Preparation and properties of Portland limestone cements

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Abstract. Limestone is a suitable substitute for economically less favourable Portland clinker in Portland blended cements. Limestone in cement not only serves as a very fine filler, but can also act as a reaction component. In this work, the properties of laboratory Portland cements with limestone were studied. The cements were prepared from two limestone types and two clinker types with a graded limestone content of up to 30 wt. %. The limestones had a different CaCO₃ content. Clinkers were distinguished by a marked difference in C₃A content and hydraulic activity. The effect of limestones on the technological properties of cements, the hydration process and the impact of separate and together grinding of limestone and clinker were studied. In this case, the type of clinker had stronger impact than the type of limestone on the technological parameters. It was also confirmed that a low limestone content has a positive effect on cement hydration.

1. Introduction
Portland cement is the most important hydraulic binder and its worldwide consumption is constantly increasing. The production was around 4.1 billion tones in 2017 [1]. Cement production is characterized by high energy and material demands. When producing one ton of cement clinker, about 0.87 tons of CO₂ is released [2]. One way to reduce cement clinker consumption and CO₂ emissions is to replace it with suitable economical and environmentally-friendly materials, called supplementary cementitious materials (SCMs). One of these materials is limestone. According to the standard EN 197-1, cements with 6–35 wt. % of limestone are called Portland-limestone cement (PLC).

Some authors divided the action mechanism of limestone in cement-based materials into two broad mechanisms of filler effect (including filler effect, nucleation effect and dilution effect) and chemical effect, while other specified filler effect, nucleation effect, dilution effect and chemical effect as distinctive mechanisms. Limestone powder can positively or negatively affect the hydration and resulting parameters of the cement binder depend on its fineness and amount. [3]

Ground limestone works as a filler if its particles are smaller than cement particles. This improves the particle size distribution and the total packing density of the cement-based material [4]. As a result, water demand in concrete is reduced and its strength and durability may be improved [5].

Since Soroka and Setter [6] introduced the limestone nucleation effect, also other authors have confirmed that fine limestone particles provide spaces for the formation of seeds of hydration products [7]. This phenomenon speeds up the hydration [8] and improves the degree of cement hydration [5]. It has been reported that the increase in C-S-H precipitation on the surface of limestone particles is due to the similarity between the planar configuration of Ca and O atoms in calcite layers and in CaO layers in C-S-H [9].
The chemical effect of limestone is mainly related to its particles size and to the content of Al₂O₃ from C₃A and C₄AF in cement. Since the aluminate phase content of the clinker is limited, the chemical effect of limestone in the cement is small. The chemical effect can be increased by the addition of Al₂O₃ from other SCMs [10]. It is reported that limestone stabilizes ettringite and reacts with Al₂O₃ to calcium carboaluminates, thereby reducing the porosity of cement mass [11, 12].

The dilution effect of limestone is that it does not have pozzolanic properties and its excess does not participate in any reaction. Therefore, there is more available free water to react with cement particles. Consequently, the degree of cement hydration is increased, which has been confirmed in various studies [4, 5, 13].

In this work, the combined effect of two types of limestone and clinkers from two cement plants on the technological parameters of the PLCs was monitored. The impact of together and separate grinding was also verified.

2. Materials and methods

2.1. Grinding together
PLCs were prepared by combination of two industrial clinkers and two limestones. Limestones are from one quarry and both limestones, according to TOC content, meet the requirements for the LL category. The limestone labelled H has a high content of CaCO₃ (94.6 wt. %) and 2.1 wt. % SiO₂. The limestone labelled L is contaminated by chert and contain 79.0 wt. % CaCO₃ (with a high content of SiO₂ – 16.5 wt. % and also Al₂O₃ – 1.6 wt. %). The clinkers are from two cement plants, they have high content of alite (C₃S), however, the content of C₃A is very different (see table 1). The clinker C was burnt from high reactivity raw meal and has fine-grained structure. Raw meal for the production of clinker M has worse reactivity and the clinker is coarse-grained (see table 1). At first, two comparative reference cements were prepared only with the addition of gypsum as a set regulator. These cements were ground to a specific surface according to Blaine to 350 m²/kg and the grinding time was measured. The addition of gypsum in case of clinker M was 5 wt. % and in case of clinker C 6 wt. %. Other cements with graduated amounts of limestone were ground for the same time as reference cements. Basic information about these cements are given in table 2 and 3.

Table 1. Quantitative phase composition of clinkers determined by optical microscopy in wt. %.

| Clinker | C₃S | C₂S | C₃A | C₄AF | Cfree | ø size of C₃S |
|---------|-----|-----|-----|------|-------|---------------|
| M       | 73.5| 7.4 | 7.0 | 9.9  | 2.2   | 31 µm         |
| C       | 70.2| 7.6 | 18.5| 3.5  | 0.2   | 20 µm         |

Table 2. Composition of PLCs with clinker M in wt. %, specific weight in kg/m³ and specific surface in m²/kg.

| Cement   | M   | M-LL 10H | M-LL 20H | M-LL 30H | M-LL 10L | M-LL 20L | M-LL 30L |
|----------|-----|----------|----------|----------|----------|----------|----------|
| Clinker M| 100 | 90       | 80       | 70       | 90       | 80       | 70       |
| Limestone H | 0   | 10       | 20       | 30       | 0        | 0        | 0        |
| Limestone L | 0   | 0        | 0        | 0        | 10       | 20       | 30       |
| Specific weight | 3087 | 3048 | 3009 | 2970 | 3052 | 3017 | 2981 |
| Specific surface | 351 | 382 | 410 | 451 | 397 | 439 | 466 |
Table 3. Composition of PLCs with clinker C in wt. %, specific weight in kg/m³ and specific surface in m²/kg.

| Cement     | C   | C-LL 10H | C-LL 20H | C-LL 30H | C-LL 10L | C-LL 20L | C-LL 30L |
|------------|-----|----------|----------|----------|----------|----------|----------|
| Clinker C  | 100 | 90       | 80       | 70       | 90       | 80       | 70       |
| Limestone H| 0   | 10       | 20       | 30       | 0        | 0        | 0        |
| Limestone L| 0   | 0        | 0        | 0        | 10       | 20       | 30       |
| Specific weight | 3075 | 3037 | 2999   | 2961   | 3041   | 3006   | 2972   |
| Specific surface | 349 | 398 | 436   | 469   | 411   | 458   | 509   |

2.2. Grinding separate

In the second part of the experiment, PLCs were prepared by combination of two industrial clinkers used in the first part and industrially ground high-purity limestone of two different types of fineness (see table 4). The limestone type 7 had specific surface 372 m²/kg and the limestone type 9 had 484 m²/kg. At first, two comparative reference cements were prepared, only with the addition of set regulator. The cements were ground to 360 m²/kg. The addition of gypsum was the same as in the first case. Other cements with graduated content of limestone were prepared by homogenization. Basic information about these cements are given in table 5 and 6.

Table 4. Granulometric characteristics of industrially produced finely ground limestones according to ČSN 72 1220 in wt. %.

| Clinker | Max. residuum on sieve 0.5 mm | Max. residuum on sieve 0.2 mm | Max. residuum on sieve 0.09 mm |
|---------|-------------------------------|-------------------------------|-------------------------------|
| Type 7  | 10.0                          | -                            | 40.0                          |
| Type 9  | -                             | 0.1                           | 5.0                           |

Table 5. Composition of PLCs with clinker M in wt. %, specific weight in kg/m³ and specific surface in m²/kg.

| Cement     | M II | M-LL 10-7 | M-LL 20-7 | M-LL 30-7 | M-LL 10-9 | M-LL 20-9 | M-LL 30-9 |
|------------|------|-----------|-----------|-----------|-----------|-----------|-----------|
| Clinker M  | 100  | 90        | 80        | 70        | 90        | 80        | 70        |
| Limestone type 7 | 0    | 10        | 20        | 30        | 0         | 0         | 0         |
| Limestone type 9 | 0    | 0         | 0         | 0         | 10        | 20        | 30        |
| Specific weight | 3087 | 3048 | 3099   | 2970   | 3048   | 3099   | 2970   |
| Specific surface | 362 | 363 | 364   | 365   | 374   | 386   | 399   |

Table 6. Composition of PLCs with clinker C in wt. %, specific weight in kg/m³ and specific surface in m²/kg.

| Cement     | C II | C-LL 10-7 | C-LL 20-7 | C-LL 30-7 | C-LL 10-9 | C-LL 20-9 | C-LL 30-9 |
|------------|------|-----------|-----------|-----------|-----------|-----------|-----------|
| Clinker C  | 100  | 90        | 80        | 70        | 90        | 80        | 70        |
| Limestone type 7 | 0    | 10        | 20        | 30        | 0         | 0         | 0         |
| Limestone type 9 | 0    | 0         | 0         | 0         | 10        | 20        | 30        |
| Specific weight | 3075 | 3037 | 2999   | 2961   | 3037   | 2999   | 2961   |
| Specific surface | 365 | 365 | 366   | 367   | 377   | 389   | 401   |
2.3. Testing methods
Compressive strengths were measured in mortars from PLCs prepared according to EN 196-1 standard, water-cured for 1, 2, 7, 28, 56 and 90 days. Mortars were prepared according to standard, i.e. with binder to sand ratio 1:3 and water to cement ratio w/c = 0.5.

The setting process of prepared PLCs was observed by a Tussenbrock method. Tussenbrock method is performed on a device with a needle similar to Vicats. Depth of submersion of six cylindrical probes of decreasing diameter in the cement paste is measured in time dependence. The depth of indentation of particular probe indicates a threshold of shearing stress (in kPa) which corresponds to consistency achieved at the moment of measurement. This method allows to capture several anomalies during the setting process such as false setting.

The influence of limestone on hydration process was observed by calorimetric measurement. Heat released during hydration process was measured within 24 hours. Observation of the course of the temperature during hydration process of prepared cement pastes was performed on semiadiabatic calorimeter [14]. From the calorimetric curves, the specific heat of cements after 24 hours hydration was calculated according to the following formula:

\[ Q_{24} = \left( \frac{C_{\text{sum}}}{m} \right) \times (t-t_0) \]  

Where:  
\( C_{\text{sum}} \) – total heat capacity of calorimeter in J.K-1 (cement, water, container);  
\( m \) – weight of cement in g;  
\( t, t_0 \) – final and initial temperature of the mixture.

The hydration heat was determined for selected samples also after 7 days of hydration using dissolution method according to EN 196-8.

3. Results and discussion
As you can see in table 2 and 3, in case of grinding together with clinker, limestone fineness significantly increases and therefore resulting cements fineness increases with increasing amount of limestone. From these values it can be also seen that limestone L has better grindability than limestone H and clinker M has better grindability than clinker C.

The most important property of the cements is their strength. The development of compressive strength of the prepared PLCs is shown in figures 1–5.
It is evident from the strength development that with increasing lime content the cement strength decreases. In case of grinding together of clinker C and less pure limestone L in the amount of 10 wt. %, only short-term strengths are slightly higher than for the reference. The same effect is reported by Menéndez et al. [15] using 10 and 20 wt. % of similarly impure limestone.

In our case, the type of clinker has stronger effect than the type of limestone. Clinker M, burnt from low reactivity raw meal, has larger recrystallized alite crystals and medium C\textsubscript{3}A content. Therefore, in terms of hydraulic activity, it can be characterized as slow. The strengths after 2 days of cement prepared from this clinker are lower and the increase in strength between 7 and 28 days is higher. On the contrary, clinker C is burnt from highly reactive raw meal, it is fine-grained with a high C\textsubscript{3}A content and it is very hydraulically active. The increase in initial strengths of the cement is large, but the increase after 7 days is not as significant.

These differences are visible on calorimetric curves as well (see figure 6 and 7). Cements from clinker C are characterized by their narrower main hydration exotherms with steeper beginning. Compared to reference C, the addition of limestone and increasing of specific surface area by grinding at a constant time led to acceleration of hydration. This corresponds to work of other authors who reported the acceleration of cement hydration by addition of fine limestone powder due to the nucleation effect [6, 16, 17]. When using impure limestone L the hydration peak is higher compared to samples with limestone H, probably due to higher fineness and increased Al\textsubscript{2}O\textsubscript{3} content. This supports
the chemical effect of limestone on cement hydration and the hydration temperature may increase [3, 18].

On the contrary, cements from clinker M had delayed hydration, and sample with 30% replacement had very low hydration temperatures with a few hours delay of the main exotherm. However, in case of these cements, the positive effect of 10% limestone addition on hydration is demonstrated by higher total hydration heat after 24 hours than that of the M reference. The values were calculated from the calorimetric curves and are shown in table 7 and 8.

From literature it is evident that the highest positive effect on cement hydration has a fine limestone powder in the amount up to 10 wt. % [3, 16, 17, 19].

Table 7. Heat of hydration of cements from clinker M released in 24 hours in the semi-adiabatic calorimeter in J/g (grinding together).

| Cement | M | M-LL 10H | M-LL 20H | M-LL 30H | M-LL 10L | M-LL 20L | M-LL 30L |
|--------|---|----------|----------|----------|----------|----------|----------|
| Q<sub>24</sub> | 367 | 371 | 350 | 193 | 398 | 334 | 231 |

Table 8. Heat of hydration of cements from clinker C released in 24 hours in the semi-adiabatic calorimeter in J/g (grinding together).

| Cement | C | C-LL 10H | C-LL 20H | C-LL 30H | C-LL 10L | C-LL 20L | C-LL 30L |
|--------|---|----------|----------|----------|----------|----------|----------|
| Q<sub>24</sub> | 450 | 456 | 409 | 329 | 442 | 431 | 341 |

Determination of the heat of hydration by the dissolution method (see table 9) shows that cements with 20% of limestone achieve a favorably low heat of hydration, and cement with 30% of limestone reaches values that classify them as cements with very low heat of hydration according to EN 14216.

Table 9. Heat of hydration of cements according to EN 196-8 with use of limestone H prepared by grinding together after 7 days of hydration in kJ/kg.

| Cement | M | M-LL 10H | M-LL 20H | M-LL 30H | C | C-LL 10H | C-LL 20H | C-LL 30H |
|--------|---|----------|----------|----------|---|----------|----------|----------|
| Hydration heat | 343 | 295 | 246 | 196 | 345 | 280 | 233 | 186 |

The biggest difference in setting were found for PLCs prepared by grinding together. In a detailed observation of setting process of the cement pastes (see figures 8 and 9) it was found that with
the increasing content of limestone, and hence also the increasing total surface area, the initial setting time is shorter. Cements prepared from more hydraulically-active clinker C have shorter initial setting time than cements from clinker M.

Voglis et al. [20] also stated shorter setting time while increasing the initial strength of cement with 15% addition of limestone compared to the reference OPC. The shortening of the cement setting time with increasing limestone content due to nucleation effect is also confirmed by other authors [21, 22, 23].

Figure 8. Setting process of cements from M clinker and limestone H (grinding together). Figure 9. Setting process of cements from C clinker and limestone H (grinding together).

4. Conclusions
The effect of limestone content (up to 30 wt. %) on PLCs technology parameters was monitored. Two types of limestone and two types of clinker were used. Limestones varied in CaCO$_3$ content (94.6 and 79.0 wt. %), clinkers were from two different cement plants and differed in particular in C$_3$A content and in hydraulic activity.

It was found that the properties of the clinkers used had a much greater impact on the parameters of the cements than the quality of the limestones used.

In terms of the influence of two types of limestone, the addition of more contaminated limestone slightly increased the strength of the cements. This can be due to its higher fineness when using together grinding or the presence of impurities in the form of Al$_2$O$_3$ and amorphous SiO$_2$.

In the case of hydraulically more active clinker with a high C$_3$A content and a low limestone content, the positive effects on cement hydration in early stages are evident.

Different preparation of cements, i.e. the addition of separately ground limestone or the together grinding of limestone with clinker, did not show a significant impact on the strength, even though the total specific surface of the cements varied considerably. Significant differences were noted only in early stages of hydration.

Furthermore, it has been found that with the increasing content of limestone the initial setting time of cements is noticeably shorter.

Cements with a high limestone content significantly save less energetically and less environmentally suitable clinker and still achieve high-quality technological parameters. In addition, they exhibit very low hydration heat, which may be beneficial in some types of applications.

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References
[1] Zinke R K and Werkheiser W H 2018 Mineral Commodity Summaries 2018 (U.S. Geological Survey, Reston, Virginia)
[2] WBCSD-CSI 2009 *Cement industry energy and CO₂ performance ‘Getting the Numbers Right’* (Conches-Geneva, Switzerland)

[3] Wang D, Shi C, Farzadnia N, Shi Z, Jia H and Ou Z 2018 *Constr. Build. Mater.* **181** pp 659–672

[4] Schutter G D 2011 *Proc. 36th Conf. on our World in Concrete & Structures (Singapore)* (Singapore: CI-Premier Pte. Ltd.)

[5] Martin C, Phillippe L and Erick R 2006 *Cem. Concr. Res.* **36**

[6] Soroka I and Setter N 1976 *Cem. Concr. Res.* **6** pp 367–376

[7] Iarrassar E F 2009 *Cem. Concr. Res.* **39** pp 241–254

[8] Craeye B, Schutter G D, Desmet B, Vantomme J, Heirman G, Vandewalle L and Kadri E 2010 *Cem. Concr. Res.* **40** pp 908–913

[9] Rode S, Oyabu N, Kobayashi K, Yamada H and Kühnle A 2009 *Langmuir* **25** pp 2850–2853

[10] Taylor H F W 1997 *Cement Chemistry* (London: Thomas Telford Publishing)

[11] De W K, Ben H M, Le S G, Kjellsen K O, Justnes H and Lothenbach B 2011 *Cem. Concr. Res.* **40** pp 279–291

[12] Lothenbach B, Maschei T, Möschner G and Glasser F P 2008 *Cem. Concr. Res.* **38** pp 1–18

[13] Scrivener K L, Lothenbach B, Belie N D, Gruyaert E, Skibsted R, Snellings J and Vollpracht A 2015 *Cem. Concr. Res.* **48** pp 835–862

[14] Brandštetr J, Polcer J, Krátký J, Holešinský R and Havliča J 2001 *Cem. Concr. Res.* **31** pp 941–947

[15] Menéndez G, Bonavetti V and Iarrassar E F 2003 *Cem. Concr. Compos.* **25** pp 61–67

[16] Vance K, Aguayo M, Oey T, Sant G and Neithalath N 2013 *Cem. Concr. Compos.* **39** pp 93–103

[17] Thongsanitgarn P, Wongkeo W, Chaipanich A and Poon C S 2014 *Constr. Build. Mater.* **66** pp 410–417

[18] Aashay A, Gaurav S a Narayan N 2016 *Constr. Build. Mater.* **102** pp 113–124

[19] Ramezanianpour A A, Ghiassvand E, Nickseresht I, Mahdikhani M and Moodi F 2009 *Cem. Concr. Compos.* **31** pp 715–720

[20] Voglis N, Kakali G, Chaniotakis E and Tsivilis S 2005 *Cem. Concr. Compos.* **27** pp 191–196

[21] Marzouki A, Lecomte A, Beddey A, Diliberto C and Ouezdou M B 2013 *Constr. Build. Mater.* **48** pp 1145–1155

[22] Valcuende M, Maco E, Parra C and Serna P 2012 *Cem. Concr. Res.* **42** pp 583–592

[23] Moon G D, Oh S, Jung S H and Choi Y C 2017 *Constr. Build. Mater.* **135** pp 129–136