SIMULATION OF CEMENT-PASTE SETTING BEHAVIOR BASED ON THE PHYSICAL PROPERTIES OF BLENDED-CEMENT POWDERS

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ABSTRACT

In this study, an empirical model was developed to simulate the setting process of cement pastes, with and without limestone. Interestingly, an excellent linear correlation was found between the time required for the cement pastes to reach penetration depths of 0 mm to 40 mm (the setting process) and the physical properties of the powders comprising those pastes. The empirical model was based on this clear, linear behavior, determined by means of linear regression analysis. The developed model offers an easy way to predict and to control the setting history of any cement paste, with and without limestone additive, by simply using the available, measured physical properties of the blended cements with limestone particles of various sizes.

KEYWORDS

cement, blended cement, limestone, setting time, linear regression

1. INTRODUCTION

Concrete is the most widely used construction material in world and cement is considered one of the main components in the concrete mixtures. However, cement highly affects greenhouse gas emissions, since the production of each ton of cement releases almost one ton of CO_2 into the atmosphere.(1,2) Globally, the production of cement contributes at least 5%–7% of all the CO_2 emissions.(3) Furthermore, cement production requires a high-temperature kiln, ~1500°C (i.e., high-energy consumption). Therefore, the development of more sustainable cements, with less CO_2 emission and energy consumption, is required in order to meet the demand for sustainability and minimal impact on the environment. One common direction is the development of blended cements by the partial replacement of the cement with mineral additives.

Blended cements with limestone are widely used in Europe. According to EN-197\1, all 27 common types of cement may have up to 5% minor additional components (MAC), typically a limestone additive. Moreover, there are four types of cement that can take a higher limestone content in two replacement ranges, CEM II A-L and CEM II A-LL (6%–20% limestone), as well as CEM II B-L and CEM II B-LL (21%–35% limestone). The motivations for reducing the clinker content are threefold: (1) the ecological benefits of the lower emission of CO_2 into the atmosphere; (2) the economic benefits of reduced costs; and (3) the existence of better scientific\

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technological solutions, yielding improved cement and concrete performances. Limestone is one of the most attractive materials, being natural, available and more cost-efficient.

Several effects of limestone powder in blended-cement were found in three main mechanisms: (i) the nucleation centers for the hydration reaction; (ii) the reactivity of limestone with clinker minerals; and (iii) the filler effect of limestone particles in cement systems. First of all, some studies reported lower initial and final setting times for blended cement with limestone, compared to original cement without limestone.(4–5) The replacement of clinker with limestone powder, which has a higher surface area than that of the clinker, increases both the number of nucleation centers and the hydration rate.(5–6) Secondly, although limestone is generally considered an inert additive, there is evidence that it is not completely inert; some additional products are formed by the limestone with the hydration products during the hydration process. However, this minor limestone reactivity produced no significant effects on the properties of the cement paste.(7–9) Thirdly, the filler effect theory applies to cement properties. Researchers have reported that the partial replacement of clinker with mineral additives influences the flow and workability of fresh cement paste.(10–14)

The properties and the performances of various cements are obtained according to the relevant standards. However, mathematical models have been developed to simulate the chemical and physical performances, in order to predict and optimize the properties of cement and concrete mixtures. For example, Lin et al.(15) formulated a model for hydration kinetics and to determine the degree of hydration of Portland cement. This model considered the effects of: the chemical composition and fineness of the cement; the water-cement ratio; the curing temperature; and the applied pressure. Based on the experimental results, an estimation equation was derived by Hwang et al.(16) to assess the compressive strength of blended cement with fly ash. Termkhajornkit et al.(17) developed a model for calculating the effects of the temperature and fineness of Portland cement on the hydration kinetics of cement paste. Although this research was done to predict the performances of the cement and concrete mixtures, less is known about how to predict and to control the setting process from the initial state of the paste until final setting is obtained of different blended cement with limestone having various sizes

In the present study, an empirical model was developed to simulate the setting histories of blended-cement pastes by assessing the physical properties of the additive powders. This empirical model was based on the linear behavior identified by linear regression analyses conducted on different sets of experimental data. The setting histories of the various blended cements with limestone, having different particle sizes and contents, were expressed by the particle-size distribution (PSD) of the powders and by the surface areas of the blended-cement and limestone contents. The determination of the setting times was obtained according to EN 196-3. The models were validated using commercially-available cements.

2. MATERIALS AND EXPERIMENTAL METHODS

In order to develop an empirical model that predicts the setting times of the blended cements, first an experimental study was performed. CEM I 52.5 R was partially replaced with limestone powders (> 99.8% $CaCO_3$) having varied particle sizes and contents. The chemical composition of the original cement is given in Table 1. This particular cement was chosen because it contains mainly clinker, with hardly any additives and, thus, it serves as a good basis for the study of the influence of limestone additives. As such, CEM I 52.5 R will be referred to here as the 'original cement'. Six different limestone powders, representing several different particle diameters, were examined; their mean sizes were: smaller than, larger than, or similar to the original cement, with an average particle diameter of 17 μm. Two different particle sizes (i.e., smaller, larger or similar) were studied for each type of limestone powder. Cement replacement was investigated using several limestone-cement mixtures in which the limestone powder comprised 0%, 5%, 10%, 20% or 30% of the mixture (by mass), where 0% represents a reference sample of the original cement (without the addition of any limestone). Additionally, two commercial cements, CEM II A-M 42.5 N and CEM I 52.5 N, were also studied for the sake of comparison and the validation of the proposed empirical models. To validate the empirical models, the properties of the powders and the fresh cement pastes were tested and measured by means of several methods.

> **Powders:** Surface area and PSD were examined for the six different limestone systems and the three cement types: CEM I 52.5 R, CEM II A-M 42.5 N, and CEM I 52.5 N. The surface area of each individual powder was determined using the Brunauer-Emmet-Teller (BET) technique with N_2. The surface areas of the cement and limestone powders were calculated by multiplying the cumulative relative weight of each powder by the surface area of the individual component in the powder mixture. PSD was determined by laser diffraction scattering (CSI-100, Ankersmid).
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> **Cement pastes:** The workability of each cement paste was determined based on normal consistency and penetration depth measurements. Each cement powder—blended or original—was mixed with the amount of water needed to obtain a normal consistency according to EN 196-3. After each sample (i.e., original cement or blended cement + limestone) was mixed with water to reach normal consistency, the samples were placed in a water bath at 20 ± 1°C. While still under water, to study the setting process, the penetration depths were measured until the final setting time was obtained using an automatic Vicat Needle Apparatus (Toni Technik).

3. PHYSICAL PROPERTIES OF BLENDED LIMESTONE-CEMENT POWDERS

3.1 Particle-size distribution (PSD)

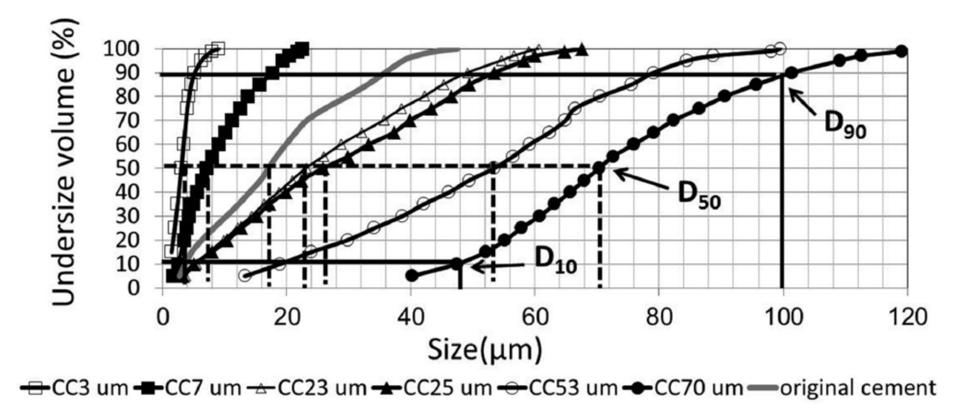
Characterizations of the PSDs of the limestone and the original cement powders were required for the empirical models. Figure 1 presents the PSD of the six tested limestone powders, as well as of the original cement. Two main methods are commonly used to characterize the PSDs of powders: (i) by D_{10}, D_{50}, D_{90} etc., and (ii) according to the Rosin-Rammler-Bennett (RRB) distribution function.

The PSDs of the limestone powders and the original cement were first characterized by D_{10}, D_{50} and D_{90}, that represent the sizes at which all the smaller particles occupy 10%, 50% and 90% of the powder's volume, respectively. The D_{50} of each limestone powder and of the original cement is represented by the dashed line. For example, only for the largest particle size (CC 70 μm), D_{10} and D_{90} are represented by continuous lines (Figure 1). The values of D_{90},

TABLE 1. Chemical composition of the original cement

Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2	K_2O	Na_2O	P_2O_5	Mn_2O_3	SO_3
%	65.07	18.96	4.5	2.46	1.16	0.36	0.33	0.21	0.32	0.30	2.86

FIGURE 1. Particle size distribution (PSD) of the tested powders (original cement and limestone).



D_{50} and D_{10} are given in Table 2 for all the tested limestone powders and the original cement, as presented in Figure 1. Three main sets of limestone sizes were examined: large particles, where D_{10}, D_{50} and D_{90} are larger than those obtained for the original cement; small particles, where D_{10}, D_{50} and D_{90} are smaller than those obtained for the original cement; and medium-sized particles, where the PSD is within that of the original cement, as may be clearly seen in Figure 1. These six different limestone powders will be identified here by their mean particle sizes (i.e., D_{50}, of 70 µm, 53 µm, 25 µm, 23 µm, 7 µm and 3 µm), each of which is signified by CCX, such that X stands for the mean particle size (e.g., CC3 is a limestone powder with a mean particle size of 3 µm).

Then, the PSDs of the powders were expressed by a mathematical equation, according to the RRB distribution function derived in Equation 1[18]:

$$R = 100\exp\left(\frac{D}{D_e}\right)^n \tag{1}$$

TABLE 2. Particle size distribution (PSD) parameters of the tested limestone powders and the original cement.

	Cement	Larger particles		Similar particles		Smaller particles	
	CEM I	CC70 µm	CC53 µm	CC25 µm	CC23 µm	CC7 µm	CC3 µm
D_{90}, µm	35.81	101.43	80.72	53.46	49.08	17.63	4.90
D_{50}, µm	17.02	70.28	53.49	25.78	23.01	7.07	3.13
D_{10}, µm	3.64	47.41	17.76	5.08	5.27	2.46	1.95
n-value	1.4987	3.9909	2.0903	1.3790	1.4202	1.5638	2.9240
D_e, µm	21.01	79.93	55.35	30.58	28.58	9.36	3.74

where R is the cumulative percentage retained on each mesh size (%); D_e is the characterized particle size that corresponds to the particle size at 36.8% of cumulative percentage retained (μm); D is the particle size (μm); and n is the uniformity coefficient index.

Equation 1 may be converted to the following form:

$$\ln\left(\ln\frac{100}{R}\right) = n\ln D - n\ln D_e \tag{2}$$

If we define the following:

$$Y = \ln\left(\ln\frac{100}{R}\right) \qquad X = \ln D \qquad b = -n\ln D_e$$

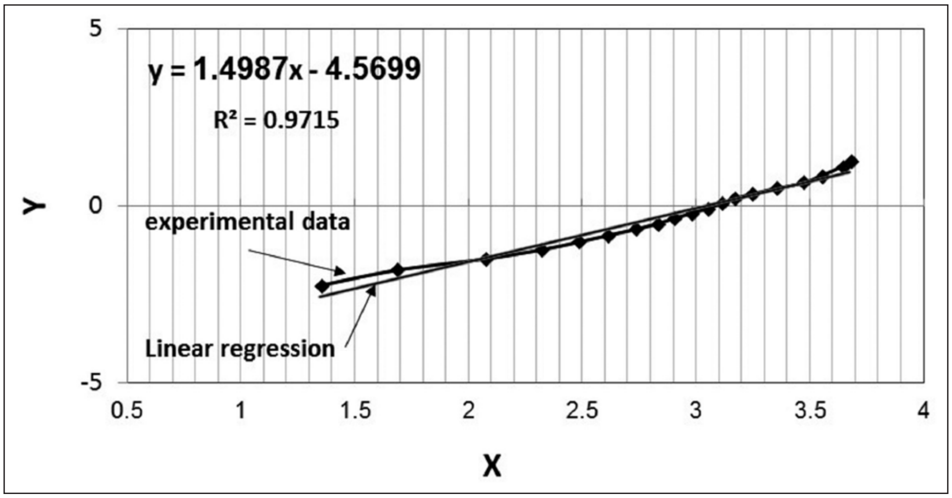
Then, Equation 2 is transformed into a linear equation:

$$Y = nX + b \tag{3}$$

where n is the slope of the linear relation.

According to Equation 2, linear regressions were performed using the PSDs presented in Figure 1 for all the tested limestone powders and original cement. Where the R values are the oversized volumes (100 – Y) presented in the y axis of Figure 1, and the D values are the particle sizes presented in the X axis of Figure 1, providing the X and Y values for Equation 3. The linear regression of all PSDs determined the value of the parameters n and b (Equation 3); then, the D_e value was calculated, based on Equation 2. Figure 2 shows, for example, the curve of the X and Y values, based on the RRB function (Equation 3) and the calculated linear regression of the original cement. This calculation gave a slope (n-value) of 1.4987 and a b-value of –4.5699 with R^2 = 0.9715; the calculated D_e was 21.01 μm. The values of n and D_e for all six limestone powders and the original cement are given in Table 2. It may be seen that the value

FIGURE 2. Linear regression of the original cement according to the Rosin-Rammler-Bennett (RRB) distribution function (Equation 3).



of D_e is well-correlated with the mean particle size (D_{50}) of the tested powders, as the values of D_e for the limestone with larger particles were larger than that of the original cement while, for the limestone with smaller particles, the values of D_e were smaller than that of the original cement. Medium-sized limestone obtained a relatively similar D_e to the value of the original cement (slightly higher). The n-values of the limestone with CC 70 µm, CC 53 µm and CC 3 µm were greater than that obtained for the original cement, but the n-values were similar to that of the original cement for CC 25 µm, CC 23 µm and CC 7 µm. Note that most of the PSD range of the limestone with CC 25 µm, CC 23 µm and CC 7 µm are within the PSD range of the original cement (Figure 1), which may explain the similarity in their n-values to that of the original cement.

3.2 Surface area

Surface area is also considered to be an important physical parameter for the characterization of powders.(12, 17) Here, the surface area was measured by the BET technique with N_2 for the original cement and all the limestone powders; the values are given in Table 3.

The surface areas of the blended cements (i.e., those comprising a blend of the original cement with limestone powders) are affected by the surface areas of: the original cement and the limestone particles, and by the relative percentages of both components in that particular blended cement. The ratio between the surface area of each blended cement (limestone + original cement) and the original cement, as a function of the limestone content, is expressed by Equation 4:

$$SA_{BC}\ [\%] = 100\ \frac{ySA_{OC} + (1-y)SA_{CC}}{SA_{OC}} \tag{4}$$

where SA_{BC} is the surface area of the blended cement (%); SA_{OC} is the surface area of the original cement; SA_{CC} is the surface area of the limestone powders; y is the relative content of the original cement in the blended cement.

The ratios between the surface-area values of the limestone-blended cements (having different sized-particles and various contents) and of the original cement are given in Table 4. Equation 4 and Table 4 indicate that the surface area of the blended cement increases relative to that of the original cement as the content of limestone with smaller particles and greater surface area is increased, while its surface area decreases with the increased content of limestone with larger particles and lower surface area than that of the original cement, as expected. Blended cements with limestone powders having a similar particle size and similar surface area (compared to the original cement) were not significantly affected by the increased limestone powder content.

TABLE 3. Surface areas of the tested powders.

	Unit	Cement CEM I	CC70 µm	CC53 µm	CC25 µm	CC23 µm	CC7 µm	CC3 µm
Surface area (BET)	m^2/gr	1.53	0.23	0.39	1.37	0.84	3.28	6.22

TABLE 4. Surface areas (%, the ratio between the blended cements with limestone and the original cement) of all the tested blended cement powders with the different limestone contents.

	Limestone content, % (by mass)			
	5	10	20	30
Particle size (CCX), µm	Surface area, %	Surface area, %	Surface area, %	Surface area, %
70	92.16	84.32	68.64	52.96
53	93.09	86.19	72.38	58.57
25	99.47	98.94	97.88	96.82
23	95.86	91.73	83.46	75.20
7	105.71	111.42	122.85	134.28
3	115.29	130.58	161.17	191.76

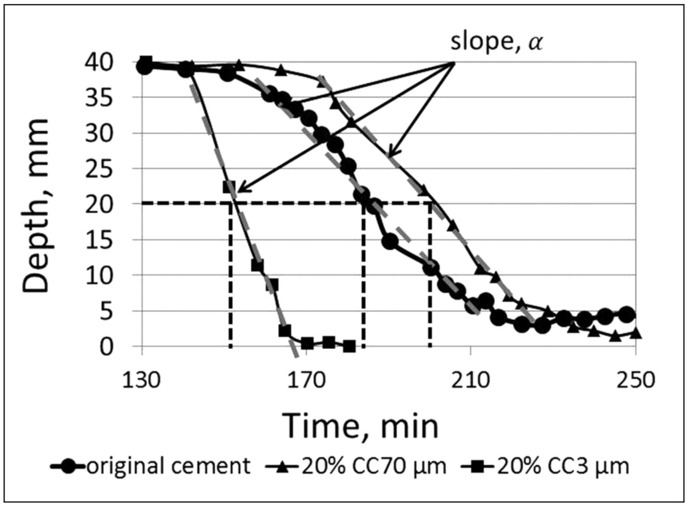
In this study, the powders are deliberately characterized by the surface areas of the blended cements (Table 4) and the PSD values of the individual limestone powders and of the original cement (i.e., D_{90}, D_{50}, D_{10} and D_e, n; see Table 2). Those powder parameters were determined to serve as predictor variables of the empirical models, to describe the setting-time process and the packing density of the limestone-blended cements with different-sized particles and varied contents.

3.3 Setting history-setting rate and time

The setting process, until final setting, was determined by the measurement of the penetration depths according to EN 196-3 for the original cement and all the blended cements with various limestone particle sizes and contents. Detailed results and discussion on the setting-history measurements of these systems may be found in a different publication.(11) For example, Figure 3 presents the penetration depths vs. the times of the original cement and of two blended cements with 20% limestone, one with large-sized (CC70 µm) and the second with small-sized (CC3 µm) particles. The times were recorded for the penetration-depth measurements taken from 40 mm until the final setting time was determined, following the standard. Observe in Figure 3 that the setting rate exhibits the linear behavior of all three systems, as represented by the grey dotted line in each system. The linear behavior of the setting rate, symbolized by α (mm/min), was observed for all the tested blended cements in this study, allowing the easy determination of the times required to reach any penetration depth between 0 mm and 40 mm. Note that the time taken to reach the penetration depth of 20 mm was found to be a relatively stable point in all the tested systems. Table 5 summarizes the setting rates, α (mm/min), and the times for reaching a penetration depth of 20 mm, $T_{PD=20mm}$, in all tested limestone-blended cements with different sized particles and contents.

Based on Table 5, for the blended cements with limestone particles smaller than those of the original cement (CC7 µm and CC3 µm) and higher surface areas, the setting rates were faster and the time needed to reach a penetration depth of 20 mm was shorter than for the original cement. An opposite trend was observed in blended cements with larger limestone

FIGURE 3. The experimental penetration depths vs. times of the original cement and blended cements with 20% limestone having smaller and larger particles (the dashed black line represents a penetration depth of 20 mm and the linear dashed grey line represents the setting rate, α, mm/min).



particles (CC70 µm and CC53 µm) and lower surface areas, which exhibited slower setting rates and longer times to reach the 20 mm penetration depth than in the original cement. In the case of a limestone-blended cement system with a particle size similar to that of the original cement (CC25 µm and CC23 µm), the setting rate and the time to a 20 mm penetration depth showed no significant change, compared to the original cement. The values of setting rate and time to 20 mm penetration depth (in Table 5) were used to develop the present model.

TABLE 5. The setting rates (α) and the times required to reach a penetration depth of 20 mm ($T_{PD=20}$) in the different blended cements (based on the example in Figure 3).

	Limestone content, % (by mass)							
	5		10		20		30	
Particle size (CCX), µm	Setting rate, α mm/min	Time, $T_{PD=20mm}$ min	Setting rate, α mm/min	Time, $T_{PD=20mm}$ min	Setting rate, α mm/min	Time, $T_{PD=20mm}$ min	Setting rate, α mm/min	Time, $T_{PD=20mm}$ min
70	−0.6312	194	−0.6012	199	−0.5335	207	−0.4192	220
53	−0.6240	201	−0.6445	209	−0.5963	215	−0.5028	228
25	−0.6113	180	−0.6104	177	−0.6621	181	−0.6265	183
23	−0.6171	180	−0.5729	189	−0.5581	193	−0.5025	202
7	−1.0302	156	−1.0915	164	−1.0906	173	−1.1772	178
3	−0.9842	166	−1.1844	168	−1.5164	152	−1.8167	152

4. MODELING

4.1 Setting history

An empirical model, simulating the setting process (in Figure 3), was developed based on linear regression analysis, using the physical parameters of the powders described above (Table 2, Table 4). Note that linear regression analysis was chosen in light of the trend observed in the experimental results, as described in the following sections.

4.1.1 Time required to reach a penetration depth of 20 mm

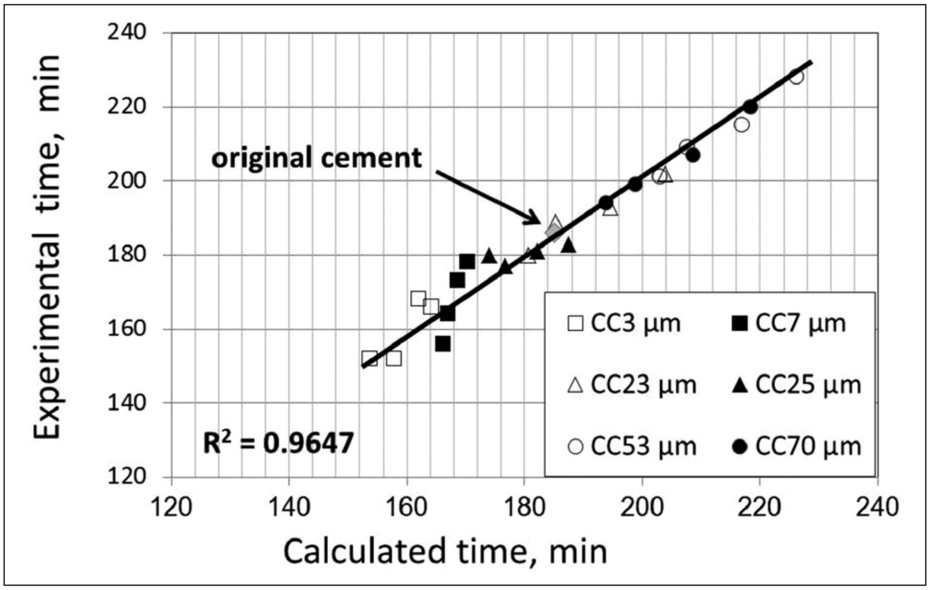
A linear regression was first performed to ascertain if there is a correlation between the time needed to reach a penetration depth of 20 mm (found to be a stable stage) and the physical parameters of the blended-cement powders: D_{90}, D_{50}, D_{10}, n and D_e values (Table 2), the limestone contents and the surface areas of the blended cements (Table 4, Equation 4).

According to the above linear regression analysis, Equation 5 describes the time taken to reach a penetration depth of 20 mm, T_{PD}, in each of the tested blended cements with the various particle sizes and contents.

$$T_{PD} = 296.099 + 1.607D_{10} + 3.775D_{50} - 2.770D_{90} - 34.267n + 0.509\ LC - 0.304SA_{BC} \quad (5)$$

The characterization parameters (D_{10}, D_{50}, D_{90}, and the n-value), the limestone contents (*LC*) and the surface areas of the blended cements (SA_{BC}%) were found to be significant parameters in line with their low p-values (less than 0.05) obtained from the linear regression analysis and were used to calculate the T_{PD} in Equation 5. However, the value of D_e was not chosen, due to its high p-value (above 0.05) obtained from the linear regression analysis. Figure 4 shows the correlation between the times measured according to EN 196-3 (Table 5) vs. the calculated times required to reach a penetration depth of 20 mm for all the investigated blended cements, using Equation 5. A good linear correlation is observed between the calculated and

FIGURE 4. Correlation between the calculated and experimental times required to reach a penetration depth of 20 mm in the different limestone-blended cements.



the experimental time values with $R^2 = 0.9647$. This good correlation clearly indicates that, by using Equation 5, it is possible to predict the time needed to reach a penetration depth of 20 mm along with the physical parameters of the powders: D_{10}, D_{50}, D_{90}, the n-values, the limestone contents and the surface areas.

4.1.2 Setting rate (*SR*)

The second parameter chosen to characterize the setting process of blended cement is its setting rate (*SR* mm/min), based on the slope presented in Figure 3. Here also, a linear regression analysis was used to find a correlation between the setting rate and the physical parameters of the tested blended-cement powders: D_{90}, D_{50}, D_{10}, n and D_e values (Table 2), the limestone contents (*LC*) and the surface areas of the blended cements (SA_{BC} %; Table 4, Equation 4).

Following the linear regression analysis, Equation 6 describes the setting rate, *SR* (mm/min), of each of the tested blended cements.

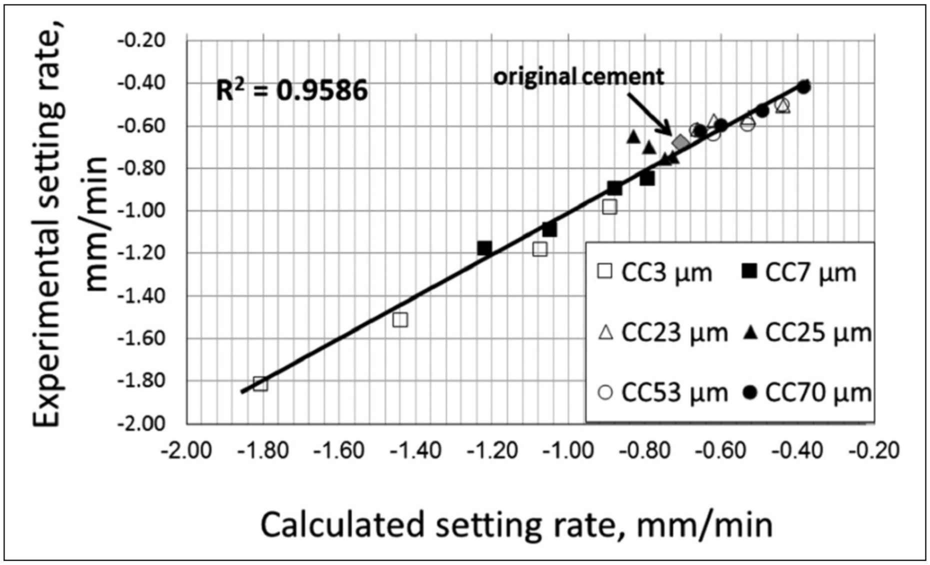
$$SR = 0.313 - 0.005\ LC - 0.010\ SA_{BC} \tag{6}$$

According to the p-values, only the limestone content and the surface area of the blended cements were found to be significant parameters for determining the setting rates. Figure 5 displays the experimental setting rates according to EN 196-3 (Table 5) and the calculated setting rates using Equation 6, for all the tested blended cements. A good linear correlation is observed between the calculated and experimental values with $R^2 = 0.9586$, indicating that, by using Equation 6, it is possible to predict the setting rates by using the limestone contents and the surface areas of the various limestone powders.

4.1.3 Modeling of the setting history

As was shown in Figures 4 and 5, good linear correlations were found between the setting rates and the times required to reach a penetration depth of 20 mm, and the physical parameters

FIGURE 5. Correlation between the calculated and experimental setting rates of the different limestone-blended cements.



of the powders: D_{90}, D_{50} and D_{10}, n, and D_e, the limestone contents and the surface areas. Therefore, the determined linear equations may be used to simulate the entire setting process of the blended cements being studied.

In order to predict the entire setting process according to EN 196-3, from 0 mm to 40 mm, it is necessary to determine the times required to reach all the possible penetration depths between 0 mm and 40 mm, in accordance with EN 196-3. Equation 7 is a suggested linear equation for the calculation of penetration depths vs. time:

$$Y = \alpha T + b \tag{7}$$

where Y represents any penetration depth (mm) from 0 mm to 40 mm; T (min) is the time required to reach a specific penetration depth of Y mm; α symbolizes the linear slope; and b symbolizes the linear constant.

The b-value of each blended cement, having a different limestone particle size and content, may be calculated by rearranging Equation 7 into the expression presented in Equation 8, where Y equals 20 mm, T is $T_{PD=20\text{ mm}}$ (Equation 5) and α is the setting rate (*SR* from Equation 6 above).

$$\begin{aligned} b = 20 - &\left(0.313 - 0.005LC - 0.010SA_{BC}\right) \\ &\left(296.099 + 1.607D_{10} + 3.775D_{50} - 2.770D_{90} - 34.267n + 0.509LC - 0.304SA_{BC}\right) \end{aligned} \tag{8}$$

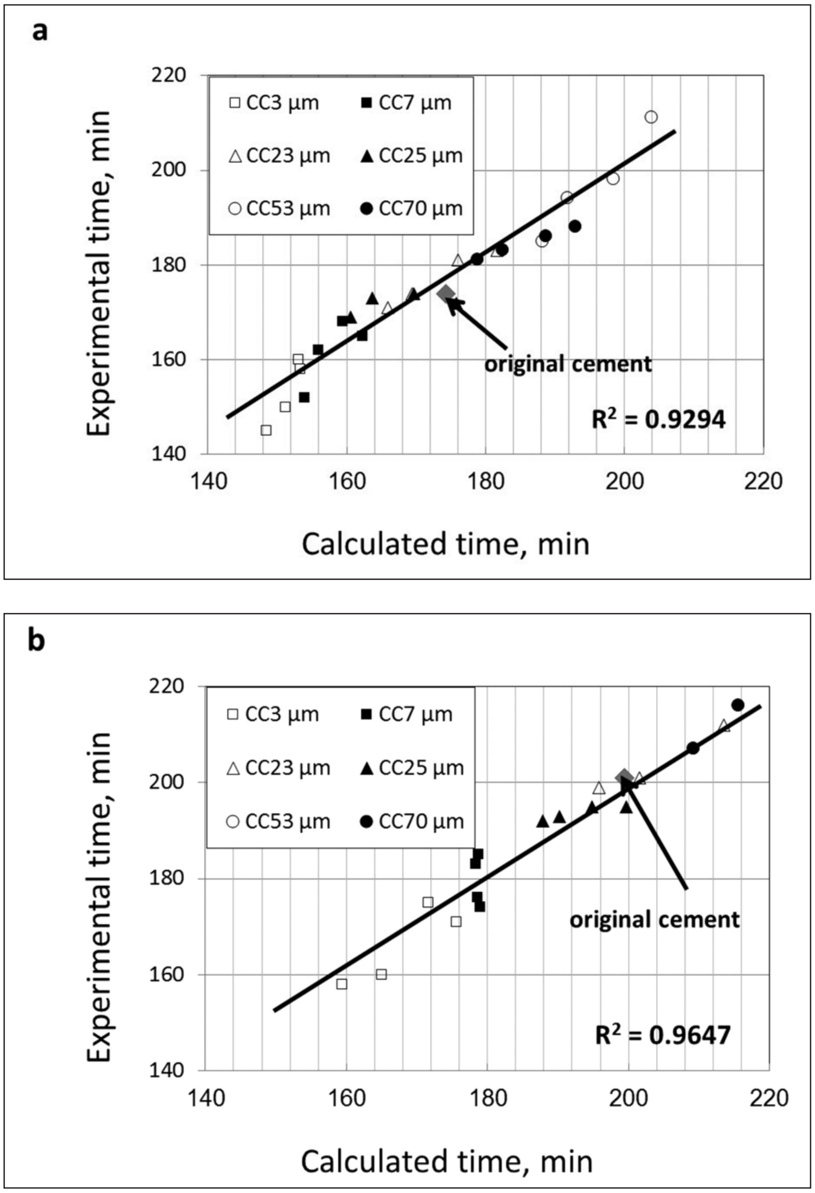
The b-values were calculated for all the tested blended cements and presented in Table 6. By the obtained values of α and b (Equation 7), it is possible to calculate the time needed to reach any penetration depth throughout the entire setting history of each blended cement (i.e., from 0 mm to 40 mm).

Figure 6 presents the experimental results (based on EN 196-3) and the calculated penetration times to depths of 30 mm and 10 mm (based on Equation 7), for all the tested blended cements. A good correlation is clearly observed between the calculated and experimental values

TABLE 6. The b-values (Equation 7) for all the tested blended cements with limestone.

	Limestone content, % (by mass)			
	5	10	20	30
Particle size (CCX), µm	b-value, mm	b-value, mm	b-value, mm	b-value, mm
70	147.62	140.07	123.37	104.52
53	155.58	149.40	135.79	120.52
25	147.54	153.18	164.79	176.84
23	140.63	135.45	123.84	110.57
7	152.54	167.33	197.32	227.85
3	167.08	194.85	248.07	298.20

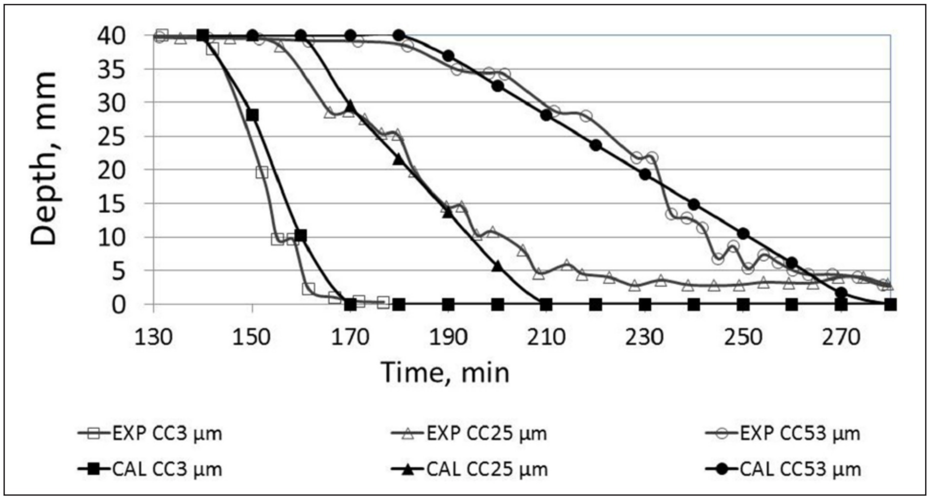
FIGURE 6. The time needed to reach the penetration depths of (a) 30 mm and (b) 10 mm, obtained experimentally in accordance with Equation 7 for all the tested limestone-blended cements.



for both these penetration depth cases, 30 mm and 10 mm, with $R^2 = 0.9294$ and $R^2 = 0.9647$, respectively. These two examples clearly show that Equation 7 may be used to calculate the penetration times to any depth from 0 mm to 40 mm, following EN 196-3. Note that this test limits the maximum possible penetration depth to 40 mm.

According to Equation 7, the entire setting process may be predicted by calculating the penetration depths from 0 mm to 40 mm vs. the times of any limestone-blended cements with various particle sizes and contents. The value of penetration depth vs. time may be calculated by transforming Equation 7 into the form presented in Equation 9 inserting the setting rate (*SR* in Equation 6) and the b-value (Equation 8).

FIGURE 7. Calculated and experimental penetration depths vs. times of blended cements with 30% limestone and particle sizes of CC53 μm, CC25 μm and CC3 μm.



$$
\begin{aligned}
Y = {} & \left(0.313 - 0.005LC - 0.010SA_{BC}\right)T \\
& + \left(-72.678 - 0.503D_{10} - 1.181D_{50} + 0.867D_{90} + 10.725n + 1.321LC\right. \\
& + 3.055SA_{BC} + 0.004LC\,SA_{BC} + 0.008LCD_{10} + 0.018LCD_{50} - 0.013LCD_{90} \\
& - 0.171LC\,n + 0.002LC^2 + 0.016SA_{BC}D_{10} - 0.037SA_{BC}D_{50} \\
& \left. - 0.027SA_{BC}D_{90} - 0.342SA_{BC}n - 0.003SA_{BC}^2\right)
\end{aligned}
\tag{9}
$$

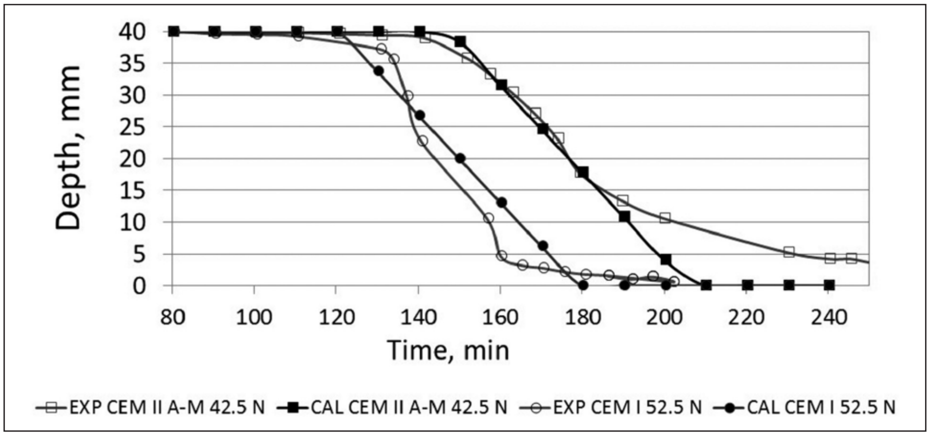
Figure 7 shows an example of the entire gamut of measured penetration depths from 0 mm to 40 mm, according to EN 196-3, and the calculated penetration depths vs. the times of three different blended cements with particle sizes: of CC53 μm, CC25 μm and CC3 μm, and 30% limestone contents.

The above developed model was validated using two additional, available commercial cements, CEM II A-M 42.5 N and CEM I 52.5 N (physical parameters in Table 7). Their setting histories were measured, based on EN 196-3, and appear in Figure 8, along with their calculated values, based on the empirical model described above (and Eq. 8). Good correlations between the experimental and calculated values are observed for both cement types, indicating the practical use of the empirical model developed here.

TABLE 7. The physical parameters of the commercial cements, CEM II A-M 42.5 N and CEM I 52.5 N.

	D_{90}, μm	D_{50}, μm	D_{10}, μm	n-value	Surface area, m^2\gr
CEM II A-M 42.5 N	40.0	21.0	5.0	1.9153	1.10
CEM I 52.5 N	36.0	10.0	1.0	1.6214	1.70

FIGURE 8. Calculated and experimental penetration depths vs. times of cement types CEM II A-M 42.5 N and CEM I 52.5 N.



Figures 7 and 8 clearly show that it is possible to model the setting-history process of different types of cements (including limestone-blended cements with different particle sizes and contents) using only the physical properties of the powders: PSDs, surface areas and contents and the set of linear equations provided above. In other words, the developed model can predict and control the setting history of any blended cement, based on linear regression parameters, by the use of the powder characteristics alone.

5. SUMMARY AND CONCLUSIONS

In this work, an empirical model was developed to predict the setting process of cement pastes with and without limestone.

An excellent linear correlation was found between the time required for the cement pastes to reach 0 to 40 mm penetration depths (setting process) and the physical properties of the powders used to compose those pastes. Similar good linear correlations were also found between the setting rates and the physical properties of those powders. The linear behavior was determined by means of linear regression analysis.

Based on these clear linear behaviors, a model was developed to predict the entire setting histories of the original and blended cements, using only the available, measured physical properties of the limestone powders: PSD values (D_{90}, D_{50}, D_{10}, n and D_e), surface areas (SA_{BC}) and limestone contents (LC).

The developed model presented in this work offers an easy and practical way to predict and to control the setting process of any cement paste, including blended cements with limestone, having different particle sizes and contents, by simply using the available, measured physical properties of the limestone powders.

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7. REFERENCES

[1] C. Mayer (2009), The greening of the concrete industry, Cement & Concrete Composites, 31, 601–605.

[2] V.M. Malhotra (2000), Role of supplementary cementing materials in reducing greenhouse gas emissions: Concrete technology for a sustainable development in the 21st century. London: E&FN Spon, pp. 35–226.

[3] C. Benjamin McLellan, P. Ross Williams, L. Janine, R. Riessen, D. Glen Corder, Cost and carbon emissions for geopolymer pastes in comparison to ordinary portland cement, J. of Clean. Prod. 19 (2011) 1080.

[4] T. Vuk, V. Tinta, R. GabrovsÏek, V. KaucÏic, The effects of limestone addition, clinker type and fineness on properties of Portland cement, Cem. Concr. Res. 317 (2001) 135.

[5] E.H. Kadri, S. Aggoun, G. De Schutterk, K. Ezziane, Combined effect of chemical nature and fineness of mineral powders on Portland cement hydration, Mater. Struct. 43 (2010) 665.

[6] H. Lv, F. Jia, Y. Cheng, Y. Li, Y. Long, J. Yang. (2011). "Study on Properties of Blended Finely Ground Limestone Powder Cement and Compressive Strength of Mortar," Advanced Material Research 168, 1449.

[7] K.D. Ingram, K.E. Daugherty, A review of limestone addition on Portland cement and concrete, Cem. Concr. Comp. 13 (1991) 165.

[8] G. Kakali, S. Tsivilis, E. Aggeli, M. Bati, Hydration products of C3A, C3S and Portland cement in the presence of CaCO3, Cem. Concr. Res. 30 (2000) 1073.

[9] J. Pera, S. Hussonb, B. Guilhot, Influence of finely ground limestone on cement hydration, Cem. Concr. Comp. 21 (1999) 99.

[10] J.L. Gallias, R. Kara-Ali, J.P. Bigas, The effect of fine mineral admixtures on water requirement of cement pastes, Cem. Concr. Res. 30 (2000) 1543.

[11] S. Fennis, J.C. Walraven, T.G. Nijland, Measuring the packing density to lower the cement content in concrete, in: J.C. Walraven, D. Stoelhorst, (Eds.), Tailor made concrete structures: New Solutions for our Society, Taylor & Francis, London, 2008, 419.

[12] Y. Peng, S. Hu, Q. Ding, Dense packing properties of mineral admixtures in cementitious material, Particuology 7 (2009) 399.

[13] W. Aiqin, Z. Chengzhi, Z. Ningsheng, The theoretic analysis of the influence of the particle size distribution of cement system on the property of cement, Cem. Concr. Res. 29 (1999) 1721.

[14] Y. Knop and A. Peled, Setting behavior of blended cement with limestone: Influence of particle size and content, Materials and Structures (accepted December 2014), 10.1617/s11527-014-0509-y.

[15] F. Lin, C. Meyer, Hydration kinetics modeling of Portland cement considering the effect of curing temperature and applied pressure, Cement and concrete Research 39 (2009) 255.

[16] K. Hwang, T. Noguchi, F. Tomosawa, Prediction model of compressive strength development of fly-ash concrete, Cement and concrete Research 34 (2004) 2269.

[17] P. Termkhajornkit, R. Barbarulo, Modeling the couple effects of temperature and fineness of Portland cement on the hydration kinetics in cement paste, Cement and concrete Research 42 (2012) 526.

[18] H. C. Henry. Wong, Albert K. H. Kwan, Packing density of cementitious materials: part 1-measurement using a wet packing method, Materials and Structures 41 (2008) 689.