



# Conceptual design of a CO<sub>2</sub> capture and utilisation process based on calcium and magnesium rich brines

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## ABSTRACT

Carbon capture and utilisation processes, CCU, are those processes aiming to produce usable products from CO<sub>2</sub>-based materials. Although there are a large number of CCU alternatives, only a few are able to propose routes for the massive production of marketable CO<sub>2</sub> based products with a negative or neutral carbon footprint in the long term. In this work, a conceptual design of a process aimed to produce a cementitious construction material, based on magnesium carbonate trihydrate, also known as nesquehonite, is discussed and experimentally tested. Desalination brines are proposed as the source of aqueous magnesium. However, these brines contain a non-negligible amount of calcium, which interferes in the development of cementitious properties from nesquehonite. In order to avoid this interference, a multi-stage precipitation is proposed, where calcium carbonate precipitates in a first stage, and pure nesquehonite can be obtained in a second stage. A thermodynamic model, based on empirical observations from the precipitation system, is proposed and the technical feasibility of three process alternatives are evaluated against the outcomes from the model. The preferred alternative, from the technical and economic point of view, is to conduct a full absorption of CO<sub>2</sub> as aqueous carbonate, which is then split in two streams for both precipitation stages. The advantage of this alternative is the applicability to different types of brines, the probably faster and more economic absorption stage, and the easier control of the reaction conditions, as pH and temperature.

## 1. Introduction

Carbon dioxide capture and storage is considered to be a key technology in the future development of low greenhouse gases economies, able to adapt and mitigate the impact of climate change [1]. However, CCS development is highly dependent on fuel prices, implementation of renewable energy and its own readiness level. Indeed, CCS is reported to be a transition technology towards a vast implementation of clean energy sources [2,3].

A variant of CCS is the so-called CCU, carbon dioxide capture and utilisation, which is a generic term for those capture processes aimed to market usable products from CO<sub>2</sub>. However, CCU alternatives are not scalable at the levels of CCS [4]. From the market point of view, a product made from e.g. CO<sub>2</sub> captured from power plants flue gases would easily flood the market with such a product. Construction

products seems to be the preferred option to encourage a massive flow of CO<sub>2</sub> in marketed products as concrete [5], but, even in that case, marketing of the product needs to be restricted to local markets to avoid the impact of transport in the greenhouse gases balance.

The capture of CO<sub>2</sub> using alkaline reagents (“alkaline capture”) is frequently proposed for the mineralisation of Mg-rich minerals in indirect capture processes. The used minerals, as serpentine or olivine, are abundant enough in nature for the long-term capture, but unable to provide a solution with low associated impact, low embodied energy and cost-effectiveness [4,6,7]. For instance, crushing Mg silicate rocks, dissolving them in HCl and reacting with CO<sub>2</sub> using alkali as catalyst consumes 23 MJ kg of captured CO<sub>2</sub>, which would have an associated emission of 1.3 kg of CO<sub>2</sub>e per kg of captured CO<sub>2</sub> [7]. In order to avoid the large impact of mineralisation, a combination of a mineralisation process and a CCU approach was proposed by Calera in order to obtain

*Abbreviations:* CCS, carbon capture and storage; CCU, carbon capture and utilization; CC\*, calcium carbonate (aragonite, calcite or monohydrocalcite); DD, disorder dolomite or magnesium calcite; HM\*, hydromagnesite and similar components; NQ, nesquehonite; STP, standard temperature pressure; x, Mg:Ca molar ratio; y, total concentration of calcium and magnesium, mol L<sup>-1</sup>

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**Table 1**  
Composition of Ras Abu Fontas desalination brine.

| Element/Compound              | Concentration, g/L (where applicable) |
|-------------------------------|---------------------------------------|
| Ca <sup>2+</sup>              | 0.7                                   |
| Mg <sup>2+</sup>              | 2.5                                   |
| Na <sup>+</sup>               | 19.4                                  |
| Cl <sup>-</sup>               | 39.3                                  |
| SO <sub>4</sub> <sup>2-</sup> | 5.1                                   |
| NH <sub>3</sub>               | 6.32 10 <sup>-4</sup>                 |
| Br <sup>-</sup>               | 0.12                                  |
| pH                            | 8.86                                  |
| TDS                           | 71.3                                  |

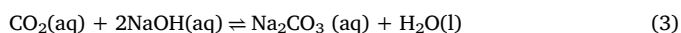
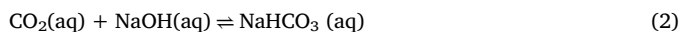
construction materials based in carbonates [8].

Our research team has proposed a route for the production of carbonate products, usable as construction materials, from captured CO<sub>2</sub> by carbonation of Mg-rich brines in alkaline aqueous media. We have successfully confirmed (i) the significant carbon capture potential of alkaline absorption of CO<sub>2</sub> using brines as the source of Mg [9] and (ii) the cementitious character of nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O) using two routes of activation [10]. During this work, this cementitious behaviour of nesquehonite was discovered unique in comparison to any outcome of any CCU or CCS mineralisation process. The great advantage of nesquehonite is its production in mild reaction conditions, i.e. there is no need for pressurised reactors or temperatures over 40 °C, which eases the economics.

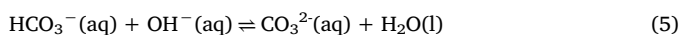
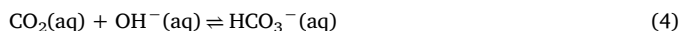
This paper proposes the conceptual design of a process able to produce nesquehonite from Mg-rich brines. In a first approach, we focused on Qatari desalination brines (see Table 1), which are rich in Mg (2.4–2.7 g/L) but with a significant amount of dissolved Ca (0.4–0.7 g/L). Calcium is an important interference in the production process of nesquehonite, since it has an impact on the development of Mg phases during its synthesis and during the development of cementitious properties, so a discussion on the ways to avoid that interference is provided. Therefore, the basic chemistry, the development of phases, and the alternatives for the design are investigated.

## 2. Chemistry of the capture process

The absorption process involves the dissolution of CO<sub>2</sub> (g) (Reaction (1), below) in an aqueous solution of elevated pH and its stabilisation as carbonate CO<sub>3</sub><sup>2-</sup> and bicarbonate HCO<sub>3</sub><sup>-</sup>. This transition to carbonate and bicarbonate accelerates the process since it sharply increases CO<sub>2</sub> solubility (Reactions (2) and (3)), although the pH to stabilise these anions needs to be increased up to 7–8 with additions of alkali, eg. sodium hydroxide, NaOH.



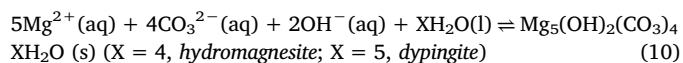
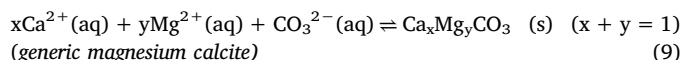
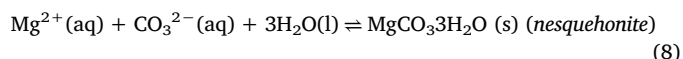
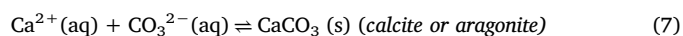
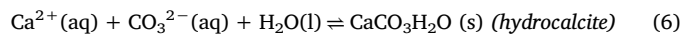
CO<sub>2</sub> establishes an equilibrium in water solutions and reacts with OH from the alkali, creating changes in pH due to water hydrolysis. Reactions (4) and (5) show the anions involved in Reactions (2) and (3):



The absorption of CO<sub>2</sub>(g) in water is limited by its solubility, which is very low at acid pH values, due to the thermodynamics of hydration of the CO<sub>2</sub> molecule. CO<sub>2</sub>(aq), also represented as carbonic acid H<sub>2</sub>CO<sub>3</sub>, is a weak acid that reduces the pH. Therefore, the main purpose of adding alkali is to increase this solubility and stabilise CO<sub>2</sub> as bicarbonate and/or carbonate.

When the Mg and Ca rich brines react with aqueous carbonates,

precipitation reactions are shown below:



These reactions occur at different rates and at different reaction conditions, which are discussed in the following sections. The stable phases for each metal under the expected conditions for CO<sub>2</sub> absorption with aqueous alkali (pressure lower than 5 atm, and temperature from 25 to 65 °C) are magnesite and calcite (Reaction (7)). However, both compounds are inhibited: first, the presence of Mg promotes the precipitation of the metastable monohydrocalcite CaCO<sub>3</sub>·H<sub>2</sub>O (Reaction (6)); and, second, the high energy required to remove the water molecules hydrating the Mg<sup>2+</sup> cation, the so-called cation barrier [11], prevents magnesite, MgCO<sub>3</sub>, and promotes the metastable nesquehonite first (Reaction (8)), and hydromagnesite-like compounds in a second stage (Reaction (10)). There are, of course, other undesired phases that may appear under uncontrolled reaction conditions. This is the case of magnesium calcites (Reaction (9)), which can be defined as calcites where part of the calcium has been substituted by magnesium in proportions close to 50% (mol/mol). The thermochemistry of these reactions is discussed in a further section below.

The literature shows several examples where the above aqueous carbonate chemistry is used for the design of a carbon capture process. A non-exhaustive list of these processes is shown in Table 2. The main development to date is the Calera process, where alkalinity is produced by the ABL process (Alkalinity Based on Low Energy), and produces a cementitious material based on amorphous carbonates of Calcium and Magnesium [8]. The main description of this development clearly discards the use of nesquehonite but focuses on materials such as bricks, drywall materials or even lightweight aggregates from the precipitation of different carbonates, e.g. CaCO<sub>3</sub>, amorphous MgCO<sub>3</sub> or Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> [8,12]. For these processes to be resource efficient, there is a strong need of alkalinity with low associated impact, so the preferred option is usually highly alkaline wastes, e.g. steel slags or fly ash [13,14]. However, one essential factor is the selection of the Mg<sup>2+</sup> source. Both carbon dioxide in flue gas and brines from desalination, as studied by several authors [15–17], are required to be locally available and close to each other in integrated power-water supply systems.

Calera failed in the development of large scale applications of the process due to doubts in the feasibility of the whole capture process. Also, recent trends in alkaline CO<sub>2</sub> capture do not focus on the production of nesquehonite as final product, but identify nesquehonite as a key solid phase in their development: for instance, during the carbonation of CO<sub>2</sub> curing concrete or cement pastes (e.g. [20]), in the development of mineral carbonation processes for storage routes [18,19], and in the production of stabilised nesquehonite only as a carbon sink [21,22]. Through the work developed by our research team, we add a new value to nesquehonite, i.e. its cementitious character, which could rebalance the design of some of these alternatives.

## 3. Experimental

In order to test the reactivity of Mg and Ca brines with carbonate and bicarbonate aqueous solutions from the alkaline absorption of carbon dioxide, several experiments have been carried out in order to quantify the yield of precipitation and identify the precipitated phases.

For each experiment, a 2L stirred reactor was used. Temperature

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