GLOBAL WARMING AND CONSTRUCTION ASPECTS
GLOBĀLĀ SASILŠANA UN TĀS STRUKTURĀLIE ASPEKTI

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Abstract. *The manufacture of cements with several main constituents is of particular importance with regard to reducing climatically relevant CO_2 emissions in the cement industry. This ecological aspect is not the only argument in favor of Portland composite cements. They are also viable alternatives to Portland cement from the technical point of view. Substitution of ordinary Portland cement (CEM I) by Portland composite cements (CEM II) and (CEM III), which clearly possess different chemical and mineralogical compositions, results in changes of their reaction behavior with additives like superplasticizers. A common admixture to CEM I in that sense is limestone (industrial $CaCO_3$). Its interaction with polycarboxylates is ignored and its inertness is taken for granted. This study provides a systematic approach in order to better understand the interaction of these polymeric superplasticizers with $CaCO_3$ by adsorption and zeta potential measurements. The results give some fundamental understanding in how far the cement industry can reduce the production of cement clinker by replacing it with limestone as admixture and consequently the CO_2-emission is reduced, which is of high political and environmental interest.*

Keywords: *Green construction – Limestone – CO_2 emission.*

Introduction

Background

During the cement clinker burning process climatically relevant gases are emitted. CO_2 accounts for the main share of these gases. Other climatically relevant gases, such as dinitrogen monoxide (N_2O) or methane (CH_4), are emitted in very small quantities [1] (Table 1).

Table 1.

Threshold values for mandatory reporting on 19 of the 37 air pollutants covered by the European Pollutant Emission Register

(sector-specific list for the industrial plants of the cement industry [1])

Pollutant	Threshold value kg/year
Carbon monoxide (CO)	500,000
Carbon dioxide (CO_2)	100,000,000
Non-methane volatile organic compounds (NMVOC)	100,000
Nitrogen oxides (NO_x)	100,000
Sulphur dioxide (SO_2)	150,000
Fine dust	50,000
Others	15,000

CO_2 emissions are both raw material-related and energy-related. The raw material-related emissions account for about 60% of total CO_2 emissions. Energy-related emissions are generated both directly through fuel combustion and indirectly through the use of electrical power. In the year 1995, the cement industry of major European countries committed itself to make its contribution to global warming prevention by up to 20%. Table 2 lists the updated proportions of CO_2 emissions accordingly [2].

The limited ability to reduce CO_2 emissions in ordinary Portland cement along with increasing governmental regulations on emissions necessitates the development of alternative cement binders. Substitution of ordinary Portland cement (CEM I) by Portland composite

cements (CEM II) and (CEM III), would lower the CO_2 emission by simply limiting the need of cement manufacturing. Admixtures, which possess different chemical and mineralogical compositions, but which still give a similar hardness like pure CEM I are used in applications like construction materials.

Table 2.

CO_2 emissions by the cement industry [2]

	Specific CO_2 emissions [t_{CO_2}/t_{cement}]			
Year	Thermal energy related (1)	Electrical energy related	Raw material related	Total
2002	0.168	0.069	0.413	0.650
2003	0.156	0.067	0.401	0.624
2004	0.155	0.068	0.428	0.651
2005	0.132	0.068	0.406	0.606
2006	0.123	0.067	0.383	0.573

(1) Only regular fuels

Table 3 shows the development of domestic scales classified by cement type [3]. It has been reported that when limestone is present in Portland cement, the rate and degree of hydration change, as does the composition of the hydrated cement paste. The literature findings are not always in close agreement but the general conclusion is that limestone participates to a certain extent in chemical reactions during hydration, not being only inert filler [4].

Table 3.

Domestic scales classified by cement types [4]

Cement type [t]	Group	2002	2003	2004	2005	2006
Portland cement	CEM I	12,816	14,173	13,728	13,226	11,189
Portland-slag cement		4,404	3,719	3,296	3,701	5,170
Portland-pozzolana cement		110	92	54	34	32
Portland-fly ash cement	CEM II	0	4	0	5	0
Portland-burnt shale cement		306	283	300	346	400
Portland-limestone cement		2,668	3,331	3,472	3,532	3,546
Portland-composite cement		0	0	45	437	1,480
Blastfurnace cement	CEM III	2,603	2,772	2,438	3,621	4,764
Other cements		246	283	259	193	263
Total		23,153	24,657	23,545	25,095	26,843

In the last century, the cement-liquefying effect of a construction-chemical additive was discovered by means of lignosulfonates. Better water retrenchments are attainable with superplasticizers. These are divided into three groups: polycondensates, polycarboxylates and small molecules. The best effect is obtained by superplasticizers of polycarboxylate-type [5]. When formulating modern durable concretes, the cement-superplasticizer compatibility becomes a source of major concern. Modification of solid-liquid interface properties and improvement of the dispersion process to avoid particle aggregation require the use of anionic polyelectrolytes. These can adsorb onto the mineral surface and act as dispersing and stabilizing agents even under unfavorable conditions [6]. Excessive adsorption of a polymer may make the use of the polymer uneconomic for application. Therefore it is important to study the adsorption behavior of a polymer before it is finally used in the field.

Generally, a certain amount of anionic superplasticizers should be adsorbed on the surface of the cement grain or its hydrated phases in order to obtain a dispersing effect. The impact of these superplasticizers can be understood considering that polycarboxylates possess many – COO^- groups and therefore a high negative charge density. The grain surface will be also negatively charged, once these superplasticizers adsorb. Due to the repulsion forces between

equal charges, a good dispersing effect is obtained and reagglomeration is avoided. Interaction between superplasticizers and ecocement has been studied by Sakai et al. [7]. The authors found that ecocement consumes more superplasticizer amount that ordinary Portmand cement.

Therefore fundamental interactions between a commercially available polymeric 1st – generation type superplasticizer and four different types of cement are studied here. Cements with different alite-, belite-, C_3A- and C_4AF-contents are used. The superplasticizer used in this study is characterized by determining its molecular weight and polymeric radius, as well as by estimating the anionic charge density in water and in the cement filtrate of four CEM I cements. The obtained results are compared with the interaction of that superplasicizer with limestone (industrial $CaCO_3$), since it resembles a common admixture to CEM I cements.

Application data of the cement-superplasticizer and limestone-superplasticizer combinations (mini-slump test) are a helpful tool to understand the surface chemistry of the superplasticizer with the binders under investigation (zeta potentials and superplasticizer adsorption).

The results of Huang et al. [8] followed the conclusion that at pH 8-11 Ca^{2+} and CO_3^{2-} are the dominating sites on the calcite surface and that H^+ and OH^- play a less important role. They further concluded that the strongly adsorbed calcium ion on the calcium carbonate surface is the dominating surface site and acts as a Lewis acid site. It is obvious that the dissolution of calcium carbonate is of great importance for its surface charge and colloidal properties as well as for its interaction with polymers. Adsorption of anionic polyelectrolytes is physical in nature. Therefore, the amount adsorbed is proportional to the size of the polymer molecule [9].

$CaCO_3$ bears a positive surface charge ranging from 20-40 mV at pH = 9 according to the particle size of the meal [10] which is very similar in its surface properties to phases of hydrated cement, particularly ettringite.

Fig. 1 shows a schematic demonstration of a hydrated cement grain. During the process of hydration, positively charged ettringite is formed upon which the anionic superplasticizers are adsorbed.
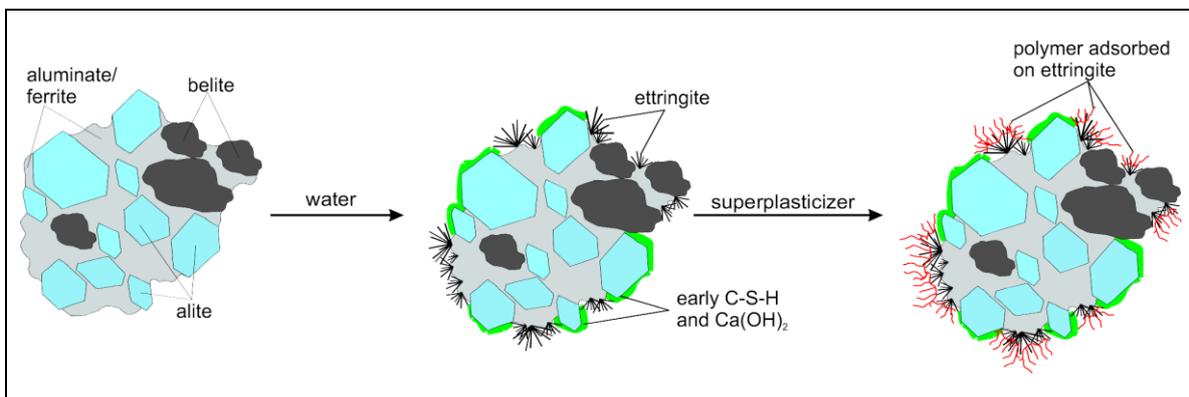
Fig. 1. **Schematic demonstration of polymer distribution on the surfaces of a hydrated cement grain**

Table 4 shows typical zeta potentials of the hydrated phases of cement and selected CEM I cement [11]. The presence of an anionic superplasticizer alters the surface potential of the cement and limestone particles. To quantify this change, zeta potential measurements provide good information.

A systematic approach in order to better understand the interaction of a polymeric superplasticizer with cement and $CaCO_3$ by adsorption and zeta potential measurements is shown here.

Table 4.

Zeta-Potential of the hydrated phases of cement and selected CEM I-cements

Hydrated phase	Zeta potential [mV]
Ettringite	+ 4,15
Monosulfate	+ 2,84
Syngenite	+ 0,49
Limestone (calcite)	+ 40,0
CEM I 32.5 R	+ 0,78
CEM 42.5 R	+ 0,45
API Class G-cement	+ 0,31

Cement vs. Limestone

After many years of discussion, in 2004, the ASTM C150 standard specification for portland cement was modified to allow the incorporation of up to a 5 % mass fraction of limestone in ordinary portland cements [12]. An extensive survey of the literature conducted by the Portland Cement Association concluded that "in general, the use of up to 5 % limestone does not affect the performance of portland cement [13]". Even higher contents of ground limestone could potentially be utilized in lower water-to-cement ratio (< 0.45) systems, where a substantial fraction of the cement clinker particles remains unhydrated, effectively acting as a rather expensive filler material [14-16].

While these and much higher levels of limestone filler substitution have been employed in Europe and elsewhere for many years, changing the ASTM standard has been a slow process. Having computational tools to assist in better understanding the influence of limestone additions on cement hydration and microstructure development should facilitate the acceptance of these more economical and ecologically blended materials. The influence of limestone substitutions on hydration rates is seen to be a strong function of water-to-solids ratio, as a 20 % limestone substitution substantially modifies the effective water-to-cement ratio of the blended mixture [17].

Numerous researchers have noted an acceleration of the hydration of cement due to the addition of fine limestone or other fine particles [17- 20]. Apparently, the surfaces of the individual filler particles provide sites for the nucleation cement hydration products such as the calcium silicate hydrate gel (C-S-H) that is the dominant hydration product in most hydrated Portland cements. Modeling the influence of limestone filler on cement hydration has been studied by Bentz [17]. It was concluded that limestone substitutions are projected to be particularly advantageous in lower w/b (<0.4) mortars and concretes. In these systems, up to 20% of the cement could potentially be substituted by limestone to economize on the usage of Portland cement clinker and to reduce the energy and the deleterious emissions associated with its production.

Materials and methods

The experiments are performed with aqueous suspensions of the different cements CEM I (A-D). Their medium particle size D_{50} is determined by using laser granulometry (Cilas 1064; Co. Cilas). The densities of these cements are established by a helium pycnometer.

The polycarboxylate used is an industrial product and is used without further purification. The solid content of the polymeric solution is established by using an IR-balance. The characterization of the polymer is made by GPC, coupled with a refractive index and light scattering detector. This equipment permits calculation of molecular weights and radii of the polymers. Moreover polymer solutions with a concentration of 10 mg / mL (with respect to the polymeric solid content) are prepared. The solvent used is a 0.1 mol/L $NaNO_3$ solution; pH = 12.0; adjusted with NaOH). The column material (Co. Waters) used contained three columns consecutively connected (Ultrahydrogel 120, Ultrahydrogel 250, Ultrahydrogel 500).

They cover a separation area of 5,000 – 400,000 Dalton. The sample is injected with a syringe containing a forwarded spaced filter (0.2 µm) in a 2-mL-GPC-sample holder, out of which the GPC-apparatus injects 100 µL into the system. Therefore the polymeric solution needed for one run is 1.0 mg. The evaluation is carried out with the GPC-Software Astra 4,908 (Co. Wyatt Technologies). To calculate the averaged molecular weights, a 3rd order fit is used.

The anionic charge of the superplasticizer under investigation is measured by means of the particle charge detector PCD 03 pH (Co. Mütek). A 100 mL standard solution of polymeric concentration of 200 mg/L is used. The filtrates of binder pastes with a water-to-binder (w/b) -value necessary to produce a flow value of 18 ± 0.5 cm (mini-slump test) is used as a solvent for the polymer to measure the anionic charge in the pore solution. The charge density is determined by means of a titration experiment with the polymer poly-dadmac (0.001 N), a cationic polyelectrolyte.

Adsorption measurements are carried out at RT by determining the organic carbon content via High TOC II analyzer (Elementar) of the centrifugate (20 min at 8500 rpm) previously produced from the cement pastes with polymeric admixtures.

The zeta potentials of the cement pastes with different amounts of polymer are measured using Model DT-1200 electro-acoustic spectrometer (Dispersion Technology, Inc.). The following mixing procedure is used to prepare the binder pastes: the binder is added to water (according to the w/b-value necessary to produce a flow value of 18 ± 0.5 cm) within 1 min. This paste is let sit for one more minute. Then, the mixture is vigorously stirred for 2 min in a casserole by using a spoon. The filtrate is taken for the measurement of the ionic background of the binder paste that is subtracted from the zeta potential values of the binder pastes containing the polycarboxylate.

Results and Discussion

Characterization of the four types of cement and limestone

The analysis of the four types of cement and limestone is performed by using the Bogue analysis- method. The results are listed in (Table 5).

Table 5.

Bogue analysis of the cements CEM I (A-D) and limestone

Binder type/ Composition	CEM I (A)	CEM I (B)	CEM I (C)	CEM I (D)	Limestone (calcite)
Alite	67.3	60.1	69.8	61.0	-
Belite	10.9	22.4	6.9	22.0	-
C_3A (cub.)	5.7	2.3	1.3	0.4	-
C_3A (orth.)	5.6	0.0	4.6	1.1	-
Na_2O	0.27	0.21	0.18	0.27	-
SiO_2	-	-	-	-	0.5
K_2O	0.67	0.63	0.72	1.27	-
C_4AF	1.7	12.2	6.8	14.0	-
Al_2O_3	4.47	3.55	3.63	4.15	0.2
Fe_2O_3	1.2	4.56	2.38	2.46	0.2
$CaSO_4*2H_2O$	0.1	2.5	0.1	1.1	-
$CaSO_4$	2.5	0.0	2.4	0.0	-
CaO free	0.3	0.2	1.1	0.3	-
$CaCO_3$	3.4	-	4.0	4.1	98.5
MgO	-	-	-	-	0.6
Water-to-binder-ratio	0.60	0.46	0.47	0.6	0.41

It can be seen that CEM I (C) possesses the highest alite content, which is a measure of early hardness. The highest belite content is found in CEM I (B), which is responsible for its late hardness. CEM I (A) has the highest C_3A content and gives rise to its fast and early hydration and reacts significantly with undesirable sulfates. The ferrite phase is responsible for the weak hardness and the slow hydration of cements of which CEM I (B) shows the highest content.

Higher positive surface potentials are expected in cases where sulfates are present due to the enhanced formation of ettringite. Limestone "Schäfer Precal 18" (Schaefer Kalk GmbH & Co K G, Diez, Germany) is used for all experiments due to its high purity of $CaCO_3$.

The density (g/cm^3) and the average particle size D_{50} (µm) of the four cements and limestone are listed in Table 6.

<div align="right">*Table 6.*</div>

The density (g/cm^3) and the average particle size D_{50} (µm) of the cements CEM I (A-D) and limestone

Binder type	Density [g/cm^3]	Average particle size D_{50} [µm]
CEM I (A)	3.12	7.5
CEM I (B)	3.14	11.28
CEM I (C)	3.14	17.49
CEM I (D)	3.14	8.81
Limestone (calcite)	0.274	9.71

Characterization of the superplasticizer under investigation

The characterization of the commercially available superplasticizer solution starts with determining its solid content, its pH-value and its molecular weight and radii determined by GPC analysis. The solid content [%] of the polymeric solution is 38.70 and its pH-value is found to be 7.97. The GPC- analysis of the 1st generation superplasticizer under investigation is resembled in Table 7.

<div align="right">*Table 7.*</div>

GPC-Analysis of the superplasticizer under investigation

Property	Value
Molecular weight [g/mol] Mn	28.050
Molecular weight [g/mol] Mw	70.180
Poly-dispersity [Mw/Mn]	2.5
R.M.S. Radius (Rg) [nm] Rgn	8.7
R.M.S. Radius (Rg) [nm] Rgw	10.1
R.M.S. Radius (Rg) [nm] Rgz	12.6
QELS Hydro dynamic Radius moment [nm] Rhn	6.4
QELS Hydro dynamic Radius moment [nm] Rhw	7.0
QELS Hydro dynamic Radius moment [nm] Rhz	8.8
QELS Hydro dynamic Radius moment [nm] Rh(avg)	6.6

In order to understand the adsorption behavior of the superplasticizers, determination of the anionic charge density is necessary [21]. The cement pastes possess high pH- values, typically 12-13. This medium accounts for the presence of polycarboxylate containing superplasticizers in the form of anionic polymers. Interaction with the positively charged binder surface takes place. Superplasticizers with a more negative charge density are attracted to a higher extent to the positively charged surface. Therefore, molecules with a higher anionic charge density show higher adsorption rates. The results of the specific anionic charge density measurements are found in Fig. 2. As expected, the polycarboxylate show in salt free water as well as in the pore water of the four cements and limestone very high anionic charge densities.

Generally, the anionic charge density of the polymers depends on the pH-value, the ionic strength and the ions present in solution (e.g. Ca^{2+}; SO_4^{2-}). The polycarboxylate under investigation shows a high anionic charge density in deionized (salt free) water which decreases in pore water of the four cements and limestone significantly. A reasonable explanation is the complexation of the carboxylate groups with the Ca^{2+} ions, a fact found with α-allyl-ω-methoxy polyethylene glycol maleic anhydride copolymer based polycarboxylate [22].
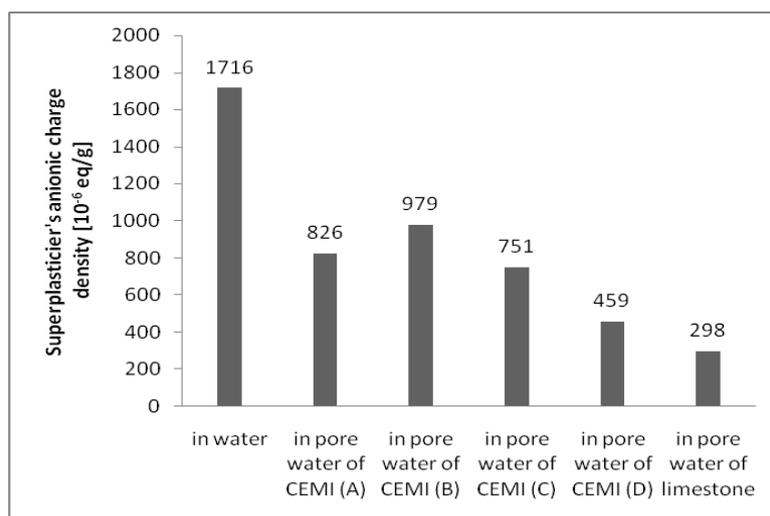
Fig. 2. **Anionic charge densities [10^{-6}eq/g] of the superplasticizer in water and in the pore water of the four cements and limestone**

Adsorption and zeta potential measurements

The superplasticizers dosage (with respect to binder) is estimated according to that necessary to produce a flow value of 26 ± 0.5 cm (mini-slump test). The blank value is a binder paste with a w/b-value at which the flow value is 18 ± 0.5 cm. By adding the superplasticizer, the dosage is adjusted such that a flow value of 26 ± 0.5 cm is obtained. The water content in the polymeric solutions is considered.

The total organic carbon (TOC) content in the pore solution without superplasticizer is estimated as background. Then the superplasticizer dosages necessary to obtain a flow value of 26 ± 0.5 cm are examined by adsorption measurements determining the TOC-content in the filtrate of non-adsorbed superplasticizer. Subtraction from starting dosages leads to the amount adsorbed. The results are shown in Fig. 3.
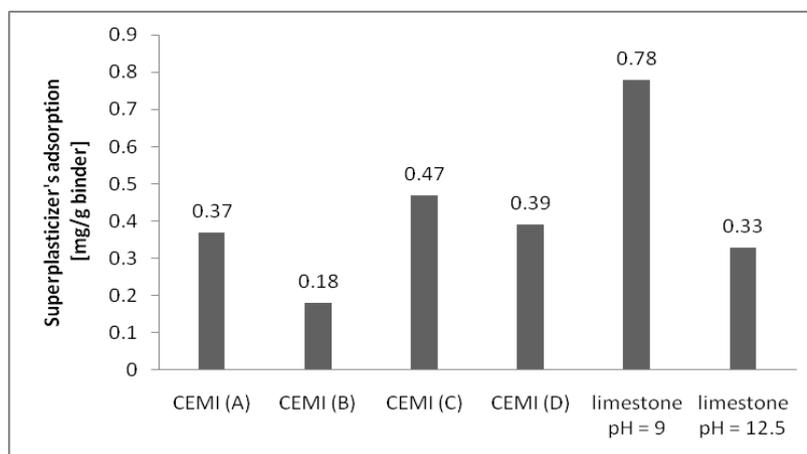
Fig. 3. **Superplasticizer adsorption [mg/g binder] on cement and limestone at a dosage necessary for a flow value of 26 ± 0.5 cm**

As expected, the C_3A-poor cement CEM I (B) adsorbed the least amount of superplasticizers, while CEM I(C) and CEM I (D) adsorbed the most. These results are consistent with the finding about dependence of adsorbed amount on the formation of ettringite [23]. In accordance with this, the high contents of sulfate and free CaO of CEM I (C) resulted in a high consumption of superplasticizers although it has a moderate C_3A-content.

The results show that the C_3A-content has a very strong influence on the adsorption of superplasticizers: the lower it is, the less the adsorption of the superplasticizers. The dependence of the adsorption on C_3A/C_4AF-content is also observed. High C_3A/C_4AF contents result in higher adsorption.

Regarding the adsorbed amount of superplasticizers, the adsorption behaviors of CEM I (D) and limestone are very similar. Consequently, this polycarboxylate is good for precast concrete, because they show a high starting liquefaction of cement pastes with low dosages. The adsorption behavior is affected by the anionic charge of the polymer in water and in the pore solutions of the four cements and limestone: The higher the anionic charge, the better the adsorption [21].

The zeta potentials are determined first without then with superplasticizer (Table 8) according to the dosages necessary to obtain a flow value of 26 ± 0.5 cm. The zeta potentials of the pure cements depend also on their C_3A-content (see blank value in Table 8). Cements with higher C_3A- and sulfate contents can form higher amounts of ettringite during the hydration process which shows a stronger positive zeta potential [24]. CEM I (C) has the least negative zeta potential of -1.9 mV. Apparently, this cement builds more ettringite due to its very high sulfate content than the CEM I (A), which is richer in the C_3A-content. This effect is even more intensified due to the fact, that CEM I (C) possesses the biggest particle size. In the contrary to that, CEM I (B) shows a very negative zeta potential, because it can form less ettringite. Besides it has a higher content of silicates that produce a negative surface charge.

Table 8.

Zeta potential [mV] of cement and limestone with and without the superplasticizer at a dosage necessary for a flow value of 26 ± 0.5 cm

Binder type	Zetapotential [mV] Blank value	Zetapotential [mV] with superplasticizer
CEM I (A)	-2.6	-3.3
CEM I (B)	-8.3	-4.3
CEM I (C)	-1.9	1.5
CEM I (D)	-2.8	0.7
Limestone at pH = 9	+40	-32
Limestone at pH = 12.5	-15	-25

The zeta potential of limestone in deionized water is +40 mV. Upon superplasticizers addition, this potential decreases to -32 mV, which lies in good accord to the adsorption onto its surface. Adjusting the pH value of $CaCO_3$ with NaOH solution, the zeta potential becomes -15 mV. Addition of the superplasticizers further decreases the zeta potential to -25 mV. The zeta potential of the different cement types is dependent on the C_3A-content. Cements of higher C_3A-contents develop a higher content of ettringite during hydration, which results in a more positive zeta potential.

Conclusion

The interaction of the superplasticizer with four different types of cement and limestone is studied. Characterization of the 1st generation type polycarboxylate under investigation showed that it possesses a very high molecular weight. On the basis of low C_3A-content it is observed that CEM I (B) show the best liquefying effect. The two cements CEM I (C) and CEM I (D) need higher dosages of superplasticizers to obtain the same result due to their high content of sulfate and free CaO. Limestone shows an evident similarity to the properties of CEM I (D) and is therefore the most compatible candidate when it comes to cement substitution by $CaCO_3$ in application. Combining limestone with the other types of cement would afford optimization of superplasticizer dosage first in order to obtain the desired characteristics of the cement-limestone mixture.

The results give an insight in how far the cement production (and consequently the CO_2 - emission) can be minimized by using economical admixtures or fillers like limestone which give good workability and compatibility to common cement types, a fact of high environmental value.

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