



## Chloride-binding capacity of hydrotalcite in cement pastes containing dolomite and metakaolin



Alisa Machner<sup>a,b,\*</sup>, Maciej Zajac<sup>c</sup>, Mohsen Ben Haha<sup>c</sup>, Knut O. Kjellsen<sup>a</sup>, Mette R. Geiker<sup>b</sup>, Klaartje De Weerd<sup>b</sup>

<sup>a</sup> Norcem AS, R&D, Setreveien 2, P.O. Box 38, 3991 Brevik, Norway

<sup>b</sup> NTNU, Department of Structural Engineering, Richard Birkelandsvei 1A, 7491 Trondheim, Norway

<sup>c</sup> Heidelberg Technology Center GmbH, Oberklamweg 2-4, 69181 Leimen, Germany

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### ABSTRACT

In this study, we investigated well-hydrated cement pastes containing dolomite and metakaolin cured at 38 °C or 60 °C, which were exposed to NaCl or CaCl<sub>2</sub> solutions of various concentrations. We determined the chloride-binding capacity, the phase assemblage and the composition of hydration phases formed. The dolomite reaction led to the formation of hydrotalcite, which contributed considerably to the chloride binding of the pastes. When the samples were exposed to CaCl<sub>2</sub>, significantly more chlorides were bound in the hydrotalcite than when the samples were exposed to NaCl. It was shown that hydrotalcite contained a similar amount of chloride per mol compared to Friedel's salt when exposed to CaCl<sub>2</sub>. By mass balance calculations, it was shown that the hydrotalcite formed in the samples containing dolomite can contribute to the chloride binding of the cement pastes to a similar extent as the Friedel's salt formed in the samples containing limestone.

### 1. Introduction

One of the main deterioration mechanisms for reinforced concrete structures is steel reinforcement corrosion. Reinforcement steel in sound concrete is passivated, i.e. does not corrode, due to the high pH of the concrete pore solution. However, in the presence of a sufficient level of chlorides, the steel is de-passivated and corrosion can occur. During the exposure to e.g. sea water or de-icing salts, chlorides ingress through the concrete cover towards the steel. Some chlorides will be free in the pore solution and some will interact with the hydrates in cement paste. In order to estimate the service life of reinforced concrete structures exposed to chlorides, we need to understand the interaction between concrete and chlorides.

Due to the increasing demand for cements and the need to reduce CO<sub>2</sub> emissions during production, new composite cements containing supplementary cementitious materials (SCMs) are being developed. In order to use these cements in reinforced concrete structures exposed to harsh environments such as marine exposure, there is a need to understand how these new binders interact with chlorides. In this study, we used dolomite and a combination of dolomite and metakaolin as SCMs to replace 40 wt% of a Portland cement. We investigated the chloride-binding capacity of the hydrate phase assemblage for these new cements.

In an ordinary Portland cement, chloride ions have been reported to be physically adsorbed on the C-S-H phase or chemically bound by the formation of chloride-containing AFm phases, e.g. Friedel's salt (3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCl<sub>2</sub>·10H<sub>2</sub>O). The use of SCMs can change the phase assemblage of the hydrated cement paste and thereby its chloride-binding capacity [1].

The addition of metakaolin has been shown to improve the chloride-binding capacity of cement paste. This has been explained with reference to the additional alumina provided by the reaction of metakaolin, which results in the formation of additional Friedel's salt [2,3]. Similar results have been reported for other alumina-delivering SCMs, such as fly ash or ground granulated blast-furnace slags (GGBFS) [1,4–7]. Moreover, the reaction of metakaolin results in the formation of additional C-S-H, which may adsorb additional chlorides [8].

The addition of dolomite has been shown, depending on curing temperature, curing time, and metakaolin content, to result in the formation of significant amounts of a hydrotalcite-like phase (in the following referred to simply as hydrotalcite) [9,10]. Hydrotalcite is a mineral in the group of layered double hydroxides (LDHs) containing magnesium and aluminium, with the general formula [Me<sub>1-x</sub><sup>2+</sup>Me<sub>x</sub><sup>3+</sup>(OH)<sub>2</sub>]<sup>x+</sup> [A<sup>m-</sup>]<sub>x/m</sub>nH<sub>2</sub>O. Its crystal structure can be derived from that of brucite. The main layer consists of metals (here abbreviated with Me), specifically magnesium (Me<sup>2+</sup>) and aluminium

\* Corresponding author at: NTNU, Department of Structural Engineering, Richard Birkelandsvei 1A, 7491 Trondheim, Norway  
E-mail address: [alisa.machner@ntnu.no](mailto:alisa.machner@ntnu.no) (A. Machner).

( $\text{Me}^{3+}$ ) hydroxide octahedra. The substitution of aluminium for magnesium in the main layer charges this layer positively. To maintain electrical neutrality, the interlayer incorporates monovalent or divalent anions (here abbreviated with A), such as  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$  or  $\text{SO}_4^{2-}$ .

Several authors observed considerable chloride binding of hydrotalcite, either synthesized as a pure phase [11–13] or formed in GGBFS cement pastes [14,15]. We will investigate the chloride binding of hydrotalcite originating from dolomite reaction in composite cements. In this system, the composition of the hydrotalcite differs from the before named studies both by the presence of carbonates and by the Mg/Al ratio of the hydrotalcite. Both factors influence the chloride-binding capacity of hydrotalcite.

Divalent ions, like  $\text{CO}_3^{2-}$  are more easily incorporated than monovalent ions, like  $\text{Cl}^-$  [11,12], so  $\text{CO}_3^{2-}$  ions are seldom exchanged with chloride ions in synthesized hydrotalcite-like phases, and the presence of carbonate ions consequently reduces the chloride-binding capacity [12,13].

A higher degree of aluminium substitution in the main layer, leading to a lower Mg/Al ratio of the hydrotalcite, increases the positive charge of the main layer. Because the interlayer seeks electrical neutrality, more anions, e.g. chlorides, are incorporated in the interlayer of hydrotalcite with a lower Mg/Al ratio [16]. The reduction of the Mg/Al ratio of the hydrotalcite can be caused by the presence of an aluminium-delivering SCM [10,17,18].

Moreover, it was reported that chlorides are also physically adsorbed on the surface of hydrotalcite adsorption [13,15].

The chloride-binding capacity of cements depends strongly on the cation associated with the chloride anion. Several authors have reported significantly greater chloride binding when samples were exposed to solutions of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  rather than  $\text{NaCl}$  [1,3,19–23]. This difference has been largely attributed to the difference in the adsorption of chlorides onto the C-S-H and larger amount Friedel's salt. We will investigate whether the cation also influences the binding capacity of the hydrotalcite.

This study focuses on the impact of the hydrotalcite formed by the reaction of dolomite fines in the cement paste on the chloride binding of composite cement pastes. For this, cement paste samples in which 40 wt % of the Portland cement was replaced by dolomite or by a combination of dolomite and metakaolin were investigated. Cement paste samples containing limestone instead of dolomite and a pure Portland cement sample were used as references. In order to be able to study the effect of hydrotalcite, we needed samples containing sufficient amounts of hydrotalcite. Therefore, we investigate binder compositions containing dolomite and little or no metakaolin and cured at elevated temperatures, which according to an earlier study yielded considerable hydrotalcite formation [10]. Chloride-binding isotherms were experimentally obtained and related to the phase assemblage and phase composition of the solids obtained with XRD, TGA, and SEM-EDS. Additionally, the contribution of hydrotalcite, Friedel's salt, and C-S-H to the chloride binding of the cement pastes was evaluated using a mass balance approach.

## 2. Experimental

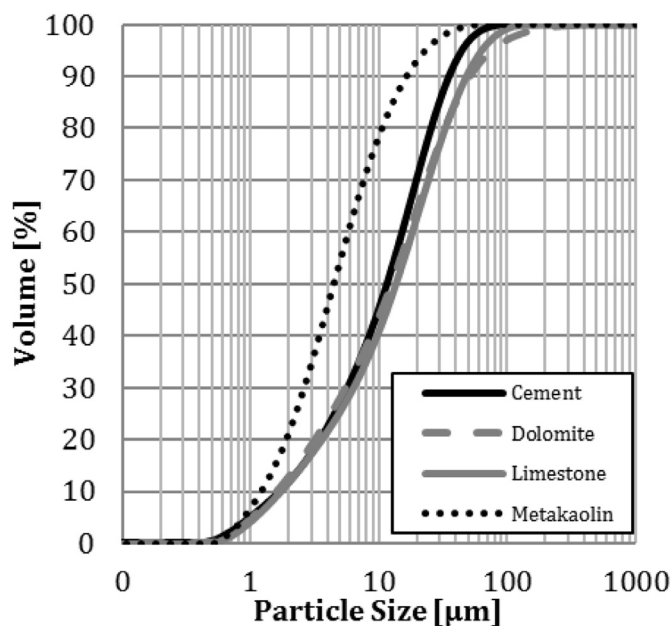
### 2.1. Materials & sample preparation

The materials used in this study were Portland cement (C) supplied by Norcem, to which gypsum but no limestone was added during grinding, natural dolomite (D), and natural limestone (L) supplied by Miljøkalk AS, and laboratory-grade metakaolin (M) supplied by Imerys (Metastar501). Table 1 shows the chemical composition, determined by X-ray fluorescence (XRF), of the materials used and their Blaine specific surface area. The particle size distributions of the materials used, determined by laser diffraction (Malvern Mastersizer 2000E), are shown in Fig. 1. Table 2 gives an overview of the various sample compositions prepared. We replaced 40 wt% of the Portland cement with either

**Table 1**

Chemical composition of the Portland cement, dolomite, limestone and metakaolin used, as determined by XRF [wt%] and their Blaine surface areas [ $\text{m}^2/\text{kg}$ ].

Oxide	Portland cement	Dolomite	Limestone	Metakaolin
$\text{SiO}_2$	19.91	0.52	0.12	52.18
$\text{Al}_2\text{O}_3$	5.15	0.01	0.06	44.92
$\text{TiO}_2$	0.282	0.00	0.00	1.14
$\text{MnO}$	0.062	0.00	0.00	0.00
$\text{Fe}_2\text{O}_3$	3.42	0.04	0.03	0.62
$\text{CaO}$	62.73	31.52	55.12	0.12
$\text{MgO}$	2.34	20.14	0.41	0.04
$\text{K}_2\text{O}$	1.09	0.00	0.01	0.18
$\text{Na}_2\text{O}$	0.48	0.00	0.00	0.17
$\text{SO}_3$	3.16	0.00	0.02	0.14
$\text{P}_2\text{O}_5$	0.109	0.01	0.00	0.07
LOI	1.07	46.79	43.57	0.29
Sum (1050 °C)	99.80	99.03	99.34	99.87
Blaine [ $\text{m}^2/\text{kg}$ ]	416	340	370	987



**Fig. 1.** Particle size distribution of the materials used determined by laser diffraction.

**Table 2**

Matrix for the mixes [wt%]. The sulphate content of the Portland cement was set to 3.2 wt %.

Name	C Portland cement	D Dolomite	L Limestone	M Metakaolin
100C	100	–	–	–
60C40D	60	40	–	–
60C35D5M	60	35	–	5
60C40L	60	–	40	–
60C35L5M	60	–	35	5

dolomite (60C40D) or a combination of 35 wt% dolomite and 5 wt% metakaolin (60C35D5M). The equivalent samples containing limestone (60C40L and 60C35L5M) and the Portland cement sample (100C) were used as references. Cement pastes were prepared with a w/b ratio of 0.5 for all binder compositions in a high-shear mixer (Braun MR5550CA). The mixing procedure was mixing for 30 s, resting for 5 min and mixing again for 60 s. The resting time of 5 min was chosen to check for false set of the paste. The resulting pastes were cast in 125 mL polyethylene screw-lid bottles, which were sealed with parafilm and stored, immersed up to their bottleneck, in water at 38 °C or 60 °C. After three months of curing, the hydrated cement pastes were removed from the

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