

# Effect of calcium-magnesium carbonate additives on cement hydration

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## Abstract

This work relates to the use of the dolomite and dolomitic limestone component as an additive in cement production, as well as to the role of the carbonate component in cement hydration. The studies focused mainly on the kinetics of hydration, which was determined by using calorimetric measurements, and on the formation of hydrated structure, especially the position of carboaluminate hydrate. Based upon some reports and our previous studies we can conclude that the applicability of dolomitic limestone as a component of cementing materials seems to be quite rational, and the details of dolomite effect on cement hydration should be highlighted. For this purpose, the mixtures of cement with limestone and dolomite, as well as the mixtures of synthetic cement phases with limestone and dolomite were produced and examined by microcalorimetry, scanning electron microscopy (SEM/BSE), X-ray diffraction (XRD), and the determination of chemical shrinkage.

**Keywords:** Cement, Dolomite, Hydration, Heat of hydration, Carboaluminate

## WPLYW WĘGLANU WAPNIOWO-MAGNEZOWEGO NA PROCES HYDRATACJI CEMENTU

Jako cel prowadzonych badań przyjęto sprawdzenie, czy dolomit może być wykorzystywany jako materiał zastępujący standardowy dodatek kamienia wapiennego. Wprowadzano dolomit i dla porównania węglan wapnia do zaczynów z cementu portlandzkiego CEM I 42,5R; badano też minerały klinkierowe i ich mieszanki (sztuczny cement „wzorcowy”). W badaniach wykorzystano mikrokalorymetrię, mikroskopię skaningową (SEM/BSE), dyfrakcję rentgenowską (XRD) i ocenę skurczu chemicznego. Wykazano, stosując w pierwszej kolejności metodę kalorymetryczną, że w mieszkach tych ma miejsce reakcja dolomitu z  $C_3A$  oraz przyspieszenie hydratacji  $C_3S$ . Stwierdzono, że dolomit tworzy, podobnie jak węglan wapnia, produkt węglanogliniany, co wpływa na kształtowanie mikrostruktury. Zastosowanie dolomitu jako dodatku do cementu wydaje się więc uzasadnione, ale należy doprecyzować opis mechanizmu oddziaływania tego dodatku na zaczyn cementowy.

**Słowa kluczowe:** cement, dolomit, hydratacja, ciepło hydratacji, węglanoglinian

## 1. Introduction

This work relates to the use of dolomite and dolomitic limestone component in cement production. This material is delivered as a by-product in the limestone and dolomite processing. There are many deposits of limestone contaminated with magnesia that differ with chemical composition and structural properties, however, their use in cement technology is not standardized.

The use of waste materials/by-products as supplementary cementing materials has been an important factor improving the sustainable development in cement and concrete technology [1, 2]. The limestone supplementary material, when used for this purpose, enables the achievement of some specific properties: the early strength of cement is similar to the reference CEM I at the additive content not higher than 10% by weight of cement, the water demand is reduced and hence the workability becomes better. The lowering of carbon dioxide and nitrogen oxides emission, due to

the partial clinker replacement and the reduction of electric energy consumption, resulting from the better grindability of the soft carbonate component, are the ecological reasons.

The production of Portland cement containing limestone, interground or blended with clinker, has increased in the past decades due to technical, economic and environmental reasons. The technical reasons mean the satisfactory physical and mechanical properties of concrete as hydrated cement based material [1–3]. The economic and environmental reasons include energy saving during the decreased clinker production, and consequently the reduction of environmental pollution by carbon dioxide [2].

The idea of using dolomite as a component of cement appeared in early 80-ties in Germany [4–6]. However, this material has not been taken into account in the European standardization process, when the limestone cement was implemented because of the potential risk of the so-called dedolomitization process in highly alkaline environment of cement paste, leading to the formation of brucite with no

binding properties. However, one should remember that this phenomenon takes place in cement paste – dolomite aggregate grain interface [7], not in the presence of randomly distributed small powdered dolomite.

In some countries the limestone deposits do not comply with the quality requirements given in the EN 197–1 standard (min. 75%  $\text{CaCO}_3$ ) because they contain inclusions of dolomite. Only a few reports dealing with dolomite usage as a cement constituent have been appeared and according to all authors [4–6, 8–10] dolomite can be taken into account as a cement component.

The usage of dolomite/dolomitized limestone is expected to increase in near future in terms of the growth of supplementary cementing materials ratio in cements, forced by reduction of carbon dioxide emission. The possible application of dolomitized limestone as a component of mixtures for geotechnical application should be considered.

The kinetics of heat evolution reflecting the early hydration in the commercial portland cement – limestone or dolomite mixtures was the starting point. Subsequently, the effect of dolomite on the kinetics of heat evolution accompanying the hydration of both alite and alite – calcium aluminate – gypsum mixture was also evaluated [9, 10]. The other studies of hydrating pastes were performed to find the way of dolomite interaction with cement systems.

## 2. Experimental

### 2.1. Raw Materials

Commercially produced standard Portland cement CEM I 42,5R was used (Blaine specific surface of  $3550 \text{ cm}^2/\text{g}$ ) with the following phase composition:  $\text{C}_3\text{S}$  – 54%,  $\text{C}_2\text{S}$  – 19%,  $\text{C}_3\text{A}$  – 10%,  $\text{C}_4\text{AF}$  – 9% by weight. The synthetic alite ( $3\text{CaO} \cdot \text{SiO}_2$  –  $\text{C}_3\text{S}$ ) was produced in the laboratory by repeated heating of the stoichiometric mixture of analytically pure limestone and silica gel at a temperature of  $1450^\circ\text{C}$ ; the stoichiometric mixture of analytically pure limestone and aluminium oxide was heated at  $1450^\circ\text{C}$  to produce the synthetic tricalcium aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  –  $\text{C}_3\text{A}$ ). The two materials were ground to the Blaine specific surface of ca.  $3550 \text{ cm}^2/\text{g}$ . The commercially available pure gypsum (standard set controlling agent) and dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$  – min. 98.0%; Blaine specific surface of about  $3000 \text{ cm}^2/\text{g}$ ) were used apart from the analytically pure limestone to produce the mixtures.

The synthetic cements were produced by mixing alite with tricalcium aluminate constituting 10 wt.% and 15 wt.% of  $\text{C}_3\text{A}$  in the mixed alite + aluminate material. The gypsum content was added as 5 wt.% of the alite + aluminate mixture. The mixtures with dolomite were subsequently produced; dolomite or limestone was introduced as a 5% to max. 20% cement material replacement by weight.

### 2.2. Experimental Procedures

An infrared particle sizer IPS UA-V2 was used to characterize the grain size distribution of cement, limestone, and dolomite. The continuous monitoring of the hydration process was carried out with help of the following techniques: calorimetric measurements, shrinkage characteristics of

hydrating pastes, X-ray diffraction (XRD) and scanning microscopy (SEM/BSE/EDS).

The rate of heat evolution was followed by means of a differential microcalorimeter of our own construction on the pastes at a water to solid ratio of 0.5. Some selected samples were subjected to evaluation of the so-called chemical shrinkage, using basic laboratory equipment (glass vials and pipettes) and a procedure similar to that given in the ASTM Standard C 1608–07. Some samples were subjected to the SEM/BSE analysis with an EDS microanalyzer (Link Isis FEI – Nanonova) to characterize the hydration products and their position in the microstructure. The phase composition of the studied synthetic cements was determined by using a Philips diffractometer.

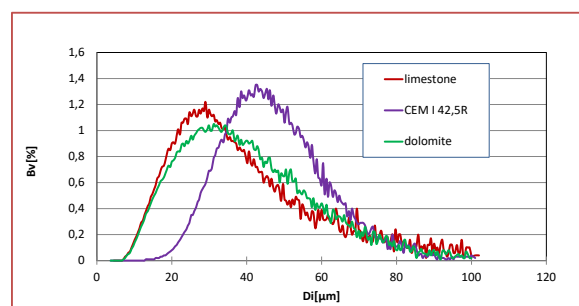


Fig. 1. Grain size distribution of limestone, dolomite, and cement. See the similarity of carbonate components characteristics.

Rys. 1. Rozkład wielkości ziaren w próbkach wapienia, dolomitu i cementu; widoczne jest duże podobieństwo uziarnienia dodatków węglanowych.

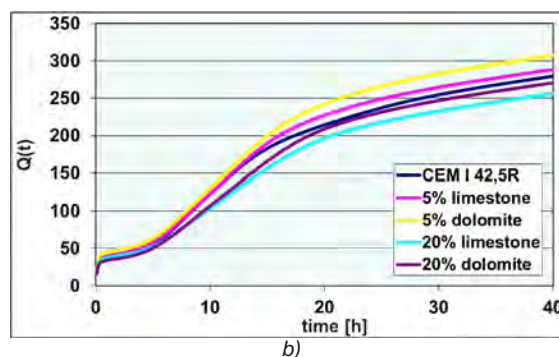
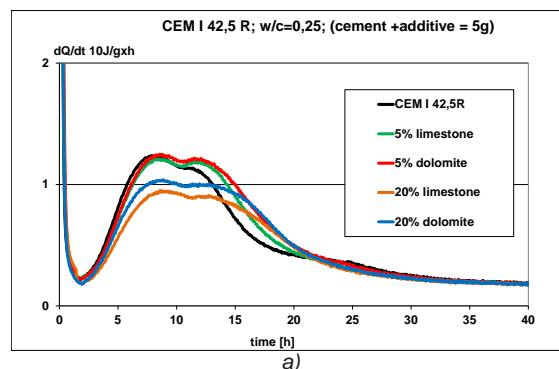


Fig. 2. Heat evolution (a) and total heat evolved (b) vs. time plots for CEM I 42,5R cement pastes hydrated with carbonate additives; calculated per 1 g cement + additive mixture.

Rys. 2. Krzywe kalorymetryczne ilustrujące szybkość wydzielania ciepła (a) i całkowitą ilość ciepła wydzielonego (b) podczas hydratacji mieszanek cementowo-węglanowych na bazie cementu CEM I 42,5R (w przeliczeniu na 1 g spoiwa cement + dodatek).

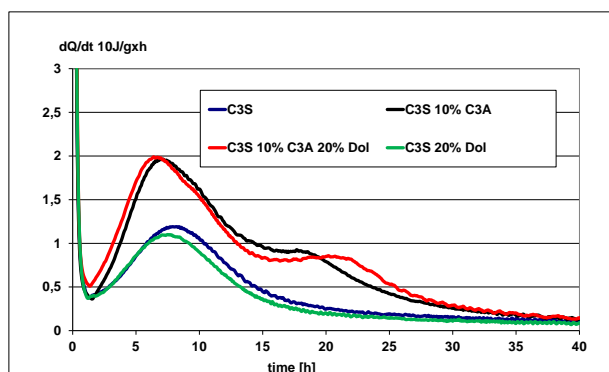


Fig. 3. Heat evolution vs. time plots for alite and alite + 10% C<sub>3</sub>A + gypsum pastes hydrated with dolomite additives; calculated per 1 g cement + additive mixture.

Rys. 3. Krzywe kalorymetryczne ilustrujące szybkość wydzielania ciepła podczas hydratacji mieszanek: alitowo-dolomitowej i syntetycznego cementu (w przeliczeniu na 1 g spoiwa cement + dodatek).

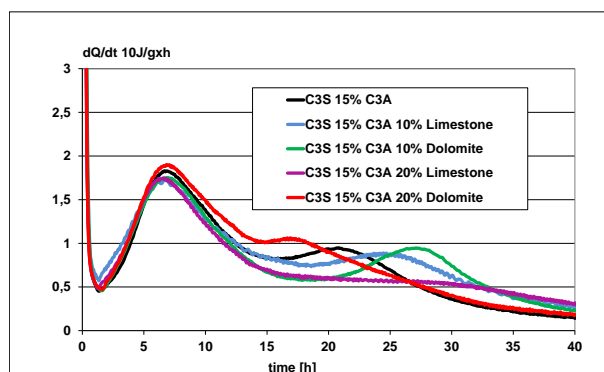


Fig. 4. Heat evolution vs. time plots for alite + 15% C<sub>3</sub>A + gypsum pastes hydrated with carbonate additives; calculated per 1 g cement + additive mixture.

Rys. 4. Krzywe kalorymetryczne ilustrujące szybkość wydzielania ciepła podczas hydratacji mieszanek syntetycznego cementu z dodatkami węglanowymi (w przeliczeniu na 1 g spoiwa cement + dodatek).

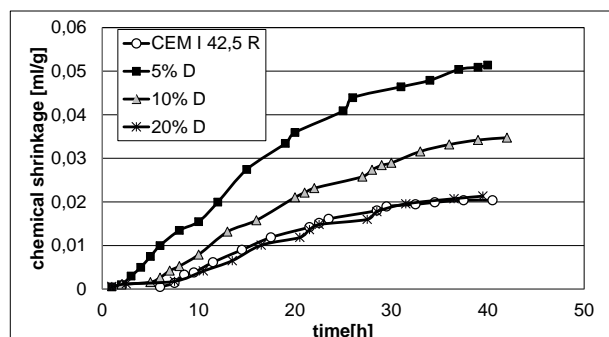


Fig. 5. Chemical shrinkage of hydrated commercial cement – dolomite mixtures.

Rys. 5. Skurcz chemiczny zaczynów cementowych z dodatkiem dolomitu.

### 3. Results and discussion

The grain size distribution of limestone, dolomite and cement is shown in Fig. 1. The heat evolution curves are shown in Figs. 2–4. The results of chemical shrinkage are plotted as Fig. 5. The example XRD pattern is shown in Fig. 6. The example SEM and BSE images together with EDS plots for 7-day and 28-day hydrated samples with 20% dolomite added as a commercial or synthetic cement replacement are presented as Figs. 7–10.

Analyzing the heat evolution data (Figs. 2–4) one can find that the induction period is not elongated in the presence of neither limestone nor dolomite additive to both commercial and synthetic cement, as well as to alite, considered very frequently as a simplified model of cement. It means that there is no especially retarded setting at the additive of up to 20% cement replacement. However, the increasing percentage of limestone or dolomite is accompanied by the lowering of maximum points of the heat evolution rate in the case of commercial cement (Fig. 2a), but the heat evolved values plots (Fig. 2b), illustrating the hydration degree vs. time, prove the similarity of all the mixtures studied; they do not decline significantly from the reference one.

The heat evolution vs. time curve for the alite sample with 20% dolomite added seems to indicate that the additive acts almost as the alite replacement (Fig. 3), as it was reported

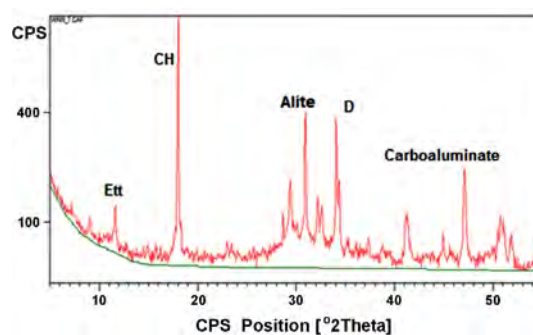


Fig. 6. XRD pattern of synthetic cement with 20% dolomite after 7-day hydration; main peaks of constituent phases indicated; Ett – ettringite, CH – calcium hydroxide, D – dolomite.

Rys. 6. Dyfraktogram rentgenowski cementu syntetycznego zawierającego 20% dolomitu po 7 dniach hydratacji ze wskazaniem głównych pików składowych faz; Ett – etryngit, CH – wodorotlenek wapnia, D – dolomit.

earlier [8, 9]. This would indicate that the hydration of silicate components is modified by the dolomite additive. Presumably the nucleation barrier is thus lowered.

The effect of the limestone component on the aluminate hydration is more pronounced because of the possible formation of carboaluminate; then the third additional peak on the calorimetric curve appears. This is visible slightly in the case of 10% calcium aluminate content (Figs. 2a and 3). In the next series of calorimetric measurements on the synthetic cement mixtures with 15% C<sub>3</sub>A, the effect attributed to the formation of calcium carboaluminate is stronger. The third peak, attributed to the hydration of calcium aluminate phase presumably with the carbonate (limestone or dolomite) component appears earlier in the case of dolomite, and is more evident; presumably the residual calcium aluminate phase, not transformed into calcium sulphoaluminate (ettringite), enters the reaction with the carbonate additive (limestone or dolomite). Analyzing the course of calorimetric curves one can find that the calcium aluminate hydration is more affected by the presence of dolomite than limestone (see Fig. 4).

At the excess of additive mixed with the constant mass of synthetic cement, the first peak attributed to the hydration of the alite phase does not decline from that for the reference



sample (see Fig. 3), while the second peak, attributed to the hydration of calcium aluminate phase with the carbonate (limestone or dolomite) component, appears earlier, especially in the case of dolomite; the higher carbonate content, the more clearly separated is the peak attributed to this process. It means that the hydration of both the silicate and aluminate phase is accelerated and modified in the presence of the carbonate additive.

The results of chemical shrinkage determination given in Fig. 5 indicate that a higher amount of water is bound in the samples with a higher percentage of additive. The higher water consumption would indicate the formation of hydrated carboaluminates of the  $C_3A \times CaCO_3 \times 11H_2O$  type

from residual  $C_3A$ , apart from the C-S-H phases and ettringite ( $C_3A \times 3CaSO_4 \times 32H_2O$ ). The position of particular plots reflects the competition for water consumption between ettringite, calcium carboaluminate and C-S-H. As a next step the XRD analysis was performed to prove the presence of these phases in the hydrating paste; the XRD pattern is shown in Fig. 6. The carboaluminate peaks occur together with those of calcium hydroxide, ettringite, and alite and dolomite as a residue.

The polished sections of cement-dolomite pastes were subjected to observations using a BSE detector accompanied by EDS analysis for chemical composition determination. The results are shown in Figs. 8–12.

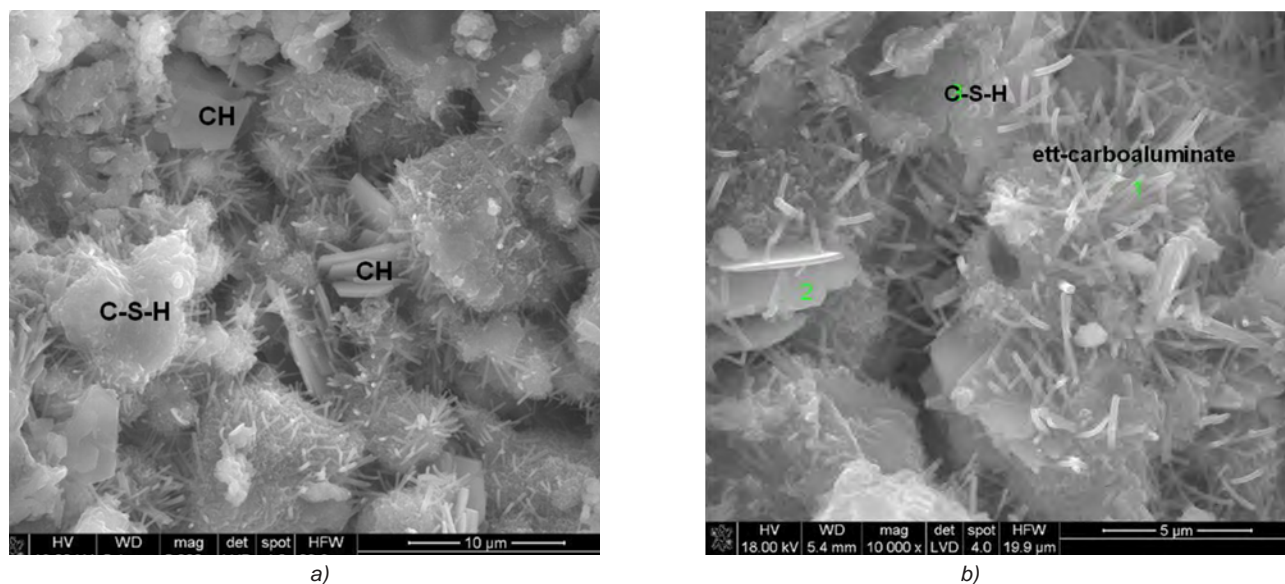


Fig. 7. SEM images of cement paste hydrated with 20% dolomite addition after 7-day maturing ( $w/c = 0.5$ ). The following hydration products are visible: a) plate-like calcium hydroxide (CH), b) ettringite-calcium carboaluminate fibres (ett-carboaluminate), a) and b) the subtle microstructure of C-S-H crystallites precipitated (C-S-H) on the dolomite grains (deduced from EDS analysis).

Rys. 7. Mikrostruktura zaczynu cementowego z 20% dodatkiem dolomitu po 7 dniach dojrzewania ( $w/c = 0.5$ ). Widoczne są produkty hydratacji: a) płytki wodorotlenku wapnia (CH), b) igielki ettringitu i węglanoglinianu wapnia (ett-carboaluminate), a) i b) C-S-H o luźnej, gąbczastej strukturze na ziarnach dolomitu (na podstawie analizy EDS).

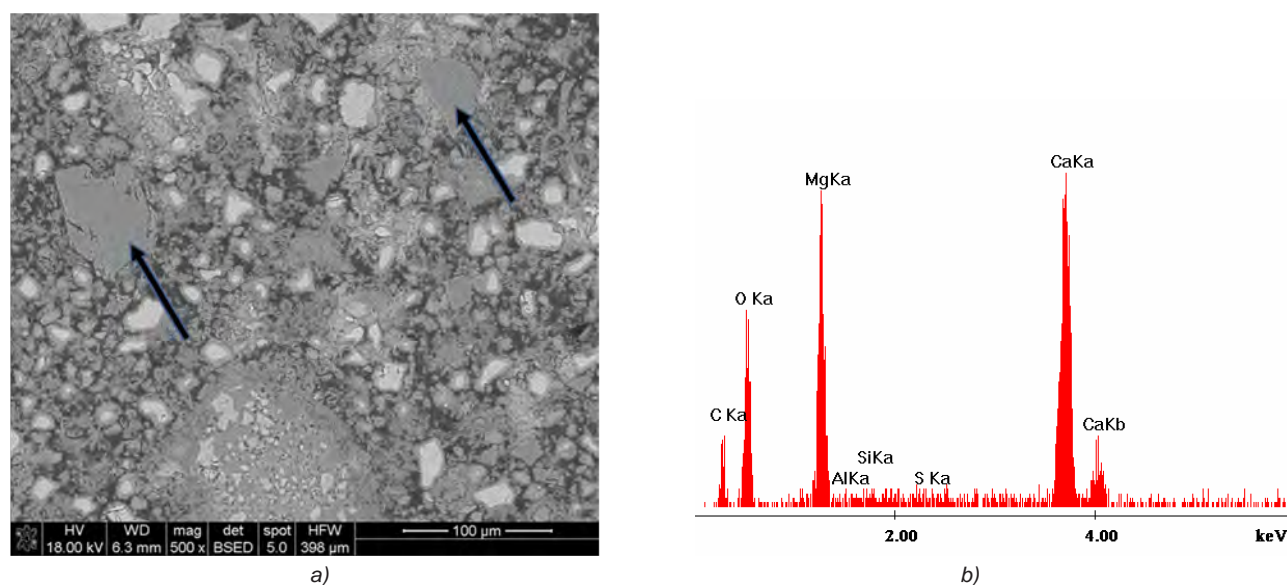


Fig. 8. Typical BSE image of polished section of cement paste with 20% dolomite (a) and EDS spectrum (b) for dolomite grains pointed out by arrows; bright, small alite grains are surrounded by C-S-H envelopes.

Rys. 8. Typowy obraz BSE zglądu zaczynu cementowego zawierającego 20% dolomitu (a) i widmo EDS (b) ziaren dolomitu wskazanych strzałkami; widoczne są drobne, równomiernie rozmieszczone ziarna alitu (jasne) z otoczkami C-S-H.

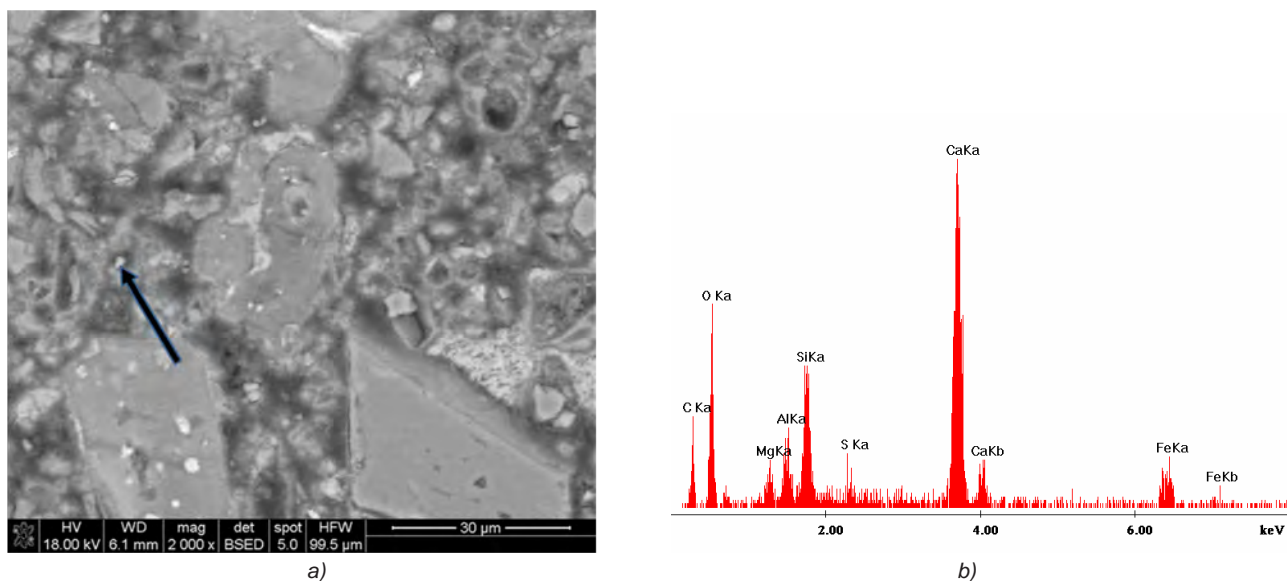


Fig. 9. BSE image of polished section of commercial cement with 20% dolomite additive (a) and EDS spectrum (b) at area indicated by arrow; the following components are visible: alite, dolomite, and the hydration products: calcium hydroxide, mixed calcium silicate hydrates together with carboaluminates and sulfoaluminates containing built-in Mg.

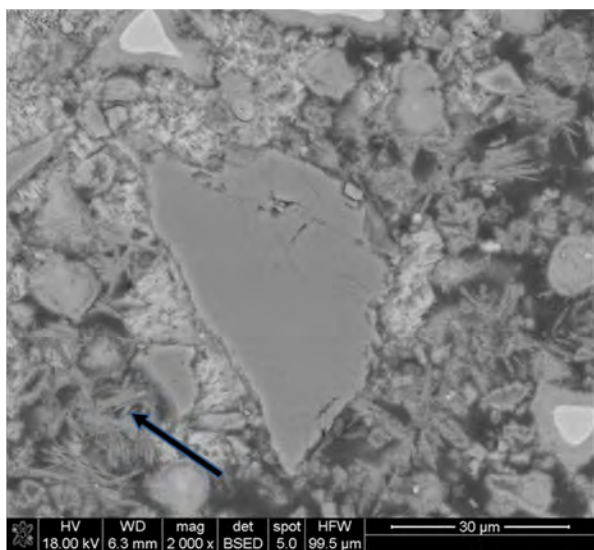


Fig. 10. BSE image of polished section of synthetic cement paste containing 15%  $C_3A$  and 20% dolomite; a dolomite grain with adjacent hydration products is visible in the image center; calcium carboaluminate and sulphoaluminate hydrate phases a visible of morphology indicated by the arrow; bright alite grains are surrounded by C-S-H envelopes.

Rys. 10. Obraz BSE zglądu zaczynu z cementu syntetycznego zawierającego 15%  $C_3A$  i 20% dodatku dolomitu; ziarno dolomitu w centralnej części otoczone jest produktami hydratacji o złożonym składzie; widoczne są obszary wodorotlenku wapnia i uwodnionych węglanoglinianów i siarczanoglinianów wapnia o morfologii wskazanej przez strzałkę; dookoła jasnych ziaren alitu widoczne są grube otoczki C-S-H.

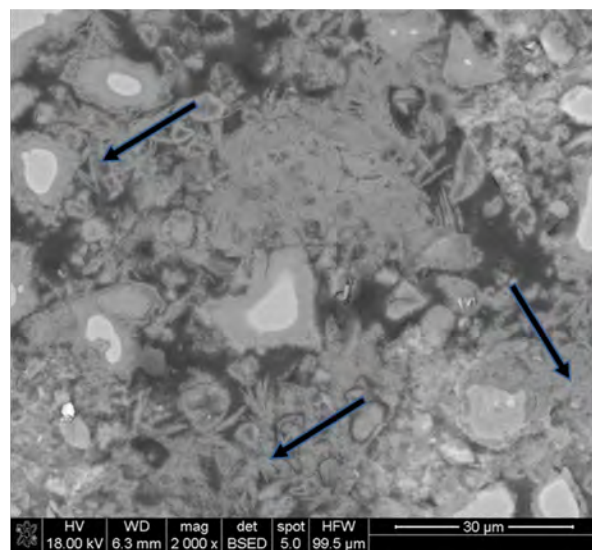


Fig. 11. BSE image of alite grains with adjacent hydration C-S-H in polished section of synthetic cement paste containing 15%  $C_3A$  and 20% dolomite; arrows indicate calcium carboaluminate and sulphoaluminate hydrate phases of fibrous and compact morphology; thick C-S-H envelopes are visible all around bright alite grains. Rys. 11. Obraz BSE zglądu zaczynu z cementu syntetycznego zawierającego 15%  $C_3A$  i 20% dodatku dolomitu; dookoła jasnych ziaren alitu widoczne grube otoczki C-S-H; strzałkami zaznaczone są obszary włóknistych i zwartych uwodnionych węglanoglinianów i siarczanoglinianów wapnia.

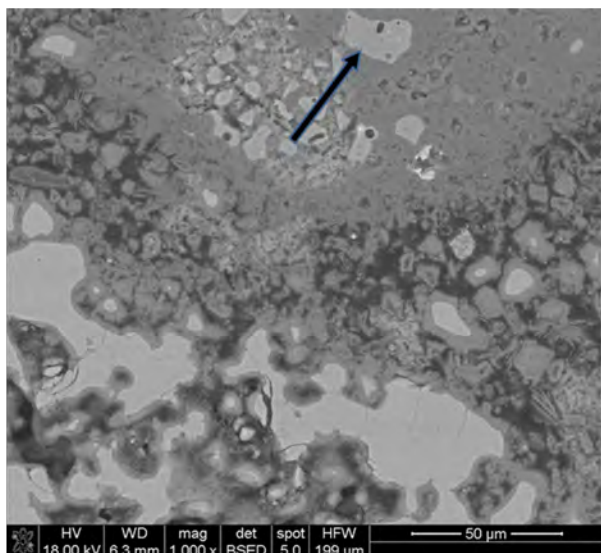


Fig. 12. Typical BSE image of polished section of synthetic cement paste containing 15%  $C_3A$  and 20% dolomite; calcium carboaluminate massive grain pointed out by arrow are visible together with bright alite grains surrounded by C-S-H envelopes.

Rys. 12. Typowy obraz BSE zglądu zaczynu z cementu syntetycznego zawierającego 15%  $C_3A$  i 20% dodatku dolomitu; dookoła ziaren alitu widoczne grube otoczki C-S-H; wskazane ziarno uwodnionego węglanoglinianu wapnia.

#### 4. Summary

The heat evolution process of commercial cement is not significantly altered in the presence of dolomite; it means that setting of paste with dolomite additive is not retarded, and the dolomite additive plays the role of active component or even acts as a cement replacement. At higher amounts, the "dilution" effect occurs.

The hydration of alite is accelerated by the dolomite additive. In the case of limestone or dolomite added to cement the effect is visible which can be presumably attributed to the reaction of the residual calcium aluminate phase, not transformed into calcium sulfoaluminate (ettringite), with the carbonate additive (limestone or dolomite). The paste is strengthened by the presence of these hydration products.

The third peak on the calorimetric curve, which is attributed to the hydration of calcium aluminate phase with carbonate component, appears earlier in the case of dolomite and is more evident. The competition mechanism in water consumption occurs between ettringite ( $C_3A \times 3CaSO_4 \times 32H_2O$ ), calcium carboaluminate (coming from residual  $C_3A$ ) and C-S-H.

The application of dolomite material as a component of non-standard material, for example for geotechnology, should be considered after examination of the binding capacity and rheological behaviour of the mixture.

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