THE EFFECT OF GROUND LIMESTONE ON THE PROPERTIES OF PORTLAND AND SLAG-PORTLAND MIXED CEMENT

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The properties were studied of Portland and slag mixed cements containing admixtures of 5 to 30 wt.% of ground limestone (as replacement of cement) with a specific surface area of 400 to 900 m^2 kg^{-1}. The decrease in strength in terms of increasing limestone content indicates that the limestone does not take part in cement gel formation. However, it is theoretically possible to prepare, from slag cement SPC 325 and 10-12 wt.% ground limestone with a specific surface area of 550 m^2 kg^{-1}, a mixed cement exhibiting higher 2-day and 7-day strengths, and a 28-day strength reduced by max. 10 % (compared to the original SPC 325 cement).

INTRODUCTION

Recently, increasing attention has been paid to the issue of mixed cements owing to the necessity of reducing the amounts of carbon dioxide produced during manufacture of Portland cement, and to the necessity of utilizing inorganic waste materials. At present, the standard ČSN ENV 197 permits the use, as admixtures to Portland cement, of classical granulated blast-furnace slag, pozzolanes, fly-ash, silica fume, calcined slate and limestones.

The addition of limestone to Portland cement for the purpose of creating the binder phase $C_4A\bar{C}H_{11}$ or some other phase, by reacting $CaCO_3$ in aqueous medium with calcium aluminates., was an idea first conceived in the thirties [1,2].

The effect of ground limestone on the structure and strength of hardened cement pastes, mortars and concretes has been amply dealt with in the literature but with no explicit results [3,4]. In the case of model pastes prepared from pure clinker minerals, the additions of ground limestone resulted in higher strength due to formation of C_4ACH_{11}. In the case of pastes and concretes, additions of ground limestone mostly improved the strength and the resistance to aggressive sulphate water. The positive effect of ground $CaCO_3$ as additive, or that of limestone gravel, on the strength of concrete is sometimes explained by the so-called "filler" effect, that is by improved grain size distribution in the mix. The improved sulphate durability of concrete or mortar containing $Ca\underline{CO_3}$ is usually attributed to possible formation of C_4ACH_{11}, a lower porosity and a reduced content of free $Ca(OH)_2$.

Importance of the following factors has been established on the basis of technological experience gained in Germany within the framework of development of the "Portlandkalksteinzement":

- C_3A content in clinker
- $CaCO_3$ content in the limestone (it should contain at least 75 wt.% $CaCO_3$ and less than 1 wt.% MgO)
- in practice, mixed limestone cement contains up to 20 wt.% limestone, although the ENV standard allows up to 35 wt.%
- the gypsum content has to be optimized for the manufacture of mixed limestone cement
- cement and limestone should be ground separately, as the grinding of a worse grindable component (here clinker) jointly with a well grindable one (limestone) narrows down the particle size distribution curve of the well grindable component, thus affecting negatively the mix workability.

According to experience, cement containing 8 to 10 wt.% limestone may attain the strength class 42.5 and can be processed in the same way as any admixture-free Portland cement. Cements with higher limestone contents (15 to 18 wt.%), belonging to strength class 32.5, require cement doses increased by approx. 10 % for attaining the same concrete strength class.

The present study had the aim to assess the effect of finely ground limestone additions on standard Portland and mixed slag cements without any previous special selection of the clinker and the limestone, while utilizing the findings described in [6].

EXPERIMENTAL PART

The effects of ground linestone additions on the properties of mixed cements were studied on Portland cements PC 400 and PC 475, and on mixed slag cement SPC 325 from standard industrial production (the cement designation corresponds to the former Czech standard that held till 1994). The high-percentage limestone used in the manufacture of cements involved in the study was used as the admixture, after grinding in a laboratory ball mill to specific surface areas ranging from 400 to 900 m^2 kg^{-1}. The chemical compositions of the cements and limestone are listed in table 1. The granulometric composition of the materials is shown in table 2. The mixed cements were prepared by blending mechanically the Portland or slag cement with the ground limestone at the given ratio ranging from 5 to 30 wt.% (as cement replacement). The gypsum content in the cements was not adjusted.

The mixed cements were used to prepare pastes (for determining the time of initial set) and mortars (for establishing the course of strength development). The mortars were prepared at a cemen-to-sand ratio of 1 : 2 with w = 0.5 (the standard procedure to ČSN 72 2117 was not precisely obeyed). All of the strength values in the text below are given as relative ones, i.e. those attained in relation to cement without limestone addition. The strengths were determined after 2, 7 and 28 days on specimens kept according to ČSN 72 2117.

The hydration products of hardened mixed cements were studied after 2, 7 and 28 days of hydration by X-ray diffraction analysis and by scanning electron microscopy. Prior to X-ray diffraction tests, the specimens were dried in vacuum.

Table 1. Chemical composition of the intitial components.

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
PC 400	59.37	22.00	5.50	2.75	3.38	2.82
PC 475	61.43	21.16	5.80	2.78	2.44	2.84
SPC 325	52.47	28.11	6.75	2.20	4.96	2.08
limestone	51.46	3.95	0.71	0.56	1.51	0.33

Table 2. Granulometry of the initial components.

material	specific median	surface area
SPC 325	300 m^2 kg^{-1}	17 μm
PC 475	350 m^2 kg^{-1}	12.8 μm
PC 400	335 m^2 kg^{-1}	15.6 μm
limestone	400 m^2 kg^{-1}	17.5 μm
limestone	580 m^2 kg^{-1}	9.4 μm
limestone	900 m^2 kg^{-1}	3.5 μm

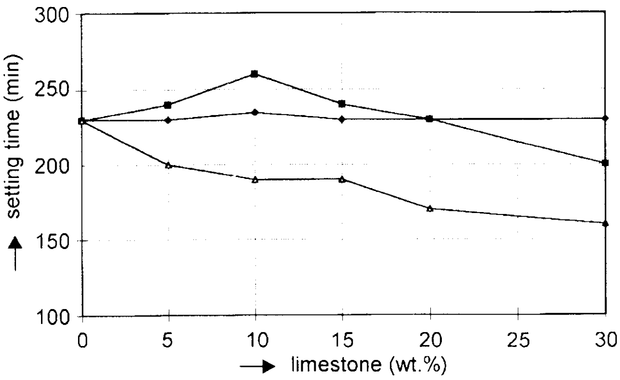

Figure 12. Effect of content of ground limestone (900 m^2 kg^{-1}) on 28-day relative strength of cements.
♦ - 400 m^2 kg^{-1}, ■ - 580 m^2 kg^{-1}, Δ - 900 m^2 kg^{-1}

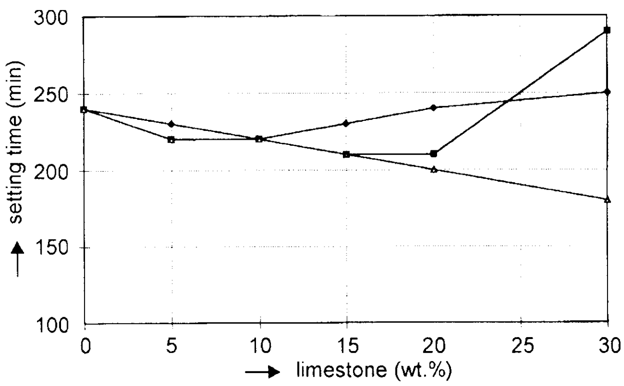

Figure 1. Effect of ground limestone content on time of initial set of slag cement SPC 325.
♦ - 400 m^2 kg^{-1}, ■ - 580 m^2 kg^{-1}, Δ - 900 m^2 kg^{-1}

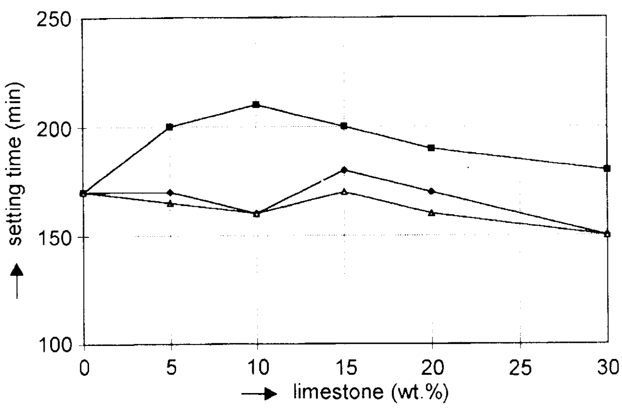

Figure 3. Effect of ground limestone content on time of initial set of Portland cement PC 475.
♦ - 400 m^2 kg^{-1}, ■ - 580 m^2 kg^{-1}, Δ - 900 m^2 kg^{-1}

RESULTS AND DISCUSSION

The experiments were concerned with the effect of ground limestone with a specific surface area ranging from 400 to 900 m^2 kg^{-1}. The limestone was not selected in compliance with the recommended criteria (it contained more than the required 1 wt.% MgO), but was of a high-lime type suitable for the manufacture of Portland and slag cements. The clinker and cement was also taken from the standard production process without using any selection. The study had the purpose to verify the possibility of simply modifying the cement from current production by adding ground limestone extracted in the cement works quarry.

The experimental results show that additions of ground limestone over the range of 5 to 30 wt.% (as cement replacement) affect the time of initial set in a variable way, and that the changes in the time of initial set are not distinct. More significant effects were exhibited by the very finely ground limestone with a specific surface area of 900 m^2 kg^{-1}, which shortened the time of initial set in all of the cases. It should be noted that the content of gypsum was not adjusted. The results allow to conclude that the $CaCO_3$ must take a part in the hydration process, because the time of initial set was not significantly reduced, and in some instances was even prolonged.

However, study of fracture surfaces of the hardened mixed cement pastes revealed no distinct changes in the morphology of the cement stone due to additions of finely ground $CaCO_3$. No formations resembling morphologically $C_4A\bar{C}H_{11}$ were found between the $CaCO_3$ grains and the cement stone matrix. The X-ray diffraction patterns of hardened cement pastes containing $CaCO_3$ indicated solely a certain possibility of the presence of $C_4A\bar{C}H_{11}$.

Another series of experiments was concerned with determining the effect of limestone ground to a surface area of 400 to 900 m^2 kg^{-1} on strength after 2, 7 and 28 days (figures 4-12). The results confirm the known fact that strength decreases with increasing $CaCO_3$ content. In some cases, an increase in strength occurred after 2 and 7 days. The reduction of 28-day strength decreases with increasing surface area of limestone and cement. The largest fall of strength was recorded with PC 400 which was found to be least suitable for the preparation of the mixed limestone cement. More favourable results were achieved with PC 475 having a larger specific surface area.

The relatively most favourable results were surprisingly obtained with slag cement SPC 325 having the lowest specific surface area. Mixed cements prepared from this cement with limestone showed large increases in 2-day and 7-day strength with limestone contents of up to 10 - 15 wt.%. A 28-day strength lower than 90 % of

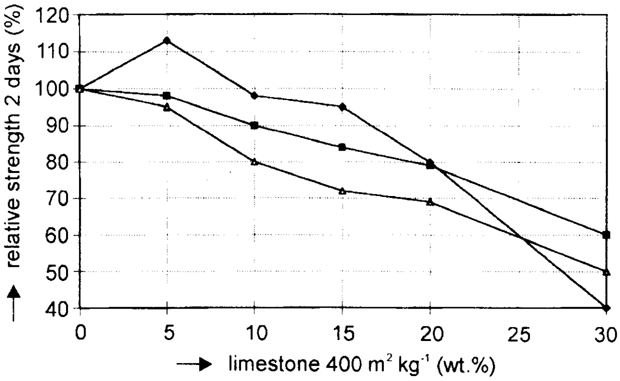

Figure 4. Effect of content of ground limestone (400 m^2 kg^{-1}) on 2-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

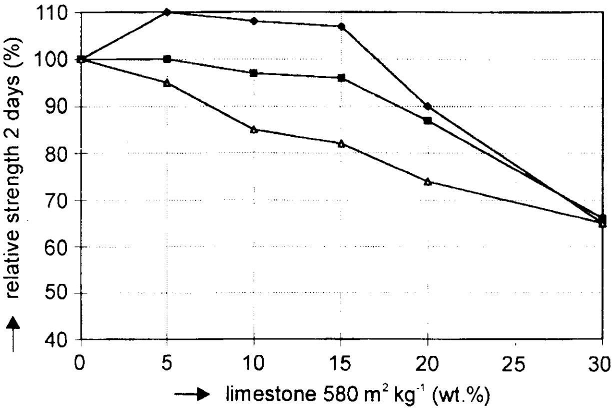

Figure 5. Effect of content of ground limestone (580 m^2 kg^{-1}) on 2-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

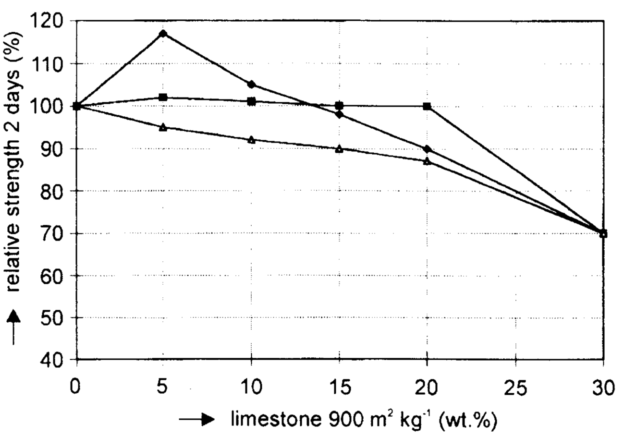

Figure 6. Effect of content of ground limestone (900 m^2 kg^{-1}) on 2-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

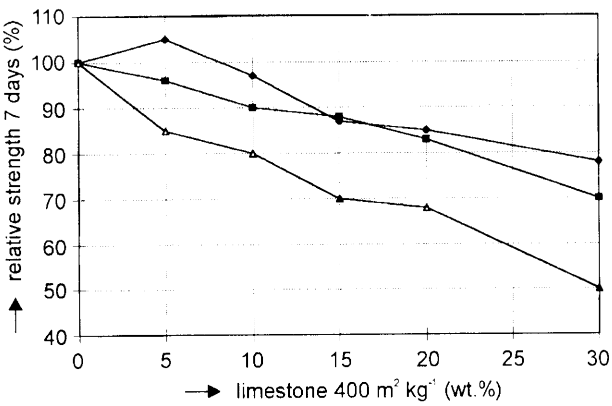

Figure 7. Effect of content of ground limestone (400 $m^2\ kg^{-1}$) on 7-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

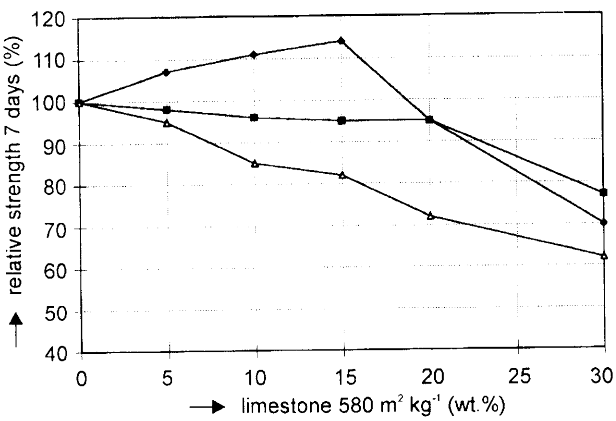

Figure 8. Effect of content of ground limestone (580 $m^2\ kg^{-1}$) on 7-day relative strength of cements.
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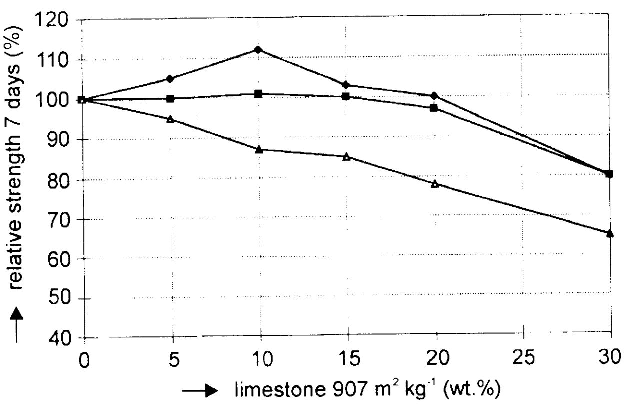

Figure 9. Effect of content of ground limestone (900 $m^2\ kg^{-1}$) on 7-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

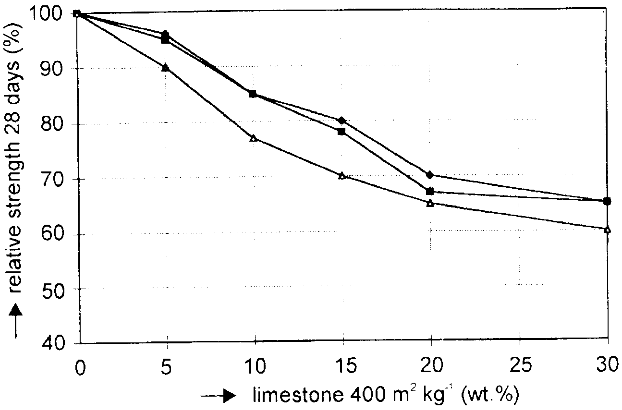

Figure 10. Effect of content of ground limestone (400 $m^2\ kg^{-1}$) on 28-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

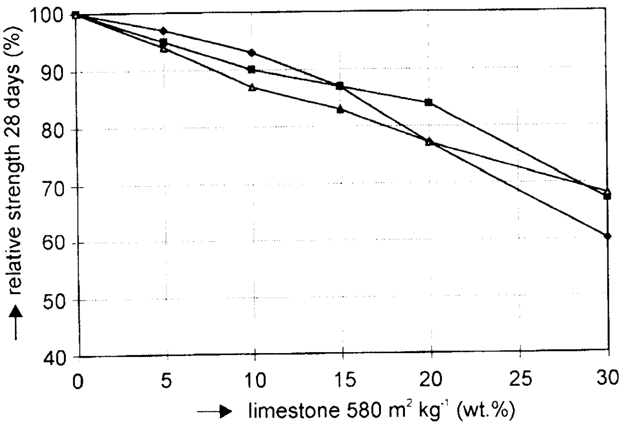

Figure 11. Effect of content of ground limestone (580 $m^2\ kg^{-1}$) on 28-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

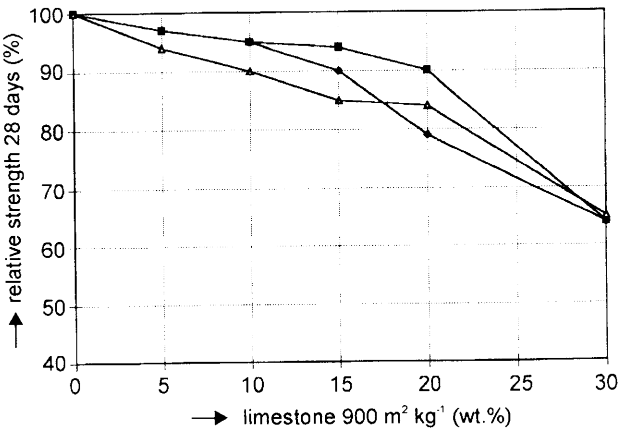

Figure 9. Effect of content of ground limestone (900 $m^2\ kg^{-1}$) on 28-day relative strength of cements.
♦ - SPC 325, ■ - PC 475, Δ - PC 400

the original one was established with limestone contents ranging from 7 to 15 wt.%, when the limestone had a specific surface area of 400 to 900 $m^2 kg^{-1}$. Using this slag cement SPC 325, it is theoretically possible to prepare a mixed cement with higher 2-day and 7-day strengths and a 28-day strength lower by max. 10 %, by adding up to 10-12 wt.% limestone ground to a surface area of 550 $m^2 kg^{-1}$.

The results obtained further show that a successful development of mixed cements requires consistent optimizing, and that it is impossible to produce a mixed cement by merely adding the ground limestone to a cement.

In our opinion, limestone-based mixed cements can best be prepared in the system Portland clinker (+ gypsum) - slag - limestone, that is by modifying slag cement, and not in the system Portland clinker (+ gypsum) - limestone. According to the literature [5], multicomponent (three-component) systems are more prospective, as they provide better opportunities for developing mixed cements with superior properties while increasing the amount of the additive. Information is available on the following types of three-component mixed cements:

Portland cement - slag - fly-ash
Portland cement - fly-ash - limestone
Portland cement - slag - silica fume
Portland cement - fly-ash - silica fume
Portland cement - fly-ash - furnace dust

As far as the systems Portland cement - slag - fly-ash, and Portland cement - fly-ash - limestone are concerned (these being topical for Czech cement works), the literature [5] points out that by consistently optimizing the content of the components and by increasing the fineness it is possible to achieve superior strengths over intervals from 2 to 28 days, as compared to the original Portland cement. Further research in this field would doubtlessly be very prospective.

CONCLUSION

1. Addition to Portland or slag cement of finely ground limestone with a specific surface area of 400 to 900 $m^2 kg^{-1}$ in amounts of 5 wt.% to 30 wt.% (as cement replacement) affects the time of initial set in a variable way, but not to a significant degree.
2. Existence of the $C_4A\bar{C}H_{11}$ phase has not been explicitly determined in hardened cement pastes containing ground $CaCO_3$.
3. Portland cement of the PC 400 class was least suitable for the preparation of limestone mixed cement, whereas better results were achieved with Portland cement PC 475.
4. On the basis of slag cement SPC 325, it is (theoretically) possible to prepare, by adding 10 - 12 wt.% of limestone ground to a specific surface area of 550 $m^2 kg^{-1}$, a mixed cement with higher 2-day and 7-day strengths and a 28-day strength lower by max. 10 % (compared to the original SPC 325).
5. It appears that the system clinker (+gypsum) - slag - limestone is more suitable for the preparation of mixed cement than the system clinker (+gypsum) - limestone.

References

1. Sprung S., Siebel E.: Zement-Kalk-Gips *44*, 113 (1991).
2. Jambor J.: Stavebnícky časopis *28*, 234 (1980).
3. Uchikawa H.: Proc. 8th Intern.Congress Chem.Cement, Vol.I., p.233, Rio de Janeiro 1986.
4. Sersale R.: Proc. 9th Intern.Congress Chem.Cement, Vol. IA, p. 261, New Delhi 1992.
5. Uchikawa H., Okamura T.: Binary and Ternary Components Blended Cements, p. 1-83, in Progress in Cement and Concrete Vol. 4 (Mineral Admixtures in Cement and Concrete), ed. S.L.Sarkar, S.N.Ghosh, Vol.4, p.1-83, ABI Book, New Delhi 1993.
6. Beutlová A.: Diploma Thesis, Department of Glass and Ceramics, Institute of Chemical Technology, Prague 1993.

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VLIV MLETÉHO VÁPENCE NA VLASTNOSTI PORTLANDSKÉHO A STRUSKOPORTLANDSKÉHO CEMENTU

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Byl studován vliv mletého vápence s měrným povrchem 400-900 $m^2 kg^{-1}$ na vlastnosti běžných portlandských a struskoportlandských cementů v rozsahu 5-30 hmot.% (jako náhrada cementu). Přísada jemně mletého vápence k portlandskému a struskoportlandskému cementu ovlivňuje počátek tuhnutí nestejnou měrou a změny v počátku tuhnutí nejsou výrazné. V zatvrdlých cementových kaších s přísadou mletého $CaCO_3$ vyplynula jen určitá pravděpodobnost přítomnosti $C_4A\bar{C}H_{11}$. Pro přípravu směsného cementu byl nejméně vhodný cement třídy PC 400 a lepších výsledků bylo dosaženo u PC 475. Z SPC 325 lze tedy teoreticky připravit směsný cement se zvýšenými pevnostmi po 2 a 7 dnech a 28 denními pevnostmi sníženými max. o 10 % s obsahem mletého vápence do 10-12 % s měrným povrchem 550 $m^2 kg^{-1}$.