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SINTEF REPORT

TITLE

COIN P1 Advanced cementing materials
SP 1.1 F Reduced CO_2 - emissions

Ternary Blended Cements with Fly Ash and Limestone
Part II: Limestone powder

State of the art

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ABSTRACT

There is a rising interest in the production of composite cements due to mounting environmental awareness and the diminishing natural resources. In composite cements considerable parts of the clinker is replaced by supplementary cementitious materials. Within two STAR's we will focus on the fly ash and limestone as replacements for part of the clinker.

This second part will discuss the influence of limestone on cement hydration and will conclude with a short overview on the available studies on the combined use of fly ash and limestone. Limestone filler addition accelerates the hydration of cement, or more precisely the C_3S phase, by acting as nuclei for CH and CSH precipitation. This accelerating effect can give rise to higher compressive strength at early age at moderate clinker replacements (≤10%). The higher the fineness of the limestone filler, the stronger the effect. Part of the $CaCO_3$ interacts with the hydration products. The reaction mechanism of C_3A is changed and calcium carboaluminates form in competition with calcium sulphoaluminates. The hydration of C_3S in the presence of carbonate results in the formation of calcium carbosilicate hydrates. It was observed that limestone filler replacements up to around 10 % (depending on the fineness) led to a more homogenous structure of the cement paste. This was attributed to a better dispersion of the hydration products as limestone particles served as precipitation sites. This denser structure could result in an improved durability performance of the cement.

Fly ash and limestone filler seems to be an interesting combination. Limestone filler can improve the early strength development, as it accelerates the hydration, and fly ash contributes to later strength development thanks to its pozzolanic reactivity. Recent studies confirm the potential of this combination. A not exploited area is the chemical interaction of fly ash and limestone. The addition of fly ash provides an additional amount of aluminate which could interact with sulphate or carbonate, and form extra binder phase, in the form of calcium carboaluminate hydrates or calcium sulphoaluminate hydrates. These phases can densify the matrix. The fineness of the limestone powder and the fly ash, the ratio between gypsum and limestone powder and the activation of the fly ash to promote the liberation of aluminate are key parameter in this research topic.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Materials technology	Materialteknologi
GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Cement	Sement
	Blended	Blandet
	Limestone	Kalkstein

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

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TABLE OF CONTENTS

1 Limestone

The addition of small amounts of limestone filler to cement is common practice. As cement plants are most often positioned in the vicinity of limestone quarries, large amounts of limestone fines are available at very low transportation costs. In France, for example, limestone powder represents the larges segment of the filler materials used in concrete industry. In 1990 the total consumption of limestone filler by the cement industry amounted to 2,400,000 tons. In the same year 450,000 tons of limestone filler were put directly in the concrete mixer in the ready-mix concrete plants, compared to only 340,000 tons of fly ash. [Bertrandy and Poitevin, 1991]

Limestone is often categorized as inert filler, meaning that its influence on cement properties is purely due to its physical nature. Or rather that if chemical interactions occur that their influence on the properties can be as good as neglected.
Other researchers claimed that limestone filler clearly showed chemical reactivity in cementitious systems and that thereby cement properties can be considerably improved.
Whether or not limestone powder is inert has been a subject of discussion for many years.
In 1948, for example, it was claimed in Norway that a certain calcareous filler (calcite) commercially known as “Aktivitt”, increased compressive strength and the resistance against sea-water. This claim gave rise to a heated discussion in the Scandinavian countries which resulted in the appointment of an expert committee by the Norwegian government to settle the validity of this claim. The committee concluded that “the calcite possesses no better filler properties than other limestone and rocks”, and “nothing in the test data indicates that any chemical reaction takes place between cement paste and calcite”. Furthermore a series of tests conducted late at the Danish State of Testing Laboratory, resulted in essentially the same conclusion, namely, “that improved properties of concrete involved, observed by addition of calcite are essentially a filler effect” presumably due to physical effects. [Soroka and Stern, 1976]

Nowadays, it is however well established that $CaCO_3$ does interact chemically with the cement components. In this state of the art an overview on the influence of limestone powder on the different cement properties will be presented.

1.1 Characteristics of limestone

In order to be suitable as filler, limestone powder has to meet certain demands. Limiting values for some critical properties were imposed to ensure adequate performance:

- The purity of the limestone should be greater than 75 % by mass of $CaCO_3$.
- Clay content determined by the adsorption of methylene blue has to be limited to 1.20g/100g.
- The organic content should be no more than 20 % by mass although values between 0.20 and 0.50 are permitted providing that their suitability for making cement is proved by adequate tests and practical experience.

According to Regourd (1986) the crystallinity of the limestone plays an important role in its reactivity. Limestone powders with disorganized crystalline structures are more effective in accelerating the strength development than limestone powder with a high level of crystallinity. Fierens et al. (1974) observed that the reactivity of a calcite surface is dependent on its crystalline orientation.

1.2 Physical impact

1.2.1 Grinding and particle size distribution

Limestone can be included in the cement by intergrinding with the clinker or by blending limestone filler with ground clinker.

Bombled et al. (1986), Tsivils et al. (1999c,2002), Von Schiller and Ellerbrock (1992) and Vuk et al. (2001) studied the intergrinding of clinker and limestone. They found that when limestone was interground with clinker, it widened the PSD of the cement (see Fig. 2). The component which was the hardest to grind, clinker, was found in the coarser fraction whilst the easier to grind component, limestone, was concentrated in the finer fraction (see Fig. 1).
The addition of limestone with a wide PSD led to a decreasing water demand per volume dry material and improved the workability.

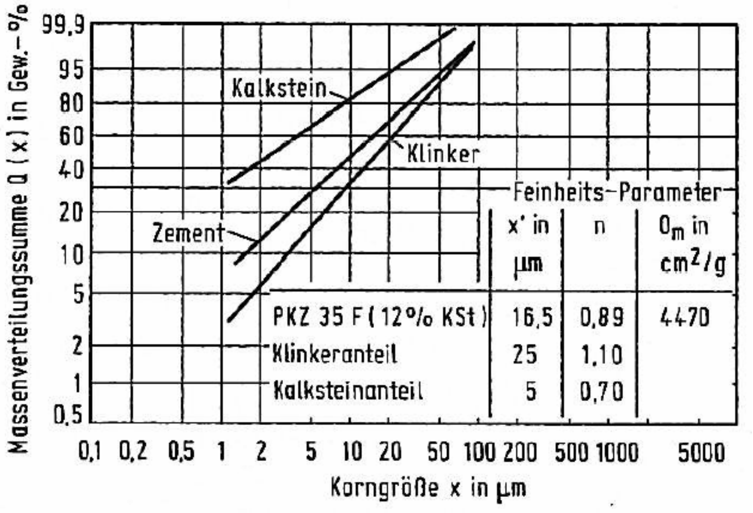


Fig. 1: Cumulative mass distribution of a limestone cement with limestone content of 12 % and of its clinker and limestone components after grinding [Von Schiller and Ellerbrock, 1992].

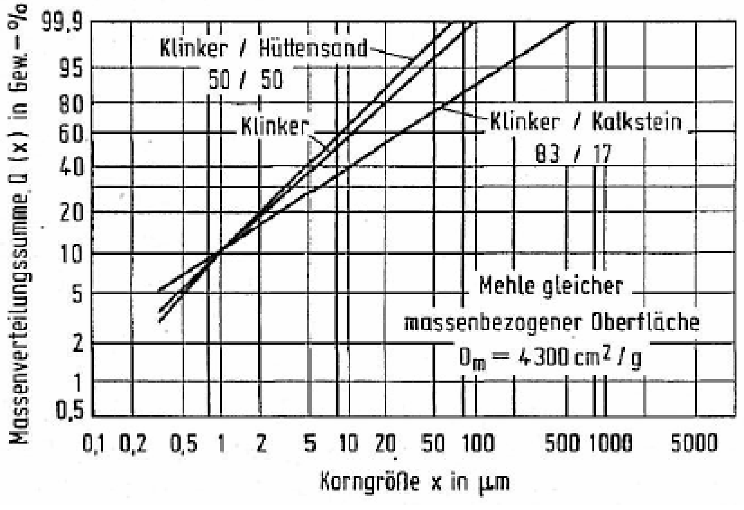


Fig. 2: Particle size distribution of interground clinker/slag and clinker/limestone with equal Blaine specific surface [Von Schiller and Ellerbrock, 1992].

Tsivils et al. (1999(3)) observed a remarkable trend during intergrinding of limestone and clinker. As the limestone content surpassed 30 %, the grinding of both clinker and limestone was inhibited. Samples containing 40 % limestone showed in spite of a higher Blaine specific surface

(due to the higher limestone content) a lower clinker and limestone fineness compared to those containing 30 %.
Von Schiller and Ellerbrock (1992) experienced a similar phenomenon when increasing the limestone content from 12 to 20 %. The fineness of the limestone cement namely decreased and its particle size distribution became narrower.

Von Schiller and Ellerbrock (1992) found that to obtain a 50MPa 28 day compressive strength the limestone cement has to be ground increasingly finer as the limestone content augmented. The limestone cement had to have a characteristic diameter x' of 30 µm for a 0 % replacement level, 26 µm for 10 %, 14 µm for 20 % and it is impossible to obtain that strength for a limestone cement containing 30 % limestone. This led to the conclusion that for a strength level of 50 MPa not more than 15-20 % limestone should be applied in limestone cement.

Voglis et al. (2005) compared blended cements produced with 15 % limestone, natural pozzolan or fly ash. The limestone cement had the highest energy consumption for grinding, required to obtain the same 28 day compressive strength. It had the highest Blaine specific surface and widest particle size distribution (lowest n).
Up to seven days the limestone cement exhibited the highest value of compressive strength, while the fly ash cement showed the lowest value in strength. The reason for this behavior is the filler effect of the fine particles of limestone, the higher clinker fineness in the limestone cement and the low rate of the pozzolanic reaction in the fly ash cement. For the period 28-540 days, the strength development is significant in case of OPC and the fly ash cement, while the limestone cement showed the lowest rate of strength development.

Separate grinding and blending of the constituents offers greater opportunity for optimization of particles size distribution and average fineness of the individual constituents and thereby for fine-tuning of the properties of the blended cements.

1.3 Chemical impact

Limestone filler appears to influence the hydration reaction of cement. In order to get a better understanding of the mechanisms behind this interaction, the effect of limestone filler or $CaCO_3$ on the hydration of the cement constituents separately, such as C_3S and C_3A, will be discussed first.

1.3.1 Effect on the hydration of C_3S

Ramachandran (1988) investigated the effect of calcium carbonate on the hydration of C_3S.
He prepared blends with a water-solid ratio of 0.4 or 0.7, and determined the amount of calcium hydroxide, non-evaporable water and calcium carbonate by thermogravimetric analysis. Some of the results are shown in Fig. 3 and Fig. 4. The addition of calcium carbonate led to an increase in calcium hydroxide formation relative to the amount of paste up to 7 days, and at all times relative to the amount of C_3S. This confirmed the accelerating effect of calcium carbonate on the hydration of C_3S. Furthermore, the accelerating effect became greater for larger calcium carbonate additions and was particularly significant at short hydration times. The non-evaporable water measurements showed similar accelerating trends as calcium carbonate was included in the system.
The particle size of limestone seemed to play an important role. As can be seen from Fig. 3, the finer the particles the greater the accelerating effect, especially at short hydration times.
The author attributed the accelerating effect of the carbonate particles to the fact that they act as nuclei. The growth of CH and C-S-H on their surfaces would decrease the concentration of Ca and Si ions in the solution phase and promote their transfer from the C_3S phase into solution.

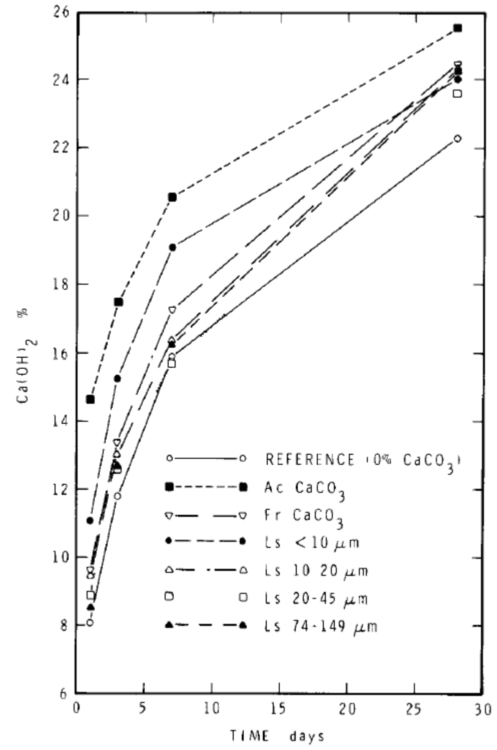


Fig. 3:Effect of particle size of $CaCO_3$ on the hydration of C_3S [Ramachandran, 1988].

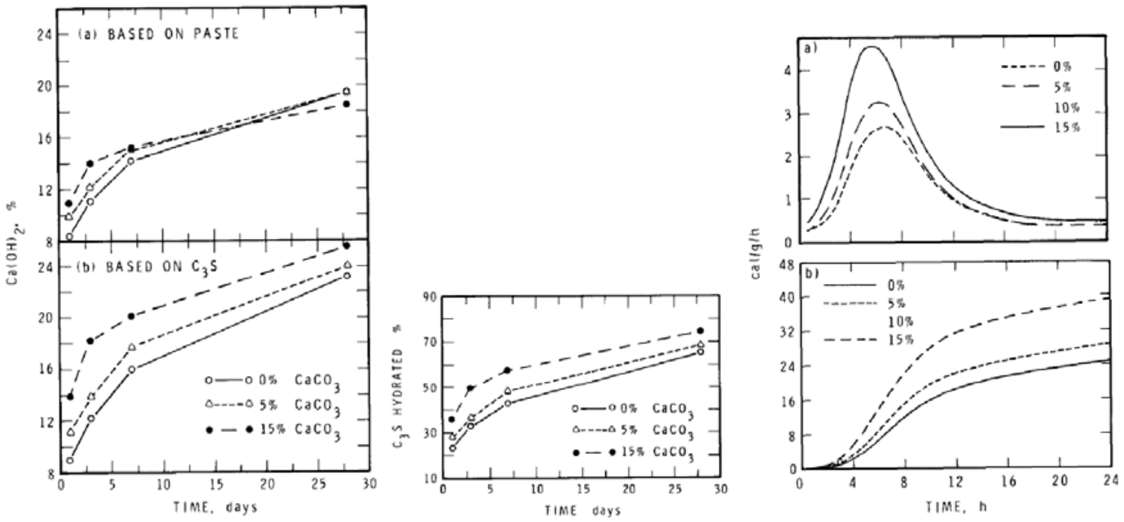


Fig. 4:Left: Formation of $Ca(OH)_2$ in C_3S paste containing different amounts of $CaCO_3$ Middle: Degree of hydration of C_3S in the presence of $CaCO_3$ Right: Conduction calorimetric curves of C_3S containing different amount of $CaCO_3$ (a) rate of heat produced, and (b) the amount of heat produced at different times. [Ramachandran, 1988]

Péra et al. (1999) and Husson et al. (1992) studied the influence of $CaCO_3$ on the hydration of C_3S by the means of isothermal calorimetry, infrared spectrometry, X-ray diffraction, SEM, differential thermal analysis and paste strength measurements. The calorimetric curves for a 50:50 blend of C_3S and $CaCO_3$, and a pure C_3S paste are shown in Fig. 5. The total heat resulting form the pure C_3S was lower than for the blend with $CaCO_3$.

SEM observations revealed a different morphology of the hydrates. Pure C_3S gave rise to platelets of calcium hydroxide and fibrils of C-S-H, whereas in the C_3S+$CaCO_3$ paste, granules of C-S-H were formed. Infrared spectrometry demonstrated the accelerating effect of $CaCO_3$ on C_3S as certain Si-O-Si stretching bands were obtained much faster in the presence of $CaCO_3$.

XRD investigations revealed the formation of a hydrated carbosilicate. The intensity of the peak (2θ=14.9°) increased with increasing $CaCO_3$ content.

DTA results showed a decrease in the decomposition peak of $CaCO_3$ with hydration time and the temperature corresponding to the maximum of this peak shifted towards smaller values.

These results indicate that $CaCO_3$ cannot be considered as an inert addition towards C_3S hydration.

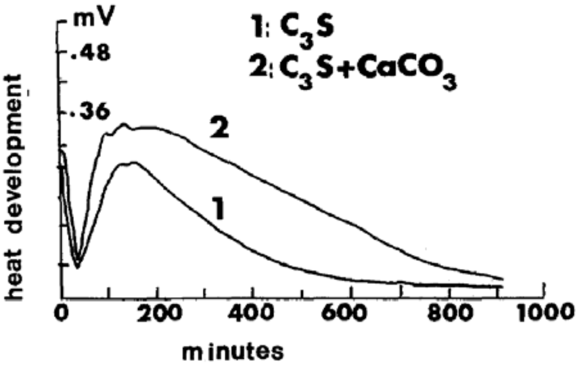


Fig. 5:Isothermal calorimetry of C_3S and $CaCO_3$ (650m^2/kg Blaine, 3600m^2/kg BET) (w/s=1) [Péra et al., 1999]

Kakali et al. (2000) also claimed to have found small amounts of carbosilicate hydrate (scawtite, $Ca_7(Si_6O_{18})(CO_3).2H_2O$) by X-ray diffraction, in a C_3S paste containing 35 % $CaCO_3$ (w/s=0,3). The XRD patterns are presented in Fig. 6.

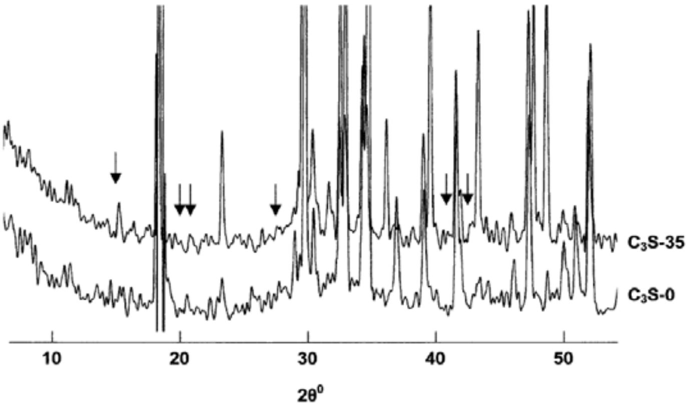


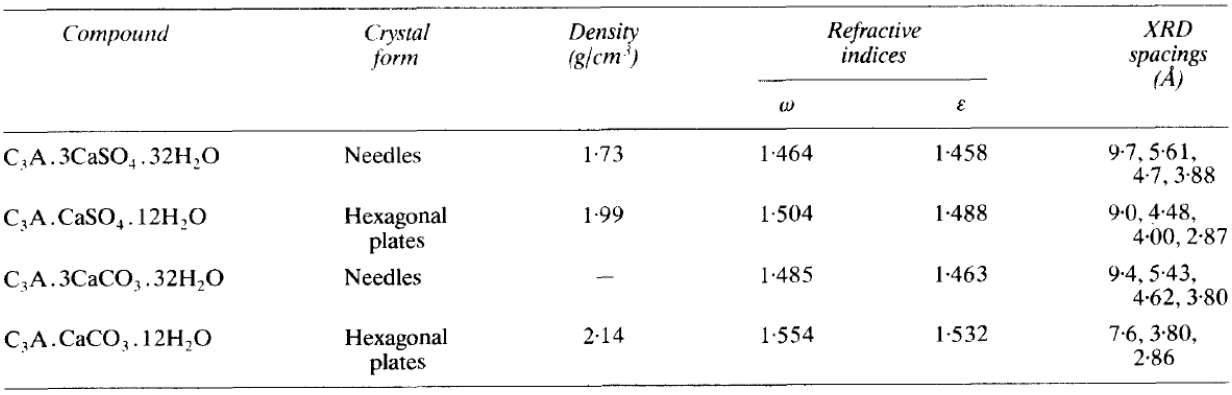
Fig. 6: XRD patterns of C_3S without (C_3S-0) and C_3S with 35 % $CaCO_3$ addition (C_3S-35) after 28 days. The arrows indicate the carbosilicate peaks. [Kakali et al., 2000].

1.3.2 Effect in the hydration of C_3A

As calcium aluminate hydrates in the presence of calcium carbonate or carbon dioxide, calcium carboaluminates form. Roberts (1968) studied the different calcium carboaluminate hydrates. He analysed the hydration products formed in hydrating calcium aluminate with increasing amount of CO_2. At first C_4AH_{19} was formed, as the addition of CO_2 increased hemicarboaluminate, than monocarboaluminate, and finally calcium carbonate and calcium hydroxide in equilibrium with monocarboaluminate precipitated.

Calcium carboaluminates have a similar structure as calcium sulphoaluminates. The physical properties of both phases are given in Table 1.

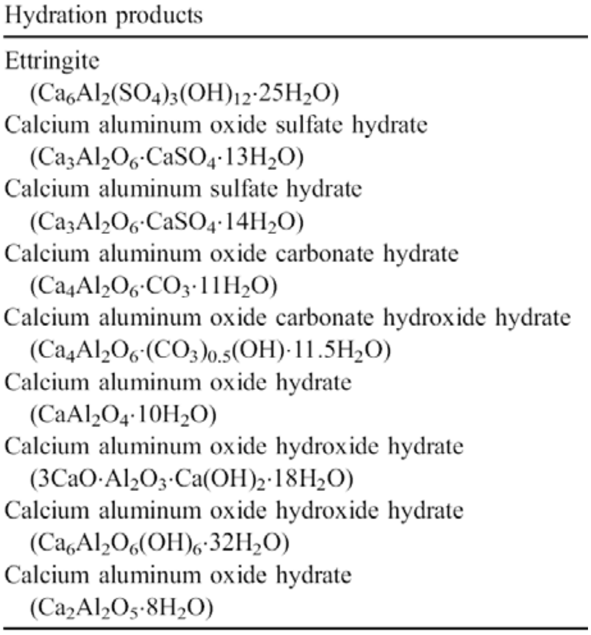
Table 1: Physical properties of calcium carboaluminates and calcium sulphoaluminates [Ingram and Daugherty, 1991].



Compound	*Crystal form*	*Density (g/cm^3)*	*Refractive indices*		*XRD spacings (Å)*
			ω	*ε*	
$C_3A.3CaSO_4.32H_2O$	Needles	1·73	1·464	1·458	9·7, 5·61, 4·7, 3·88
$C_3A.CaSO_4.12H_2O$	Hexagonal plates	1·99	1·504	1·488	9·0, 4·48, 4·00, 2·87
$C_3A.3CaCO_3.32H_2O$	Needles	—	1·485	1·463	9·4, 5·43, 4·62, 3·80
$C_3A.CaCO_3.12H_2O$	Hexagonal plates	2·14	1·554	1·532	7·6, 3·80, 2·86

Besides sulphate and carbonate, calcium hydroxide also played an important role in the hydration of calcium aluminate [Bonavetti et al. (2001), Kakali et al. (2000), Poellmann and Kuzel (1990) and Poellmann (1992)]. Table 2 shows the hydration products observed by Kakali et al. (2000). The presence of calcium hydroxide gives rise to the formation of different hydration products. It can be concluded that calcium hydroxide should not be left out the system when one wants to simulate the hydration of the C_3A in cement.
Bonavetti et al. (2001) on the other hand observed the formation of calcium hemicarboaluminate in the C_3A-$CaCO_3$-CH-H_2O system containing calcium hydroxide. This hydration phase was however not observed in limestone blended cement paste.

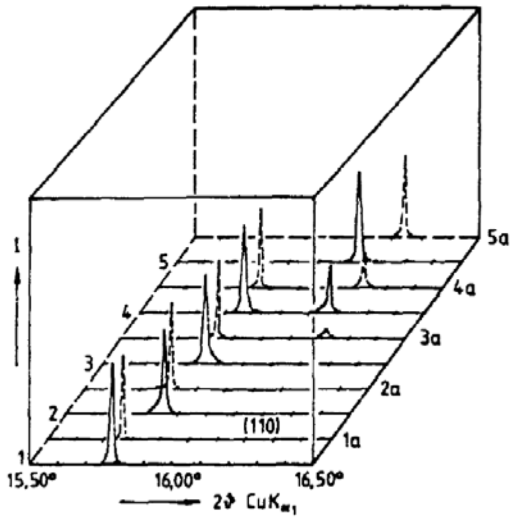
Table 2: Hydration products observed by Kakali et al. (2000) in a C_3A – $CaCO_3$ – $CaSO_4$ - H_2O – $Ca(OH)_2$ system.



Hydration products
Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 25H_2O$)
Calcium aluminum oxide sulfate hydrate ($Ca_3Al_2O_6\cdot CaSO_4\cdot 13H_2O$)
Calcium aluminum sulfate hydrate ($Ca_3Al_2O_6\cdot CaSO_4\cdot 14H_2O$)
Calcium aluminum oxide carbonate hydrate ($Ca_4Al_2O_6\cdot CO_3\cdot 11H_2O$)
Calcium aluminum oxide carbonate hydroxide hydrate ($Ca_4Al_2O_6\cdot (CO_3)_{0.5}(OH)\cdot 11.5H_2O$)
Calcium aluminum oxide hydrate ($CaAl_2O_4\cdot 10H_2O$)
Calcium aluminum oxide hydroxide hydrate ($3CaO\cdot Al_2O_3\cdot Ca(OH)_2\cdot 18H_2O$)
Calcium aluminum oxide hydroxide hydrate ($Ca_6Al_2O_6(OH)_6\cdot 32H_2O$)
Calcium aluminum oxide hydrate ($Ca_2Al_2O_5\cdot 8H_2O$)

Table 1 and Table 2 only show the top of the ice berg of the variety of hydration products.

Poellmann and Kuzel (1990), Poellmann (1992), and Trezza and Lavat (2001) proved the existence of a whole variety of ettringites having different substitution of carbonate and hydroxide for some of the sulphate in the channels of the ettringite structure, by both X-ray and FT-IR analysis. Fig. 7 shows different types of ettringite together with their X-ray dispersion spectrum.



1. $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
2. $3CaO \cdot Al_2O_3 \cdot 2.1CaSO_4 \cdot 0.9CaCO_3 \cdot 32H_2O$
3. $3CaO \cdot Al_2O_3 \cdot 1.2CaSO_4 \cdot 1.8CaCO_3 \cdot 32H_2O$
4. $3CaO \cdot Al_2O_3 \cdot 0.9CaSO_4 \cdot 2.1CaCO_3 \cdot 32H_2O$
5. $3CaO \cdot Al_2O_3 \cdot 3CaCO_3 \cdot 32H_2O$
1. $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$
1a. $3CaO \cdot Al_2O_3 \cdot 2.7CaSO_4 \cdot 0.3Ca(OH)_2 \cdot 32H_2O$
2a. $3CaO \cdot Al_2O_3 \cdot 2.1CaSO_4 \cdot 0.9Ca(OH)_2 \cdot 32H_2O$
3a. $3CaO \cdot Al_2O_3 \cdot 1.48CaSO_4 \cdot 1.52Ca(OH)_2 \cdot 32H_2O$
4a. $3CaO \cdot Al_2O_3 \cdot (x\ 1.5)CaSO_4 \cdot (x\ 1.5)Ca(OH)_2 \cdot 32H_2O$
6. $3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot 32H_2O$

Fig. 7: Different compositions of ettringite and their X-ray intensities (110) [Poellmann and Kuzel, 1990].

Carboaluminates can, besides electron microscopy, X-ray analysis and FTIR, be detected by means of thermal analysis.

Differential thermal analysis was applied by Bushnell-Watson and Sharp (1985) to detected calcium carboaluminates. Monocarboaluminate and calcium aluminate hydrated appeared to give endothermic DTA peaks in the same temperature range. When relatively large amounts of either phase are present, an endothermic peak at between 180°C and 200°C is observed. The minor phase may produce a shoulder on this peak at a lower temperature. Approximately equal amounts of both phases sometimes produce a more obvious doublet. To avoid possible misinterpretation of an endothermic peak in the range 160°C and 200°C, DTA should be backed up by XRD data. Fig. 8 shows DTA curves of aluminate cement containing 1/5 $CaCO_3$, hydrated for different times at 40°C. The evolution of the endothermic peak between 160°C and 200°C, as the relative amounts of monocarboaluminate and calcium aluminate hydrate change over time, is clearly demonstrated in this example.

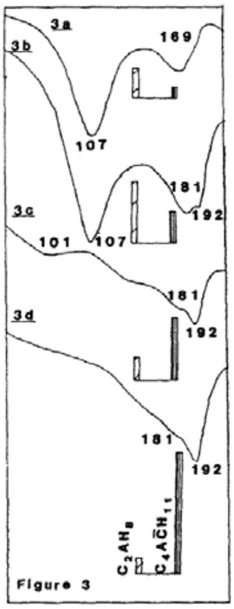


Fig. 8: DTA curves of aluminate cement and $CaCO_3$ (1:5 ratio) hydrated at 40°C at different hydration times: (3a) 6hrs. (3b) 1day, (3c) 2days, (3d) 5days [Bushnell-Watson and Sharp, 1985].

Singh (1977) and Cussino and Negro (1980) associated monocarboaluminate hydrate with an endothermic peak in differential thermal analysis curves at 180°C. This is in agreement with the findings of Bushnell-Watson and Sharp (1985). Cubic calcium aluminate hydrate seemed to relate to an endothermic peak at 330°C.

1.3.2.1 The system $C_3A – CaCO_3 – H_2O$ (– $Ca(OH)_2$)

Soustelle et al. (1985a, 1985b) and Bachiorrini et al. (1986) investigated the system $CaO – Al_2O_3 – CO_2 – H_2O$. According to the thermodynamic analyses the following phases, in the order of increasing stability, would form: $C_4A\underline{C}H_{11}$(calcium monocarboaluminate hydrate), C_2AH_8 and CAH_{10}. The phases would precipitate in the opposite order. In the thermodynamic study it is assumed that the concentrations are uniform. It is this assumption which causes the difference between the composition of hydration products calculated thermodynamically and the phases observed in the paste. Concentration gradients of the different ions are inherent to paste due to the different interfaces. The carbonate gradient close to the surface of the calcite particles leads to dissolution of previously formed C_2AH_8 and CAH_{10}, and formation of $C_4A\underline{C}H_{11}$, although the previous hydration products would be more stable in a homogeneous solution. Fig. 9 shows the different hydration phases formed in function of time, in the system $CaO – Al_2O_3 – CO_2 – H_2O$, determined by X-ray diffraction. The reason that thermodynamically less stable phases can form, is the concentration gradient in the solution due to the water/calcite interface. An increase in water/solid ratio or changes in gradients, decrease the effect of local carbonate concentrations.

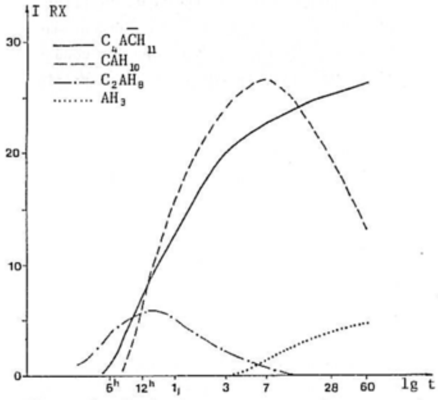


Fig. 9: The different hydration phases in function of time in the system $CaO – Al_2O_3 – CO_2 – H_2O$ [Bachiorrini et al., 1986].

Bachiorrini et al. (1986) studied the effect of limestone addition on the hydration of aluminate by isothermal calorimetry. Limestone was compared with quartz. The results are depicted in Fig. 10. The hydration reaction starts much faster as part of the calcium aluminate is replaced by calcium carbonate. Quartz on the other hand only seemed to dilute the hydration of calcium aluminate.

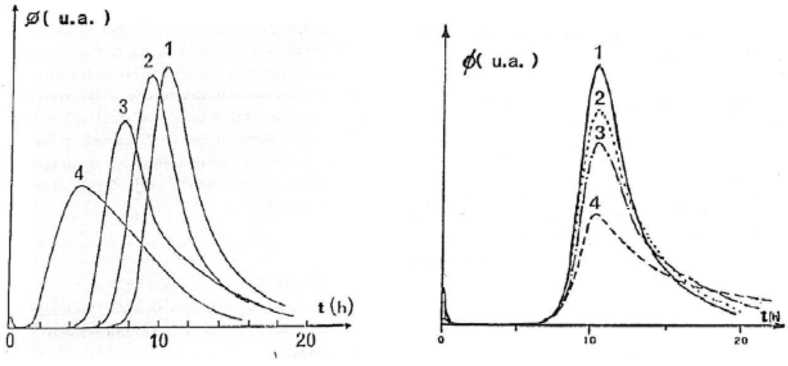


Fig. 10: Rate of heat of hydration for different combination of CA and $CaCO_3$ (left), and CA and quartz (right)
(1) CA, (2) 90/10, (3) 82.6/17.4 and (4) 50/50 [Bachiorrini et al., 1986].

Jambor (1980) observed cubic calcium aluminate hydrate (C_3AH_6) as the main hydration product of C_3A after 1 and 28 days of curing. Minor amounts of unhydrated C_3A and C_4AH_{19} were detected and a small quantity of calcium carboaluminate hydrate had formed due to reaction with CO_2 from the air.
Calcium carboaluminate hydrate was the main hydration product in the pastes containing $CaCO_3$ (see Fig. 11). Secondary phases such as unhydrated C_3A, C_3AH_6 and $CaCO_3$ were also detected. However no calcium tricarboaluminate hydrate was observed. Bonavetti et al. (2001) observed no calcium tricarboaluminate hydrate either, during the hydration of the C_3A-$CaCO_3$ system.
Jambor (1980) found that calcium carboaluminate hydrate possessed a spectacularly higher binding capacity than the cubic calcium aluminate hydrates. Compressive strength up to 17 MPa after 1 day and 29 MPa after 28 days were measured on mortar prisms prepared with 60/40 $C_3A/CaCO_3$ binder. Without $CaCO_3$ the compressive strength could not exceed the 1MPa limit.

Fig. 11:Calcium carboaluminate hydrate [Jambor, 1980].

Cussino and Negro (1980) investigated the effect of limestone sand (500m^2/kg) and limestone aggregate on the hydration of aluminate cement. Aluminate cement can exhibit strength loss over time due to transformation of hexagonal calcium aluminate hydrate to cubic calcium aluminate hydrate (CAH). Mechanical tests showed that calcareous aggregates or fine calcareous replacement of the cement (25 %) could attenuate or eliminate the loss of mechanical strength in mortar and concrete. This appeared to be due to the exclusion of cubic CAH formation, or in some cases very limited formation but than in combination with calcium carboaluminate hydrates. Calcium carboaluminate hydrates have a higher molar volume and might thereby fill part of the pores formed due to the transformation from hexagonal to cubic CAH phases. This was confirmed by porosity measurements which showed a clear decrease in porosity as calcium carboaluminate hydrate was formed.

Fentiman (1985) found that calcium carboaluminate hydrate formation in a carbo-aluminous cement (30 % calcium carbonate) depends on the curing temperature. Fig. 12 shows the different phases observed by X-ray analysis after 24 hours of curing. Carbo-aluminous cement differs from aluminous cement in that monocarboaluminate forms at the expense of C_2AH_8 and C_3AH_6 in the temperature range from 25°C to 60°C. Curing temperature less then 10°C results in the formation of CAH_{10} as the main hydration product.

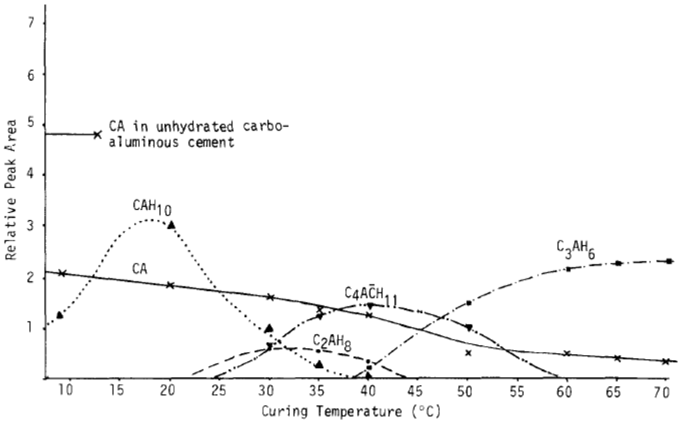


Fig. 12: Hydration phases formed in carbo-aluminous cements cured at different temperatures, determined by XRD (30 % $CaCO_3$)[Fentiman, 1985].

Méndez and Vázquez (1984) observed a similar temperature dependency of the different aluminate hydrate phases. They prevented the deleterious transformation from CAH_{10} to C_3AH_6, by heating the samples during the hydration so the cubic calcium aluminate hydrate (C_3AH_6) formed at once (see Fig. 12). Addition of calcium carbonate or carbonation treatment with CO_2 increased the compressive strength even more.

1.3.2.2 The system $C_3A – CaCO_3 – CaSO_4$ - H_2O (– $Ca(OH)_2$)

Ramachandran (1986, 1988) studied the influence of calcium carbonate on the hydration of aluminate (C_3A) with and without gypsum. Without gypsum aluminate first hydrates to a hexagonal metastable calcium aluminate hydrate (C_2AH_x-C_4AH_x) and transforms subsequently to the stable cubic phase (C_3AH_6). Calcium carbonate inhibits the formation of the hexagonal phase and promotes the formation of some type of complex. The formation of the cubic phase on the other hand is delayed or suppressed by calcium carbonate.

When aluminate hydrates in the presence of gypsum, first ettringite forms. If gypsum is depleted before all aluminate has reacted, ettringite will react with the aluminate and form calcium monosulphoaluminate hydrate (in short hereafter monosulphoaluminate). $CaCO_3$ addition to this system accelerates the formation of first ettringite and than monsulphoaluminate. This can be clearly seen from the DSC-curves in Fig. 13 as gypsum gives rise to an endothermic peak at 100°C, ettringite at 130°C and monosulphoaluminate at 165-180°C.

According to the author, the accelerating effect might be due to the formation of a carboaluminate complex on the surface of C_3A particles. This layer may be less compact and more permeable than the Ettringite layer normally occurring in the C_3A-gypsum system.

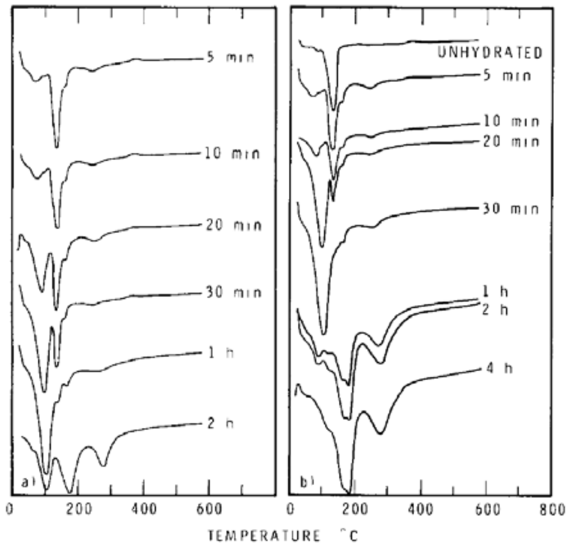


Fig. 13: DSC curves of aluminate with gypsum (25 %). Left: without $CaCO_3$. Right: with $CaCO_3$ (12.5 %) [Ramachandran, 1988].

Vernet (1986) results were not in line with those obtained by Ramachandran. Vernet observed suppression of monosulphoaluminate formation and retardation of the hydration reaction. He prepared a blend of 100g C_3A, 100g calcium carbonate, 5-50g gypsum. In the first stage of hydration ettringite was observed. The reaction was basically the same as in the absence of limestone. But as soon as the gypsum is depleted, it is the limestone which dominates the reactions. Monosulphoaluminate was not observed, instead a solid solution of C_4AH_{13} containing sulphate and carbonate was formed. As all C_3A becomes depleted an equilibrium composition of ettringite and carboaluminate forms.

The reaction with C_3A with low gypsum content is strongly retarded by limestone addition meaning that limestone powder also could act as a set regulator. A micrograph of concrete with limestone filler is shown in Fig. 14. It can be seen that calcium carboaluminate hydrates (here after carboaluminates) have crystallized in the vicinity of the aluminate grains and thereby shield the C_3A grains. This might explain the retarding effect of calcium carbonate on C_3A.

Ingram and Daugherty (1991) suggested that an increase in the rate of ettringite formation by the incorporation of carbonate, might be caused by an increase in apparent starting material for reaction.

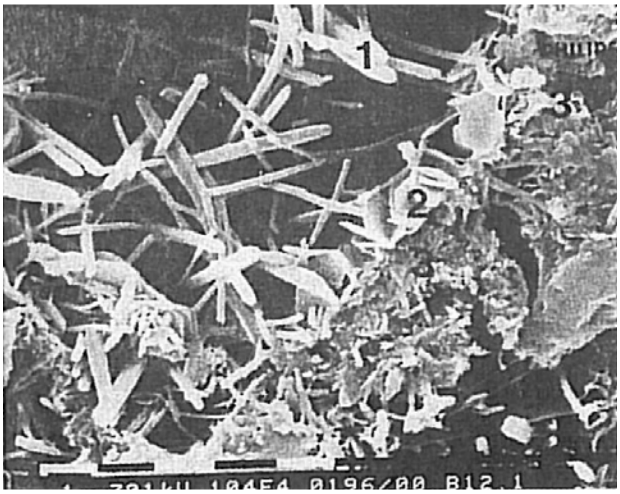


Fig. 14: Concrete with limestone filler. (1) ettringite, (2) carboaluminate and (3) clinker grain [Vernet, 1986].

Kakali et al. (2000) and Singh (1977) confirmed the results from Vernet (1986). Kakali et al. (2000) observed that calcium carbonate suppressed the conversion of ettringite to monosulphoaluminate and favoured the replacement of monosulphoaluminate by monocarboaluminate, in a C_3A-$CaCO_3$-gypsum system. This was according to Kakali et al. (2000) due to the greater insolubility and therefore the greater stability of monocarboaluminate.
When gypsum is excluded from the system, monocarboaluminate hydrate forms at the start of hydration.
Singh (1977) added 2 % thallous carbonate (Tl_2CO_3) to a calcium aluminate (C_3A) blend containing 20 % gypsum. The hydration was monitored by isothermal calorimetry and thermal analysis. Tl_2CO_3 appeared to retard the hydration. Raising the addition to 4 % amplified the retardation effect. According to the author this was due to the formation of calcium carboaluminate and calcium carbonate, which precipitated during the hydration.

Vernet and Norworyta (1992) investigated the competition between the formation of monocarboaluminate and monosulphoaluminate hydrates in a C_3A - $Ca(OH)_2$ - $CaSO_4.2H_2O$ - $CaCO_3$ - H_2O system. Calcium aluminate hydrated at 25°C in the presence of on excess of calcium hydroxide. The amounts of added calcium carbonate and calcium aluminate were varied. The hydration kinetics were monitored and solids and liquid phases analysed. Fig. 15 shows the kinetic diagrams for one of the tested combinations.

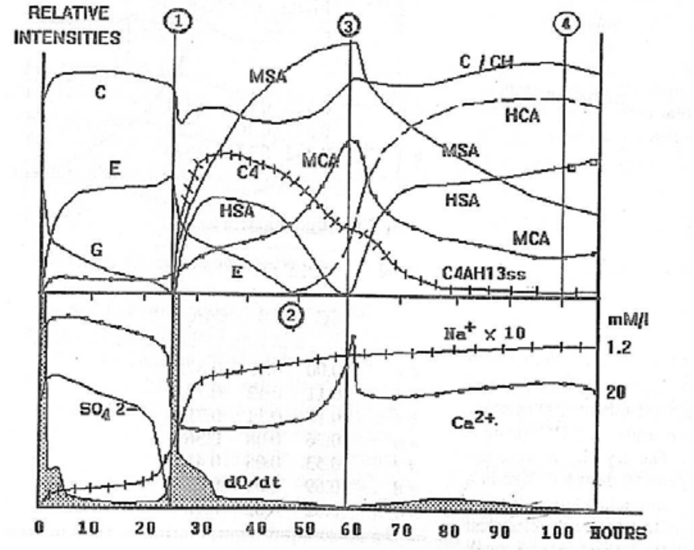


Fig. 15: Kinetic diagram for a C_3A - $CaSO_4.2H_2O$ - $CaCO_3$ H_2O system with molar ratio of 0.365 – 0.142 – 0.492. C=conductometer curve, E=ettringite, G=gypsum, MSA=monosuphoaluminate, MCA=monocarboaluminate, HSA=hemisuphoaluminate, HCA=hemicarboaluminate, CH=portlandite, C4= C_4AH_{13} solid solution [Vernet and Noworyta, 1992].

It was found that in the quarternary system, monosulpho- and monocarboaluminate can coexist at equilibrium with portlandite and calcium aluminate hydrate, for adequate initial compositions. Nevertheless the evolution of the system remains far from equilibrium, as long as C_3A is present, and this allows the formation of metastable phases.

Kuzel and Pöllmann (1991) made a systematic study on the hydration of C_3A in the presence of $Ca(OH)_2$, $CaSO_4.2H_2O$ and $CaCO_3$. They varied the molar ratios (indicated as e.g. 1:1:1) of the different constituents. Fig. 16 gives the evolution of the hydration products over time of some of the tested combinations.

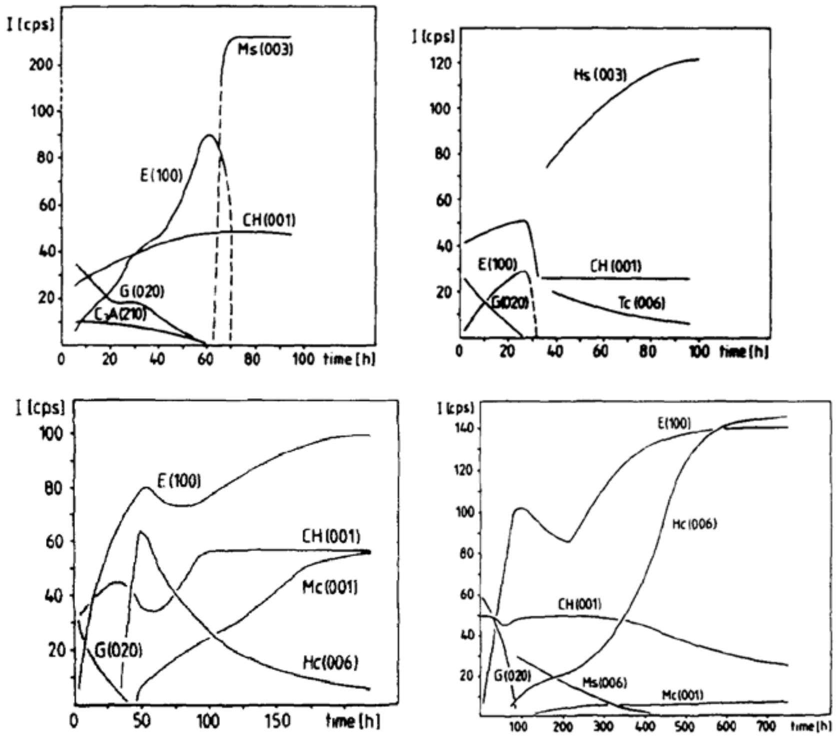


Fig. 16: Relative amounts of the hydration products for:
Left up: C_3A – CaO– $CaSO_4 \cdot 2H_2O$ → 1:1:1
Right up: C_3A – CaO – $CaSO_4 \cdot 2H_2O$ → 1:1:1/2
Left down: C_3A – CaO – $CaSO_4 \cdot 2H_2O$ – $CaCO_3$ → 1:1:1:2/3
Right down: C_3A – CaO – $CaSO_4 \cdot 2H_2O$ – $CaCO_3$ → 1:1:1:1/3
[Kuzel and Pöllmann, 1991].

The system C_3A – CaO– $CaSO_4 \cdot 2H_2O$ → 1:1:1 is depicted in the left upper corner of Fig. 16. Calcium oxide hydrates till calcium hydroxide (CH), and ettringite (E) forms gradually during the dormant period. After 65 hours when the aluminate (C_3A) is depleted the ettringite rapidly transforms into monosulphoaluminate (Ms). During the whole hydration no change in the amount of calcium hydroxide was observed.

For the C_3A – CaO – $CaSO_4 \cdot 2H_2O$ → 1:1:1/2 system, the induction period lasts only 32 hours and hemisulphoaluminate (Hs) is formed instead of monosulphoaluminate (see Fig. 16 right upper corner). Calcium hydroxide is consumed by the formation of $C_3A \cdot Ca(OH)_2 \cdot 18H_2O$ (Tc). The decomposition of ettringite in the C_3A – CaO – $CaSO_4 \cdot 2H_2O$ → 1:1:3/4 system after 45h and a member of the extended solid solution between monosulphoaluminate and ettringite was formed.

In the following carbonate system, C_3A – CaO – $CaCO_3$ → 1:1:1/3, the main hydration product observed after 3 hours was $C_3A.Ca(OH)_2.18H_2O$ (Tc). It gradually converted over time to hemicarboaluminate. At $CaCO_3/C_3A$ ratios greater than 1, monocarboaluminate $C_3A \cdot CaCO_3 \cdot 11H_2O$ and $CaCO_3$ were present, but tricarboaluminate was not observed.

The hydration mechanism of C_3A – CaO – $CaSO_4 \cdot 2H_2O$ – $CaCO_3$ → 1:1:1:2/3 is depicted in the lower left corner of Fig. 16. At first ettringite forms around C_3A particles. After 40 hours sulphate ions are depleted, but no transformation to monosulphoaluminate or hemisulphoaluminate takes place. These are suppressed in the presence of $CaCO_3$. Hemicarboaluminate is formed and which on its turn converts steadily to monocarboaluminate. At equilibrium monocarboaluminate, ettringite and $Ca(OH)_2$ are found.

In the C_3A – CaO – $CaSO_4 \cdot 2H_2O$ – $CaCO_3$ → 1:1:1:1/3 system the $CaCO_3$ is to low to prevent the crystallization of monosulphoaluminate at end of induction period. But monosulphoaluminate

disappears due to a topochemical interlayer exchange forming hemicarboaluminate (see lower right corner of Fig. 16).
Due to the low sulphate content in the system C_3A – CaO – $CaSO_4 \cdot 2H_2O$ – $CaCO_3$ → 1:1:1/4:1/4, a small amount of $C_3A \cdot Ca(OH)_2 \cdot 18H_2O$ was formed. At equilibrium hemisulphoaluminate and a solid solution between the former and hemicarboaluminate were found.

Based on the above mentioned observation Fig. 17 was constructed.

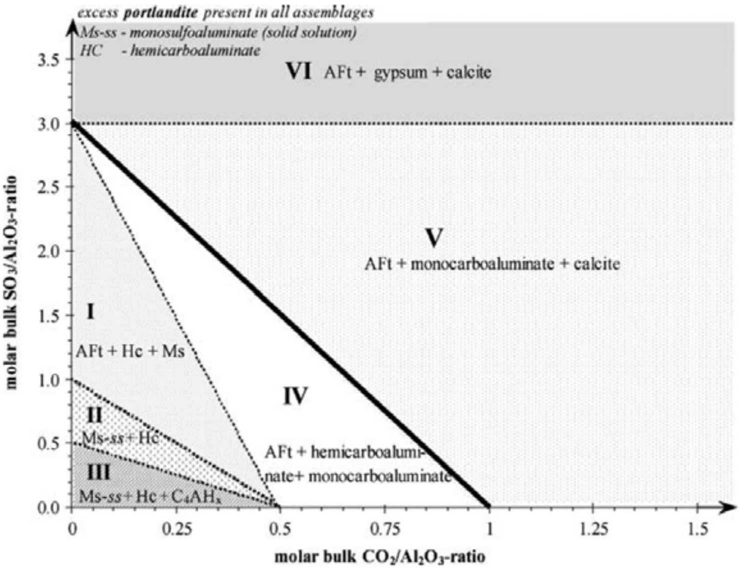


Fig. 17:Calculated phase assemblage of a hydrated mixture consisting of C_3A, portlandite and varying initial sulphate (SO_3/Al_2O_3) and carbonate ions ($CaCO_3/Al_2O_3$) at 25°C in molar units [Matschei et al., 2007].

Fig. 17 does not enable the amount of phases to be calculated. For that reason Matschei et al. (2007) converted the data determined by Kuzel and Pöllmann into graphs of which Fig. 18 is an example. From these graphs one can read of the amount of the different phase for a given sulphate/aluminate ratio.

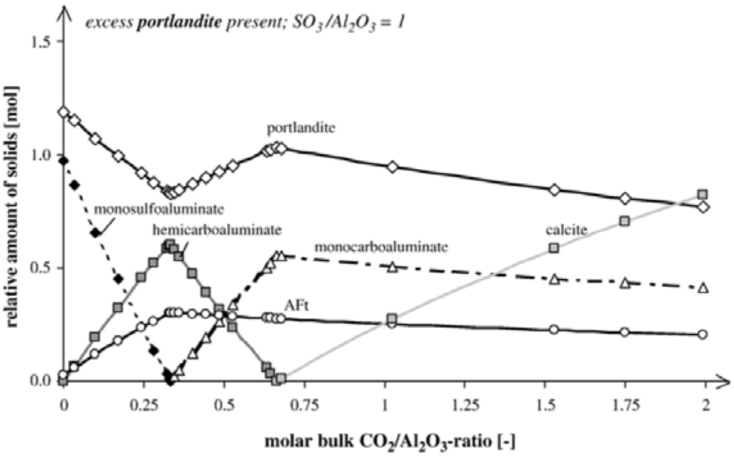


Fig. 18: Relative amount of hydrate phases of a model mixture consisting of C_3A, portlandite, with fixed sulphate ratio ($SO_3/Al_2O_3=1$) and in function of changing carbonate ratio (CO_2/Al_2O_3) at 25°C (constant amount of solids $C_3A + CaSO_4 + CH + Cc = 3.25$ mol, reacted with 500g water; data expressed in molar units) [Matschei et al., 2007].

Volume change of the hydrates was calculated by combining the density of the different phases with their amount. The results are shown in Fig. 19. The effect of calcite addition and its subsequent reaction initially increase the molar volume of the solids and consume water. At low additions calcite is reactive, free calcite forms carboaluminates and displaces thereby sulphate form AFm (abbreviation for calcium monosulphoaluminate hydrate) to ettringite. The high water binding capacity and low density of ettringite give rise to an increase in volume of the solids. The maximum solid phase volume is achieved at a carbonate ratio of approximately 0.33. This is considerably less than the maximum amount of reactive calcite, namely 0.66.

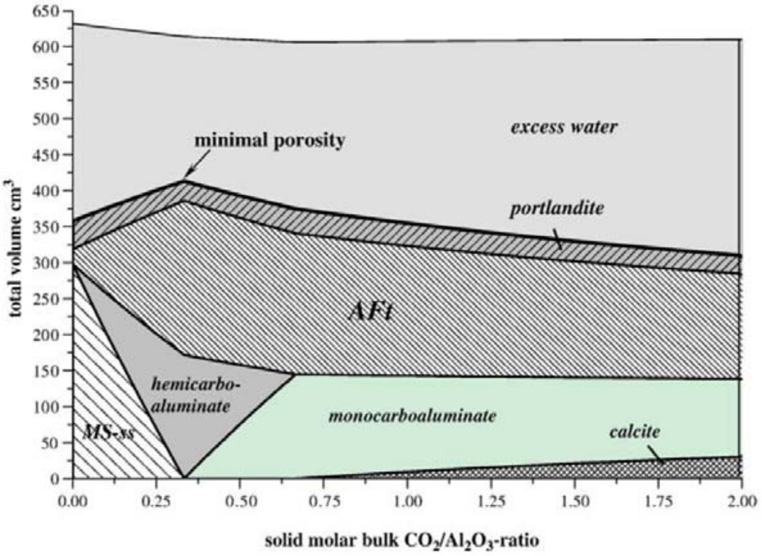


Fig. 19: Volume changes of hydrated phases of a model mixture consisting of C_3A, portlandite, with fixed sulphate ratio ($SO_3/Al_2O_3=1$) and in function of changing carbonate ratio (CO_2/Al_2O_3) at 25°C (constant amount of solids $C_3A + CaSO_4 + CH + Cc = 3.25$ mol, reacted with 500g water; data expressed in molar units) [Matschei et al., 2007].

The calculations implicitly assume that volume changes as a consequence of the calcite reaction occur after the paste has hardened. As the phases are not expansive no external volume changes take place. If these suppositions are correct, calcite would reduce the porosity by the creation of hydration products.

1.3.3 Effect on the hydration of Portland cement

Bonavetti et al. (2001) followed the development of the different hydration phases in a limestone-blended cement by the means of XRD. Calcium monocarboaluminate hydrate was immediately detected after hydration began. The transformation of monosulphoaluminate to monocarboaluminate occurred after 28 days while the conversion from ettringite to monosulphoaluminate is deferred.

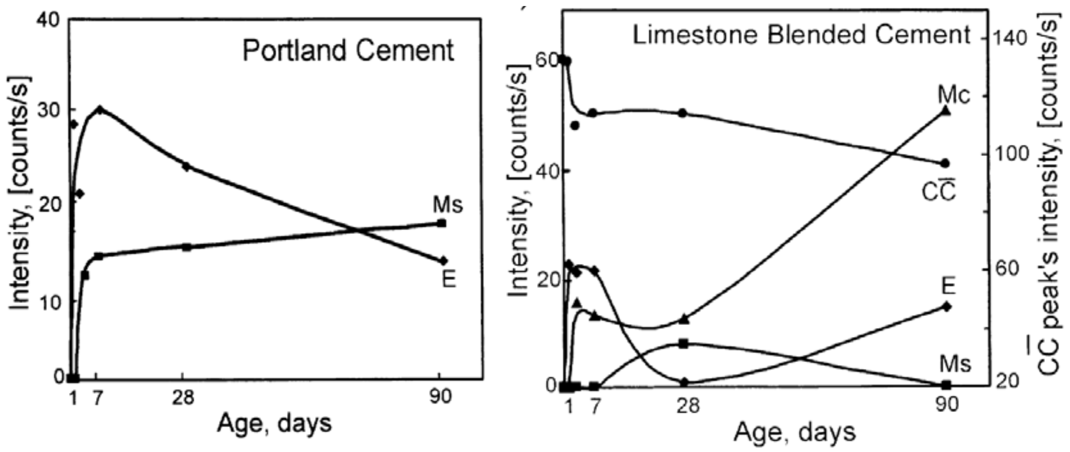


Fig. 20:Evolution of hydration products in OPC (Left) and limestone blended cement (Right) in function of time (Ms = monsulphoaluminate, E = ettringite, Mc = monocarboaluminate, CC' = calcite) [Bonavetti et al. 2001].

In Fig. 20 the evolution of the hydration products in OPC is compared with those in limestone blended cement (20 % replacement level).

In OPC ettringite had formed after one day and it transformed to monosulphoaluminate after 3 days.

In limestone blended cement ettringite was also detected after 1 day but its conversion to Monosulphoaluminate was delayed until 7 days. After 3 days, however, monocarboaluminate was observed and approximately 15 % of the $CaCO_3$ had been consumed. After 28 days the monosulphoaluminate level starts to drop and an ettringite and monocarboaluminate commence to form again. The initial conversion of ettringite to monosulphoaluminate, in the paste containing limestone filler, occurs due to the lack of gypsum in the paste. At later ages a conversion of monosulphoaluminate to ettringite occurs due to the presence of a new source of sulphate ions. In this case the sulphates are provided by the monosulphoaluminate. Carbonate ions supplied by limestone filler produced the monosulphoaluminate-monocarboaluminate transformation because the last compound is more stable according to its solubility products.

After 90 days about three-quarters of the carbonate supplied by the limestone had not reacted.

Fig. 21 shows the difference in phase composition of hydrated cement paste after 28 days with or without limestone powder as determined by XRD/Rietveld analysis [Hirao et al., 2007].

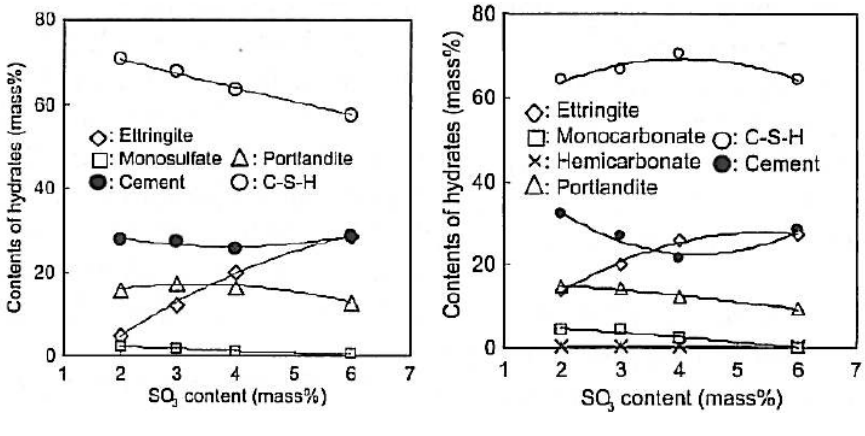


Fig. 21:Phase composition of hydrated cement paste after 28 days in function of the sulphate content. Left: without limestone powder. Right: with 4 % limestone powder (1000m^2/kg) replacement. [Hirao et al., 2007].

The amount of C-S-H is no longer dependent on the sulphate content as limestone powder is added. The amount of ettringite at low sulphate levels is increased significantly and instead of Monosulphoaluminate, monocarboaluminate and hemicarboaluminate are formed.
The volume ratio of the different phases was calculated. The results are depicted in Fig. 22.

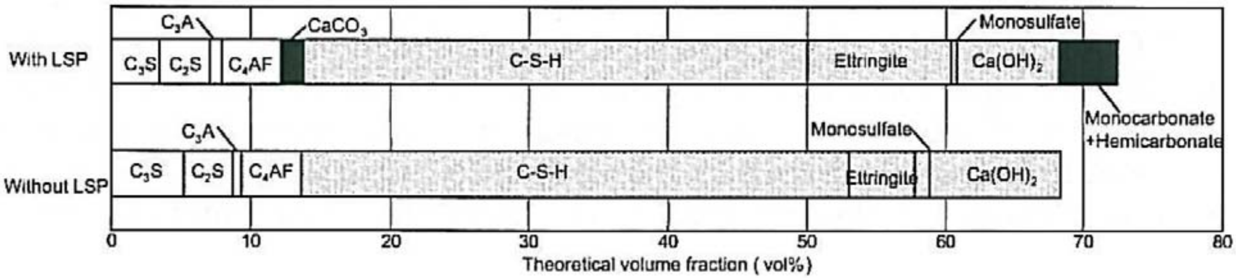


Fig. 22: The volume ratio of minerals and hydrates in cement paste with (4 %) and without limestone powder (LSP) and a 2 % sulphate content after 7days [Hirao et al., 2007].

The amount of unhydrated C_3S decreases as limestone powder is included. This is in agreement with the previously discussed effect of limestone powder on the hydration of alite. The volume of the aluminate hydrates does not decrease after the consumption of gypsum as ettringite is not consumed. This gives rise to an increase in total volume.

Péra et al. (1999) prepared an OPC-limestone powder blend with weight ratio 1:1. The heat produced by the reaction between OPC and limestone is about double that from plain OPC (see Fig. 23). XRD analysis revealed the presence of calcium carboaluminate hydrate and calcium carbosilicate hydrate. Monosulphoaluminate, on the other hand, had disappeared. The compressive strength was maintained or even increased in pastes containing 10 % $CaCO_3$, High replacement levels of $CaCO_3$ gave rise to a decrease in strength.

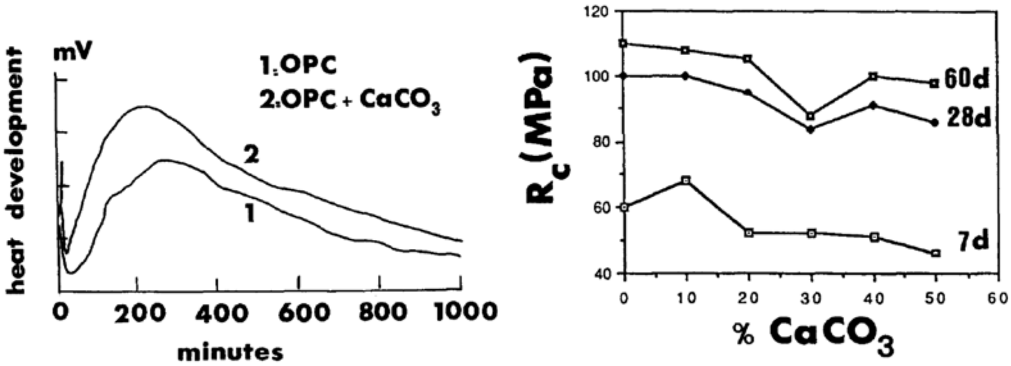


Fig. 23: Left: Isothermal calorimetry curves for OPC and OPC+CACO$_3$ (w/s=1). Right: Compressive strength of cement paste containing different amounts of $CaCO_3$ (w/s=0.25-0.28) [Péra et al., 1999].

Dweck et al. (2000) studied the changes in the weight loss peak, attributed to $CaCO_3$ as measured by DTG, in hydrating limestone cement. The calcium carbonate peak goes from one-step to a two-step decomposition peak. Since $CaCO_3$ was the only crystalline carbonate phase observed by XRD, the first $CaCO_3$ DTG peak will probably be due to the formation of a non-crystalline calcium carbonate phase during the hydration process. The non-crystalline $CaCO_3$ decomposes at lower temperatures causing the appearance of the two observed peaks. For longer hydration times, it can be seen that the peak which occurs at lower temperatures increases in area, probably due to the higher CO_2 mass evolved from carboaluminates formed during hydration. This effect is much more visible in the DTG than in the DTA curves.
Ingram and Daugherty (1992) used this technique to determine the consumption of carbonate during cement hydration. They measured the weight loss between 550°C and 850°C. It was found that only a small part of the calcium carbonate of the limestone is consumed during the cement

hydration. An OPC with an aluminate content of 6.59 % only incorporated 0.69 % carbonate when 5 % limestone was added after 28 days and 4.02 % for a 25 % limestone addition. The presence of gypsum and higher aluminate content in the clinker enhanced the uptake of carbonate. An addition of 3 % of gypsum gave rise to an uptake of 5.84 % carbonate for a 10 % limestone addition. A cement with high aluminate content (12.5 %) consumed 3 % carbonate when 5 % limestone was added.

Rahhal and Talero (2005) compared the effect of limestone filler (L) and quartz filler (Q) on the hydration of two different cements. One cement has a high aluminate content, 6,4 % (PC1), and the other has a relatively low aluminate content, 1,5 % (PC2). Isothermal calorimetric curves for replacement levels of 20 % and 40 % are depicted in Fig. 24. The peak following the main peak of hydration, observed in the calorimetric curves of PC1, is attributed to the transformation of ettringite to monosulphoaluminate. The mineral additions stimulate the hydration reactions of Portland cement components, but after the first few hours this effect begins to diminish and the dilution effect caused by the percentage replacement becomes more evident

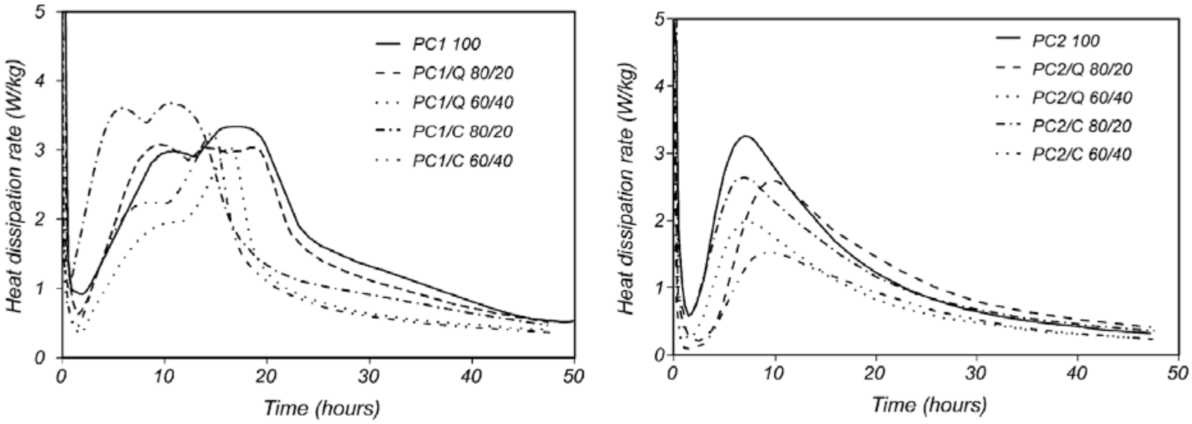


Fig. 24:The influence of limestone filler(L) and quartz filler (Q) replacement on the hydration of: Left: cement with relatively high aluminate content / Right: cement with low aluminate content [Rahhal and Talero, 2005].

For the limestone filler the optimal replacement level, according to the acceleration effect, appeared to be 20 %. In the case of quartz, it seemed to depend on the cement type used. In the high aluminate cement, the 20 % replacement level gave a better accelerating effect than the 40 % level, whereas in the low aluminate cement the opposite effect was observed.

The total amount of dissipated heat (per cement weight) after two days of hydration, appeared to decrease as the replacement level increased from 20 % to 40 % but was in general still higher than for the reference without replacement. The amount of non-evaporable water, determined on two day old samples, increased with increasing replacement levels.

X-ray diffraction analysis revealed the presence of carbonated hydrated calcium silicate and both the tri- and mono-variant of carboaluminate hydrate.

The formation of the ettringite analogue of calcium carboaluminate hydrate was also observed by Sharma and Pandey (1999) during the initial period of hydration (13.24°). It was observed up to 28 days, but it later converted into the more stable monocarboaluminate hydrate.

Kakali et al. (2000), and Sharma and Pandey (1999) determined the amount of bound water and the calcium hydroxide content by thermogravimetric analyses. They both appeared to increase relative to the amount of clinker and gypsum as limestone was added. This can be explained by the fact that limestone particles act as nucleation sides for calcium hydroxide and C-S-H. This on its turn gives rise to an acceleration of the clinker hydration.

Ingram and Daugherty (1992) performed some XRD analyses on OPC with 5 % limestone addition or a 5 % gypsum addition after 140 days of hydration. Limestone appeared to give rise to a greater C-S-H peak and a smaller portlandite (CH) peak compared to gypsum. The authors explained this phenomenon by the precipitation of CH on the surface of the limestone particles. This gives rise to an acceleration of the rate C-S-H formation and prevents CH from forming large crystals. The rapid covering of the limestone particles by CH might explain the limited amounts of carbonate available in the initial hydration.

Soroka and Setter (1977) observed a reduction in the amount of combined water as 30 % very fine ground limestone filler (1030 m^2/kg) was added to OPC compared to more coarse limestone filler additions with finenesses such as 360 m^2/kg or 670 m^2/kg. According to the authors this was due to the formation of monocarboaluminate on the surface of the C_3A grains, which according to them would suppress the reaction. This would lead to a reduction in the amount of chemically bound water as aluminates bind relatively large amounts of water.
The reduction in the amount of chemically bound water was not reflected in reduced strength. The authors explained this by the fact that strength is governed by C-S-H formation, which was not reduced by the limestone powder addition. Therefore the authors concluded that calcium carboaluminate formation is irrelevant for the strength aspect.

Barker and Cory (1991) investigate the effect of a 5 % and 25 % limestone addition to OPC and RHPC. The fineness of the limestone fillers varied between 350 and 530 m^2/kg. The pastes were prepared with a 0.50 water-cement ratio. The samples were analysed with thermogravimetric analysis (TGA), X-ray diffraction (XRD) and electron microscopy (SEM).
The addition of 5 or 25 % limestone to Portland cement accelerated the hydration reaction. The finer ground limestone cement showed a greater accelerating effect. Limestone had only little effect on the CH produced when added to the cements with low alite content.
Micrographs showed that a 25 % limestone addition influences both the size and distribution of regions of CH, as larger regions of CH were observed which were more unevenly distributed throughout the paste. Another significant change in the microstructure, in the presence of limestone, was the formation of a hydration rims of calcium silicate surrounding C_3S particles. Similar micro structural effects of limestone addition were observed by Gegout et al. (1986).
Barker and Cory (1991) detected, at earlier age, increasing amounts of ettringite are formed with increasing level of limestone addition. Monosulphoaluminate on the other hand was not observed in the pastes containing 5 and 25 % limestone. As hydration progresses, there is a trend towards the formation of larger amounts of monocarboaluminate with increasing level of limestone addition. In the cements with higher C_3A content larger amounts of carboaluminate were formed.

1.4 Physico-chemical impact

1.4.1 Effect on the initial and final setting time

Negro et al. (1986) composed a cement of 94 % clinker (C_3A=8.49 %, SO_3:1.45 %) and 6 % of a mixture of gypsum or limestone powder. Gypsum and limestone were combined as follows 6-0, 4.5-1.5, 3-3 1.5-4.5 and 0-6. No large difference in setting time was observed (initial = 2 h 35 min – 2 h 55 min, final = 4 h 40 min – 4 h 50 min) for the cements except for the cement without gypsum (initial = 0 h 20 min, final = 1 h 50 min). X-ray diffraction analysis revealed the presence of carboaluminates and calcium aluminate hydrates in the limestone containing cements. It appeared possible to replace 50 % of the gypsum by limestone powder without changing the cement performance such as setting, water demand, rheology, compressive strength and shrinkage. A 25 % replacement of gypsum by limestone gave even rise to a slight improvement in the cements characteristics. It should be stressed that the optimum replacement level of gypsum by limestone according to the compressive strength is variable and depends on the aluminate and sulphate content of the cement. The author experienced with another clinker, with a 6.98 % aluminate and 2.35 % sulphate content, that all gypsum could be replaced by limestone without changing setting and strength characteristics.

Vuk et al. (2001) observed a considerable decrease in initial and final set when a small amount of limestone (5 %) was interground with clinker containing 5 % of gypsum. Two different cement types were used, mainly differing in alite and belite amounts. The blended cements were ground to two different finenesses, 2 % residue on the 90 μm sieve or a 5 % residue. The limestone addition reduced the initial setting time by 30-50 min and the final set by 40 to 60 min. The effect of the limestone addition depended more on the clinker type than on the fineness of the blended cement.

Tsivilis et al. (1991a) produced limestone cements by intergrinding limestone additions ranging from 5 to 35 % together with clinker and 5 % gypsum to finenesses varying between 300 and 550 m^2/kg. No drastic changes in setting time were observed compared to the reference without limestone.

1.4.2 Effect on the interfacial transition zone

Grandet and Ollivier (1980) studied the interaction of calcareous aggregates and cement paste at the interface. Cement paste prepared with an OPC (10 % C_3A and 7 % C_4AF) and a water/cement ratio of 0.50. The cement paste was cast against a piece of marble.

The evolution of the amount of aluminate hydrates and carboaluminates formed is determined by X-ray diffraction analysis. The results are shown in Fig. 25. At first aluminate hydrate phase detected had the following composition: $C_4A \cdot \frac{1}{2}CO_2 \cdot 12H_2O$ (8.2Å). The CO_2 in this compound does not seem to come from dissolution of carbonate from limestone since it was observed with other aggregates as well. After almost one week monocarboaluminate, $C_3A \cdot CaCO_3 \cdot 11H_2O$ (7.6Å), starts to form and the amount of aluminate hydrate decreases. The amount of aluminates formed in the interfacial zone seems to stagnate after 9 weeks of curing.

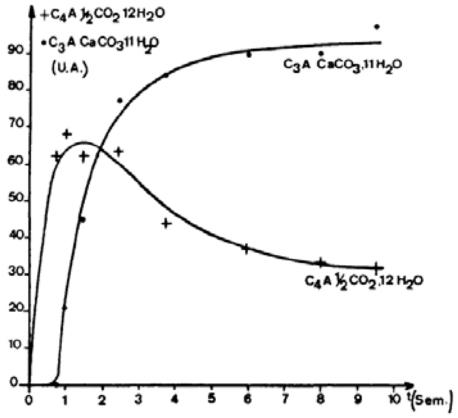


Fig. 25: Evolution of the amount of aluminates and carboaluminate in function of time at the paste-aggregate interface [Grandet and Ollivier, 1980].

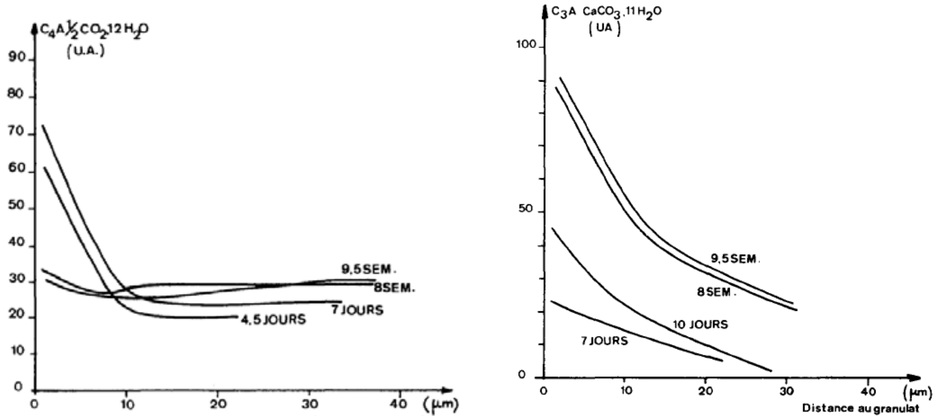


Fig. 26: Evolution of the amount of aluminate hydrate (Left) and carboaluminate (right) in function of the distance from the aggregate at different curing times [Grandet and Ollivier, 1980].

The amount of aluminate decreases regularly towards the bulk of the binder. Meaning that the aluminate reaction takes place preferably in the vicinity of the limestone particles. Fig. 26 shows that the formation of carboaluminates stays an interfacial phenomenon over time. The carbonate ions go slowly into solution and react steadily with the cement paste.

The dissolution of the calcite into the cement paste depends on the crystallographic orientation and the calcite grains. The diffusion of carbonate ions, liberated by the limestone, through the paste progresses slowly. Their concentration decreases fast from the interface towards the bulk cement paste.

SEM micrographs prevailed the hexagonal crystals of monocarboaluminate. The monocarboaluminates led to inferior crystallinity of portlandite in the interfacial zone. As a consequence, the contact surface between the paste and the aggregate and its roughness increased. The portlandite film was only observed on the surfaces of aggregates which had not reacted.

Tests were performed with a lower w/c ratio (0.29). The formation of calcium carboaluminate appeared to be much slower. No aluminate hydrate was observed at early age. Hence the w/c ratio of the paste is an important parameter in determining the rate of formation of monocarboaluminate at the interfacial zone.

Bachiorrini and Murat (1987) found that the interfacial transition zone formed between calcareous aggregates and an aluminous cement paste evolutes over time. Calcium carboaluminate crystals growing epitaxically on the calcium carbonate were observed with electron microscopy. This interaction between the paste and the aggregates became apparent when studying the crack propagation. Initially the cracks were intergranular and followed intergranular paths. But after some months the cracks formed transgranular through the calcareous aggregates. In case of siliceous aggregates the paths stay intergranular.

The evolution of the binding mechanism between aluminous cement paste and calcareous aggregates in time is depicted in Fig. 27. It is clear that the formation of a good bound requires quite some time.

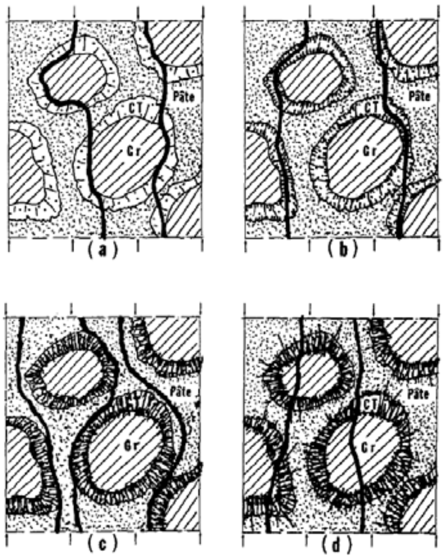


Fig. 27: Schematic presentation of different ways of propagation of cracks through aluminous cement mortar containing calcareous aggregates
(a) before 7 days of curing, (b) between 7 and 28 days, (c) after 28 days and (d) after 6 months to one year [Bachiorrini and Murat, 1987].

Monteiro and Meht (1986) observed interaction between carbonate rocks and alite cement containing no aluminates. XRD analysis show the formation of a calcium carbonate-calcium hydroxide compound at the interface. The substitution of the large and highly oriented crystals of calcium hydroxide by a compound having smaller crystals appears to be main reason for the strengthening of the transition zone.

Conjeaud et al. (1980) detected monocarboaluminate in the transition zone between the paste and calcareous aggregates but that did not seem to influence the binding capacity between them after 90 days. The shape of the aggregates appeared to be much more important.

1.4.3 Effect on the permeability

Tsivilis et al. (1999b, 2000 and 2003) investigated the porosity of limestone Portland cement with replacement levels up to 30 % after 9 months of curing, by mercury intrusion. The mortars were prepared with a w/c ratio 0.50 and sand:cement ratio of 3:1. The porosity decreased at a 10 % limestone replacement level but increased for levels higher than 20 %. As a consequence improved anti-corrosive protection has been observed.

The improvement in microstructure of concrete containing cement with a 10 % limestone replacement was confirmed by a study of thin sections. Water was better dispersed resulting in a homogenous structure.

Limestone cement exhibits higher gas permeability values compared to ordinary Portland cement. Water permeability and sorptivity properties on the other hand are improved.

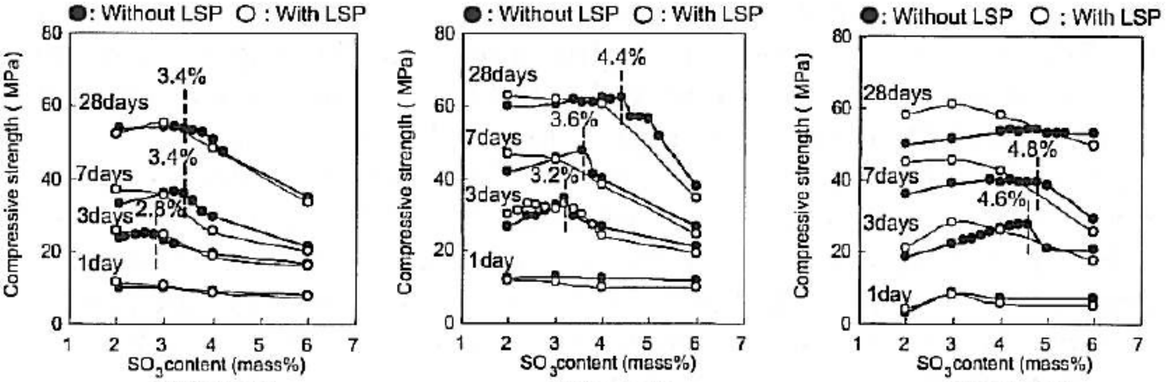
Sellevold et al. (1982) used ultra fine $CaCO_3$ powder, with the main body of particles smaller than 1µm, to replace 12 % of a white Danish cement (high alite, and low aluminate and ferrite content). The mercury intrusion data for mature paste with and without $CaCO_3$ were compared. The $CaCO_3$ addition appeared to reduce to the total pore volume and gave rise to a finer pore structure. This was attributed to the fact that fine limestone particles provide a large amount of additional nucleation sites which results in a more homogeneous distribution of C-S-H and thus a less open structure.

1.5 Mechanical impact

1.5.1 Influence on the strength development

The sulphate content in cement is optimised according to the strength development, volume stability and setting. Hirao et al. (2007) studied the influence of limestone powder addition on the optimum sulphate content. Finely ground limestone powder (1000 m^2/kg) was applied at a replacement level of 4 % and the sulphate content was varied between 2.0 and 6.0 % by reagent grade calcium sulphate hemi-hydrate (758 m^2/kg). Three different cements were tested with different alite and aluminate content. Mortars were prepared with a w/c ratio of 0.5 and 1:3 sand cement ratio.

The limestone powder did not influence the setting and expansion properties at sulphate dosages lower than 4 %. The compressive strength on the other hand clearly increased at lower sulphate contents. The effect on the compressive strength for the three tested cements is depicted in Fig. 28. The optimum sulphate content without limestone powder addition is marked.



(1) Cement 1 (2) Cement 2 (3) Cement 3

Fig. 28: Mortar compressive strength of the three tested cements in function of the sulphate content with (4 %) and without limestone powder replacement [Hirao et al., 2007].

It appears that the limestone addition increases the compressive strength at sulphate levels lower than the optimum content without limestone, and decreases it once this value is surpassed. This effect is most significant for Cement 3 with the highest aluminate content.

Soroka and Stern (1976) compared the effect of different filler replacements of OPC on the compressive strength development of mortar. The fillers used were limestone filler, two pozzolanic fillers and one non-hydraulic, non-calcareous filler (CaF_2). The mortar prisms were prepared with a 1:2.75 binder-sand ratio and a water/blended cement ratio ranging between 0.57 and 0.61.

At first ground limestone was compared with the two pozzolans, trass and ground scoria. All fillers improved significantly the compressive strength. This improvement was time dependent, being more pronounced at earlier rather than at later age. Only at early age the observed effect on strength was related to the type of filler involved. In later age, however, this difference in the filler effect was less evident, becoming virtually non-exsistent at 28 days when all three brought approximately the same improvement in strength.

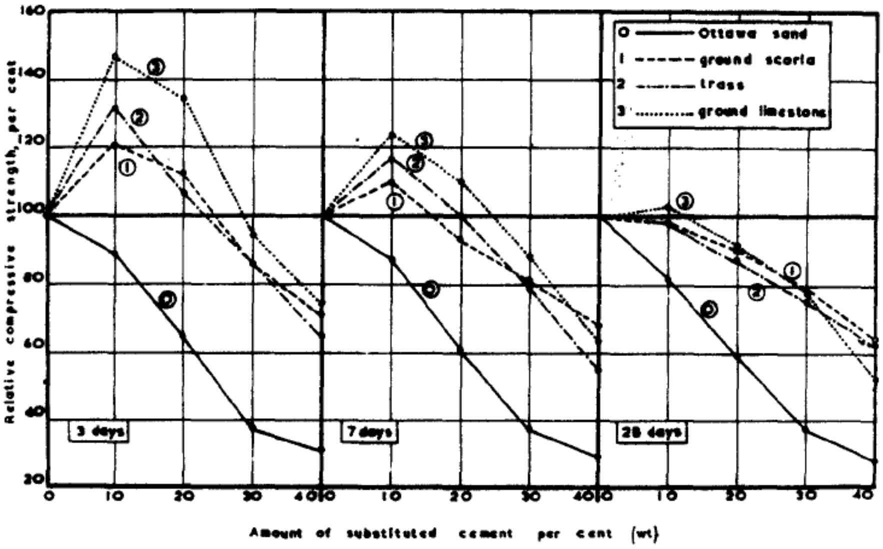


Fig. 29:Relative compressive strength of mortars composed with blended cements at after 3, 7 and 28 days of hydration in function of the replacement level (0 %, 10 %, 20 %, 30 % and 40 %) [Soroka and Stern, 1976].

A second test series was performed in order to eliminate the pozzolanic effect at later age. The effect of limestone filler (900 m^2/kg) was compared with that of CaF_2 (1,800 m^2/kg). Due to the fineness of the fillers the w/c ratio was raised up to 0.75. Both fillers improved the compressive strength significantly at early age. Greater improvement in the strength of the $CaCO_3$ containing mortars was evident only at 3 and 7 days. At later age the effect of both fillers on strength was virtually the same irrespective their difference in chemical composition and fineness.

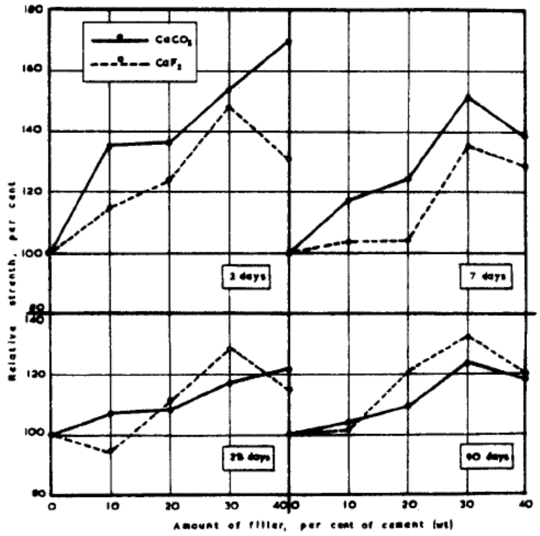


Fig. 30: Relative compressive strength of mortars composed with blended cements ($CaCO_3$ or CaF_2) at after 3, 7, 28 and 90 days of hydration in function of the replacement level (0, 10 %, 20 %, 30 % and 40 %) [Soroka and Stern, 1976].

The effect of filler addition on the strength was mainly due to their accelerating effect on the rate of the cement hydration. The fillers act as crystallization nuclei and thereby increase the crystallization rate of portlandite, and consequently also the rate of cement hydration. This effect is essentially the same for all filler studied irrespective their specific composition. It was observed that the calcareous filler were superior in improving the compressive strength at early age. This might be due to their structure which is more compatible with the crystallizing phase so that epitaxial growth can occur. The data, on the other hand, did not provided information on the possible formation of calcium carboaluminate when calcareous fillers were involved. It did suggest, however that if such a formation did take place the cement compressive strength was not necessarily affected. Because if calcium carboaluminate would result in strength increase, this effect should been evident at all ages and not only at early age.

Tsivilis et al. (1999a) composed different limestone cements with 3 kinds of limestone and 2 kinds of clinker. The major differences between the limestones used were calcite content, dolomite content and quartz/clay content. The cements differed most in alite and aluminate content. Limestone was added in portions ranging form 5 to 35 % and 5 % gypsum was included in all cements. The cements were produced by intergrinding in a pro-pilot plant ball mill with a capacity of 5kg.

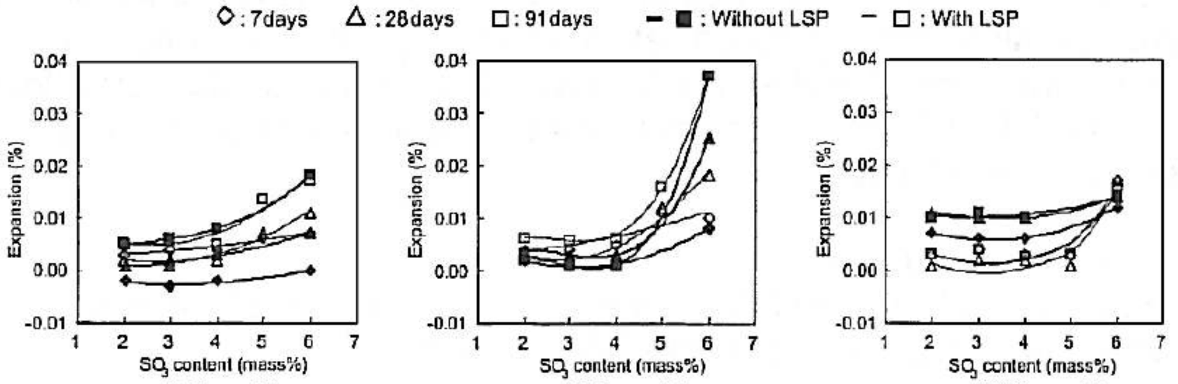
Addition of 10 % limestone did not significantly alter the compressive strength at any age up to a fineness of 430 m^2/kg, further increase of cement fineness led to the production of limestone cements having a compressive strength lower than the pure ones. Cements with 35 % limestone addition reached strengths between 27 and 35 MPa after 28 days of curing for Blaine finenesses ranging between 500 and 600 m^2/kg.

The clinker with the high aluminate content is generally more reactive when limestone is present but the limestone with high dolomite content was best combined with the low aluminate clinker. The effect of fineness on the clinker reactivity and strength development varies in relation to clinker and limestone quality. Therefore it can be concluded that the combination of the different materials is more important than the characteristics of the individual materials.

1.5.2 Influence on the volumetric stability

Hirao et al. (2007) investigated the effect of a 4 % limestone powder replacement on the expansion (when submerged) and drying shrinkage characteristics for three different cements with varying sulphate content.

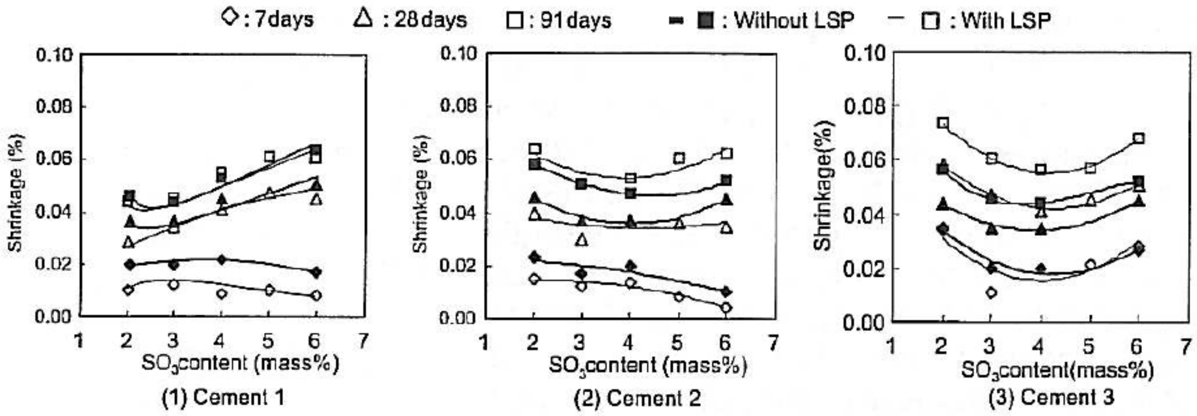
The expansion in water of the mortars containing limestone showed almost the same trend as the once without limestone. However, the expansion of Cement 3, which has the highest aluminate content, became smaller a lower sulphate contents.



(1) Cement 1 (2) Cement 2 (3) Cement 3

Fig. 31: Expansion of mortars in water for varying sulphate content and with (4 %) or without limestone powder (LSP) [Hirao et al., 2007].

The shrinkage, at early age and at low aluminate content, decreases by the addition of limestone powder. At later age and for higher aluminate contents, limestone powder increases the shrinkage. According to the author this might be due to the influence of limestone powder on the type of hydrates, on the strength development and porosity but further investigation is required on this subject.



(1) Cement 1

(2) Cement 2

(3) Cement 3

Fig. 32: Drying shrinkage of mortar for varying sulphate content and with (4 %) or without limestone powder (LSP) [Hirao et al., 2007].

Tsivilis et al. (1991(1)) produced limestone cements by intergrinding limestone additions ranging from 5 to 35 % with clinker and 5 % gypsum to fineness varying between 300 and 550 m^2/kg. The linear expansion and linear shrinkage at 28 days were definitely smaller than for the reference cements without limestone addition.

1.6 Durability

1.6.1 Sulphate attack

González and Irassar (1998) investigated the effect of limestone filler on the sulphate resistance of low C_3A Portland cements. Three different cements with varying chemical composition were applied and limestone replacements of 0 %, 10 % and 20 %. They found that the addition of limestone filler could increase or decrease the sulphate performance of blended cements depending on the mineralogical composition of Portland clinker, the amount of filler replacement, and the equilibrium between the increase of hydration degree before exposure and the water-cement increases by filler addition. A 10 % replacement of limestone filler had a favourable effect on cements containing unstable compounds in a sulphate environment, but did not cause significant improvement in the sulphate performance of already relative sulphate sustainable cements.

The authors suggested three mechanisms by which limestone could influence the sulphate resistance: (1) increase the early hydration rate and a subsequent decrease in the porosity at early age, on the other hand higher amounts of calcium hydroxide will crystallize on the surfaces of aggregates and filler particles which on their turn will form potential spaces for delayed ettringite formation; (2) dilution of C_3A by replacing part of the cement, this improves the resistance slightly for high or moderate C_3A cement but is insufficient to obtain sulphate resistant cement; (3) formation of carboaluminate might contribute to a denser structure, but in high sulphate environments ettringite could be a more stable phase than carboaluminate.

Ingram and Daugherty (1991) found that the improvement of the sulphate resistance by limestone addition was most significant for cements with higher C_3A contents. This is in agreement with González' and Irassars (1998) second mechanism.

Livesey (1991) observed that the type of clinker was more important than the kind and amount of filler.

1.6.2 Carbonation

Ingram and Daugherty (1992) found that low levels of carbonate addition to OPC increase the resistance against atmospheric carbonation (see Fig. 33).

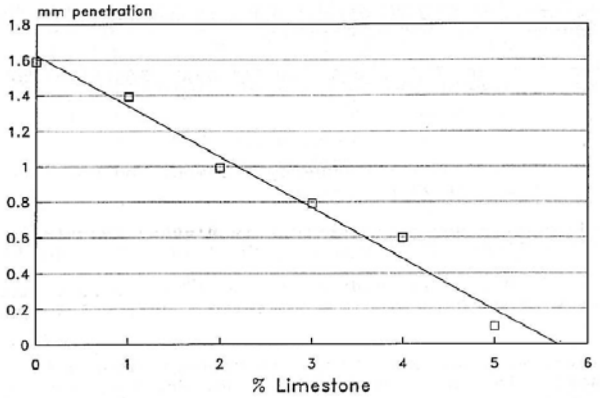


Fig. 33: CO_2 penetration of 140 days cement sample [Ingram and Daugherty, 1992].

Tezuka et al. (1992) found similar results for 5 % limestone addition. But for limestone additions higher than 10 % increased carbonation depths were observed.
Tsivilis et al. (2000) replaced up to 35 % of clinker by limestone (w/c=0.5) and found no sign of carbonatation after 12 months. The reference on the other hand showed a carbonatation depth of 5mm.

1.6.3 Chloride diffusion

Tezuka et al. (1992) prepared cement pastes with a water/solid ratio of 0.4 and with limestone additions ranging between 5 and 35 %. It was found that the diffusion coefficient for Cl ions decreased for a limestone content of 5 %, and increased for limestone levels higher than 10 %. According to the authors the differences were within the usual limits for OPC and blended cements. So they concluded that the diffusion coefficient of cement paste with limestone addition is similar to that of OPC.

Tsivilis et al. (2000) tested the rapid chloride permeability of limestone cements with replacement levels up to 35 %. The concretes were classified as highly permeable to chloride but this should be attributed to the high w/c ratios applied (0.70).

The type of clinker is more important than the kind and amount of filler according to Livesey (1991).

1.6.4 Freeze-thaw

Tsivilis et al. (2000) observed inferior freeze-thaw resistance in limestone concrete with limestone replacing up to 35 % of the clinker but this might be due to the high value of the w/c ratio applied namely, 0.70.

Livesey (1991) observed a reduced freeze thaw resistance of high filler cements and stresses the need for air entrainment.

1.7 Conclusion

Limestone can be included in the cement by intergrinding with the clinker or by blending limestone filer with ground clinker. As limestone is interground with clinker, the particle size of the cement widens. As a consequence a decrease in water demand and an improved

Limestone filler addition accelerates the hydration of cement, or more precisely the C_3S phase, by acting as nuclei for CH and CSH precipitation. This accelerating effect gives rise to higher compressive strength at early age, and shorter initial and final setting times. Limestone fillers with a higher fineness, have the strongest effect.

Part of the $CaCO_3$ interacts with the hydration products. The reaction mechanism of C_3A is changed and calcium carboaluminates form in competition with calcium sulphoaluminates. The hydration of C_3S in the presence of carbonate results in the formation of calcium carbosilicate hydrates.

It was observed that limestone filler replacements up to around 10 % (depending on the fineness) led to a more homogenous structure of the cement paste. This was attributed to a better dispersion of the hydration products as limestone particles served as precipitation sites. This denser structure could result in an improved durability performance of the cement. At higher replacement level the reduction in hydration products overrules the homogenizing effect.

1.8 Future research

When developing an all-round blended cement the amount and the fineness of the limestone addition should be optimised according to setting, strength, volumetric stability and porosity, keeping in mind the importance of the $SO_4\backslash CO_3$ ratio.

2 Combination limestone and fly ash

Very little is published on the ternary blends containing both limestone and fly ash, although this appears to be a logical combination, as limestone improves early strength development by its acceleration effect, but does not contribute to the strength at later age, and whereas fly ash reduces early strength by dilution but increase later strength development by pozzolanic reaction forming partly calcium aluminate hydrates that calcium carbonate can react with.

Elkhadiri et al. (2002) used a combination of limestone filler and fly ash. They were interground with the clinker until 2.5 % was retained on the 80 μm sieve. This resulted in good packing and mechanical properties. A 10 % fly ash and 13 % limestone replacement gave rise to a compressive strength of 17.8 MPa after 2 days and 45.9MPa after 28 days.

Sato and Beaudoin (2007) investigated the effect of nano-sized $CaCO_3$ addition on the hydration of cement paste containing high volumes of fly ash. 50 % of the OPC was replaced by FA and 10 or 20 % of micro-sized or nano-sized $CaCO_3$ was added. SEM images of both micro-sized and nano-sized $CaCO_3$ are depicted in Fig. 34 their average particle sizes are respectively 5 to 20 μm, and 50 to 120 nm. The BET surface area were respectively 350 m^2/kg and 20500 m^2/kg.

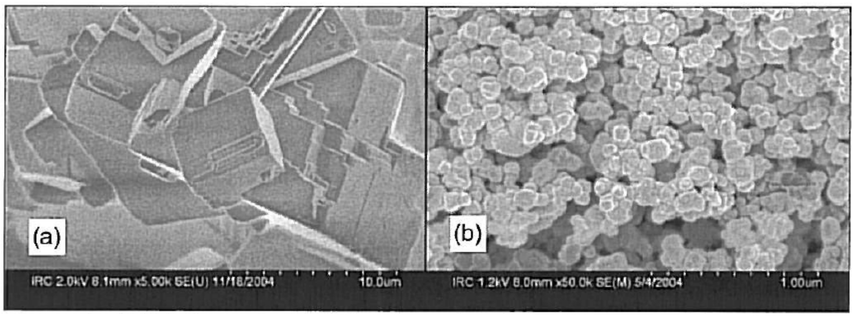


Fig. 34:SEM images of (a) micro-sized $CaCO_3$ and (b) nano-sized $CaCO_3$ [Sato and Beaudoin, 2007].

At first the effect of micro- and nano-$CaCO_3$ on OPC without fly ash replacement was investigated.

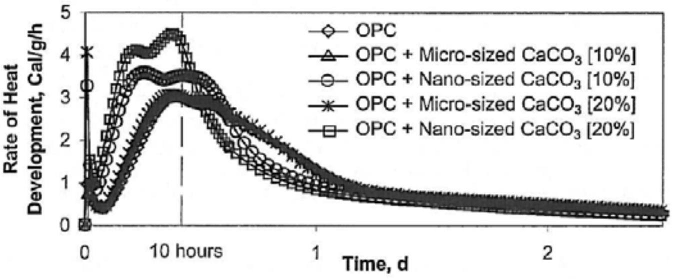


Fig. 35: Conduction calorimetry curves for OPC and OPC with micro- and nano- $CaCO_3$ (w/c=0.50) [Sato and Beaudoin, 2007].

Fig. 35 shows the conduction calorimetry curves for OPC and OPC with micro- and nano-$CaCO_3$. The curve of the control OPC is almost identical to those of the OPC with additions of both 20 % and 20 % micro-sized $CaCO_3$, indicating that macro sized $CaCO_3$ has little or almost no effect on the hydration of OPC in terms of rate of heat development. It is evident, however that the addition of both 10 % and 20 % nano-sized $CaCO_3$ significantly accelerate the early hydration of OPC. The higher the amount the greater the effect.

The shoulder following the main peak of hydration is enhanced through the addition of nano-sized $CaCO_3$. According to the author this might be due to enhanced ettringite formation or a mixture of ettringite and calcium carboaluminate.

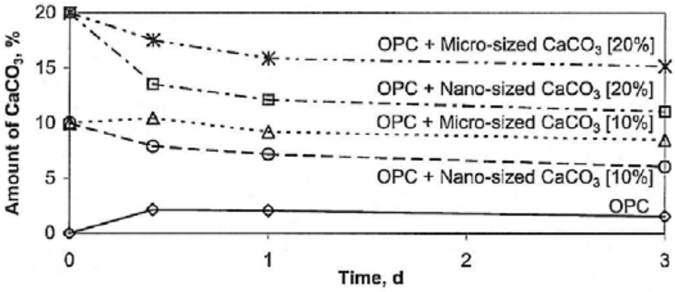


Fig. 36: The amounts of $CaCO_3$, determined by TGA, for OPC and OPC with the addition of micro- and nano-sized $CaCO_3$ for w/c 0.50 hydrated for 10 hours, 1 day and 3 days [Sato and Beaudoin, 2007].

The TGA was conducted for the same series of specimens in order to determine the amount of $CaCO_3$. The results are shown in Fig. 36. There is about 2 % of $CaCO_3$ in the control OPC constantly observed throughout the hydration up to 3 days, indicating that the anhydrous OPC powder might have been carbonated during the storage period. The amount of $CaCO_3$ in each specimen is lower than the amount added to the specimen and decreases as the hydration takes place. This suggests that some portion of $CaCO_3$ added to the specimen might have reacted in the hydration process.

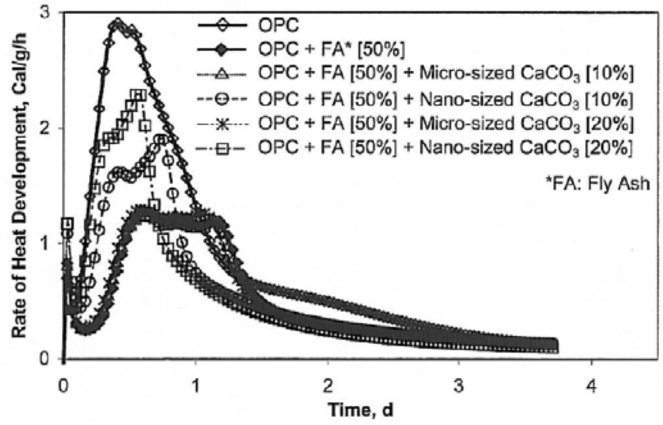


Fig. 37: Conduction calorimetry curves for OPC, OPC containing 50 % fly ash and OPC containing 50 % fly ash with additions micro- and nano- $CaCO_3$ for w/c=0.50 [Sato and Beaudoin, 2007].

From Fig. 37 it can be seen that the hydration of OPC containing 50 % fly ash is significantly delayed compared to that of OPC itself. The curve of OPC containing 50 % fly ash is almost identical to those of the OPC containing 50 % fly ash with the additions of 10 % and 20 % micro-sized $CaCO_3$. It is clearly evident, however that the additions of nano-sized $CaCO_3$ accelerate and compensate for the delayed early hydration of OPC containing 50 % fly ash. When 20 % nano-sized $CaCO_3$ is added the OPC containing 50 % fly ash hydrates almost as fast as the control OPC.

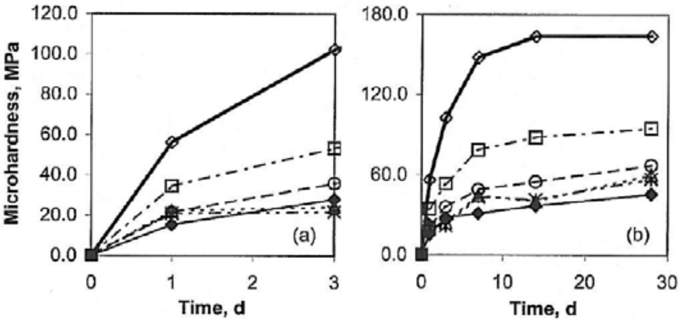


Fig. 38: Micro-hardness values for OPC, OPC containing 50 % fly ash and OPC containing 50 % fly ash with additions micro- and nano- $CaCO_3$ for w/c=0,50 for (a) 3 days and (b) 28 days [Sato and Beaudoin, 2007].

Fig. 38 shows the micro-hardness values of OPC, OPC containing 50 % fly ash and OPC containing 50 % fly ash with the additions of micro- and nano-sized $CaCO_3$ hydrated up to 3 and 28 days. The addition of nano-sized $CaCO_3$ remarkably improved the micro-hardness. The formation of calcium carboaluminate hydrates might not be relevant for the strength improvement, according to the authors. The strength enhancement can primarily attributed to the acceleration of the C_3S hydration, as nano-sized $CaCO_3$ particles serve as nucleation sites. This is visualised by the increase of the main hydration peak in the calorimetric curves. The addition of nano-sized $CaCO_3$ did not only affect the early hydration, but also the long term hydration as it significantly improved the 28 day strength.

Härdtl et al. (2007) prepared a cement containing 72 % clinker, 17 % limestone and 11 % fly ash. The specific surface was 501m^2/kg. A compressive strength of 28.7MPa was obtained after 2 days and 59.7 MPa after 28 days. Tests were conducted on carbonation, Cl-migration, freeze-thaw and frost de-icing sustainability. According to the authors, the durability appeared to be on a similar level compared to ordinary Portland cement and well-known blended cements.

2.1 Conclusion and suggestions for future research

The fly ash and the limestone filler content have to be optimized with regard to strength. Limestone filler improves the early strength development, as it accelerates the hydration, and fly ash contributes to later strength development due to its pozzolanic reactivity.

A very interesting research topic, concerning ternary cements containing limestone and fly ash, is the interaction of the aluminate phase of fly ash and calcium carbonate of the limestone. The aluminate content of fly ash generally ranges between 20 and 30 %. This is considerably higher than aluminate content of ordinary Portland clinker which is about 4-6 %. The additional amount of aluminate provided by the fly ash could interact with sulphate or carbonate, and form extra binder phase, in the form of calcium carboaluminate hydrates or calcium sulphoaluminate hydrates. These phases can densify the matrix and might contribute to strength.

The fines of the limestone powder and the fly ash, the ratio between gypsum and limestone powder and the activation of the fly ash to promote the liberation of aluminate are key parameter in this research topic. The effect of limestone particle size is of importance in such a study, and even nano-sized or at least precipitated calcium carbonate, in particular with respect to timing of reactions as long as early strengths are needed by the building sector.

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