

Insights into Phase Assemblage in MgO-Al₂O₃-(SiO₂)-CO₂ Systems

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ABSTRACT

The decarbonization of cement industry will require a versatile portfolio of different alternative cements. In contrast to other known and popular alternatives, cements based on MgO-rich hydrates remain unexplored topic and little is known about the formation and stability of Mg-Al LDH as the main binding phase in a cement. In this work, we report on experimental work on the phase assemblage of MgO-Al₂O₃-(SiO₂)-CO₂-H₂O system via the hydration of an amorphous magnesium aluminate (AMA) in the presence of different magnesium carbonates and metakaolin. The data reveal that hydrotalcite is the main hydrate of the cement with relatively fast reaction kinetics in which AMA is fully hydrated after 7 days of curing in ambient water. Additionally, more detailed phase assemblage will be beneficial in the better understanding and in improving the thermodynamic data for the MgO-Al₂O₃-SiO₂-CO₂-H₂O system and of interest to shed light on the long-term stability of this cement.

Keywords: hydrotalcite; low-CO₂ cement; Mg-Al LDH; thermodynamic modelling

INTRODUCTION

Cements based on Mg chemistry have been attracting great attention in recent years. This is due to the unique yet not fully known properties of many MgO-bearing phases such as M-S-H and magnesium carbonates[1]. These cements can significantly lower the carbon footprint and may even reach carbon negativity with controlled feedstocks and processes. Among various MgO-bearing phases, Mg-Al layered double hydroxide (LDH) [2] offers interesting characteristics due to the possibility to steer its formation and stability through the flexibility in interlayer anions. Here, we report the formation and the stability of such Mg-Al LDH as the main binding phase in the MgO-Al₂O₃-(SiO₂-)CO₂-H₂O system. The study initiates a new venue for discussion and further investigation on this novel binder in order to achieve lower net carbon emissions with comparable performance.

EXPERIMENTAL INVESTIGATION

Materials

Hydrotalcite (CAS Number: 11097-59-9) was commercially obtained for the source of MgO and Al₂O₃. The phase was calcinated at 700 °C for 12 hours to obtain an amorphous magnesium aluminate (AMA) with formula Mg₄Al₂O₉.

Nesquehonite was used as the source of MgO and CO₂ in which the crystal was synthesized via wet carbonation of brucite (purity 99.7%, CAS number: 1309-42-8) at 20 °C. Brucite was used as 0.7 mol/l of solution while the CO₂ gas was bubbled into the suspension with a flow rate of 100 cm³/min for a total duration of 6 hours.

Metakaolin was obtained from the calcination of kaolin (CAS Number: 1332-58-7) at 700 °C for 12 hours. All dry powders were stored in sealed plastic bottles prior to use.

Mix recipe

The mix recipe is shown in Table 1. The water to binder (W/B) ratio was kept the same for all mixes at 1 and an extra 1 wt% Na₂CO₃ was added in the dry powder to facilitate the faster formation of M-(A-)S-H as reported previously in Ref. [3,4].

Table 1. Mix recipe of the developed binders

Mix ID	AMA [g]	NQ [g]	MK [g]	Na ₂ CO ₃ [g]	H ₂ O [g]
Ref	100	-	-		
Ht-NQ	50	50	-	1	100
Ht-MK	50	-	50		

Sample preparation and characterization

Powders are weighed following the recipe in Table 1 and later homogenized using a mixer for 2 hours prior to use. Paste samples were prepared and cast into mold to obtain 1×1×4-cm³ prism samples. Samples were cured in a humidity chamber (23 °C and 95–98 RH%) for 24 hours before demolding and further curing in water at room temperature for the next 27 days. Hydrated pastes of the developed mixes were collected after 28 days of hydration using solvent exchange with isopropanol and later characterized by XRD and TGA.

XRD. The XRD measurements were performed with a Rigaku SmartLab 9 kW using Co-K α radiation (K α 1 = 1.78892 Å; K α 2 = 1.79278 Å; K α 1/K α 2 = 0.5). The scan was set at a scan rate of 3°/min in the range 5°–90° (2 θ) and 0.02°/step. Powdered samples were sieved through a 63- μ m sieve. Data were further analyzed using X'pert Highscore Plus software version 5.1 coupled with PDF-4+ 2023 database.

TGA. TGA/DTG analyses were done with a SDT 650 (TA Instruments) for roughly 40–50 mg of powdered sample. Alumina crucibles were used and the temperature range was set from 23 °C to 1000 °C at a heating rate of 10 °C/min in a nitrogen atmosphere with a flow rate of 20 ml/min.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffractograms of the developed mixes after different hydration times. AMA was found to be reactive (reference mix), reaching full reaction extent after 7 days (Fig. 1a) to form hydrotalcite (with characteristic reflection at 13.3° 2θ Co)[5] as the main hydrate in the samples. In contrast, samples blended with NQ and MK exhibited a more complex phase assemblage in which the hydrotalcite was found in both mixes albeit with broader reflexes (Fig. 1b and c). This indicates that the hydrotalcite formed in these blends with lower crystallinity. Hydromagnesite [6] was found in the Ht-NQ sample after 28 days of hydration which indicated a part of NQ converted to hydromagnesite over time. In the Ht-MK sample, besides the formation of poorly crystalline hydrotalcite, there was likely the formation of M-(A-)S-H which is known as a nano crystalline phase with the broad humps between $20\text{--}40^\circ$ 2θ Co [7]. The differences in phase formation among sample were also observed in TG/DTG data (Fig. 2). Specifically, it is easier to quantify hydrotalcite by TG/DTG with its characteristic water losses at $175\text{--}220$, $340\text{--}360$ and $390\text{--}420^\circ\text{C}$. Here, total water losses attributed to hydrotalcite are about 43 wt% (at 800°C) in the reference system and about 47 and 27 wt% in the Ht-NQ and Ht-MK systems, respectively. These findings indicated that the hydrotalcite represents approximately 62 wt% in Ht-MK while the overlapping in decarbonation of NQ poses challenges in the quantification of hydrotalcite content in Ht-NQ which will require other characterizations e.g., ^{27}Al MAS NMR. In addition, further investigation is needed to shed light on the involvement of MK and NQ in the formation and structure of hydrotalcite formed in the binder.

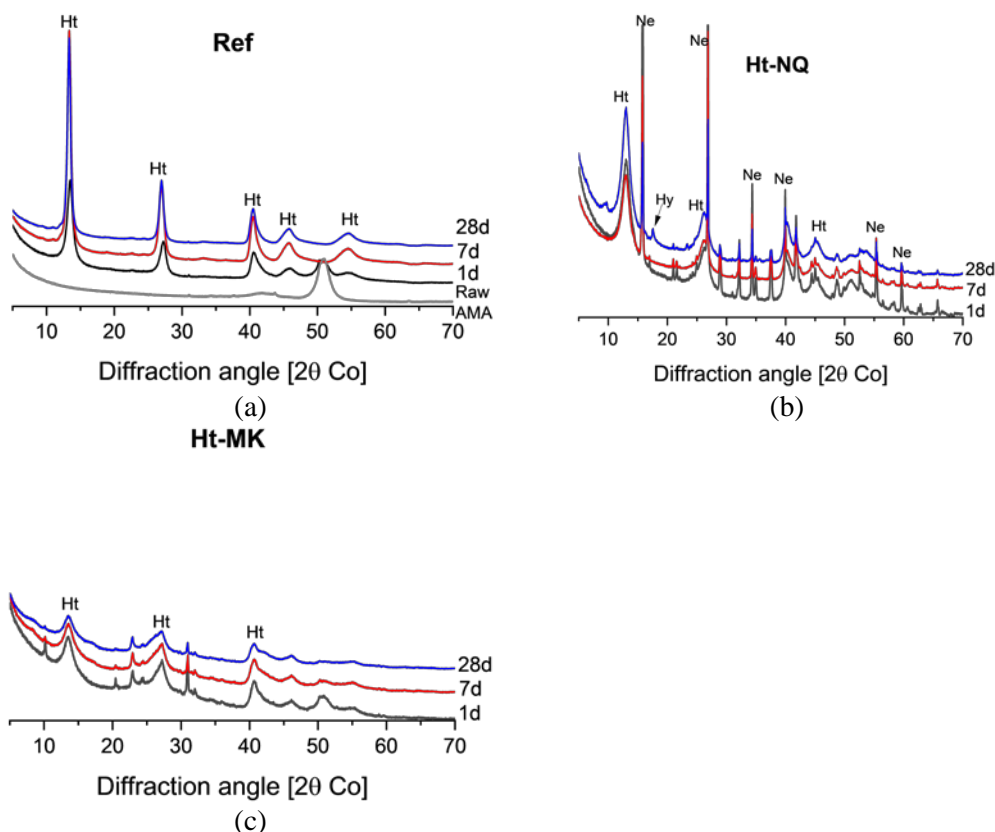


Fig.1 - Phase formation of Ht-based cement and its blends. Ht = hydrotalcite, Ne = nesquehonite and Hy = hydromagnesite

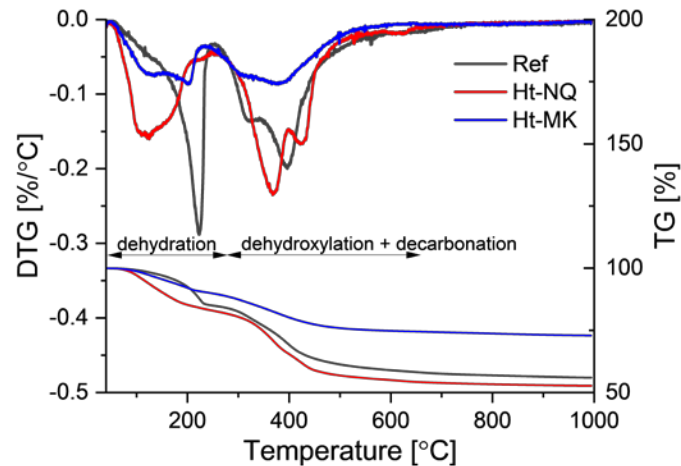


Fig. 2 - TG/DTG of pastes after 28 days of hydration

CONCLUSIONS AND OUTLOOK

In this work, we reported the phase assemblage and the binding properties of different Mg-Al-(Si)-CO₂ systems upon hydration. The reactive amorphous magnesium aluminate Mg₄Al₂O₇ can solely hydrate which can potentially be utilized to provide sufficient strength for some applications in construction (e.g., plaster). However, once the AMA is blended with other sources of carbonates or alumino silicates, there are opportunities to tune the formation of Mg-Al LDH for better mechanical performance as well as durability. The driving force for this phenomenon needs a thorough investigation to address the role of Mg-Al LDH as well as other hydrates/carbonates formed in these blends.

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