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Chemical, microstructural and strength development of calcium and magnesium carbonate binders☆

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ABSTRACT

The influence of magnesium on the chemistry of calcium carbonate formation has been studied. It was found that the type of carbonate formed by subjecting compacts of $Ca(OH)_2$ and $Mg(OH)_2$ to carbon dioxide (up to 20 atm CO_2 pressure) for variable periods of time is largely controlled by the molar proportion of calcium to magnesium in the initial mixture. Increasing magnesium content in the initial mixture favours the formation of nesquehonite and other carbonates containing both calcium and magnesium. The compressive strength of the carbonate is improved with the presence of nesquehonite and/or other magnesium-containing phases. Curing time and CO_2 exposure influence the strength differently, depending on the initial Ca/Mg ratio of the initial mixture. The formation of magnesium-containing carbonate phases is particularly favoured at higher CO_2 pressures combined with prolonged exposure times.

1. Introduction

Calcite ($CaCO_3$), aragonite ($CaCO_3$), magnesian calcite ($(Ca,Mg)CO_3$), dolomite ($CaMgCO_3$), Ca-magnesite ($(Ca,Mg)CO_3$) and magnesite ($MgCO_3$) are considered as the main rock-forming carbonate minerals in nature [1–3]. Evolution of these minerals, in nature, takes place in a variety of geological and chemical environments and is basically a crystallisation process. The confining pressures of overlaying sediments, temperature, the relevant ionic concentrations, and the presence of foreign ions and other impurities all contribute by some degree to the maturing and soundness of the carbonate structure. The physical and chemical conditions of the environment in which they are formed are reflected in their composition.

It has been shown previously [4] that calcium carbonate binders with good physical properties can be developed in the laboratory using controlled experimental conditions, and that the binder properties would mainly depend on the crystalline morphology and microstructure of the product. Any crystallisation process can be influenced by the presence of substrates (foreign particles) and/or by other foreign ions in the system. Some substrates can act as suitable nucleation sites for the crystallising species controlling the crystallisation process and hence the microstructure of the final product. Some foreign ions can also be chemically involved in the reaction process, resulting in alterations in the chemical composition and hence the microstructure of the product.

The foreign ions that are well known to have an impact on calcium carbonate formation are Mg^{+2}, OH^{-1} and SO_4^{-2}. Their concentrations and rate of carbonate formation mainly determine the chemistry and morphology of the product. Among these foreign ions, magnesium can be considered as the most influential ion in calcium carbonate formations [5–10]. Depending on the Mg/Ca ratio at the start, different carbonate phases are known to be formed.

The use of magnesium carbonates or calcium magnesium carbonates as cementitious binders is not very common to date, and not much literature is available on the subject. Improvement in the strength of lime mortars by the incorporation of $Mg(OH)_2$ or magnesia (MgO) followed by exposure to an air/CO_2 environment, for example, has been attributed to the formation of hydromagnesite ($Mg(OH)_2.4MgO.4CO_2.4H_2O$) during the curing process [11].

In addition to the relevance of these systems as binders, $MgCO_3$ is also known to be the main product in the CO_2 sequestration process by magnesium-containing minerals. Serpentine ($Mg_3Si_2O_5(OH)_4$) and brucite ($Mg(OH)_2$) are Mg-rich lamellar minerals that are being investigated worldwide in relation to the CO_2 sequestration process [12]. Overall, the availability and low cost of these minerals, combined with the exothermic nature of the carbonation process, provides exciting potential for economically viable product development.

This work investigated the role of magnesium ions, incorporated as magnesium hydroxide into the hydrated lime carbonation processes, on the physical properties of the resulting products. The underlying chemistry of the process when different Mg/Ca ratios were involved was systematically studied under different CO_2 environments. The

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☆ The experimental part of this work was carried out at CSIRO Materials and Manufacturing Laboratories at North Ryde, Sydney, Australia.

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Table 1
Chemical composition (%) of hydrated lime.

Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	Na_2O	SiO_2	LOI
0.28	72.4	0.16	0.17	0.42	0.08	0.61	25.2

different CO_2 environments were created by applying different CO_2 pressures for various curing time periods. The study correlated the type of carbonate phase formed to the physical performance of the product based on compressive strength measurements.

2. Materials and experimental procedure

The hydrated lime used had the chemical composition given in Table 1. Laboratory-grade magnesium hydroxide was used as the magnesium source and industrial-grade CO_2 gas was used throughout the work. The equipment used allows samples to be compacted and subsequently exposed to CO_2 at different gas pressures. Details of the equipment are given by De Silva *et al.* [4].

Different mix formulations, as shown in Table 2, were prepared at a water/solid (W/S) ratio of 0.25, by changing the ratio of magnesium hydroxide and calcium hydroxide to obtain different Mg/Ca molar ratios. A known amount of the mixture was then compacted at 2 MPa mechanical pressure for 2 min and exposed to different CO_2 pressures, (ambient, 1 and 20 atm), at 23 ± 2 °C temperature for different time intervals (0, 0.5 and 6 h). The compact (sample after compaction) dimensions were 16 mm diameter and 25 mm height, and the weight of the sample mixture was chosen so that the height of the cylinder was about 25 mm after each compaction. (The density of the initial compacts was about 1390 kg m^{-3}). As the CO_2 exposure was carried out in a sealed environment, the moisture was conserved.

After exposure to CO_2, the compacts were kept at 23 ± 2 °C and 50 ± 5% RH for 24 h before being subjected to strength measurements and solid phase analysis by X-ray diffraction (XRD), scanning electron microscopy (SEM) in conjunction with electron dispersive X-ray analysis (EDAX) and differential thermal analysis (DTA). Gold-coated samples were used in the SEM analysis. The compacts exposed to ambient conditions were considered as controls.

A separate set of specimens of different Mg/Ca ratios, as shown in Table 2, were also exposed to 20 atm CO_2 pressure for 0.5 h and were kept at 23 ± 2 °C and 50 ± 5% RH to evaluate the strength at 28 days.

3. Experimental results

3.1. Compressive strength development

3.1.1. Effect of Mg/Ca ratio

Compressive strength development of compacts CH, MC_4, MC, M_4C, $M_{10}C$ and MH exposed to 20 atm CO_2 pressure for different time intervals are shown in Fig. 1. With limited exposure to CO_2 (0.5 h), an increase in Mg content in the starting mixture significantly increased the compressive strength of the product.

With prolonged exposure to CO_2, the strength improvement was negligible for samples with an Mg/Ca ratio up to about 1:1 and, in these samples, most of the strength (50–75%) was gained in the first 0.5 h of exposure. However, the compacts with higher magnesium contents (Mg/Ca ratio higher than 1:1), showed continuous increase in strength with exposure time. The strength of the compact with only magnesium hydroxide (MH), reached 70 MPa after 6 h of CO_2 exposure, which was about twice the strength gained by this compact at 0.5 h exposure. In contrast, the strength at 6 h of the compact with only calcium hydroxide (CH) was less than half of that at 0.5 h. In other words, the compacts containing more magnesium benefit from longer CO_2 exposures.

Table 2
Mg/Ca molar ratios in the initial compositions.

Mix identity	CH	MC_4	MC	M_4C	$M_{10}C$	MH
Mg/Ca (molar ratio)	Only $Ca(OH)_2$	1:4	1:1	4:1	10:1	Only $Mg(OH)_2$

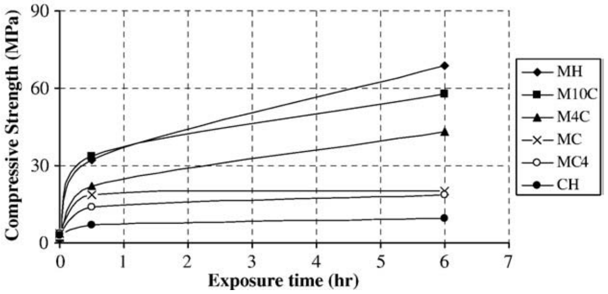

Fig. 1. Effect of CO_2 exposure time on the compressive strength of compacts made with different Mg/Ca ratios (CO_2 pressure = 20 atm).

3.1.2. Effect of CO_2 gas pressure

The compressive strength development of the CH, MC and MH compacts exposed to 1 and 20 atm CO_2 pressures are shown in Fig. 2. It can be seen that increasing CO_2 gas pressure from 1 to 20 atm enhanced the strength of all the compositions studied. However, the magnitude of strength increase with increasing CO_2 pressure was different, depending on the magnesium content of the initial mixture. For example, for the compact with only magnesium (MH), at 6 h exposure the strengths were about 15 and 70 MPa at 1 and 20 atm respectively, which is about a fivefold increase. For the MC and CH compacts, the comparable strength gains were 3 and 1.5 times respectively. Therefore, the compacts with high magnesium contents benefited more from increasing CO_2 pressure.

3.1.3. Long-term strength characteristics of Mg/Ca compacts

The compressive strength characteristics, up to 28 days, of compacts made with different Mg/Ca ratios and exposed to 20 atm CO_2 pressure for 0.5 h are shown in Fig. 3.

The compacts containing high magnesium content (MH and $M_{10}C$) and already exposed to 20 atm CO_2 for 0.5 h, kept at ambient conditions, show virtually no change in strength up to 28 days. However, when the calcium content in the initial mixture was high, an increase of strength was seen at 28 days. It is hard to draw any direct relationship between the magnitude of strength increase and the original calcium content of the compacts, but the change was certainly

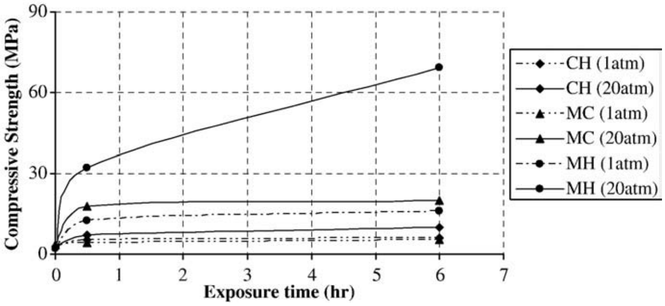

Fig. 2. Effect of CO_2 gas pressure on compressive strength of compacts made with different Mg/Ca ratios.

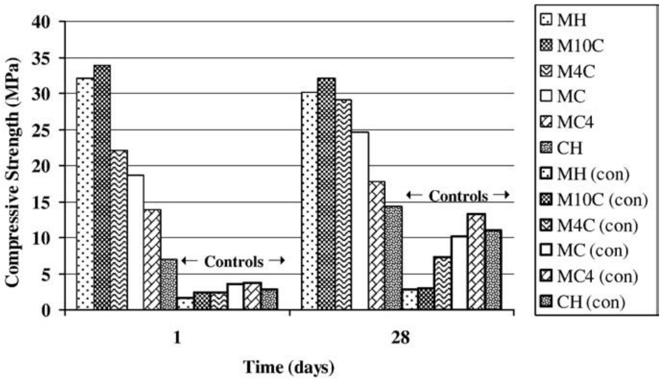

Fig. 3. Compressive strength up to 28 days of the compacts exposed to CO_2 at 20 atm for 0.5 h (con = control).

related to the initial calcium content. The more calcium present in the sample, higher the reactivity in the low CO_2 (ambient) environments and this might possibly lead to increase in product strength.

Control samples also showed a gradual increase in strength, the magnitude of which was associated with the calcium content of the initial mixture. The control samples with very high magnesium contents (MH and $M_{10}C$) show virtually no strength improvement at 28 days. These results again show the slow or zero reactivity of high Mg-containing compacts at low CO_2 (ambient) environments.

3.2. Solid phase development

3.2.1. XRD analysis

The XRD patterns of compacts MH, M_4C, MC, MC_4 and CH, exposed to 20 atm for 6 h, are shown in Fig. 4. The presence of phases in the different mixtures, as identified by XRD, is also summarised in Table 3.

It can be seen that compacts CH, MC_4 and MC contained peaks corresponding to $CaCO_3$ or $(Ca,Mg)CO_3$ (magnesian calcite). (Calcite and magnesian calcite generally show similar 2-theta values and are hard to distinguish by XRD. However, as will be shown in the microstructural analysis in the next section, it can be confirmed that magnesian calcite was present in the mixtures containing both calcium and magnesium.) When the initial Mg/Ca ratio increased, especially greater than 1:1, a new phase corresponding to nesquehonite ($MgCO_3.3H_2O$) started to appear, with the gradual disappearance of the $(Ca,Mg)CO_3$ phase. Correspondingly, compact MH predominantly contained unreacted $Mg(OH)_2$ and nesquehonite. Therefore, it is conceivable that the strength enhancements associated with increasing Mg/Ca in the initial mixture were due to the development of magnesium-containing carbonate phases in these compacts.

Table 3
Phases present in different mixtures as identified by XRD.

Mixture	Primary phases identified by XRD
CH	$CaCO_3$, $Ca(OH)_2$ (traces)
MC_4	$(Ca,Mg)CO_3 + Ca(OH)_2 + Mg(OH)_2$ (trace amounts)
MC	$(Ca,Mg)CO_3 + Mg(OH)_2 + MgCO_3.3H_2O$ (trace amounts)
M_4C	$(Ca,Mg)CO_3$ (traces) $+ MgCO_3.3H_2O + Mg(OH)_2$
MH	$MgCO_3.3H_2O + Mg(OH)_2$

An XRD analysis was also carried out on compacts MH, MC and CH, exposed to 20 atm CO_2 for 0.5 h and then kept at ambient conditions for 28 days, which showed the presence of nesquehonite, magnesian calcite and/or calcite phases in these systems (graph not presented). This indicated the stability of these carbonated phases in the long-term.

3.2.2. Differential thermal analysis

DTA patterns of mixtures MC and MH exposed to 20 atm CO_2 for 6 h are presented in Figs. 5 and 6 respectively. In mixture MC (Fig. 5), the endothermic peaks around 390 °C and 750 °C are due to the decomposition of unreacted $Mg(OH)_2$ and a magnesian calcite phase present in the product, respectively. The decomposition of nesquehonite generally occurs in two stages [13]. First it starts to lose its structural water around 200 °C and transform to magnesite ($MgCO_3$), which decomposes in the range of 400–550 °C. The very small peaks present in the DTA pattern in the regions of 200–300 °C and 460 °C can be attributed to these two transformations (as shown in the XRD patterns, in this sample nesquehonite was present in trace amounts). The endothermic peak around 100 °C may be an indication of either the presence of moisture in the sample or perhaps the start of loss of structural water in the nesquehonite.

The DTA pattern of mixture MH exposed to CO_2 (Fig. 6), shows peaks corresponding to the decomposition of nesquehonite (200 °C and 520 °C) and $Mg(OH)_2$ (415 °C).

The chemical reactions representing the decomposition of these different phases are shown in Table 4.

3.3. Morphology and microstructure

SEMs of compacts CH, MC and MH exposed to 20 atm for 6 h are shown in Figs. 7, 8a and 9a respectively. It can be seen that the overall microstructure was different depending on the Mg/Ca ratio of the

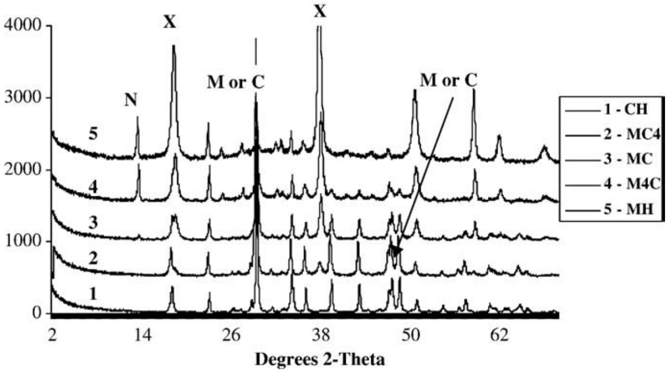

Fig. 4. XRD spectra of compacts exposed to CO_2 at 20 atm for 6 h (N = nesquehonite, M = magnesian calcite, C = calcite, X = magnesium hydroxide).

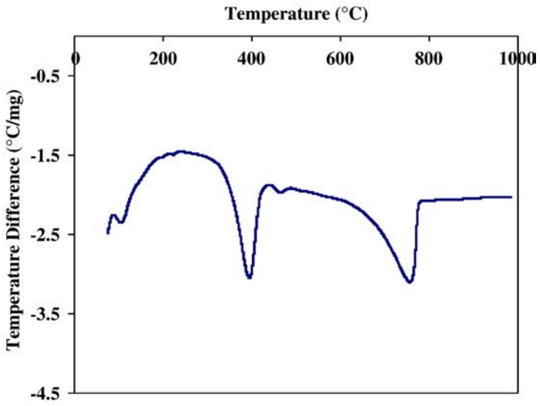

Fig. 5. DTA pattern of compact MC exposed to CO_2 at 20 atm CO_2 for 6 h.

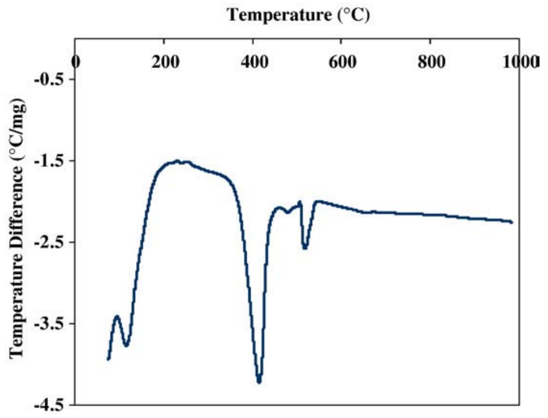

Fig. 6. DTA pattern of compact MH exposed to CO_2 at 20 atm CO_2 for 6 h.

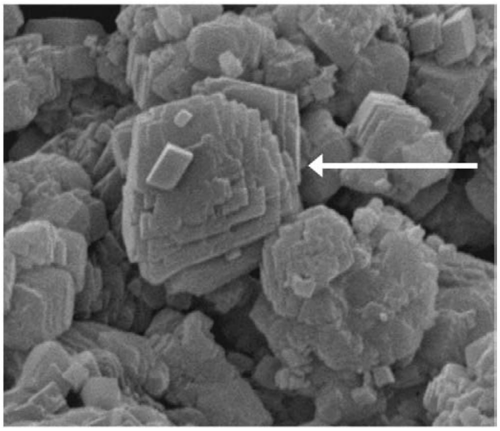

Fig. 7. SEM of carbonated mixture CH showing calcium carbonate phase.

initial mixture. The microstructure of the carbonated mixture CH (Fig. 7) contained plate-like crystalline calcium carbonate morphologies.

Fig. 8a presents an SEM of the carbonated MC compact, which consisted of morphologies of crystalline appearance. EDAX spectra of these phases (Fig. 8b and c) showed that they were carbonate phases containing both Ca and Mg. Therefore, it is more likely these were the magnesian calcite phases identified by XRD. It should also be noted that the Ca/Mg ratios in these carbonate phases was inconsistent (Fig. 8b and c)—some actually reaching 1:1, which is similar to dolomite.

Fig. 9a presents an SEM of the carbonated MH compact. The microstructure consisted of conglomerates of plate-like morphologies that were intimately mixed with unreacted magnesium hydroxide. This plate-like morphology was very much similar to that of nesquehonite, as shown in the literature [14]. The results of an EDAX analysis on this phase are shown in Fig. 9b which confirm the presence of nesquehonite in the carbonated MH compact.

4. Discussion

This work shows that the incorporation of magnesium hydroxide into hydrated lime carbonation has a considerable impact on the chemistry of the process. Magnesium becomes chemically involved in the reaction process, resulting in carbonate phases containing magnesium and thereby changing the performance (strength) characteristics of the carbonate binder. The incorporation of magnesium into a system greatly enhances the strength of the carbonate binder, the magnitude of which is observed to be proportional to the amount of magnesium hydroxide added to the initial mixture. This strength increase is possibly due to the formation of magnesium-containing carbonate phases in the high magnesium environments. Also it is clear from the results that to obtain magnesium containing carbonate phases environments high in CO_2 have to be used.

When a system contains only calcium hydroxide, the carbonate phase obtained is calcite. As the Mg/Ca ratio in the initial mixture increases, the main carbonate phases observed are magnesian calcite or/and hydrated magnesium carbonate, namely nesquehonite. A system with only magnesium hydroxide produces nesquehonite during exposure to CO_2. The chemical reactions for these formations can be written as follows:

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O}$$

$$\mathrm{Ca(OH)_2 + Mg(OH)_2 + CO_2 \rightarrow (Ca,Mg)CO_3 \text{ and/or } MgCO_3.3H_2O + H_2O}$$

$$\mathrm{Mg(OH)_2 + CO_2 \rightarrow MgCO_3H_2O}$$

Nesquehonite is categorised as a hydrated magnesium carbonate as it contains three water molecules in its structure [15]. The main magnesium carbonate phases that can present in an $MgO–CO_2–H_2O$ system are magnesite, nesquehonite and hydromagnesite. The stability of these carbonates depends on the CO_2 pressure and water vapour pressure of the environment. Nesquehonite was found to be stable at higher CO_2 pressures [15].

As shown in this study, high CO_2 pressure facilitates the formation of nesquehonite and, once it is formed, it remains stable in a system. However, the amount of water present in the system could also be a key factor that controls this formation, as water is a part of the molecular structure of nesquehonite.

The type of carbonate phase formed mainly depends on the availability of Mg^{+2} (or the solubility of magnesium hydroxide) for the reaction. The solubility of magnesium hydroxide (0.009 g/100 mL water) is extremely low compared to calcium hydroxide (0.185 g/100 mL water). Therefore, in ambient conditions the reaction of magnesium hydroxide with ambient CO_2 is much lower than that of calcium hydroxide. This is likely to explain the pattern of strength development of the control samples with different Mg/Ca ratios up to 28 days, in which the samples that had high magnesium contents did not show any strength improvement when exposed to ambient conditions.

Magnesium hydroxide is reactive in acidic environments. Increasing CO_2 pressure, which increases the acidity of the medium, makes more Mg^{+2} available to the reaction, resulting in carbonate phases containing magnesium and hence increasing the strength of the binder. The extent of exposure time, at high CO_2 pressures, also seems to play a part when the magnesium content in the sample is high. The longer exposure times facilitate the reactivity of magnesium hydroxide. Therefore, higher Mg/Ca ratios benefit more from the combination of higher CO_2 pressures and longer exposure times.

Even though magnesium incorporation favours the strength characteristics of the carbonate binder, the thermal stability of these phases may limit their applications. As shown by DTA data, magnesian calcite and calcite both decompose in a similar temperature range

Table 4
Decomposition reactions of different phases.

Chemical reaction	Temperature, °C
$Ca(OH)_2 \rightarrow CaO + H_2O$	400–500
$Mg(OH)_2 \rightarrow MgO + H_2O$	375–450
$CaCO_3 \rightarrow CaO + CO_2$	650–800
$(Ca,Mg)CO_3 \rightarrow CaO + MgO + CO_2$	650–800
$MgCO_3.3H_2O \rightarrow MgO + CO_2 + 3H_2O$	200–550
$MgCO_3 \rightarrow MgO + CO_2$	400–550

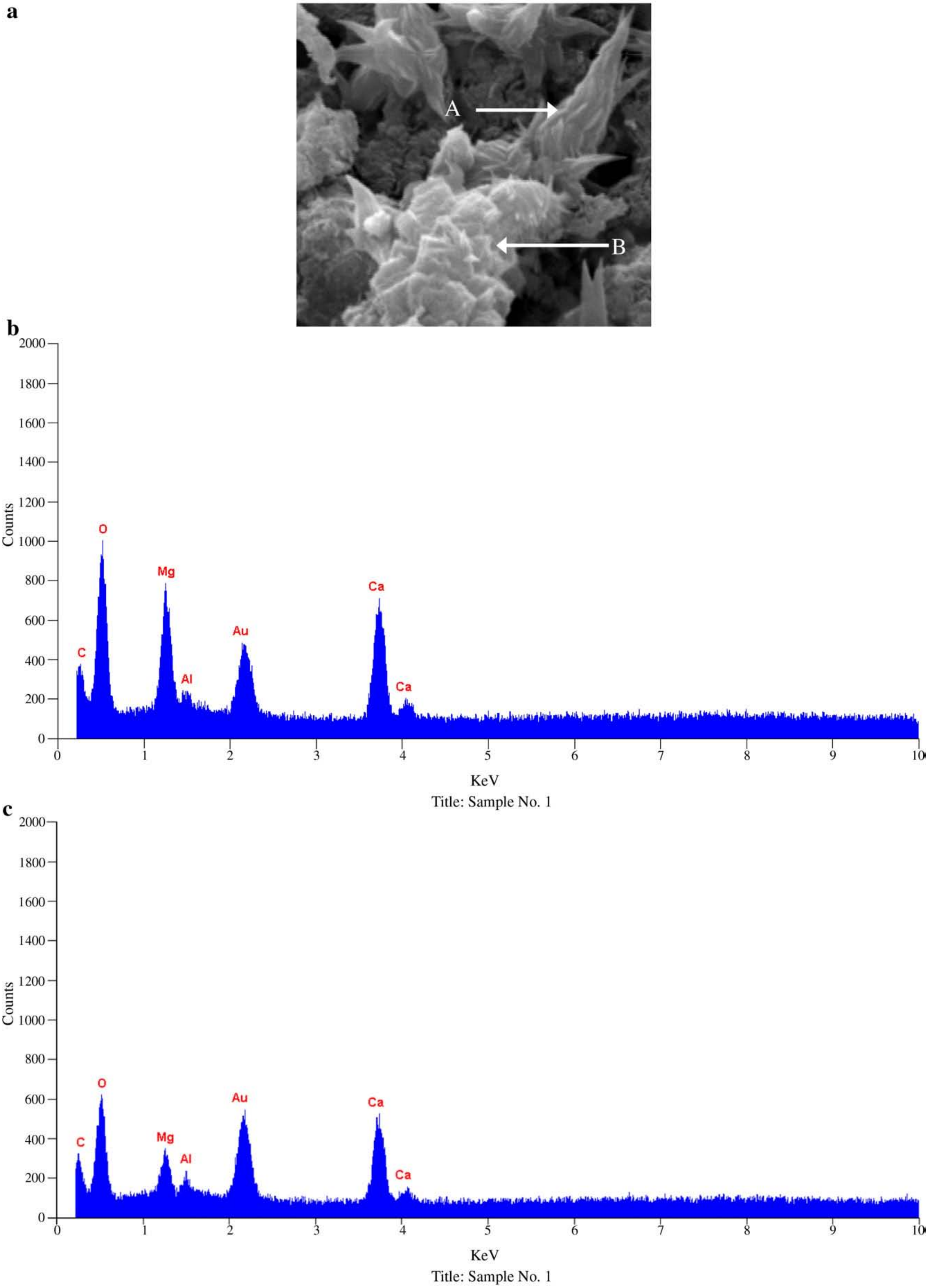

Fig. 8. a. SEM of carbonated MC compact showing calcium magnesium carbonate phases A and B. b. ED spectra of phase A in a. c. ED spectra of phase B in Fig. 7a.

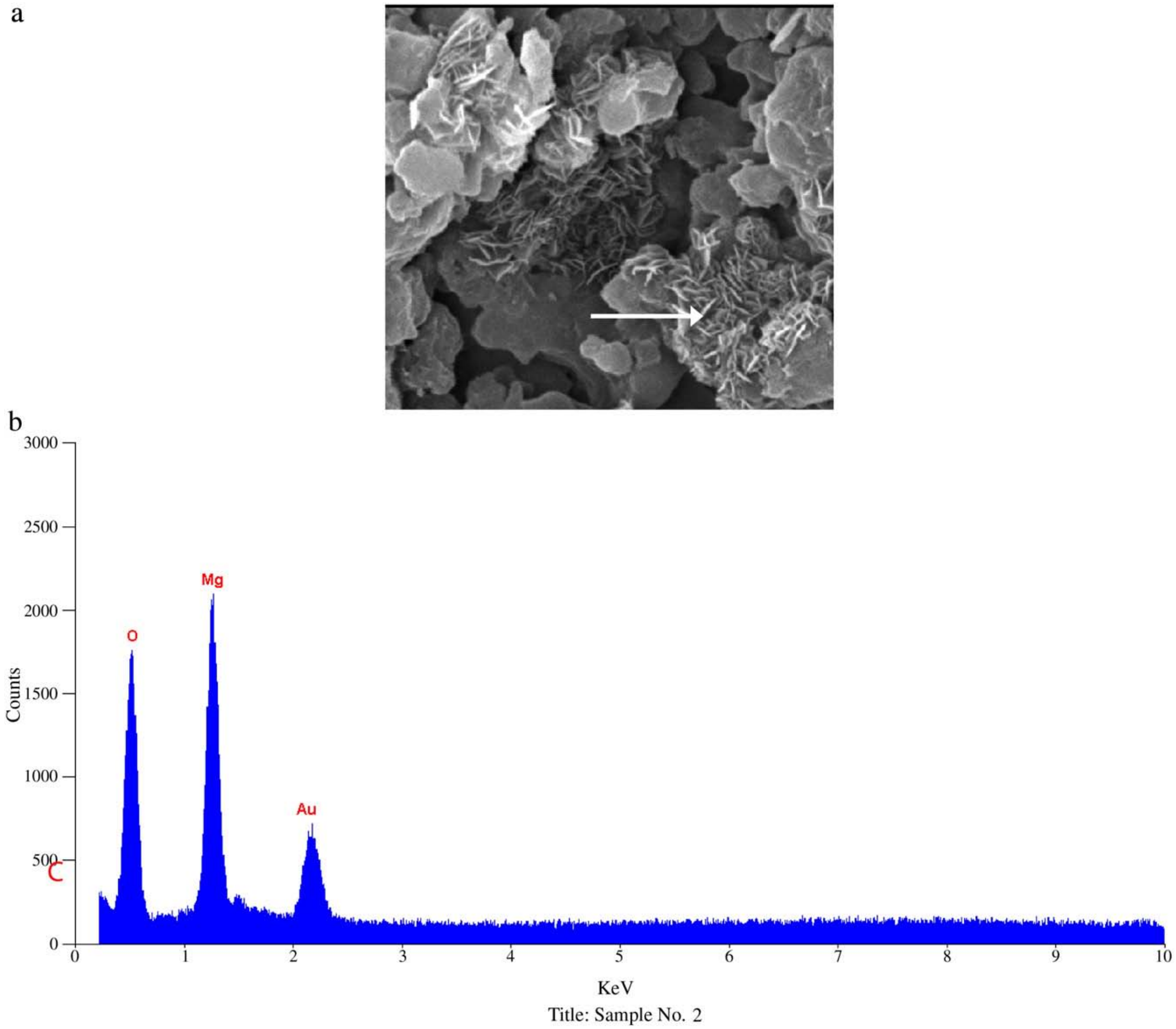

Fig. 9. a. SEM of carbonated mixture MH showing nesquehonite phase. b. ED spectra of nesquehonite phase shown in a.

(around 750 °C, but nesquehonite has a relatively lower decomposition temperature (200 °C) compared to calcite or magnesian calcite.

5. Conclusions

This study discloses that magnesium-containing carbonate binders can be obtained by incorporating magnesium, as magnesium hydroxide, into the $Ca(OH)_2/CO_2$ system. The carbonate phases of magnesium only, or both magnesium and calcium, show better physical performance, as measured by strength, than equivalent calcium systems. The performance (strength) of the binders varies with the chemical composition or the type of carbonate binder. This trend is mainly dependent on the Mg/Ca ratio of the initial mixture. Curing time and CO_2 exposure influence the strength characteristics differently, depending on the Ca/Mg ratio of the initial mixture. Higher CO_2 pressures combined with prolonged exposure times appear to facilitate the formation of magnesium-containing carbonate phases.

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