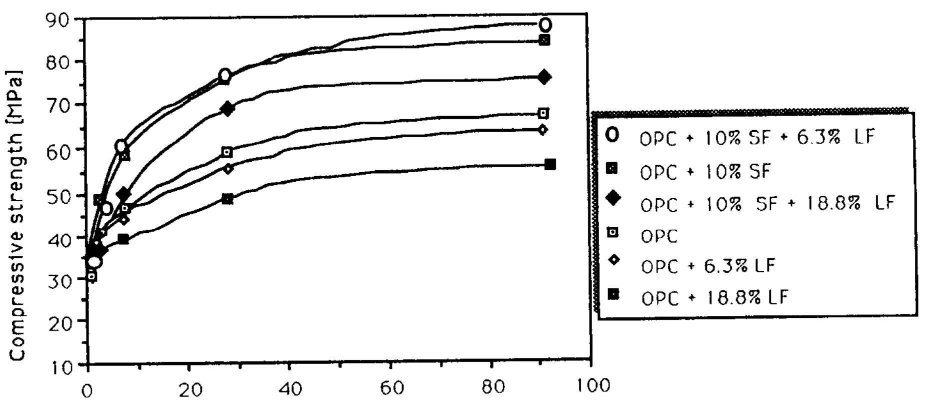


FIG. 4
Comparison of the compressive strength of mortars made with different fillers (w/b = 0.33).

of pure OPC, OPC + LF, OPC + 10% SF and OPC +10% SF + LF mortars. Blending SF and LF simultaneously with cement brought about significant strength improvements compared to the pure OPC and OPC + LF systems, and compared to the OPC + 10% SF system at some LF proportions. This opens up the possibility of partially replacing portland cement by industrial byproducts combined with non-processed fillers. Pozzolanic industrial byproducts can provide long term strength while carbonate additions can increase the early age strength. This can perhaps decrease the required cement production without compromising the overall performance of the cementitious binder.

It is worth mentioning that it is not advisable to extrapolate the results above outside the experimental domain investigated or to other combinations of materials. Although they describe the behavior inside the domain, they do not substitute for other necessary experiments outside this domain or for using other materials.

<u>Cost Effectiveness.</u> The costs of mortars in the following discussion are expressed in Canadian dollars. Only the cost of the binder and the HRWR were considered in the cost estimation of the mortars since the amount of sand was constant in all mixes. Costs of $100/ton for cement and 2$/L for the HRWR were considered generally representative of the trends in the Canadian

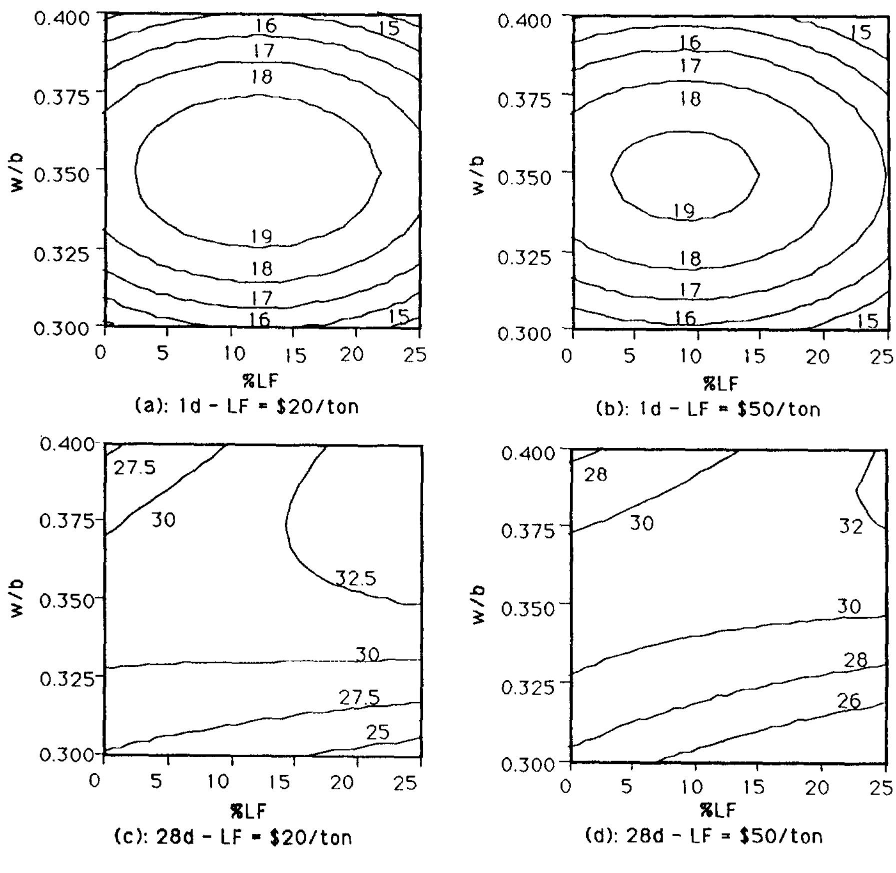


FIG. 5.
CEF isoresponse curves for the OPC+ LF binder [MPA/$ × 100].

market. As the price of SF varies significantly in North America, two values, namely: $300/ton and $500/ton were analyzed. In addition, two tentative costs were investigated for the LF, namely: $20/ton and $50/ton, to assess up to what price the replacement of cement by LF is cost effective. The cost effectiveness for the various binders was considered at early age (1d) and at mature age (28d), because of the different implications of both conditions in the construction site. As a basis for comparison, a cost effectiveness factor (CEF) has been defined. The higher the CEF, the more cost effective is the binder:

$$CEF_i = \frac{fc_i}{C} \times 100 \qquad (1)$$

where CEF_i is the cost effectiveness factor at age i [MPa/$ × 100], $f'c_i$ is the compressive strength of the mortar at age i [MPa], and C is the cost of 1 m^3 of mortar [$ CAN]. The isoresponse curves for the CEF are presented in Fig. 5, Fig. 6 and Fig. 7 for the non SF mortars, the $300/ton SF mortars and the $500/ton SF mortars, respectively.

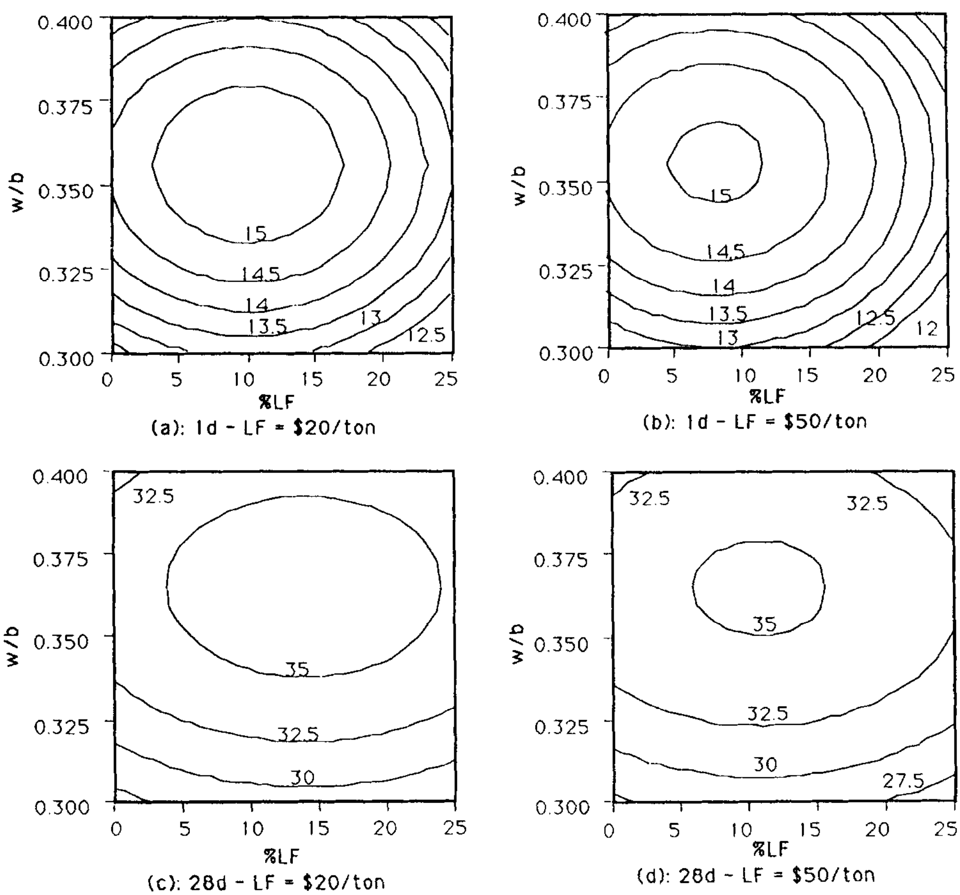


FIG. 6.
CEF isoresponse curves for the OPC + 10% SF + LF binder (SF = $300/ton) [MPa/$ × 100].

Invariably, the CEF at 1d increased with increasing LF up to about 10 to 15%, then tended to decrease for higher addition rates. Optimal conditions were generally observed at the mid-range w/b ratios, and these optimal conditions covered larger areas of the experimental domain when the cost of the LF was lower. The most cost effective mortars at 1d were the non SF ones, which had CEF ranging from 15 to 19 as compared to 12 to 15 and 10.5 to 13.5 for the $300/ton SF and the $500/ton SF, respectively.

At 28d, the CEF for the non SF mortars increased as the LF increased only at the higher and mid-range w/b ratios. The effect was not significant at lower w/b ratio for the $20/ton LF (Fig. 5-c), and was even reversed for the $50/ton LF (Fig. 5-d). For the SF mortars however, the 28d CEF increased with LF up to about 10 to 15%, then tended to decrease for higher addition rates.

Optimal conditions were again observed at mid-range w/b ratios at 5 to 20% LF for the $20/ton LF, and around 10% for the 50$/ton LF. Contrary to the early age behavior, the $300/ton SF mortars were now the most cost effective. Their CEF ranged from 27.5 to 35, as compared to 25 to 32.5 and 25 to 31, for the non SF mortars and the $500/ton SF mortars, respectively.

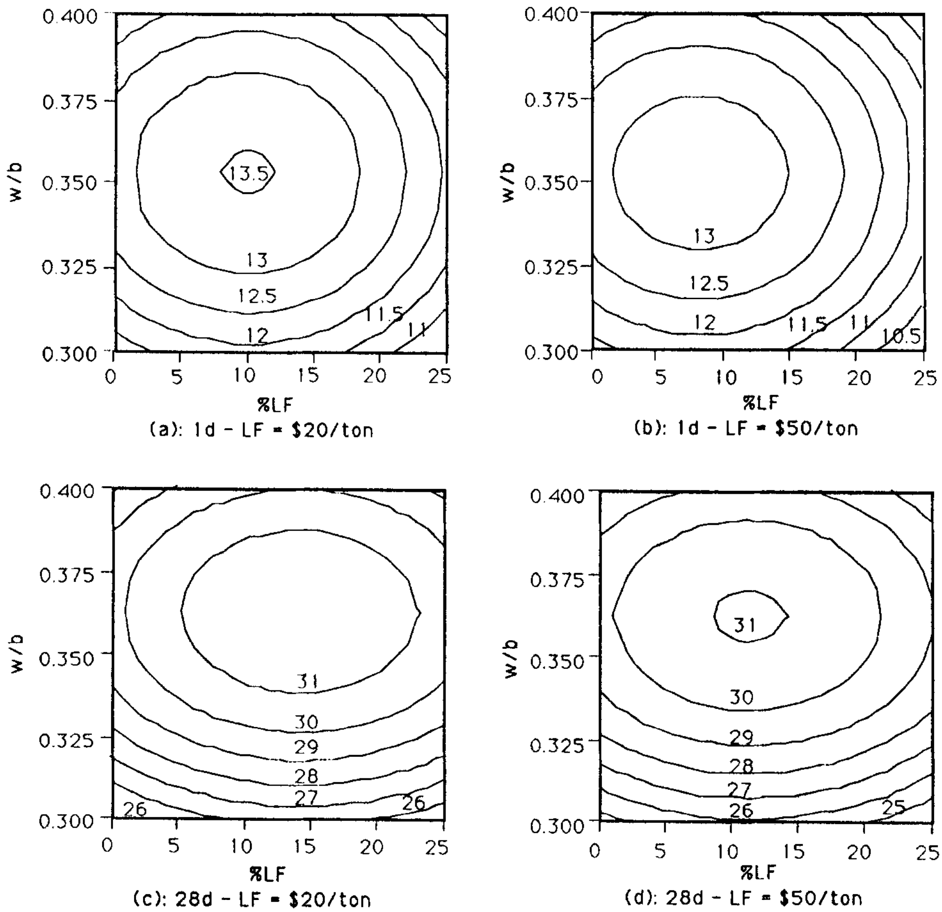


FIG. 7.

CEF isoresponse curves for the OPC + 10% SF + LF binder (SF = $500/ton) [MPa/$ × 100].

It should be realized that the CEF presented above does not account for the energy saved when cement is replaced by LF, nor does it account for the environmental impact of reducing the hazardous emissions released to the air. In addition, this optimization work did not include the potential positive effect of a finer grinding of the clinker to be used in this kind of composite cement. It is also reasonable to expect a much finer LF to play a better role in high strength mixes, though this would increase its cost.

Conclusions

The effect of 0 to 25% limestone microfiller replacement of cement on the compressive strength and cost effectiveness of 0.3 to 0.4 w/b ratio superplasticized cement mortars was investigated in silica fume and non silica fume systems. The experiments were designed based on a statistical model which allowed the isoresponse curves for the various responses to be obtained over the experimental domain. The modeling and prediction of the response of other experimental points in the experimental domain were therefore possible. The following conclusions can be drawn (results should not be extrapolated outside the experimental domain or to other combinations of materials):

1. LF replacement of cement did not significantly affect the strength of mortars at early ages up to about 10 to 15% by volume. Higher levels of LF caused significant strength losses, which were more significant in the SF mixes. At later ages, LF replacement of cement beyond 10 to 15% caused strength losses which were more significant.
2. Blending silica fume and limestone powder simultaneously with cement was efficient in maintaining high 28d compressive strength, which for some LF proportions compared to an OPC + 10% SF system.
3. The early age strength of cement mortars was most cost effective in an OPC system containing about 10 to 15% LF, and can be improved in an OPC + 10% SF triple blended cementitious binder by adding up to 10% LF.
4. The 28d compressive strength of cement mortars was most cost effective in an OPC + 10% SF + LF triple-blended binder containing up to 10 to 15% LF for a $300/ton SF, and can be improved in a $500/ton silica fume triple blended system by adding up to 10% LF.
5. Partial replacement of cement by combined pozzolanic industrial byproducts and unprocessed microfillers may provide a more efficient use of cement, with less energy consumed and less hazardous emissions released in the air, without compromising the fundamental characteristics of the cementitious binder.

Acknowledgment

This work was supported by the National Science and Engineering Research Council, through *Concrete Canada*, The Network of Centers of Excellence on High Performance Concrete.

References

1. Nehdi, M., Mindess, S. and Aïtcin, P.-C., "Use of ground limestone in concrete: a new look", Buil. Res. Jour., 43, 4, p. 245 (1995).

2. Mehta, P.K., "Rice husk ash: A unique supplementary cementing material", Adv. Concrete technology, CANMET, Malhotra, V.M., ed., 2nd. edition, p. 407 (1994).
3. Feng, N-Q., Li, G-Z. and Zang, X-W., "High-strength and flowing concrete with a zeolitic mineral admixture", Cem. Conc. and Aggr., 12, 2, p. 61 (1990).
4. Bentur, A., Bonen, D. and Goldman, A. , Discussion of a paper by Cong, X. et al., "Role of silica fume in compressive strength of cement paste, mortar and concrete", ACI Mat. Jour., July-Aug., p. 376 (1993).
5. Detwiler, R.J. and Mehta, P.K., "Chemical and physical effects of silica fume on mechanical behavior of concrete", ACI Mat. Jour., 86, 6, p. 609 (1989).
6. Goldman, A. and Bentur, A., "Properties of cementitious systems containing silica fume or non reactive microfillers", Advn. Cem. Bas. Mat., 1, p. 209 (1994).
7. Gutteridge, W.A. and Dalziel, J.A., "Filler cement: The effect of the secondary component on the hydration of Portland cement: Part I: A fine non hydraulic filler", Cem. Concr. Res., 20, p. 778 (1990).
8. de Larrard, F., "Ultrafine particles for the making of very high strength concretes", Cem. Concr. Res., 9, p. 161 (1989).
9. Fidjestøl, P. and Frearson, J., "High performance concrete using blended and triple blended binders", ACI-SP-149, Proc. Int. conf., Malhotra, V.M., ed., p. 135 (1994).
10. Do, T.S. and Rui, F.D., "Blended cement using zeolite and limestone as fine fillers", Silicates Industriels, 6, p. 127 (1983).
11. Montgomery, D.C., Design and Analysis of Experiments, John Wiley and Sons, New York, pp. 460-470 (1984).
12. JMP Statistics and Graphics Guide, Statistics Made Visual, SAS Institute Inc, NC, USA (1994).
13. Ramachandran, V.S. and Chun-Mei, Z., "Dependence of fineness of calcium carbonate on the hydration behavior of tricalcium silicate", Dur. Buil. Mat., 4, p. 44 (1986).
14. Husson, S., Gulhot, B. and Pera, J., "Influence of different fillers on the hydration of C_3S", 9th. ICCC, New Delhi, Vol. IV, p. 430 (1992).
15. Barker, A.P. and Cory, H., "The early hydration of limestone filled cements", Proc. Blended Cements in Construction, Swamy, R.N., ed, p. 107 (1991).
16. Feldman, R.F., Ramachandran, V.S. and Sereda, J.P., "Influence of $CaCO_3$ on the hydration of $3CaO.Al_2O_3$", Jour. Amer. Cerm. Soc., 48, 1, p. 25 (1965).
17. Manabe, T., Kawada, N. and Nishiyama, M., "Studies on $3CaO.Al_2O_3.CaCO_3.nH_2O$", CAJ. Review, pp. 48 (1961).
18. Ramachandran, V.S. and Chun-Mei, Z., "Hydration and microstructural development in the $3CaO.Al_2O_3$-$CaCO_3$ - H_2O system", Materials and Structures, 19, 114, p. 43 (1986).
19. Evrard, O. and Chloup, M., "Réactivité chimique des calcaires en milieu basique: application aux ciments et bétons", Annales ITBTP, 529, Série 316, p. 83 (1994).