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Communication

The effects of limestone addition, clinker type and fineness on properties of Portland cement

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Abstract

Full factorial experimental design was applied to evaluate the effect of 5% limestone addition on various properties of cement in relation to clinker type and fineness. Two clinkers, differing only in lime saturation factor (LSF), were used, and cements with two levels of fineness were prepared. The experiment was performed in real-scale conditions on a ball mill with a capacity of 15 t/h. Effects of different factors on compressive strength, heat of hydration, setting times and water demand as well as the interactions between factors were evaluated.

Keywords: Portland cement; Fineness; Limestone; Hydration; Mechanical properties

1. Introduction

Limestone is an important material for cement manufacture. The addition of limestone to Portland cement may significantly improve several cement properties such as compressive strength, water demand, workability, durability [1–7], and can also decrease production costs. The effects of small limestone additions on both compressive strength and on heat of hydration are relatively well known, but less is known about the dependence of these effects on clinker properties (for example C_3S content), fineness of cement and other factors. There is evidence that the influence of limestone depends on C_3A content of clinker because $CaCO_3$ produces calcium carboaluminate hydrate during the reaction with C_3A [1,8,9]. There is also some evidence that finely ground limestone influences C_3S hydration [10–13] but the influence of C_3S content in clinker on the effect of limestone addition is not so well documented.

The aim of this study was to evaluate possible interactions between limestone addition, C_3S content in clinker, and fineness. The question was how the effect of limestone depends on clinker quality and fineness. Experimental design technique was applied in order to evaluate these possible interactions. Studies of the influence of limestone additions have usually been done using laboratory-scale experiments whereas in our case all experimental runs were performed under real-scale conditions. Eight different cement samples were obtained by grinding them in an industrial ball mill. In most studies, the effect of limestone addition is examined in combination with clinkers having relatively high lime saturation factor (LSF), while in our study two clinkers with LSF below 0.87 were used. This study not only examines the interaction between LSF and limestone addition but also tries to extend the knowledge of limestone-addition effects to a wider interval of LSF. A special condition of the experiment was that the two clinkers used differed almost exclusively in LSF, so that the effects studied could be easily extracted.

2. Methods

The experiment was performed according to the 2^3 factorial experimental design, where the three factors were limestone content, clinker type and cement fineness measured as a residue on a 90-μm sieve. The experimental design module of Statistica software (STATISTICA for Windows, 1998 Edition, StatSoft, Tulsa, OK, USA) was

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Table 1
Factors in experimental design

Run	Clinker type	Fineness (%)	Limestone addition (%)
1	A	2	0
2	A	2	5
3	A	5	0
4	A	5	5
5	B	2	0
6	B	2	5
7	B	5	0
8	B	5	5

used for data evaluation. Experimental runs with factor values used are presented in Table 1.

In every run the mixture was prepared in a ball mill with a capacity of 15 t/h. Cement was produced for at least 3–4 h, so that the conditions in the ball mill stabilized. Then a larger amount of sample was removed and stored in plastic bags that were placed into 100-l plastic containers.

In the experiment two clinkers with relatively low LSF were used; their mineralogical and chemical compositions are shown in Table 2. Both clinkers used also had rather low heat of hydration; the main difference between them was in LSF, that is, in the ratio between C_3S and C_2S content. C_3A and C_4AF contents were practically the same for both clinkers.

Good-quality limestone with at least 85% $CaCO_3$ and with low TOC and clay content was used (chemical composition, 5% of gypsum: 7.2 SiO_2, 1.9 Al_2O_3, 0.8 Fe_2O_3, 48.8 CaO, 1.0 MgO, 0.2 SO_3). $CaCO_3$ in limestone was of good crystallinity according to the results of X-ray diffraction analysis. Five percent of gypsum was also interground with each sample.

Table 2
Mineralogical and chemical compositions of clinkers A and B and corresponding heats of hydration

	A	B
Composition (%)		
LSF	0.82	0.87
SiO_2	24.7	23.4
Al_2O_3	3.7	3.9
Fe_20_3	5.0	5.3
CaO	63.1	63.9
MgO	1.5	1.5
SO_3	0.4	0.5
Free lime	0.6	0.6
C_3S	35	46
C_2S	45	32
C_3A	1.3	1.4
C_4AF	15	16
Heat of hydration (J/g)		
After 3 days	211	227
After 14 days	273	295

Mineralogical compositions were calculated according to Bogue equations.

Compositions were ground to two different fineness levels, determined as a residue on a 90-μm sieve. Two levels of fineness were 5% and 2% of residue.

Compressive strength of standard mortars was measured according to the EN 196-1 standard, and the heat of hydration was determined by the solution method according to the prEN 196-8 [14,15]. Specific surface area, the standard consistency and the setting time were also determined according to EN standards [16,17].

3. Results and discussion

Several characteristics of eight cement samples are shown in Table 3.

It is evident that Blaine surface area was increased by limestone addition for the same residue on the 90-μm sieve. On the average surface area increased approximately by 45 m^2/kg.

Also, the addition of 5% of slimestone decreased water content for standard consistency of paste by an average of 0.5% in absolute scale, but the most important effect on water demand was that of the fineness. Changing fineness from 2% to 5% residue on the 90-μm sieve decreased water demand by approximately 1.5% in absolute scale.

The addition of limestone also exhibited a strong effect on the initial and final setting measured by the Vicat method. Limestone decreased both setting times, but the effect on the initial setting depended on clinker type. Specifically, in combination with clinker A (low C_3S) the initial setting time was shortened by approximately 50 min, while in combination with clinker B (high C_3S) the decrease was only 25 min. Both setting times decreased with fineness and LSF of clinker used, but the influence of clinker type was more pronounced in combination with low fineness of cement. It seems that the lower the fineness of cement, the stronger the effect of clinker composition on setting time.

The results of tests on compressive strength and the heat of hydration are presented in Figs. 1 and 2.

Data for compressive strength after 2, 7 and 28 days show that at the beginning the addition of limestone increased the compressive strength, but after 28 days the compressive strength decreased. The influence of limestone

Table 3
Relevant data on eight cement samples

Sample	Blaine specific surface area (m^2/kg)	Water demand (%)	Initial setting time (min)	Final setting time (min)
1	404	25.0	255	345
2	437	25.3	205	300
3	307	24.5	300	400
4	367	24.1	250	340
5	395	26.3	190	280
6	438	25.8	170	240
7	313	24.3	210	300
8	354	23.8	180	250

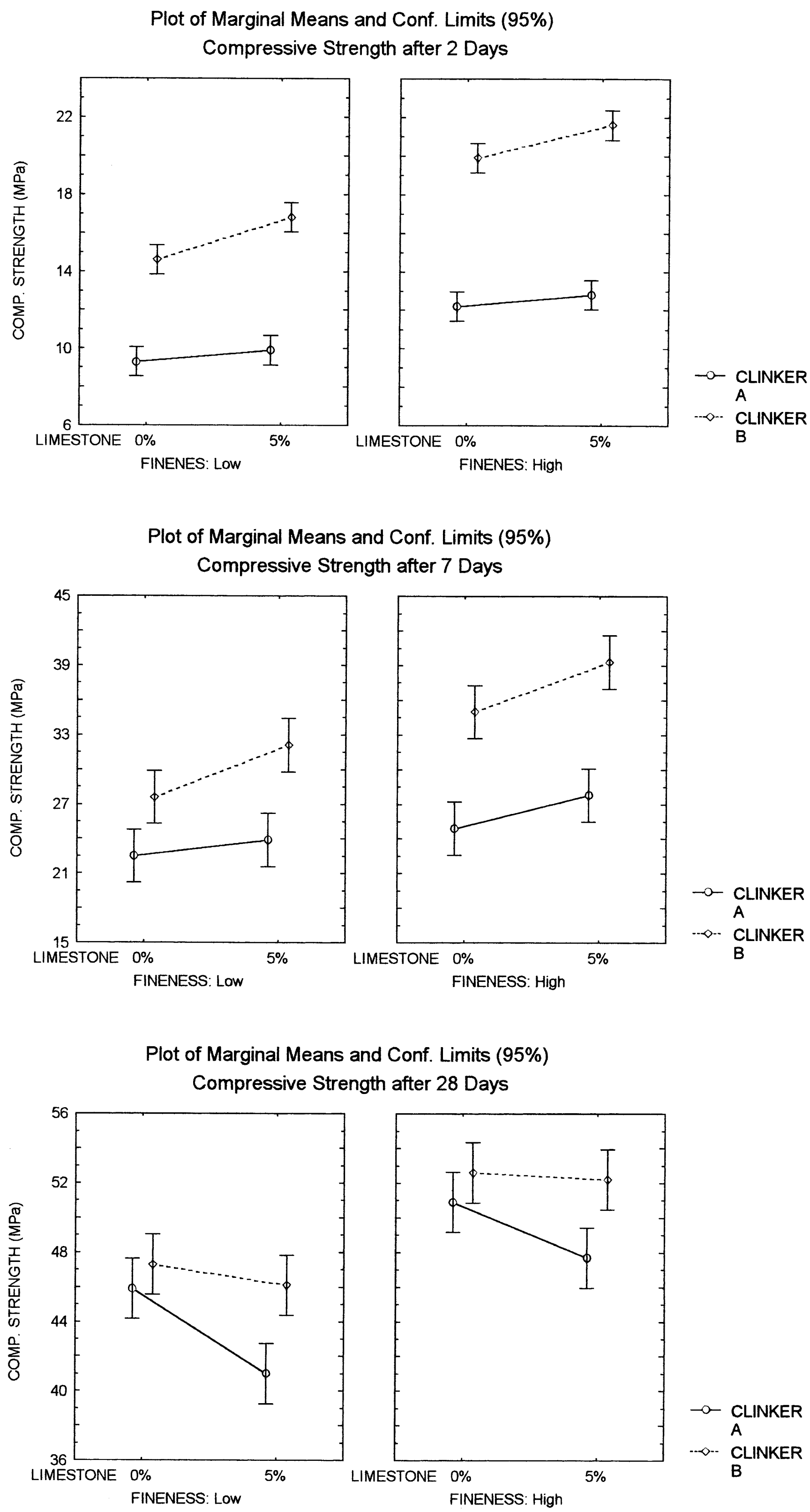

Fig. 1. The effect of limestone addition on the compressive strength at different times.

strongly depended on clinker type used. At the beginning limestone had a stronger effect in combination with clinker B, so the compressive strength increased more in the case of clinker B by the limestone addition. Finely ground limestone evidently promoted the hydration of C_3S, and the higher the content of C_3S in the clinker, the stronger was the

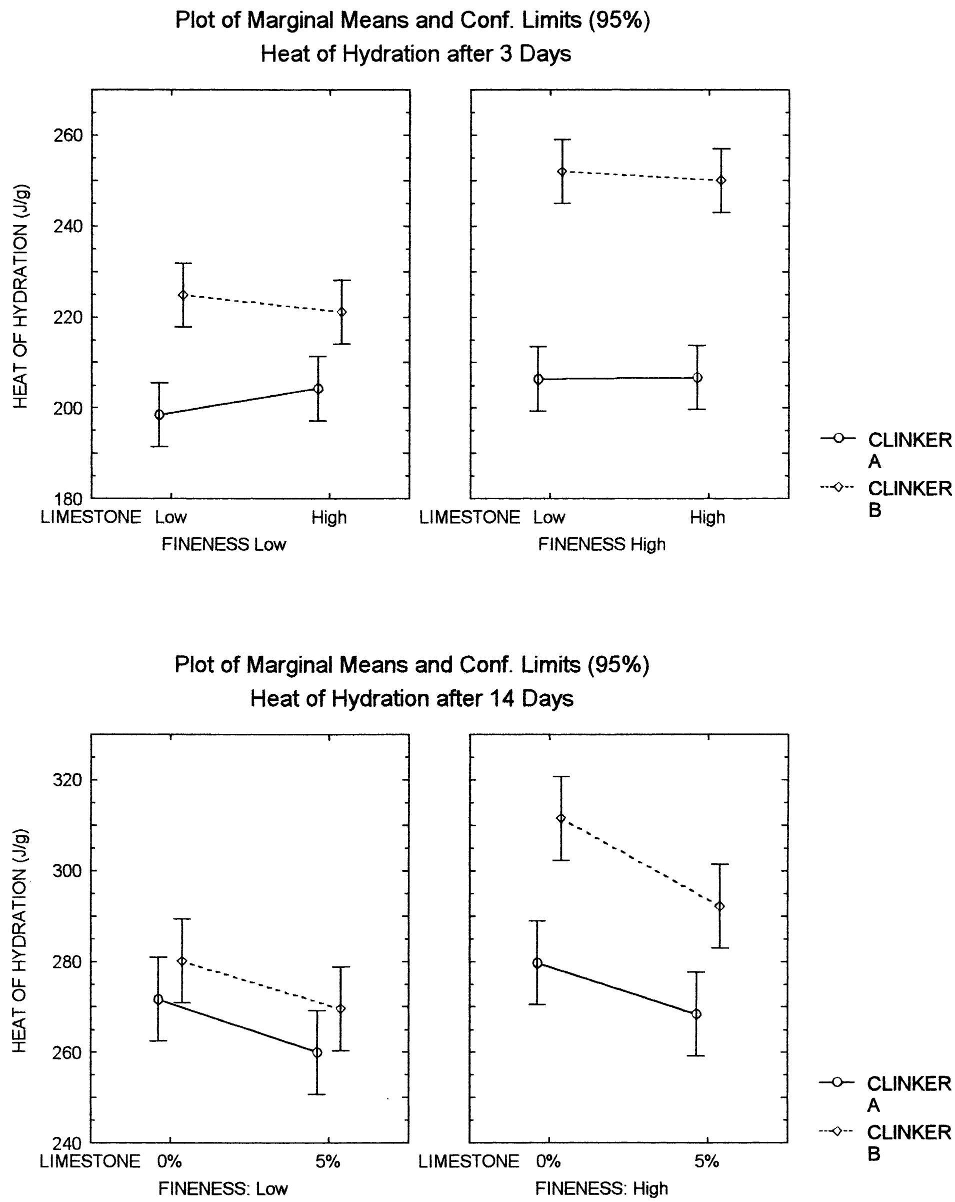

Fig. 2. The effect of limestone addition on heat of hydration at different times.

effect of limestone on hydration and compressive strength. After 28 days the compressive strength slightly decreased in the case of clinker B, while in combination with clinker A the decrease caused by limestone addition was much more pronounced. It is evident that limestone addition acted less negatively in combination with clinker containing more C_3S. It seems that cements with small additions of limestone could be expected to have better performance if they have higher C_3S content.

At the beginning of the hydration (up to 3 days) limestone did not significantly change the heat of hydration (already noted in Ref. [18]), similarly, later (up to 14 days) the heat of hydration decreased less than the reduction in clinker content. These facts indicated that limestone certainly did not act as an inert material, but rather it had to be considered to be an active part of the hydrating system. Limestone can enhance the reactivity of individual phases in cement clinker and, in addition, can react with them. As reported in other papers [1,7,19,20], in the reaction between C_3A and $CaCO_3$ carboaluminate hydrates are produced and, recently, it was found that carbosilicate hydrates might form in the reaction between $CaCO_3$ and silicate phases of clinker [12,13].

The influence of limestone addition on the heat of hydration did not significantly depend on the other two factors considered in this study. On the other hand, it could be established that the effect of clinker type varied with the cement fineness. At a higher level of cement fineness, clinker type influenced hydration heat to a greater extent; this could be explained by the multiplicative effect of fineness and clinker reactivity (C_3S content). It can be stated that the effect of clinker type was most important at early stages of hydration; however, the effect slightly decreased later on while the effect of fineness remained more or less constant during hydration time. As has been stated before, the addition of limestone significantly changed the heat of hydration only at later stages of hydration.

4. Conclusions

Limestone addition considerably influences some characteristics of cement, but this influence depends also on other factors. By the use of an experimental design technique, synergistic effects of limestone addition, fineness and clinker type were detected. The effect of limestone addition depended more on clinker type than on its fineness. The addition of limestone to clinker having high LSF influenced predominantly early compressive strength, while the addition of limestone to clinker having low LSF influenced mostly the compressive strength after 28 days and the initial setting time. The effect of clinker on many properties depended on fineness (compressive strength, setting time, heat of hydration), which could be partly explained by the multiplicative action of both factors. Considering data on compressive strength and the heat of hydration it can be concluded that an increase in early compressive strength caused by limestone addition could only be partly accounted for by enhanced hydration since the heat of hydration remained unchanged. To completely explain this phenomenon one must also consider the changes in hydration products and the physical action of limestone. It can also be observed that the experimental design technique represents a valuable research tool especially for the detection of interactions between different factors that could otherwise be difficult to evaluate.

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