

Research note

Studies on Main Properties of Ternary Blended Cement with Limestone Powder and Microsilica

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Abstract

The ternary system of Portland cement-microsilica-limestone has been studied by investigating its set and strength behaviours. A number of different cementitious systems comprised of 0, 10, 15, 20, 25, and 30% limestone powder and 0, 4, 6, 8, 10, 12, 14, and 16% microsilica were designed and prepared. The cementitious systems were then characterized by determining their relative workability and measuring their initial and final setting times and also their 7- and 28-day compressive strengths using paste specimens prepared at a constant W/C-ratio of 0.38. Total 77-day shrinkage of the systems was also measured. The obtained results reveal that both 7- and 28-day compressive strengths increase with increasing microsilica up to 12% and decrease with increasing the percentage of limestone powder. A comparison of the results confirms the possibility of replacing Portland cement by a proportioned mixture of microsilica and limestone powder for enhancing the strength behaviour or producing composite cements containing relatively high proportions of limestone powder with no loss in 7- and 28-day compressive strengths compared to plain cement.

Keywords: *Microsilica, Limestone, Compressive strength*

1- Introduction

The production of blended cements has gained more importance during the last decades. Blended cements are simply produced by adding pozzolanic materials or some suitable minerals like limestone to Portland cement. Most of the pozzolanic materials being utilized nowadays are from industrial wastes. The utilization of these materials in the production of blended cements not only relieves the need for land-filling, hence avoiding the consequent environmental pollution, but also provides a number of benefits both for cement

producers and for consumers. Sometimes, there are possible improvements in strength behaviour and durability of cement, which in turn could reduce the amount of cement consumption [1]. In addition to the blended cements of the binary type, i.e. Portland cement with only one additive material, an increasing tendency has emerged for developing and producing composite Portland cements or blended cements consisting of Portland cement and two or more additive materials [2]. Composite Portland cements are usually produced by the partial replacement of Portland cement with a

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mixture of artificial and/or natural pozzolanic materials.

Microsilica, an important pozzolanic additive for Portland cement, was initially a waste material produced in Ferrosilicon-alloys industries. At the beginning, microsilica was added to cement for just avoiding any atmospheric pollution caused by emissions. Later, the technical benefits of microsilica for Portland cement, including strength enhancement and increased durability against acid-water and sulfate attacks, rapidly developed its application in cement-based materials [3].

Limestone is a non-pozzolanic material currently being considered as a suitable additive for Portland cement. The use of limestone in the production of blended cement dates back to the 1970s [4]. At the beginning, limited amounts of limestone, i.e. up to 5%, was being used as a neutral filler. Later, however, results of research works have clearly revealed its useful physical and chemical interactions with Portland cement phases. The allowable amount for limestone addition to Portland cement therefore has been considerably increased [5]. The present European standard for composition, specifications and conformity criteria for common cements, EN 197-1, has defined four types of Portland limestone cements which could be simply produced by incorporating suitable types of limestone into Portland cement up to 35% replacement.

Although the individual utilization of microsilica and limestone as suitable additive materials for cement and concrete has been practiced for quite a long time, the simultaneous incorporation of these two materials into Portland cement and the production of composite Portland cement is quite a new topic for research.

The first study on such composite cements dates back to the year 1996, in which Nehdi et al [6] investigated the properties of cement mortars including microsilica and limestone. They concluded that after 7 days, the compressive strength of mortars consisting of

10 to 15% limestone and 10% microsilica exceeds that of the control sample. Later in 1999 and in different studies, Zelic et al [7,8], confirmed that the addition of silica fumes to limestone blended Portland cement leads to considerable improvements of mechanical properties and the sulfate resistance of cement mortars by utilizing special properties such as high pozzolan activity and large specific surfaces. In their studies, they considered the influence of the combined action of silica fume and limestone on strength development, porosity, pore structure, and morphological features in the system where 15 wt% of cement was substituted by finely ground limestone. Silica fume was added in amounts of 0, 2, 5, 8, 11 and 15 wt% on a cement basis, respectively. Their results showed that replacement of Portland cement by 15 wt% of limestone caused a reduction in the compressive strength. When silica fume was added together with limestone, the mortars containing up to 8 wt% of silica fume showed a considerable increase in the earlier compressive strength. After 28 days of hydration, mortars containing more than 8 wt% show a higher strength than mortar containing no silica fume. Also, these researchers studied the effect of silica fume on corrosion resistance to sulfate attack of Na_2SO_4 and MgSO_4 solutions in Portland cement mortars containing limestone and mortars containing no limestone [8]. The expansion and changes in the elasticity modulus of mortars as a function of silica fume content were investigated. The presence of monocarbonate and the absence of monosulfate were detected in the mortars containing limestone. The addition of silica fume resulted in less CH formed by the hydration process and, consequently, less gypsum and ettringite during the sulfate immersion of mortars. In 2002, Vuk et al [9] investigated the influence of mineral admixtures such as silica fume on sulfate resistance of limestone cement pastes aged in cold MgSO_4 solution. It was found that the

addition of silica fume to limestone cement significantly improved its sulfate resistance. It was shown that the absorption of sulfate and the formation of sulfate minerals in the cement paste was decreased by the addition of silica fume. In 2003, Pandey et al [10] investigated the durability of a number of blended cements containing silica fume by exposing the mortar cubes separately in 5% Na₂SO₄ and 5% NaCl solutions till the age of 90 and 180 days. The performance was observed by compressive strength development criteria after various lengths of exposure. Results have been discussed and it was found that the durability of blended cements containing silica fume is higher than the ordinary Portland cement.

This study investigates the simultaneous contribution of microsilica and limestone on set, compressive strength, and shrinkage behaviours of Portland cement and introduces the potential of microsilica and limestone for producing ternary composite

cements with relatively high percents of replacements and no loss in strength behaviour based on 7- and 28-day compressive strengths.

2- Experimental

2-1- Materials

Portland cement, Type II ASTM standard, limestone, and microsilica were used in this work. Limestone was first ground in a laboratory ball mill to a Blaine specific surface area of 320 m²/kg in accordance with ASTM standard C204 [11]. Microsilica containing 96.12% SiO₂ and having a BET specific surface area of 18000 m²/kg was prepared from Iranian ferro-alloys industries. The chemical composition and physical properties of the materials are given in Table 1. Details of the mix proportion for the studied composite systems containing different levels of microsilica and limestone are given in Table 2.

Table 1. chemical composition and physical properties of the materials.

	Portland cement (PC)	Limestone (L)	Microsilica (MS)
Chemical Composition			
SiO ₂	20.83	0.79	96.12
Al ₂ O ₃	4.56	0.1	0.82
Fe ₂ O ₃	3.69	0.12	-
CaO	63.9	55.36	-
MgO	2.65	0.8	-
SO ₃	2.07	-	-
K ₂ O	0.59	-	-
Na ₂ O	-	0.12	0.4
LOI	1.95	42.78	0.63
Bogue's Potential Phase Composition			
C ₃ S	63.39		
C ₂ S	11.97		
C ₃ A	5.84		
C ₄ AF	11.23		
Specific Surface Area (m²/kg)	295 (Blaine)	320 (Blaine)	18000 (BET)
Density (kg/m³)	3.130	2.750	0.318

Table 2. Mix proportions of ternary composite systems.

System	Portland Cement (wt%)	Limestone (wt%)	Microsilica (wt%)	System	Portland Cement (wt%)	Limestone (wt%)	Microsilica (wt%)
1	100	0	0	25	80	20	0
2	96	0	4	26	76	20	4
3	94	0	6	27	74	20	6
4	92	0	8	28	72	20	8
5	90	0	10	29	70	20	10
6	88	0	12	30	68	20	12
7	86	0	14	31	66	20	14
8	84	0	16	32	62	20	16
9	90	10	0	33	75	25	0
10	86	10	4	34	71	25	4
11	84	10	6	35	69	25	6
12	82	10	8	36	67	25	8
13	80	10	10	37	65	25	10
14	78	10	12	38	63	25	12
15	76	10	14	39	61	25	14
16	74	10	16	40	59	25	16
17	85	15	0	41	70	30	0
18	81	15	4	42	66	30	4
19	79	15	6	43	64	30	6
20	77	15	8	44	62	30	8
21	75	15	10	45	60	30	10
22	73	15	12	46	58	30	12
23	71	15	14	47	56	30	14
24	69	15	16	48	54	30	16

2-2- Test Procedure

Systems of Portland cement, limestone powder, and microsilica at given proportions were firstly prepared manually by mixing each system for 10 minutes and then homogenized using an electric mixer of the type SANA SGG-3001 (180 W) and mixing each system separately for a few minutes. Water-to-dry binder ratio was taken constant at 0.38 for all systems. With such water-to-dry binder ratio, the spread diameter in the flow table test was in the range 13.55 to 18.25 cm for paste specimens. The prepared pastes were characterized by measuring their initial and final setting times using a Vicat needle in accordance with ASTM standard C191-82 [12], and determining their relative workability using a flow table. The pastes were cast into specimens of $2 \times 2 \times 2$ cm³ in size and the moulds were kept in an atmosphere of more than 95% relative humidity at 25°C for the first 24 hours. The

moulds were then opened and the specimens stored in water at 25°C for further curing.

From each system and for each compressive strength measurement, three specimens were used. The average of the three values was reported as the result of compressive strength measurement. Total 77-day shrinkage of the systems was also measured using a digital caliper (AACO) with an accuracy of 0.01 mm.

3- Results and Discussion

3-1- Setting times

Results of the initial and final setting times are shown in figures 1 and 2 respectively. As seen in both cases, the incorporation of microsilica and any increase in its percentage result in a reduction of the setting time. In a system without limestone, a 16% replacement of Portland cement with microsilica reduces both initial and final

setting times by 80 and 95 minutes respectively compared to the reference system, i.e. the system containing plain cement. The incorporation of limestone could also affect both the initial and the final setting times, but to a lesser extent compared

to microsilica. At relatively lower percentages of replacement, up to 15%, limestone increases the setting times. However, at higher dosages, limestone results in reductions in setting times.

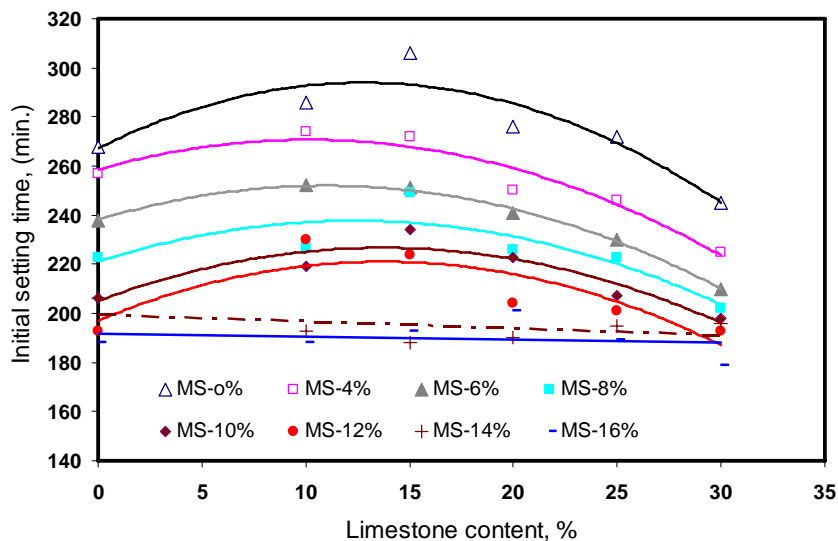


Figure 1. Initial setting times of ternary blended cements with limestone powder and microsilica

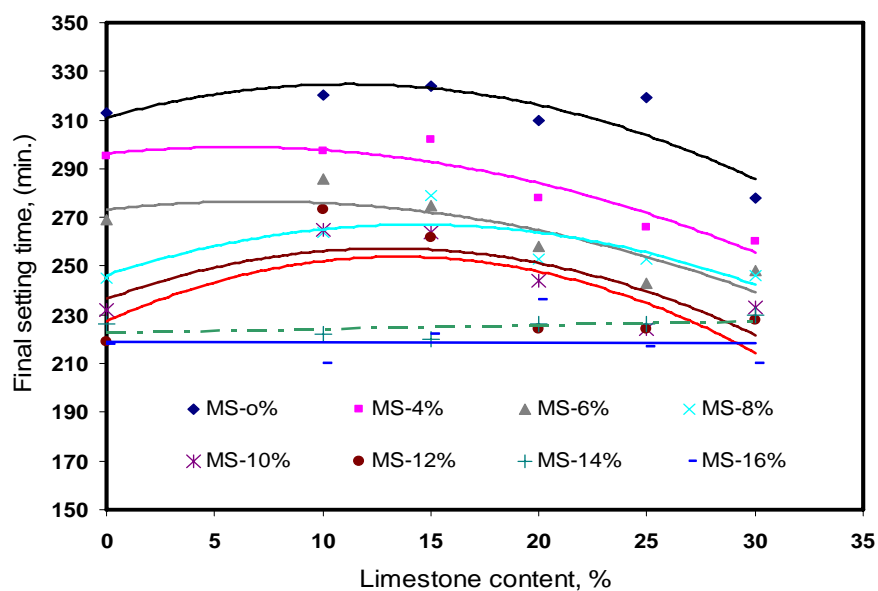


Figure 2. Final setting times of ternary blended cements with limestone powder and microsilica

The effects of microsilica on setting times could be attributed to its capability in water absorption and its effect on the hydration of cement phases [6,...,10,13,14,15]. Microsilica consists of very small particles, i.e. submicron, providing a very high specific surface area and enabling a relatively high capacity of water absorption [15]. Any addition in the percentage of microsilica therefore results in a higher amount of water absorption, which in turn not only worsens the paste workability, but also reduces both the initial and the final setting times. Very small particles of microsilica could also play the important role of nucleation center for hydration products of cement pastes [15]. Microsilica, therefore, could also reduce both the initial and the final setting times by accelerating the hydration reactions of cement phases.

Limestone is not an inert and react with calcium-aluminate phase (C_3A) producing a binding compound, i.e. calcium-carbo-alumino hydrate, which is similar to sulfo-aluminate from the reaction between gypsum and C_3A . At relatively lower dosages therefore, limestone could increase the setting times not only due to the formation of

calcium-carbo-alumino hydrate, but also due to lessening the C_3A concentration. On the other hand, at relatively high dosages, limestone could accelerate the hydration reactions of the cement phases, particularly the C_3S phase. It is reported that limestone, when incorporated at relatively high percentages, could react with C_3S producing calcium-silico-carbonate [16,17]. Limestone therefore reduces both the initial and the final setting times when incorporated at relatively high percentages, i.e. higher than 15%.

3-2- Compressive Strength

Results obtained for 7-day compressive strength are presented in figure 4. As seen, an increase in the percentage of limestone always decreases the 7-day compressive strength, whereas for microsilica an optimum in the percentage of replacement is observed. Up to 12%, any increase in the percentage of microsilica increases the 7-day compressive strength, and replacement at high percentages results in a decrease in 7-day compressive strength. Figure 4 presents the results obtained for 28-day compressive strengths. Quite similar trends are seen in comparison to what is seen in figure 3.

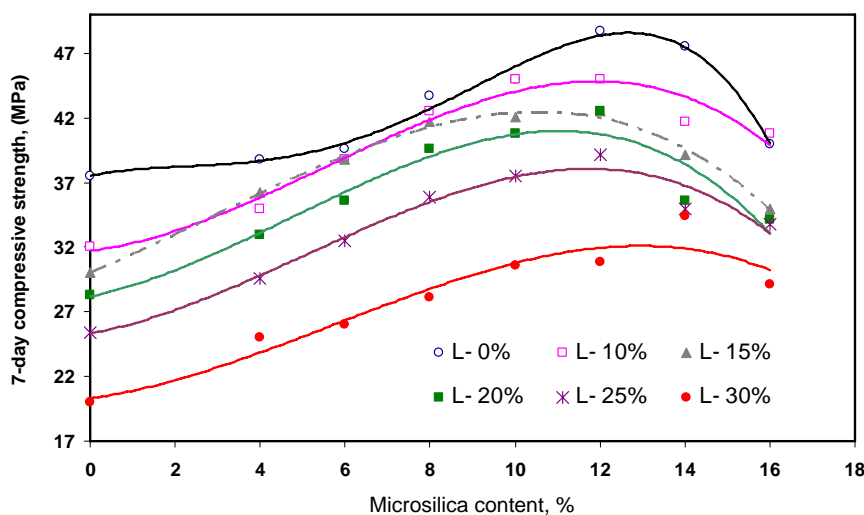


Figure 3. 7-day compressive strengths of ternary blended cements with limestone powder and microsilica

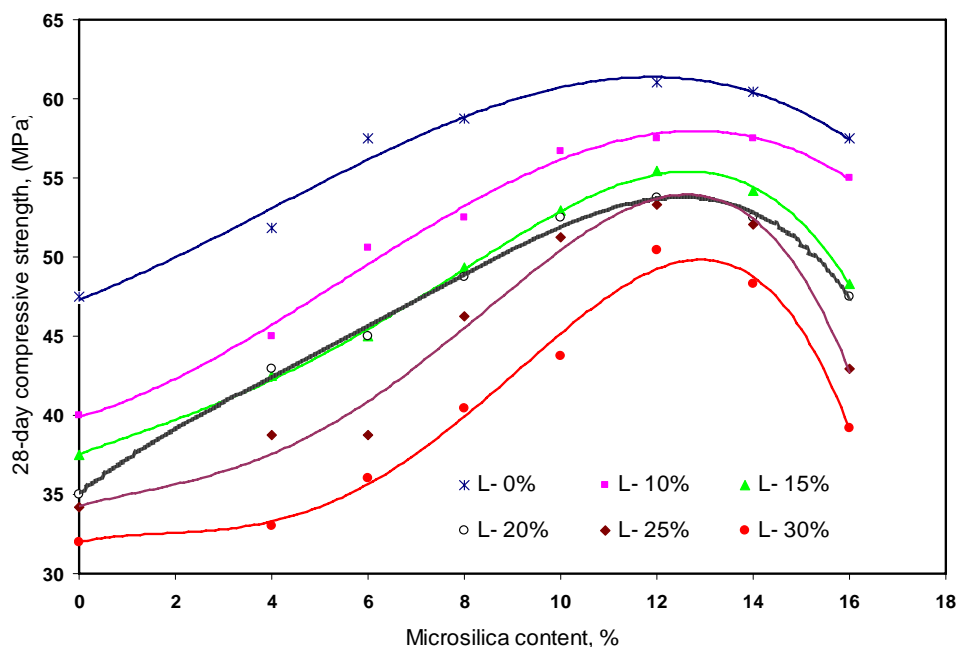


Figure 4. 28-day compressive strengths of ternary blended cements with limestone powder and microsilica

Microsilica is a highly reactive pozzolanic material consisting of almost 96% amorphous silica. When incorporated into Portland cement, it reacts with calcium hydroxide generated in the hydration reactions of the alite and belite phases. The reaction of microsilica with calcium hydroxide results in the formation of some additional calcium-silicate hydrate, which is quite similar to the hydration product of the alite and belite phases. This additional calcium-silicate hydrate could effectively densify the microstructure of the cement paste and therefore strengthen its mechanical behaviour [13,14,15]. Any increase in the replacement percentage of microsilica up to the optimum value, i.e. 12%, therefore increases both 7- and 28-day compressive strengths due to the formation of additional calcium-silicate hydrate.

At percentages higher than the optimum value, i.e. 12%, it is hypothesized that microsilica separate cement grains [13]. Such

a separation between cement grains, along with the water absorption capacity of microsilica, could significantly decelerate the cement hydration reactions, hence weakening the 7- and 28-day compressive strengths.

Limestone powder is not a pozzolanic material and the incorporation of which at percentages higher than 10 always weakens the compressive strengths [16,17]. A comparison of the results confirms the possibility of replacing Portland cement with a proportioned mixture of microsilica and limestone powder for enhancing the strength behaviour or producing composite cements containing relatively high proportions of limestone powder with no loss in 7- and 28-day compressive strengths compared to plain cement. As seen, the composite ternary system comprised of 25% limestone powder and 12% microsilica, i.e. a total replacement of 37%, exhibits the same 7- and 28-day compressive strengths as the plain cement.

The same conclusions were also reported by

other researchers [6,7,8]. It was well established that limestone addition considerably increases the total porosity of mortars. However, if introduced together with microsilica, porosity decreases and this in turn results in an increase in compressive strength. The addition of microsilica at percentages higher than the optimum values increases the porosity again. It is also reported that the quantity of limestone incorporated was affected by the microsilica content. Although the general conclusions reported in the literature are the same and confirm each other, the optimum values reported for the limestone and microsilica are different. Nehdi et al [6] concluded that after 7 days, the compressive strength of mortars consisting of 10 to 15% limestone and 10% microsilica exceeds that of the control sample. According to Zelic et al [7,8], mortars containing up to 8 wt% of silica fume and 15 wt% limestone showed a considerable increase in the earlier compressive strength. After 28 days of hydration, mortars containing more than 8 wt% show a higher strength than mortar containing no silica fume. Such differences in the optimum values of limestone and microsilica based on compressive strengths can be attributed to the physical, chemical, and mineralogical characteristics of the materials used. The differences in fineness, chemical composition, and mineralogical phase composition can be considered as the main factors determining the optimum addition percentage for any additive material.

3-3- Paste workability

The effects of microsilica and limestone powder on the workability of cement paste were investigated by measuring the spread diameter increase in a flow-table test [18]. The obtained results for the plain cement, binary system containing 12% microsilica, binary system containing 25% limestone powder, and ternary system comprised of 12% microsilica and 25% limestone powder are presented in figure 5.

As seen, both microsilica and limestone powder lower the spread diameter of the cement paste. The effect of microsilica however is so strong that it could worsen the workability of cement paste more than limestone powder, even at a percentage less than half of limestone powder, i.e. 12% compared to 25%. Such a strong effect in the case of microsilica is due to its relatively high capacity of water absorption caused by its very high specific surface area [13]. Microsilica has a specific surface area of 18000 m²/kg, almost 56 times higher than that of limestone powder, i.e. 320 m²/kg.

3-4- Total Shrinkage

Figure 6 represents the results obtained for total 77-day shrinkage including both autogeneous and drying shrinkage. The specimens were kept at environmental conditions after 28 days of curing in water. The total 77-day shrinkage decreases with increasing the replacement percentage of microsilica up to almost 6%. From 6%, any increase in microsilica percentage results in an increase in the total 77-day shrinkage. The decrease in total shrinkage due to the incorporation of microsilica could be attributed to the physical filling effect and pozzolanic chemical reaction of microsilica [11]. The increase in the total shrinkage at relatively high percentages of microsilica is due to its water absorption. At these percentages a significant proportion of added water is trapped by microsilica and the separated cement grains are hydrated to a lesser extent. The trapped water therefore could be dried later, slowly, resulting in a higher drying shrinkage.

4- Conclusions

- 1- Both 7- and 28-day compressive strengths of the ternary system; Portland cement-limestone powder-microsilica increase with increasing microsilica up to 12% and decrease with increasing the replacement percentage of limestone powder.
- 2- It is possible to replace Portland cement

by a proportioned mixture of microsilica and limestone powder for enhancing the strength behaviour or producing composite cement containing relatively high proportions of limestone powder with no loss in both 7- and 28-day compressive strengths compared to plain cement.

3- Incorporation of microsilica and any

increase in its percentage always result in a reduction in both the initial and final setting times. Limestone, however, increases the setting times at relatively lower percentages of replacement, i.e. less than 15%. Higher dosages of limestone also results in reductions in setting times.

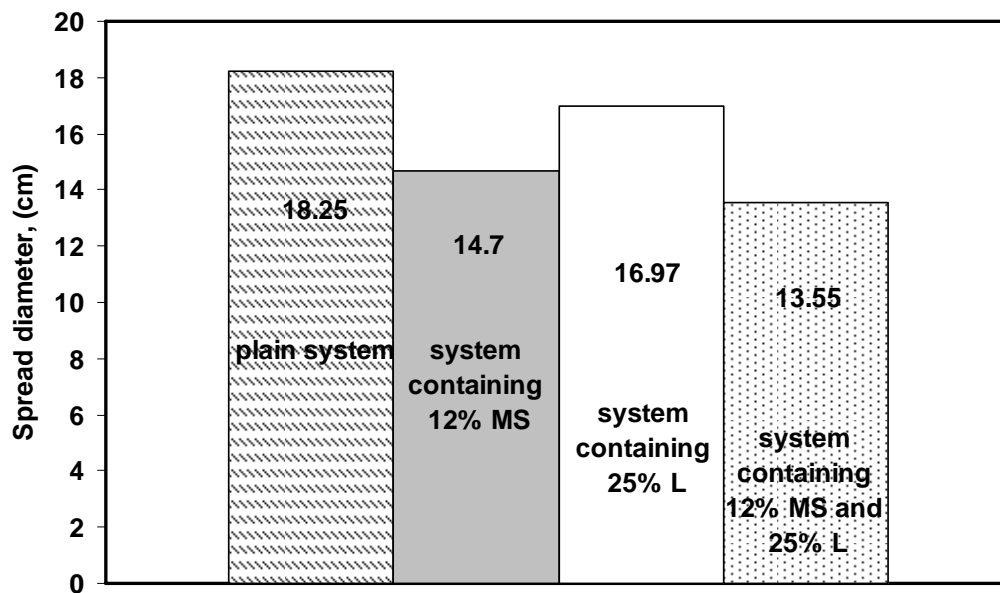


Figure 5. Spread diameter measured in flow-table test

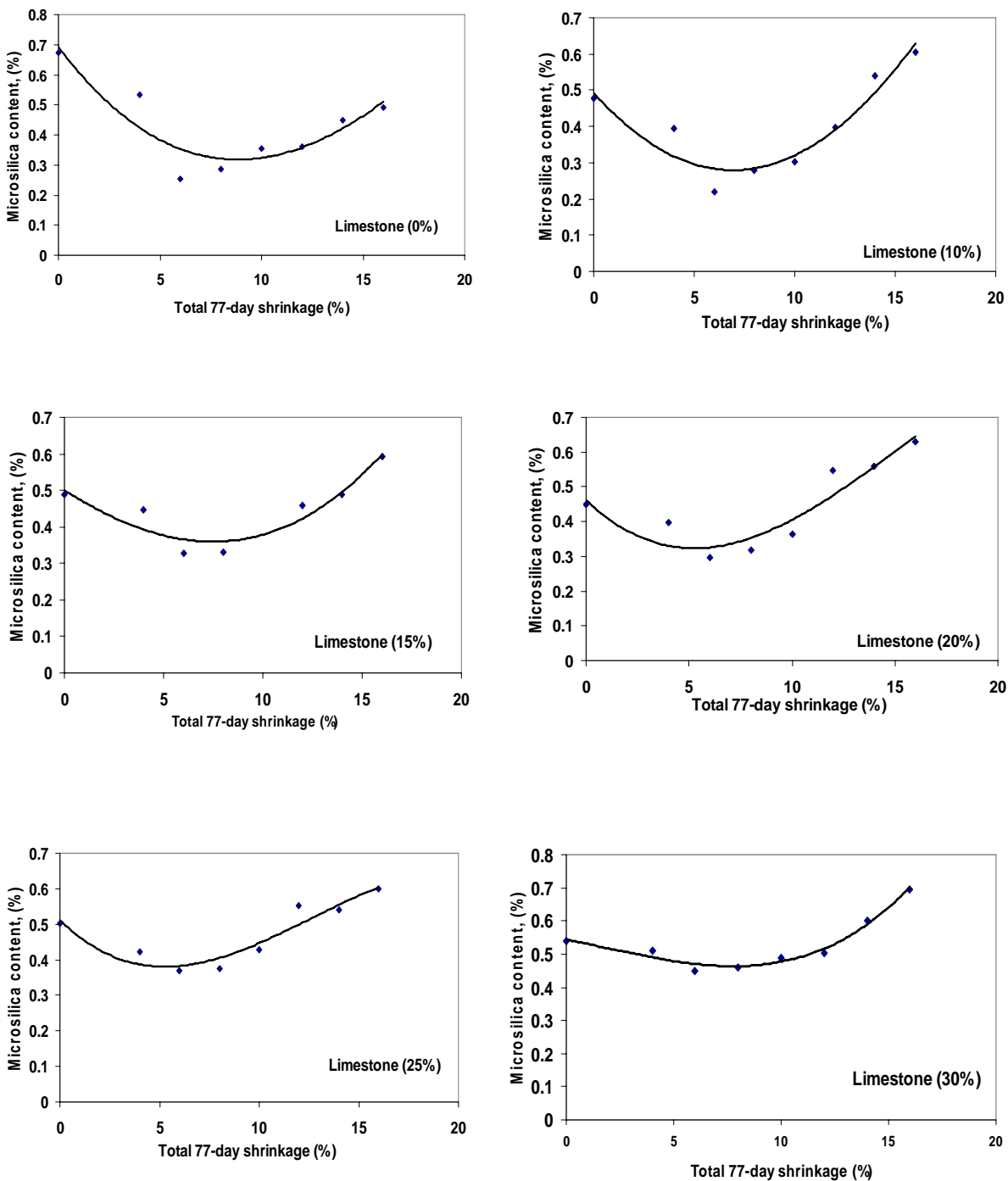


Figure 6. Total 77-day shrinkage of ternary blended cements with limestone powder and microsilica

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