Production optimization of composite cements with low environmental footprint

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1. Introduction

Various strategies are applied in order to reduce the green-house gas-emissions, such as optimizing the process of clinker production, the use of alternative fuel and the partial substitution of the clinker in composite cements by the so-called supplementary cementitious materials (SCM). Currently, the most suitable SCMs from the available materials are semi-hydraulic or pozzolanic materials such as granulated blast-furnace slags (herein "slag") and fly ashes from coal combustion process [1]. Application of, limestone, is limited because of its little contribution on the performance [2]. Ternary systems (herein "composite cement") simultaneously containing more than one SCM besides Portland cement clinker contribute to the reduction of CO_2 emissions due to further decrease of the clinker content. Recent research work on quaternary systems revealed that use of slag and fly ash in combination with limestone may lead to the further increase of the cement clinker replacement ratio [3] [4].
The main processes taking place during the hydration of Portland cements (OPC) are well understood. In contrast, the hydration of composite cements are more complicated. As both, part of the Portland cement and the added SCMs react simultaneously. This leads to their interaction and thus influencing the reactivity of each other.
HeidelbergCement launched the research program aiming at the understanding of the parameters that allow maximizing the clinker replacement by slag and limestone while keeping adequate cement performances. Understanding the interactions between the reacting clinker, slag and limestone [4] [5] allowed the development and the optimization of production methods of the composite cements at a clinker replacement of up to 50%. These efforts have led to the establishment of the know-how allowing the optimization of the cement composition and properties. During the Endurcrete project (EU funded project Horizon 2020), the methods of optimization were used to produce composites cement with low environmental footprint for improved durability.
This contribution presents the optimization of the multicomponent cement for this purpose maximizing the cement performance evolution while minimizing its environmental impact.

2. The model

The modelling concept applied within this work involves several intermediate models. Results obtained at each calculation step constitute the input for the next step. The modelling concept includes

- an empirical model that describes the dissolution of the clinker phases coupled with a thermodynamic equilibrium model that assumes equilibrium between the solution and the hydrates
- the results are afterward transferred to an empirical model relating the porosity with the strength, the evolution of the compressive strength can be linked to the initial cement composition and time from mixing with water.

Additionally, the intermediate modelling results may be used as an indication and facilitate the explaining of the durability performance. The described approach is derived from the combination of different modeling approaches developed in previous investigations [3] [6] [7] [8].

The modelling of the compressive strength evolution as a function of the cement composition and time is based on the:

- Definition of the composition of the composite cement, including the composition of the clinker and supplementary cementitious materials. The composition of the materials used within these studies were similar to those investigated earlier [9] [4].
- Calculation of the kinetics of the dissolution of the reactive phases. The input was based on experimentally determined dissolution kinetics of clinker phases and slag, as reported in earlier studies [9] [4].
- Thermodynamic calculations using a consistent thermodynamic dataset, based on the GEMS software [10].
- Calculation of the compressive strength based on the predicted porosity; the relationship was fitted for the data presented in [11] and in [12].

3. Results of the modelling; compressive strength

The modelled total porosity is plotted in Figure 1. The lowest porosity is calculated for the systems rich in cement clinker and the slag. The positive effect of the calcite and alumina bearing phases [3] [4] is visible; the lowest porosity is registered for the samples characterized by about 5 wt.-% of limestone. The increase of the slag content to more than 30 wt.-% results in the increase of the porosity. The increase of the limestone content to more than about 5 wt.-% results always in porosity increase.

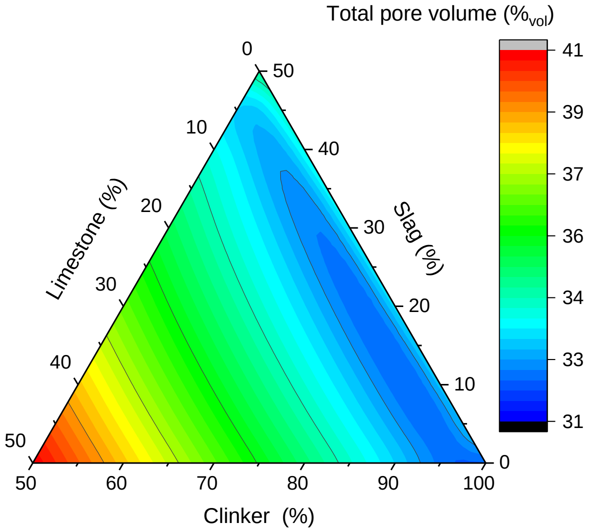

Figure 1: Calculated porosity at 28 days of hydration

The predicted compressive strength is shown in Figure 2 at three hydration times; 7, 28 and 180 days. The early compressive strength is dominated by the content of the clinker. The higher the clinker, the higher is the compressive strength. This observation is related to the kinetics of the reaction of the different materials. Thus, at the early times mainly reaction of the clinker contributes to the formation of the microstructure and resulting compressive strength. However, it is noticeable that already at that time some small presence of limestone has a positive impact on the compressive strength according to the mechanisms described in [2] [3] [4].

At 28 days, the highest compressive strength is visible for the cements containing up to 30 wt.-% of slag. Further increase of the slag content results in a reduction of the compressive strength since the reaction degree of the slag at 28 days is not able to compensate for the dilution of the cement linker. However, at 180 days of hydration, the higher the slag content the higher the compressive strength.

For all investigated cements, the increase of the limestone content by more than ~ 10 wt.-% results in the decrease of the compressive strength [3] [6] [11]. Limestone contribution is only limited to the formed microstructure by interacting with alumina bearing phases [3] [6].

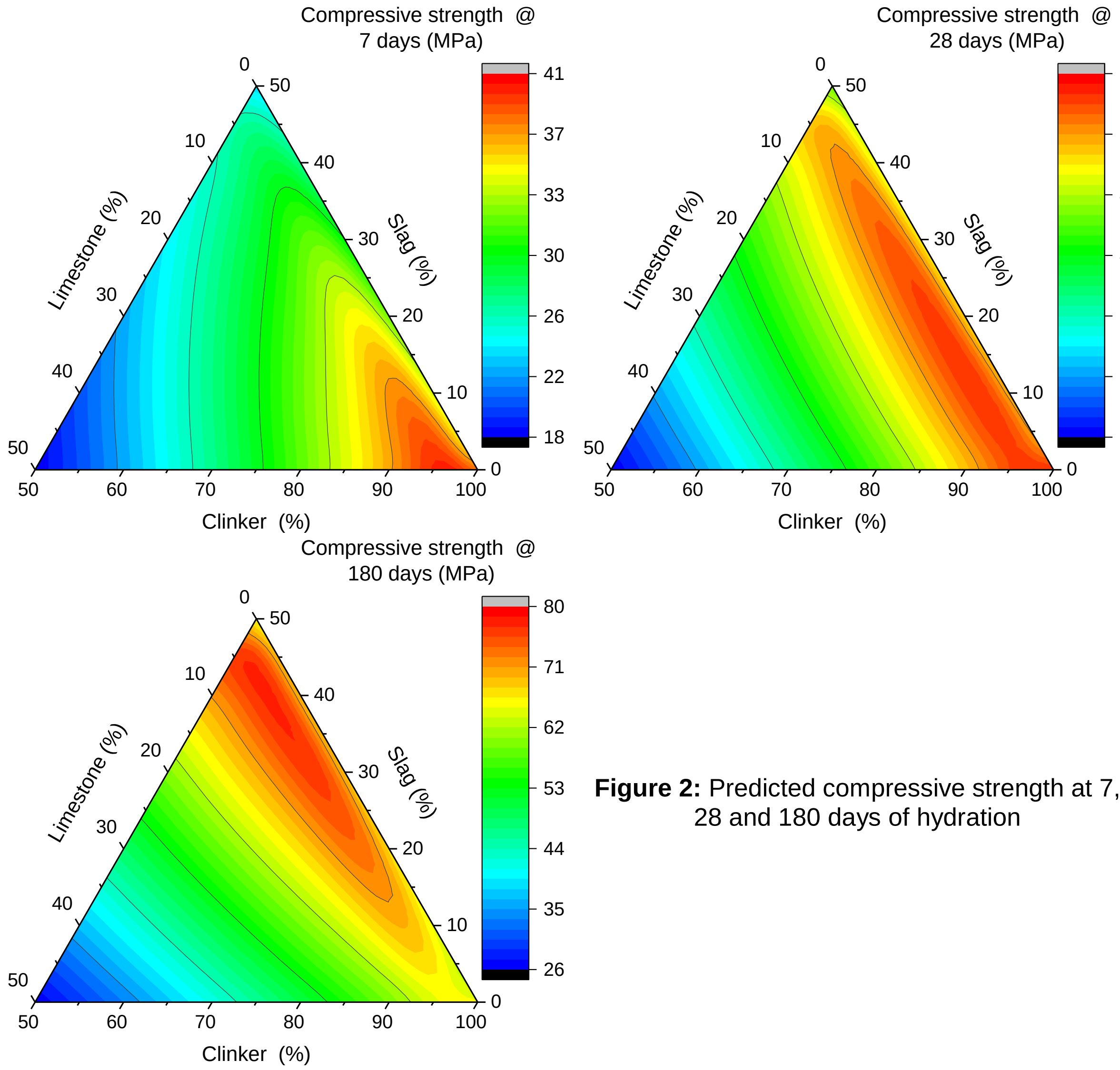

Figure 2: Predicted compressive strength at 7, 28 and 180 days of hydration

4. Experimental verification

4.1. Performance of the cement mortars

The cements were prepared in the laboratory by blending the cement components in a laboratory mixer. The experimental conditions were as well similar to the investigation used for the calibration of the modelling. Mortar bars were cast according to EN 196-1 procedure, at constant w/c of 0.50.The results of the strength measurements are re-plotted in Table 1 and Figure 3.

The tested cements are characterized by the clinker replacement ratio of 40 and 50 wt.-%, respectively, contain 20-40 wt.-% slag, 10 and 20 wt.-% of limestone. In order to prepare these cements, industrial CEM I 52.5R was mixed with the ground slag and ground limestone and calcium sulfate (anhydrite).

Table 1: Composition of the cements used for the mortar preparation (wt.-%), following the definitions of EN 197-1

	Clinker	**Slag**	**Limestone**	**SO_3**
60-20-20	60	20	20	3.0
60-30-10	60	30	10	3.0
50-30-20	50	30	20	3.0
50-40-10	50	40	10	3.0

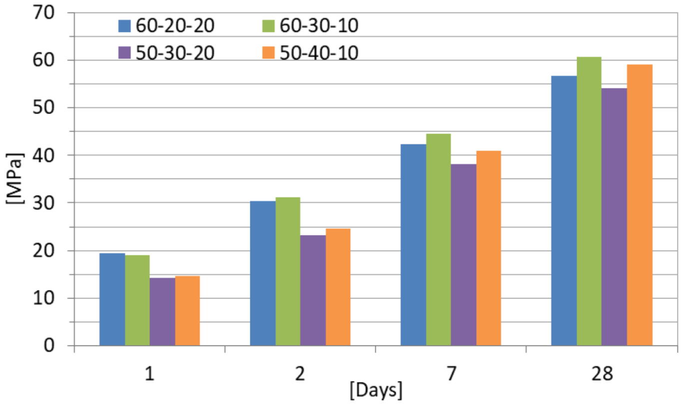

Figure 3: Compressive strength according EN196-1

At early hydration times the slag and limestone mostly dilutes the cement clinker and the strength decreases with increased Portland cement clinker substitution. Improvement of the strength is noticeable for the low limestone contents. As hydration time progresses, the contribution of the slag increases.

This comparison confirms that adopted modelling approach can correctly account for the interactions in the reacting multicomponent cement, microstructure features and consequently, it correctly predicts the compressive strength evolution.

While the measurements data are collected for limited range of the composition, the modelling tools provide significantly higher resolution and are hence capable to precisely find the optimal compositions.

The beneficial effect of increasing the fineness of ground slag on early compressive strength, is less pronounced as compared to the effect of a finely ground ordinary Portland cement fraction. Therefore a few mixtures were tested with increasing amount of fine clinker particles. The tested cements are characterized by a clinker replacement ratio of 50 wt.-%, and contain 40 wt.-% slag and 10 wt.-% of limestone. In order to prepare these cements, the ground slag and ground limestone were mixed with industrial CEM I 42.5R and industrial CEM I 52.5R respectively and additional calcium sulfate (anhydrite).

Table 2: Composition of the cements used for the mortar preparation (wt.-%), following the definitions of EN 197-1

	CEM I 52.5R (5400 cm²/g)	**CEM I 42.5R (3900 cm²/g)**	**Slag**	**Limestone**	**SO_3**
D 55/45	27.5	22.5	40	10	2.8
D 70/30	35.0	15.0	40	10	2.8
D 85/15	42.5	7.5	40	10	2.8
D 100/0	50.0	0.0	40	10	2.8

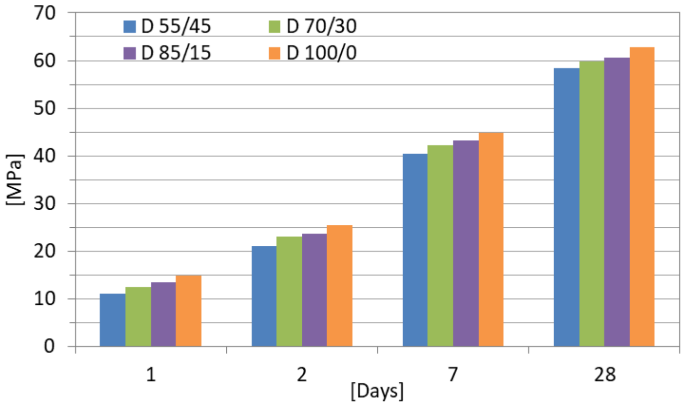

Figure 4: Compressive strength according EN196-1

4.2. Performance of the optimal cement compositions in concrete

In order to verify the performance of the composite cements, the laboratory composite cements were tested in concretes. The tested cements are characterized by the clinker replacement ratio of 40 and 50 wt.-%, respectively, and contain 10 wt.-% of limestone. In order to prepare these cements, industrial CEM I 52.5R was mixed with the separately ground slag, limestone and calcium sulfate. Additionally, commercially produced reference composite cements, which are well established on the European market, were investigated (e.g. for Germany [13] these are CEM II/A-S and CEM II/A-LL and CEM III/A). The composition of the tested cements is given in Table 1. The target strength class of the cement was 42.5 according EN 197-1 norm.

Table 1: Composition of the cements used for the concrete preparation (wt.-%), following the definitions of EN 197-1

	Cement clinker	slag	limestone	SO_3
LabCEM1	60	30	10	2.9
LabCEM2	50	40	10	2.9
CEM II/A-S 42.5R	82	18	-	3.0
CEM II/A-LL 42.5R	82	-	18	3.2
CEM III/A 42.5N	60	40	-	2.8

The following concrete performances were tested: evolution of the compressive strength, carbonation resistance, resistance of the concrete to the chloride attack and freeze-thaw resistance.

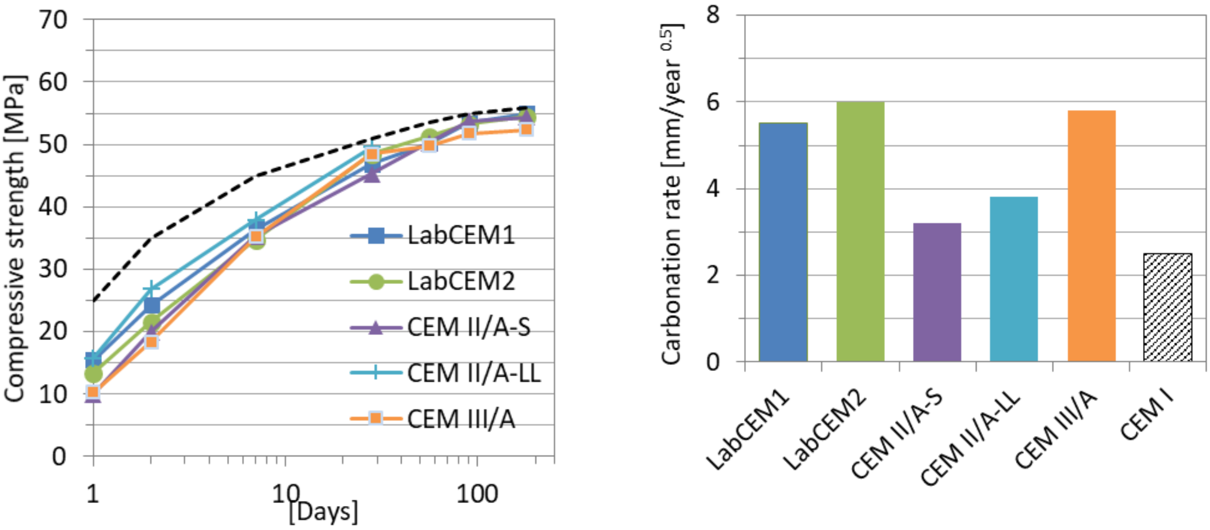

Figure 5: Concrete (Cement 320 kg/m³, w/c 0.50) strength evolution and carbonation rates. The dashed line shows the results for concrete based on CEM I 52.5R cement, used for the preparation of the LabCem's.

The compressive strength evolution of the concrete is given in Figure 5. The compressive strength of the two investigated laboratory made cements is similar to the currently commercially available CEM II/A-S and CEM III/A of the same strength class. However the strength is initially lower when compared to the cement CEM II/A-LL. At 90 days from mixing with water, all the cements are characterized by the same compressive strength.

The carbonation rates are presented in Figure 5-right. The rates are inversely proportional to the clinker content of the cements. The carbonation rates of optimized composite cements are comparable to the commercial CEM III/A and higher than CEM I and CEM II cements.

The resistance of the concretes to the freeze-thaw with and without de-icing salt was examined. The results of the scaling are plotted in Figure 6. The concrete samples based on the cement containing slag are characterized by the similar performance. The scaling during the CIF test was significantly below the limit of 1000 g/m^2 after 56 freeze-thaw cycles as given in [14]. The resistance of the concretes to the freeze-thaw with de-icing salt was tested according to CDF (capillary suction, de-icing agent and freeze thaw) test. The results are shown in Figure 6. All the tested concretes are characterized by a lower scaling than 1500 g/m^2 after 28 freeze-thaw cycling as required by [15].

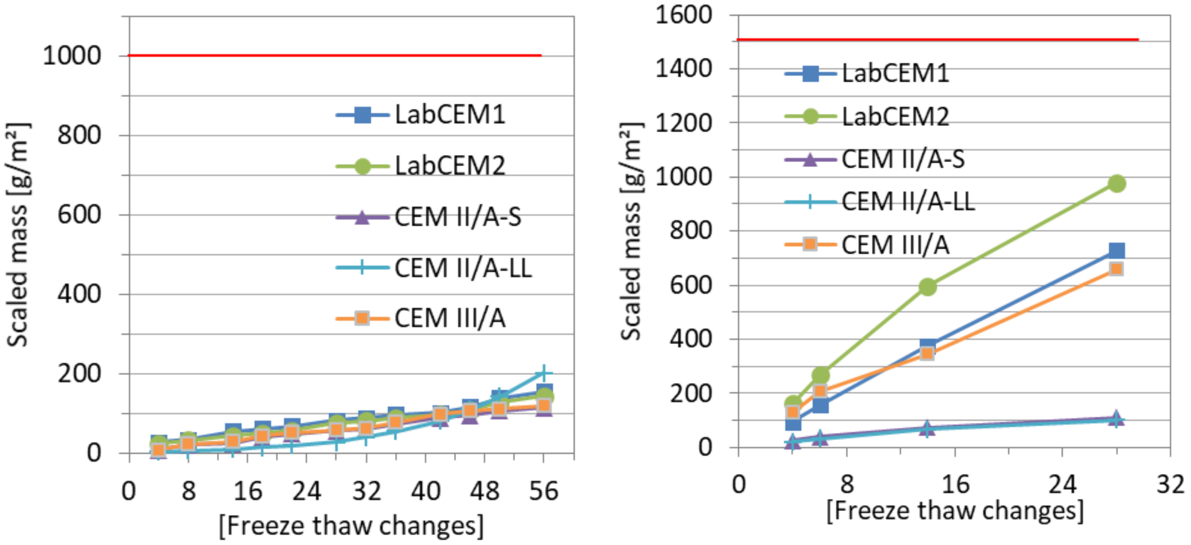

Figure 6: Evolution of the scaled material during the freeze-thaw testing (CF) and the freeze-thaw testing with de-icing agent (CDF). The read lines gives the limits for the exposure resistance classes. The dashed line shows the results for concrete based on CEM I 52.5R cement used for the preparation of the LabCem's.

The presented results agree well with the available literature data. Generally, the freeze-thaw performance of the cement containing slag is similar or inferior when compared to the neat Portland cements (CEM I) [16]. Limestone, when used at the higher replacement ratio, has a negative impact on the resistance to freeze-thaw cycles. These differences can be well explained with the help of the modelling results shown in [5].

The replacement of the cement clinker by the slag results in a reduction of the portlandite content and the increase of the C-S-H. Therefore, in the case of the slag this is the C-S-H phase that is more prone to carbonation, resulting in the shrinkage and opening of the microstructure [18]. In the case of OPC, the portlandite is the main carbonating phase which results in the increase of the solid volume and decrease of the porosity. For the lower limestone dosages, it has no pronounced impact and the cements with limestone generally fulfil the requirements [5] [17].

The results of rapid chloride migration tests are shown in Figure 7. The penetration of chloride into the mortars is lower for the cements containing slag, when compared to the limestone cement and lower or similar to the CEM I. In general, the slag is improving the resistance of the cement mortars and concretes to the chloride migration because of the finer porosity, the higher chloride binding; both related to the increase of the C-S-H. It also increases capacity to chemical binding because of the formation of the Friedel salt [19]. Thermodynamic modelling reveals that in the investigated composition range, the mechanism related to the cement densification and physical adsorption is dominating since the AFm phase content is similar for a given limestone content.

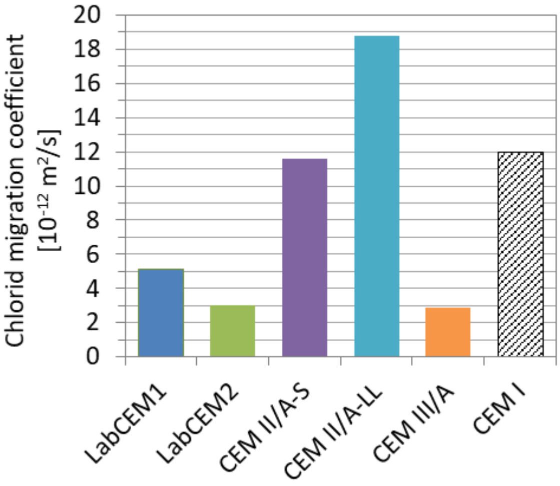

Figure 7: Rapid chloride migration coefficient determined at 28 days. Additionally the chloride migration coefficient is given for the same CEM I 52.5R.

Overall the investigation of the mortars and concretes performance reveal that the LabCEM1 and LabCEM2 are characterized by performance which is in many cases lower that the CEM I used for the production of these cements. However, their performance is comparable or superior to the cements currently available in market such as CEM II/A-S and CEM III/A, which are of the same strength class. Compared to these cements, the optimized cements offer a significant improvement of the effective global warming potential.

5. Conclusions

Recent research work revealed that use of slag in combination with limestone may lead to the further increase of the clinker replacement ratio while keeping the slag content constant. The present contribution demonstrates an optimization tool for composition of multi-component cement enabling minimizing the clinker content while maximizing the performance of the cement.

The impact of the initial cement composition on the phase assemblage and resulting porosity was investigated by means of the thermodynamic modelling supporting by the hydration kinetics models. The approach used accounted for the specific interactions among the clinker, slag and limestone. Knowledge of the microstructure features in the investigate systems enabled the prediction of the compressive strength at different hydration times. The modelling predictions were verified by the testing of laboratory cements by means of method provided by the existing standards. The general agreement between predictions and measured performance evolution had confirmed the accuracy of the developed models as well as of the general concept of the composite cement optimization. This revealed that composite cements characterized by the approximatively 50 wt.-% of cement clinker, 40 wt.-% of slag and 10 wt.-% of limestone are characterized by the appreciable performance. Since the prediction of the durability performance is not possible, this was tested. This investigation showed that the optimized cements despite the lower clinker factor are characterized by durability performance comparable or superior to the commercial composite cements. The modelling results further provided valuable insights into the underlying phenomena that helped to analyze the experimental observations related to the concrete performance parameters.

It is important to note that the developed model is flexible with respect to the cement composition and its kinetics of the hydration. Any composition of Portland composite cements of known hydration kinetics can be modelled and the performance predicted.

1. Literature

[1] B. Lothenbach, K. Scrivener, and R. D. Hooton, “Supplementary cementitious materials,” *Cem. Concr. Res.*, vol. 41, no. 12, pp. 1244–1256, 2011.

[2] B. Lothenbach, G. Le Saout, E. Gallucci, and K. Scrivener, “Influence of limestone on the hydration of Portland cements,” *Cem. Concr. Res.*, vol. 38, no. 6, pp. 848–860, Jun. 2008.

[3] K. De Weerdt, M. B. Haha, G. Le Saout, K. O. Kjellsen, H. Justnes, and B. Lothenbach, “Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash,” *Cem. Concr. Res.*, vol. 41, no. 3, pp. 279–291, Mar. 2011.

[4] S. Adu-Amankwah, M. Zajac, C. Stabler, B. Lothenbach, and L. Black, “Influence of limestone on the hydration of ternary slag cements,” *Cem. Concr. Res.*, vol. 100, pp. 96–109, Oct. 2017.

[5] G. Bolte and M. Zajac, “Limestone requirements for high-limestone cements,” *ZKG Int.*, vol. 69, no. 4, pp. 54–60, 2016.

[6] B. Lothenbach, G. Le Saout, E. Gallucci, and K. Scrivener, “Influence of limestone on the hydration of Portland cements,” *Cem. Concr. Res.*, vol. 38, no. 6, pp. 848–860, Jun. 2008.

[7] B. Lothenbach and F. Winnefeld, “Thermodynamic modelling of the hydration of Portland cement,” *Cem. Concr. Res.*, vol. 36, no. 2, pp. 209–226, Feb. 2006.

[8] J. Skocek, M. Zajac, C. Stabler, and M. Ben Haha, “Predictive modelling of hydration and mechanical performance of low Ca composite cements: Possibilities and limitations from industrial perspective,” *Cem. Concr. Res.*, vol. 100, pp. 68–83, Oct. 2017.

[9] M. Whittaker, M. Zajac, M. Ben Haha, F. Bullerjahn, and L. Black, “The role of the alumina content of slag, plus the presence of additional sulfate on the hydration and microstructure of Portland cement-slag blends,” *Cem. Concr. Res.*, vol. 66, pp. 91–101, Dec. 2014.

[10] D. Damidot, B. Lothenbach, D. Herfort, and F. P. Glasser, “Thermodynamics and cement science,” *Cem. Concr. Res.*, vol. 41, no. 7, pp. 679–695, Jul. 2011.

[11] M. Zajac, J. Skocek, S. Adu-Amankwah, L. Black, and M. Ben Haha, “Impact of microstructure on the performance of composite cements: why higher total porosity can result in higher strength,” *Submited Cem. Concr. Compos.*

[12] M. Zajac and M. Ben Haha, “Experimental investigation and modeling of hydration and performance evolution of fly ash cement,” *Mater. Struct.*, vol. 47, no. 7, pp. 1259–1269, Jul. 2014.

[13] VDZ-Publikation, “Zementindustrie im Überblick 2017.” [Online]. Available: https://www.vdz-online.de/publikationen/zementindustrie-im-ueberblick/. [Accessed: 01-Dec-2017].

[14] B. für Wasserbau, *BAW-Merkblatt: Frostprüfung von Beton*. Karlsruhe, 2012.

[15] M. J. Setzer and R. Auberg, “Freeze-thaw and deicing salt resistance of concrete testing by the CDF method CDF resistance limit and evaluation of precision,” *Mater. Struct.*, vol. 28, no. 1, pp. 16–31, 1995.

[16] P. Utgenannt and P.-E. Petersson, “Frost Resistance of Concrete Containing Secondary Cementitious Materials . Experience from Field and Laboratory Investigations.” .

[17] S. Palm, T. Proske, M. Rezvani, S. Hainer, C. Müller, and C.-A. Graubner, “Cements with a high limestone content – Mechanical properties, durability and ecological characteristics of the concrete,” *Constr. Build. Mater.*, vol. 119, pp. 308–318, Aug. 2016.

[18] J. J. Chen, J. J. Thomas, and H. M. Jennings, “Decalcification shrinkage of cement paste,” *Cem. Concr. Res.*, vol. 36, no. 5, pp. 801–809, May 2006.

[19] R. Luo, Y. Cai, C. Wang, and X. Huang, “Study of chloride binding and diffusion in GGBS concrete,” *Cem. Concr. Res.*, vol. 33, no. 1, pp. 1–7, 2003.