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Sequestering CO_2 by Mineralization into Useful Nesquehonite-Based Products

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The precipitation of magnesium hydroxy-carbonate hydrates has been suggested as a route to sequester CO_2 into solids. We report the development of self-cementing compositions based on nesquehonite, $MgCO_3{\cdot}3H_2O$, that are made from CO_2-containing gas streams, the CO_2 being separated from other gases by its high solubility in alkaline water, while magnesium is typically provided by waste desalination brines. Precipitation conditions are adjusted to optimize the formation of nesquehonite and the crystalline solid can readily be washed free of chloride. Products can be prepared to achieve self-cementation following two routes: (i) thermal activation of the nesquehonite then rehydration of the precursor or (ii) direct curing of a slurry of nesquehonite. The products thus obtained contain ~30 wt% CO_2 and could form the basis for a new generation of lightweight, thermally insulating boards, blocks, and panels, with sufficient strength for general construction.

Keywords: CO_2 sequestration, desalination brines, mineralization, magnesium carbonates, construction products

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INTRODUCTION

In order to mitigate the impacts of the continuously rising atmospheric CO_2 levels (Earth System Research Laboratory, 2016), short- to medium-term measures are needed to cope with increasing CO_2 emissions, while, in the longer term, strategies have to be developed to decarbonize society. The conventional approach to the sequestration of carbon dioxide involves the separation of CO_2 from other gases, its liquefaction, transportation, and storage underground; the technology is well known and several large scale projects have been reported (Global CCS Institute, 2016). However, the cost of such process is at present still high and some uncertainties regarding the permanence of storage sites for liquid CO_2 remain.

An alternative approach to achieve CO_2 sequestration is to use mineralization, i.e., to make solid products related in composition, structure, and engineering properties to naturally occurring minerals while insuring a permanent and safe storage of the CO_2 (Haywood et al., 2001; Lackner, 2002; Mazzotti et al., 2005; Teir et al., 2007; Styring et al., 2011; Olajire, 2013). For this reason, we have considered "MHCH" (shorthand for magnesium hydroxy-carbonate hydrate) phases, which exist as natural minerals and/or synthesis products, to be suitable targets for mineralization; **Table 1** lists the name, formula, and composition of the most common MHCH phases. The fact that these phases, like their natural analogs, can be used by the industry (Constantz et al., 2010; Hull et al., 2011; Camire et al., 2012; Unluer and Al-Tabbaa, 2013) is important as a favorable economic balance is necessary to make any industrial CO_2 sequestration process viable on the long term.

TABLE 1 | Commonly synthesized MHCH phases.

Name	Formula	Composition (wt%)		
		MgO	CO_2	H_2O
Nesquehonite	$MgCO_3 \cdot 3H_2O$	29.1	31.8	39.1
Dypingite	$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$	41.5	36.2	22.3
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	43.1	37.6	19.3

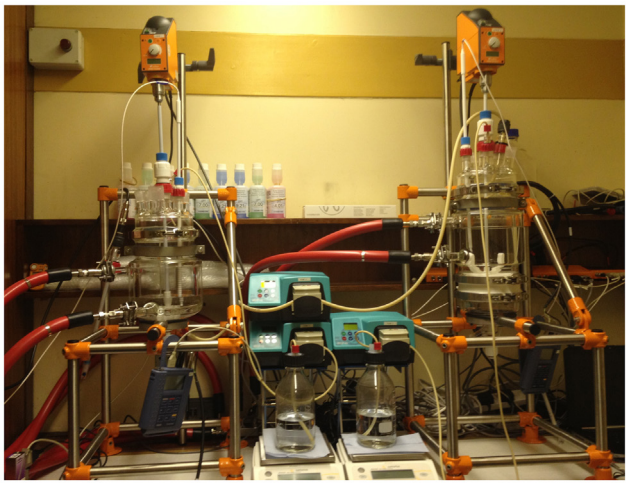

FIGURE 1 | Photo of the lab-scale reactor used for the synthesis of MHCH phases (the total height is about 1.3 m and the two double-walled reactors have a 2-L internal capacity).

Our objective was to develop a process, from collection of CO_2 to product, where previous separation from other gases is not required while synthesizing products with the following characteristics:

- Low initial cost, using where possible waste materials.
- Making products that could enter established large volume markets, of which building and construction seemed a potential target.
- Developing functional products which look and are handled like competitive materials, concentrating on replacing traditional materials with high embodied energy costs.

This contribution presents our progress to date and describes briefly future plans.

MATERIALS AND METHODS

A lab-scale reactor (**Figure 1**) allowing the control and recording of experimental parameters for batch syntheses (e.g., addition rates of reagents, reaction temperature, etc.) was designed in consultation with Radleys (UK). When using a commercial gas cylinder as the source of CO_2, reaction occurs in two stages: (i) a dissolution stage in which CO_2 is sparged in a solution kept at an alkaline pH with NaOH and (ii) a second stage in which the carbonate/bicarbonate solution obtained in the first stage reacts with a Mg-containing solution, e.g., $MgCl_2$ in most cases. In the trials described here, the first stage was replaced by the direct use of an aqueous solution of $NaHCO_3$ + Na_2CO_3. The second stage typically lasts 4 h, starting from the addition of the Mg-rich solution to the CO_2-rich solution (addition time of 30 min), with constant stirring at room temperature (i.e., 20–25°C) and ambient pressure (i.e., 1 atm) prior to washing and filtering the nesquehonite product. The holding stage allows crystallization to complete thus producing a coarse and readily filterable product. The yield of the reaction was calculated on the basis of recovered Mg, which was determined by atomic absorption using a Varian AAS. The concentrations of $MgCl_2$ and Na_2CO_3 + $NaHCO_3$ were ~0.1–0.2 mol L^{-1} and all experiments were performed with an equimolar Mg:CO_2 ratio. The thermal analysis of the solid product was performed in static air in ovens and with a Stanton Redcroft DTA/TG apparatus typically at 5–10°C min^{-1} under flowing nitrogen atmosphere (at ~50–60 mL min^{-1}).

Cubes of nesquehonite-based products were prepared using the following two methods: (i) nesquehonite is thermally activated between 100 and 250°C then the resulting solid is mixed with water, the product shaped then cured under humid conditions at ambient temperature and (ii) nesquehonite is mixed directly with water, the product is then shaped and cured under humid conditions at 60–80°C. The compressive strength of the cubes was measured with a Hounsfield universal press using a loading speed of 1 mm min^{-1} and a 10-kN sensor. Thermal conductivity was measured with a Lasercomp FOX 603 Heat Flow Meter using a reduced-area multi-thickness measurement method (Patterson, under review)[1], which accounts for the effects of resistance to heat flow at the interface between the apparatus and the sample surface (Tleoubaev and Brzezinski, 2008) but uses a reduced sample size and so requires less material.

X-ray diffraction (Panalytical X'Pert Pro using Cu-K_α radiation; power parameters were 45 kV and 40 mA) was used at the different stages of the process to characterize the solids formed while their morphology was assessed by Scanning Electron Microscopy (Hitachi S-520 using 20 kV acceleration voltage).

RESULTS

Production of Nesquehonite

Nesquehonite was successfully obtained as the only solid phase using the Radleys reactor. **Figure 2** shows the typical product morphology of sharply faceted long needles. The X-ray powder diffraction pattern of nesquehonite (**Figure 3**) conforms to that reported in the literature [e.g., Kloprogge et al. (2003) or Ma and Yoon (2013)].

With the experience of operating the Radleys reactor, it was found that precipitation conditions for making nesquehonite were relatively robust and reproducible in the range 20–25°C. Therefore, a larger facility, which is composed of a ~50-L plastic tank equipped with a pump and a motorized stirrer, was used to make nesquehonite in kilogram batches using Na_2CO_3, $NaHCO_3$, and $MgCl_2$. Yields calculated on the basis of recovered Mg were

[1] Patterson, N., Yoon, S., Macphee, D. E., and Imbabi, M. S. The cuboid method for measurement of thermal properties of cement-based materials using the guarded heat flow meter. (under review, Constr. Build. Mater, 2015).

typically around 75–80% and did not differ significantly from those obtained in the Radleys reactor; the product could in both cases be made phase pure and with the same morphology.

Properties of Nesquehonite

Thermal Decomposition of Nesquehonite

The thermal analysis of nesquehonite shows that volatiles, i.e., water and carbon dioxide, are lost in stages beginning at about 100°C (Dell and Weller, 1959; Davies and Bubela, 1973; Lanas and Alvarez, 2004; Vagvolgyi et al., 2008; Ballirano et al., 2010; Jauffret et al., 2015). The low temperature decomposition stages (below 250°C) are of most interest to a thermal activation process that also avoids loss of structural CO_2. Three incompletely resolved stages of water loss occur in the course of DTA (**Figure 4**). The nesquehonite structure begins to break down during the loss of its first water molecule and the resulting product obtained at about 2 H_2O is an ill-crystallized phase we termed "phase X" as its X-ray diffraction pattern is unlike any others reported for known MHCH phases, including that of barringtonite, which also has the formula $MgCO_3{\cdot}2H_2O$ (Jauffret et al., 2015).

FIGURE 2 | Typical low magnification SEM photo of nesquehonite, $MgCO_3$ $3H_2O$ (synthesis conditions: 25°C, 4 h, 0.1 mol of $MgCl_2$ and Na_2CO_3, total volume 1.1 L).

Reconstitution of Nesquehonite

One of the interesting characteristics of the thermally activated solids is that, upon mixing with water and allowing the wet paste to age at ~20–25°C, nesquehonite can be regenerated (Morrison et al., 2014; Jauffret et al., 2015). This suggests that sufficient structural motifs of nesquehonite are preserved during thermal activation to facilitate its reformation. The morphology of the precursor nesquehonite is certainly well preserved throughout the decomposition and subsequent reconstitution so that the morphology of the reconstituted product resembles that of the precursor. However, considerable heat is released in the course of reconstitution and recrystallization. The reconstitution reaction is cementitious and is initiated spontaneously by mixing the solid precursor powder with water and curing at room temperature, preferably with retention of water, for several hours.

Stability of Nesquehonite

Although nesquehonite persists up to 100°C, it is unstable upon prolonged storage in moist atmospheres at temperatures above 60°C. Additional data on its persistence and the extent of the hysteresis loop between P/T conditions for hydration–dehydration cycles have been reported (Morgan et al., 2015). Nesquehonite

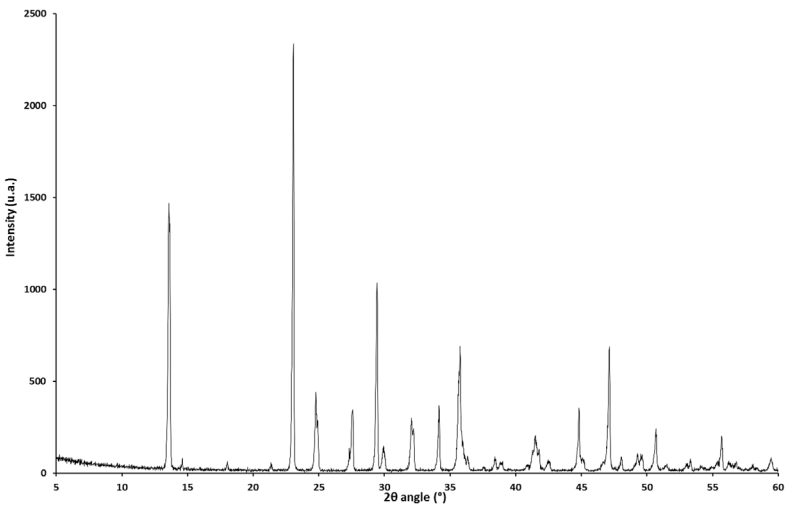

FIGURE 3 | XRD pattern of nesquehonite (synthesis conditions: 25°C, 4 h, 0.1 mol of $MgCl_2$ and Na_2CO_3, total volume 1.1 L) in agreement with PDF #00-020-0669 (differences in intensity could be explained by the preferred orientation of the crystals).

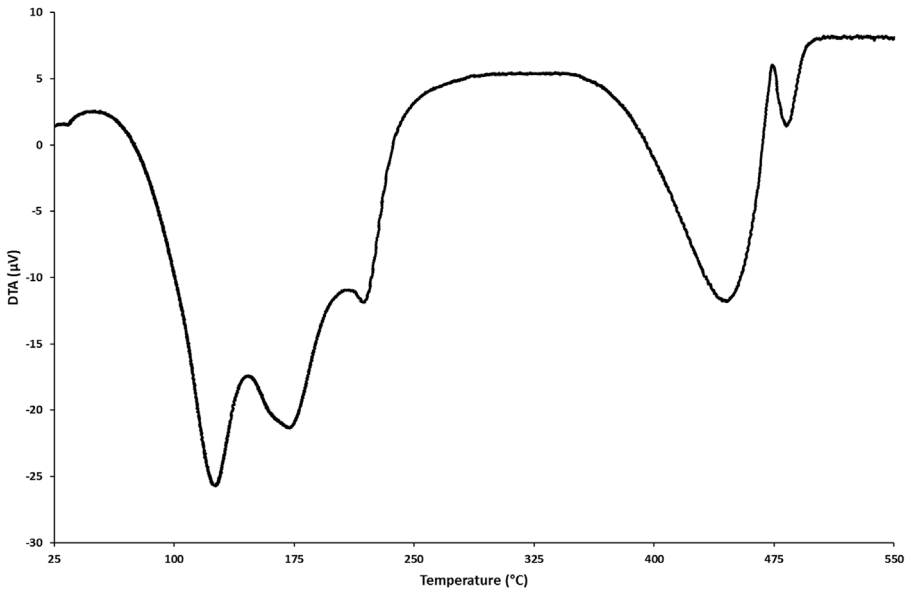

FIGURE 4 | DTA pattern of nesquehonite (synthesis conditions: 25°C, 4 h, 0.2 mol of $MgCl_2$ and Na_2CO_3, total volume 1.2 L) obtained with a heating rate of 5°C min^{-1} under a flowing N_2 atmosphere (55 ± 5 mL min^{-1}); sample mass was ~24 mg.

slowly decomposes with the evolution of water and carbon dioxide to a dypingite-like phase, $Mg_5(CO_3)_4(OH)_2{\cdot}nH_2O$ (with $n > 5$), then to dypingite itself ($n = 5$) and hydromagnesite ($n = 4$). Reaction may require several months to approach completion at room temperature (~20–25°C) but this delay decreases to only several hours or days in the course of curing under humid conditions at temperatures in the range 60–80°C.

Preparation and Properties of Nesquehonite-Based Products

The two methods used for the preparation of nesquehonite-based products are described in Section "Materials and Methods" above. Products are fabricated broadly by the same methods used for clay or cement: a liquid suspension can be poured into molds, or, if using stiffer mixes, compacted in molds by vibration or pressing. Fabrication methods are also important as vibrated and pressed samples typically require less water and could thus achieve higher strengths than cast products. In the case of products prepared with thermally activated nesquehonite, shapes gradually harden as the added water progressively evaporates and part of it is chemically combined to regenerate nesquehonite. In the case of products prepared with the second method, shapes made from nesquehonite gradually gain strength as conversion to dypingite and hydromagnesite occurs which, as explained above, leads to a net loss of structural water and of ~20% of the CO_2 initially sequestered in the solid; however, the CO_2 thus released could be looped back to an earlier stage. Both methods result in an extensive microstructural and mineralogical reconstitution, which is the subject of an ongoing study.

Compressive strength values up to 8 MPa were obtained for cubes prepared with both methods, which shows that sufficient strength could be achieved for product applications such as panels and blocks. Measured thermal conductivity values were found to lie in the range 0.21–0.33 W K^{-1} m^{-1} for products made from thermally activated nesquehonite; these results, combined with bulk densities in the range 600–900 kg m^{-3}, suggest a promising use for the products as thermal insulation materials. For example, a 1 m × 1 m, 0.4 m thick panel (i.e., containing 0.4 m^3 of material) with a bulk density of 700 kg m^{-3} will weigh 280 kg so ~600 kg less than a comparable panel made of ordinary concrete with a bulk density of ~2200 kg m^{-3}, i.e., weighing ~880 kg; since such panel will contain ~30 wt% carbon dioxide, the amount of CO_2 thus sequestered in insulating a typical residential unit would be significant.

DISCUSSION

MHCH Phases

Much effort was expended in developing conditions leading to precipitation of phase pure, or nearly pure, nesquehonite. In an industrial context, the source of CO_2 could be any flue gas stream, ideally rich in CO_2, and the source of Mg could be a desalination brine. Desalination brines can differ significantly in composition depending on plant design, but for economic reasons the reject water stream is usually not concentrated by more than a factor of ~2 relative to seawater and is thus close to 1M NaCl and 0.1M Mg; in practice, waste brines are often discharged warm (at 40–45°C). For example, Calera has patented a process for obtaining several specific carbonate phases using seawater as the source of Mg (Constantz et al., 2010; Camire et al., 2012), but this process is seen as uneconomical due to the high alkali requirements and large seawater volumes needed (Unruh, 2010).

TABLE 2 | Saturation indexes (SI) of the phases potentially precipitating in the case of the reaction at 25°C and 1 atm of a brine containing 2.4 g L^{-1} $Mg2^+$, 23.0 g L^{-1} Na^+, and 42.6 g L^{-1} Cl^- with a carbonate solution at a Mg:CO_2 molar ratio of 1; the initial alkalinity of the system was adjusted to pH = 7.5 with 0.1 g L^{-1} HCO_3^- .

Phase	SI (log IAP–log Ks)	log IAP	log Ks
Brucite	6.65	−4.52	−11.17
Magnesite	3.08	−4.75	−7.83
Hydromagnesite	14.38	−23.96	−38.34
Nesquehonite	0.87	−4.82	−5.69

The ionic activity products (IAP) and solubility products (Ks) were calculated with PHREEQC (United States Geological Survey, 2015) using the Pitzer database.

Theoretically, the reaction of a brine rich in Mg^{2+} ions with an effluent from the absorption of CO_2 by sodium hydroxide, i.e., a solution of sodium carbonate and bicarbonate, would produce magnesite (**Table 2**). However, some of the expected phases are kinetically inhibited due to the relatively low temperature of reaction (e.g., hydromagnesite) or the presence of energy barriers (e.g., magnesite). Brucite is also predicted to appear by thermodynamic modeling, but its presence could not be confirmed experimentally due to its expected very low concentration in the solid phase.

Numerous reports of the synthesis of MHCH phases have been made. Precipitation is mainly done by mixing an aqueous solution of Mg salts, e.g., $MgCl_2$, with an aqueous solution of $NaHCO_3$ and/or Na_2CO_3 (Kloprogge et al., 2003; Haenchen et al., 2008; Case et al., 2011; Ma and Yoon, 2013). $NaHCO_3$/Na_2CO_3 solutions would be obtained when NaOH is used for the dissolution of CO_2 into an aqueous solution but other bases such as aqueous ammonia solutions have been also used (Ferrini et al., 2009; De Vito et al., 2012). The physical chemistry of the precipitation of MHCH phases has been much studied and it appears that metastability is widespread among the precipitated products (Dell and Weller, 1959; Bender and Sprague, 1965; Langmuir, 1965; Davies and Bubela, 1973; Canterford et al., 1984; Haenchen et al., 2008; Hopkinson et al., 2008, 2012; Case et al., 2011; Ballirano et al., 2013).

Relatively few uses have been reported for the precipitated MHCH phases, one possibility being simply to landfill the MHCH. But we sought higher value applications and so developed a process for making self-cementing MHCH compositions. The choice of MHCH phase is important as their crystal structures differ especially in the role of "water" and this bonding gives insights into their subsequent potential for self-cementation. Not all the relevant crystal structures are known but two families of MHCH phases occur: one in which water is present exclusively as molecular water (e.g., nesquehonite) and another in which "water" occurs as mixtures of molecular water and charge-balancing OH groups (e.g., hydromagnesite). Some contention arises about the structure of nesquehonite because partial structural information, for example, derived from FTIR patterns, has been interpreted in terms of bonding and purport to show that "water" in nesquehonite is present partly as a mixture of molecular water and OH groups (Hales et al., 2008; Frost and Palmer, 2011; Hopkinson et al., 2012). However, the X-ray crystal structure shows unequivocally that species such as HCO_3^- and OH^- are absent: the correct picture is that all protons are combined as water in nesquehonite (Stephan and MacGillavry, 1972; Giester et al., 2000). The binding state of the "water" in the phases is important as it affects their subsequent evolution in the course of thermal treatment and enables control over the development of cementitious properties: so far, only nesquehonite (i.e., an MHCH phase containing only molecular water) was found to develop cementitious properties when treated, as described above.

Next Steps

Much work has been done on the relationships between porosity and microstructure but without as yet gaining a full understanding of the complex relationships. From the low bulk densities obtained (usually 600–900 kg m^{-3}) and the densities of the solid phases (1840 kg m^{-3} for nesquehonite and 2240 kg m^{-3} for hydromagnesite), the porosity of the products is high, typically around 60%. Despite that, strength remains relatively high. Characterization data and a mechanistic account of the relationships between porosity, permeability, and strength will be presented in a subsequent paper.

We have published a preliminary study of the GHG balance of the process (Galvez-Martos et al., 2016); in this study, it is shown that the carbon footprint of the developed product only becomes negative when the carbon footprint of other construction materials that are replaced, such as gypsum plasterboard, is taken into account.

One of the key economic costs associated with the process is the relatively high cost of the sodium hydroxide required to run the process. Further optimization, aiming to minimize alkali consumption, is therefore necessary: we have started to search for other means of adjusting the pH in the course of the CO_2 dissolution and MHCH precipitation stages.

We are presently beginning the design of a pilot plant for making nesquehonite to be located in Qatar. The intention is to use reject desalination brines from a nearby desalination plant as the source of magnesium and to capture CO_2 from a diesel engine exhaust (the engine is operated for an entirely unrelated process and its exhaust would normally be discharged into the atmosphere). It is anticipated that the pilot plant will be commissioned in mid-2016. The experience thus gained will be used to evaluate product properties and process economics: actual operational experience will be used to get a much firmer estimate of cost, including a more realistic costing of capital investment. It is also intended to make an actual demonstration of a construction using products from the pilot plant.

Other Developments

Significant progress has been reported in using Mg-containing minerals, e.g., periclase, magnesite, olivine, or serpentine, as targets for mineral sequestration. Several minerals are responsible for the observed CO_2 capture but, using thermally activated serpentine rocks, nesquehonite is almost invariably observed to form in the course of the reaction of the activated rocks at ambient temperature with water and carbon dioxide; serpentine will therefore be considered to be an important target phase for sourcing Mg.

Until now, we have considered that we will have to make nesquehonite and, to that end, have developed precipitation routes from aqueous sources. These sources, which can be terrestrial as

well as marine, would include formation waters or production brines from the oil and gas industry.

However, the formation of nesquehonite-based cementitious products is essentially a free-standing process, independent of the source of nesquehonite or Mg. It is therefore apparent that a process based on Mg-containing rocks, formation waters, or production brines could be adapted so as to produce an aqueous stream suitable for the precipitation of nesquehonite in relatively phase pure form. This would enable useful solids to be obtained as by-products of the sequestration process, thus elevating the sequestration products from wastes to useful, value-added construction materials.

AUTHOR CONTRIBUTIONS

FG directed the preparation of the paper. FG and MI directed the work carried out by GJ, JM, J-LG-M, and NP.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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