Investigation of the products of the dolomite reaction in Portland cement pastes

Alisa Machner	Maciej Zajac
Industrial PhD student	Mohsen Ben Haha
Norcem AS	Heidelberg Technology Center
NTNU Department of Structural Engineering	DE – 69181 Leimen
NO – 7034 Trondheim	maciej.zajac@htc-gmbh.com
alisa.machner@ntnu.no	mohsen.ben.haha@htc-gmbh.com

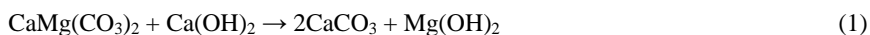|	
Knut O. Kjellsen	Mette R. Geiker, professor
R&D Manager	Klaartje De Weerdt, professor
Norcem AS	NTNU Department of Structural Engineering
FoU	NO – 7034 Trondheim
NO – 3991 Brevik	klaartje.d.weerdt@ntnu.no
knut.kjellsen@norcem.no	mette.geiker@ntnu.no

ABSTRACT

The formation of potentially deleterious reaction products from the reaction of dolomite fines in Portland cement pastes was investigated. It was shown that the reaction of dolomite fines did not follow the commonly accepted dedolomitization reaction. Instead, similar hydration phases as reported for the Portland cement containing limestone are observed, with the exception that also hydrotalcite is formed. It was shown with SEM-EDS and XRD that hydrotalcite is the only magnesium containing hydration product of the dolomite reaction, as no brucite or M-S-H were detected. In the next step of this study this reaction will be investigated in Al-rich systems.

1. INTRODUCTION

Due to the scarceness of high-quality limestone as required for CEM II Portland-limestone cements, other carbonate sources, like dolomite ($CaMg(CO_3)_2$), are in the focus as alternative mineral replacement for cement clinker. However, dolomite is assumed to undergo the so-called dedolomitization reaction in high-pH environments. In this reaction, dolomite reacts with calcium hydroxide (portlandite) to form calcium carbonate (calcite) and magnesium hydroxide (brucite) [1-3], as shown in equation 1.

$$CaMg(CO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 \tag{1}$$

There is still an ongoing discussion whether this reaction is harmful to concrete made with dolomitic aggregates. It was recently shown, that in cementitious systems, where other ions are present (Al, Si), the reaction of dolomite results in products similar to those of hydrating Portland-limestone cement with the exception of additional hydrotalcite [4]. The aim of this study was to investigate the influence of replacement of Portland cement clinker by dolomite on the phase assemblage. This was done with focus on whether other magnesium-containing and potentially harmful phases are formed during the reaction of dolomite i.e. brucite (expansive) or

M-S-H (low cementing properties). In a next step of this study the influence of additional aluminium by the addition of metakaolin on the dolomite reaction will be investigated.

2.   EXPERIMENTAL

The cement pastes investigated in this study were prepared by replacing 40 %wt of a Portland cement clinker by natural dolomite. Precipitated gypsum was added, when mixing, in order to achieve a sulphate content of 2.5 %wt per gram of binder. The cement clinker was ground in a laboratory ball mill until a Blaine surface of approx. 400 m^2/kg was achieved. The dolomite was used as received (Blaine surface: 340 m^2/kg). The chemical compositions of the major elements of the materials used are given in Table 1. The paste samples were prepared with a w/b ratio of 0.45 and were stored under sealed conditions at a relative humidity of 100% at 38 °C or 60 °C for 360 days.

Table 1 – Chemical composition of the clinker and dolomite used.

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O	SO$_3$	LOI
Clinker	20.6	5.6	3.12	63.26	2.66	1.23	0.51	1.37	-
Dolomite	0.52	0.01	0.04	31.52	20.14	0.00	0.00	0.00	46.79

In order to investigate the phase assemblage and microstructure of the samples with scanning electron microscopy (SEM), a 3 mm slice was cut off the cured cement paste and immersed in isopropanol for min. 1 week. Polished and carbon coated sections of the paste samples were prepared for SEM analysis. Elemental mapping and spot analyses were carried out using a Hitachi S-3400N microscope equipped with an energy dispersive spectrometer (EDS) from Oxford. Prior to X-ray diffraction (XRD) analyses, the hydration of the cement pastes was stopped by double solvent exchange using isopropanol and petroleum ether. For the XRD analyses a D8 Focus diffractometer from Bruker was used for the measurements with a Bragg-Brentano θ – θ geometry and Cu-Kα radiation (approx. 1.54 Å).

3.   RESULTS AND DISCUSSION

Figure 1 shows the BSE images and the elemental maps of magnesium, aluminium, oxygen, calcium and silicon for the investigated sample cured at 38 °C and 60 °C. The large uniform grains (length up to 70 µm) in both images contain magnesium and calcium and are poor in silicon and aluminium. These particles are unreacted dolomite grains. For the sample cured at 60 °C (Figure 1 – upper row) a darker reaction rim can be observed within the original grain boundaries of the dolomite grains. These rims appear to be enriched in magnesium compared to the original dolomite grains. Additionally they contain high amounts of aluminium but are poor in silicon and calcium. High oxygen levels were measured in these rims, indicating that the products formed in them are hydrates. The original grain boundaries of the dolomite grains are still visible because a bright thin layer of C-S-H phase has precipitated around them at early ages. This layer then persisted even after the dolomite started to react at later ages. The dark thick reaction rims within the former dolomite grain boundaries indicate a high reaction degree of the dolomite at 60 °C, which results in complete reaction of the smaller dolomite particles. The sample cured at 38 °C shows almost no reaction of the dolomite (Figure 2 – lower row). Only around small cracks in the dolomite particles and directly at the surface, aluminium and oxygen are slightly increased. This is in-line with the findings of Zajac et al. [4], who reported a notably higher reaction degree for dolomite in a composite cement when cured at 60 °C compared to 38 °C. Also other authors reported an increased dissolution rate of dolomite at elevated curing temperatures [2,3]. From the elemental map of magnesium it can be seen, that magnesium is present only inside the former dolomite grain boundaries. This is probably due to

the low mobility of magnesium in high pH environment. The results of the SEM-EDS point analyses of the reaction rims are plotted in Figure 2 as the Mg/Si over the Al/Si ratio. The data points for the sample cured at 38 °C coincide with the y-axis. This is probably due to the limited rim thickness, which results in the measurement of the unreacted dolomite rather than an actual reaction product. In the case of the sample cured at 60 °C, the data points describe a linear line. This indicates that the reaction product has a fixed Mg/Al ratio and does not contain silicon. It can therefore be concluded, that no M-S-H has formed during the reaction of dolomite. The reaction product can be identified as hydrotalcite ($Mg_{4+x}Al_2(CO_3)_y(OH)_{16}\cdot4(H_2O)$) [5]. The Mg/Al ratio of the hydrotalcite formed was 3.2 in this study. Zajac et al [4] measured a lower Mg/Al ratio of approx. 2 in their samples, probably due to the lower dolomite addition they used in their mixes as they used a similar clinker.
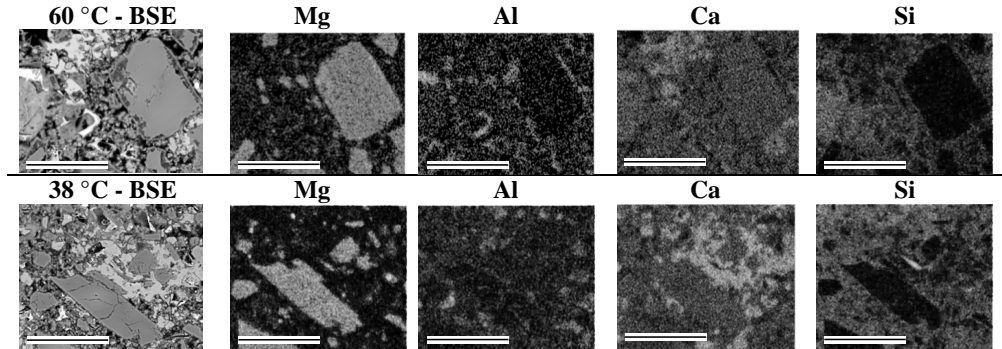

Figure 1 – BSE image and elemental maps of Mg, Al, O, Ca and Si of the sample 60C40D cured at 60 °C (upper row) and 38 °C (lower row) for 360 days. The scales (white bars) represent a length of 50 μm.
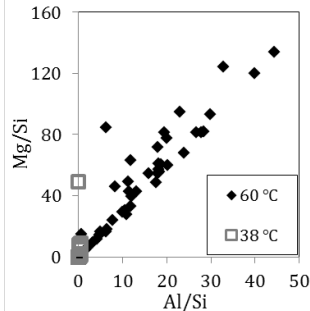

Figure 2 – Mg/Si over Al/Si ratio of the reaction rim in the samples cured at 60 °C or 38 °C.
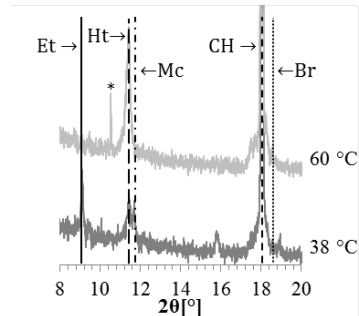
Figure 3 – XRD plots of the samples cured at 60 °C or 38 °C for 360 days. (* indicates a peak of unknown origin)

Figure 3 shows the XRD plots for the samples cured at 38 °C and 60 °C in the range of 8 to 20 °2θ. The main reflections of ettringite (Et) (9.1 °2θ), hydrotalcite (Ht) (11.4 °2θ), monocarbonate (Mc) (11.7 °2θ), portlandite (CH) (18.1 °2θ) and brucite (Br) (18.6 °2θ) are indicated. The sample cured at 38 °C, shows a clear ettringite peak and small peaks of hydrotalcite and monocarbonate. The reaction of dolomite delivers CO_2 to the system, which can stabilize ettringite by the formation of monocarbonate at 38 °C. This is in agreement with the findings of Zajac et al. [4]. At 60 °C, the stable phases differ significantly from those at

38 °C. The ettringite peak is not observed as this phase is not stable at 60 °C [6]. Moreover, monocarbonate is not detected. The main diffraction peak observed is hydrotalcite, which shows a notably higher and sharper peak at 60 °C compared to the sample cured at 38 °C. This is in good agreement with the observations made by SEM-EDS, which showed a notably higher reaction degree of dolomite at 60 °C compared to 38 °C. In both samples no clear brucite peaks could be observed by XRD. Hydrotalcite is therefore assumed to be the only magnesium-containing reaction product of the dolomite reaction. The proposed reaction based on our observations of dolomite in a cementitious system is given in equation 2.

$$CaMg(CO_3)_2 + Ca(OH)_2 + [Al(OH)_4]^- \rightarrow Mg_{4+x}Al_2(CO_3)_y(OH)_{16} \cdot 4(H_2O) + CaCO_3 + CO_3^{2-} \quad (2)$$

The dolomite will react with portlandite and alumina in the pore solution to form hydrotalcite and provides carbonate ions to the system which might partially react further to calcite or carbonate AFm. No potentially harmful phases such as brucite or M-S-H were observed.

4.   CONCLUSION
It has been shown that the reaction of dolomite fines, when used as replacement for Portland cement clinker, results in the formation of hydrotalcite, especially at 60 °C. Additionally, at 38 °C the stabilization of ettringite due to the formation of monocarbonate can be observed. Contrary to the commonly assumed reaction of dolomite in high-pH environments no brucite was detected. Hydrotalcite was the only magnesium containing product of the dolomite reaction. The reaction of dolomite fines in cementitious systems is therefore not assumed to form any deleterious hydration products. In a next step of this study we will investigate the influence of additional aluminium by the addition of metakaolin on the dolomite reaction.

5.   ACKNOWLEDGEMENTS

REFERENCES
1.   E. Garcia, P. Alfonso, M. Labrador, S. Galí, Dedolomitization in different alkaline media: Application to Portland cement paste, Cem Concr Res 33 (2003) 1443–1448.
2.   S. Galí, C. Ayora, P. Alfonso, E. Tauler, M. Labrador, Kinetics of dolomite-portlandite reaction - Application to Portland cement concrete, Cem Concr Res 31 (2001) 933–939.
3.   X. Zhang, F.P. Glasser, K.L. Scrivener, Reaction kinetics of dolomite and portlandite, Cem Concr Res 66 (2014) 11–18.
4.   M. Zajac, S.K. Bremseth, M. Whitehead, M. Ben Haha, Effect of $CaMg(CO_3)_2$ on hydrate assemblages and mechanical properties of hydrated cement pastes at 40 °C and 60 °C., Cem Concr Res 65 (2014) 21–29.
5.   M. Ben Haha, B. Lothenbach, G. Le Saout, F. Winnefeld, Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag — Part I: Effect of MgO, Cem Concr Res 41 (2011) 955–963.
6.   B. Lothenbach, F. Winnefeld, C. Alder, E. Wieland, P. Lunk, Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes, Cem Concr Res 37 (2007) 483–491.