

Magnesium chloride as a leaching and aragonite-promoting self-regenerative additive for the mineral carbonation of calcium-rich materials



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ABSTRACT

Two approaches for the intensification of the mineral carbonation reaction are combined and studied in this work, namely: (i) the calcium leaching and aragonite promoting effects of magnesium chloride (MgCl_2), and (ii) the passivating layer abrasion effect of sonication. The alkaline materials subjected to leaching and carbonation tests included lime, wollastonite, steel slags, and air pollution control (APC) residue. Batch leaching tests were conducted with varying concentrations of additives to determine extraction efficiency, and with varying solids-to-liquid ratios to determine solubility limitations. Aqueous mineral carbonation tests, with and without the use of ultrasound, were conducted applying varying concentrations of magnesium chloride and varying durations to assess CO_2 uptake improvement and characterize the formed carbonate phases. The leaching of calcium from lime with the use of MgCl_2 was found to be atom-efficient (1 mol Ca extracted for every mole Mg added), but the extraction efficiency from slags and APC residue was limited to 26–35% due to mineralogical and microstructural constraints. The addition of MgCl_2 notably improved argon oxygen decarburization (AOD) slag carbonation extent under sonication, where higher additive dosage resulted in higher CO_2 uptake. Without ultrasound, however, carbonation extent was reduced with MgCl_2 addition. The benefit of MgCl_2 under sonication can be linked to the preferential formation of aragonite (85 wt% of formed carbonates), which precipitates on the slag particles in the form of acicular crystals with low packing density, thus becoming more susceptible to the surface erosion effect of sonication, as evidenced by the significantly reduced carbonated slag particle size.

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1. Introduction

Mineral carbonation is an attractive route for the storage of CO_2 due to the geochemical stability of the formed carbonates, and is also a potentially viable route for the valorisation of alkaline waste or low-value materials, such as industrial slags, ashes and tailings, due to the reduction of basicity, the predominant stabilization of leaching, and the formation of more marketable mineral products (Bobicki et al., 2012; Pan et al., 2012; Sanna et al., 2012; Bodor et al., 2013; Kirchofer et al., 2013). Much work has been done in recent years to identify suitable materials for mineral carbonation, to understand the fundamental mechanisms that control kinetics and conversion, and to develop processing routes that intensify the reaction whilst reducing energy demand (Zevenhoven et al., 2011; Santos and Van Gerven, 2011). Two main mineral carbonation

routes have been established: (i) indirect carbonation, wherein the alkaline-earth components (mainly Ca and/or Mg) are first extracted from the solids into an aqueous solution, which is then contacted with CO_2 for precipitation of the carbonates, and (ii) direct carbonation, wherein the solids (dry, wet or in aqueous slurry) are directly reacted with CO_2 , and thus the carbonate products are formed together with the inert and residual minerals. In either case, the mobility of the alkaline-earth elements from the solids is a major limitation for achieving high conversion rates and CO_2 uptake.

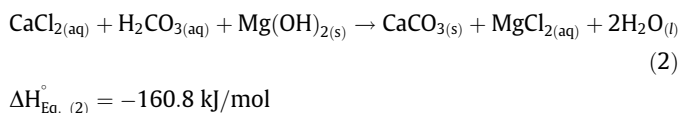
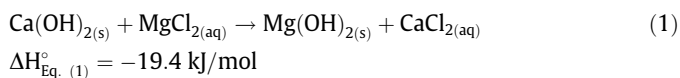
To overcome this problem, researchers have turned to finding suitable leaching agents, which ideally should have high extraction efficiency, but at the same time should have less affinity for the alkaline-earth elements than the carbonate ion (CO_3^{2-}), to allow the precipitation of carbonates upon pH-swing. Acetic acid (CH_3COOH) has been successfully applied for the production of precipitated calcium carbonate (PCC) from steel slag (Eloneva et al., 2008), but after extraction it is necessary to add a strong base

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(e.g. NaOH) to neutralize the acid and promote carbonate precipitation; the neutralized acetate can potentially be regenerated into acetic acid, but at a large processing cost. To avoid regeneration, [Eloneva et al. \(2009\)](#) also tested the efficacy of ammonium salts (NH_4Cl , $\text{CH}_3\text{COONH}_4$, NH_4NO_3) and found positive results with steel converter slag, but the efficiency was poorer for blast furnace and ladle slags; this was attributed to calcium being predominantly bound as silicates in these materials (as opposed to free lime (CaO) in converter slag). The loss of ammonia (NH_3) in the off-gas also becomes an added concern when using these additives ([Eloneva et al., 2011](#)).

In the present work, a novel approach to enhancing calcium mobility is investigated, namely the use of magnesium chloride (MgCl_2) as a leaching agent. This concept has its roots in a recent study conducted by our group ([Santos et al., 2012](#)) on the sonochemical synthesis at low temperatures of pure aragonite precipitates possessing novel crystal morphology (*hubbard squash-like*). Aragonite is a polymorph of calcium carbonate typically formed at higher temperatures (90–450 °C) and in marine environments ([Kitano and Hood, 1962](#); [Passe-Coutrin et al., 1995](#); [Santos et al., 2013b](#)). The strategy of using MgCl_2 to promote aragonite during mineral carbonation had been described in earlier studies ([Ahn et al., 2007](#); [Hu et al., 2008](#)), with the mechanism being tentatively attributed to the binding of Mg^{2+} to the calcite polymorph crystal surface, thus inhibiting its growth, and to the reduction in supersaturation with respect to $[\text{CO}_3^{2-}]$ as a result of pH reduction. [Santos et al. \(2012\)](#) found that by combining MgCl_2 with ultrasound, it is possible to obtain high purity aragonite at temperatures as low as 24 °C. It was also observed, in agreement with reported findings of [Xiang et al. \(2006\)](#), that MgCl_2 also acts as a calcium leaching agent, as upon its addition to a slurry of $\text{Ca}(\text{OH})_2$, the calcium becomes solubilised, while the magnesium precipitates as $\text{Mg}(\text{OH})_2$ (Eq. (1)). Subsequently, upon carbonation, the calcium precipitates as CaCO_3 , while the magnesium returns into solution with the chloride (Eq. (2)). Both steps are exothermic, but most of the reaction heat is released in the carbonation step.



These reaction steps are illustrated in [Fig. 1](#) with crystallographic data from [Ceulemans \(2011\)](#). At first, when magnesium chloride is added to a slurry of calcium hydroxide (portlandite), formation of brucite ($\text{Mg}(\text{OH})_2$) is seen. Once CO_2 is introduced into the slurry, carbonic acid reacts with dissolved calcium, forming calcite and aragonite polymorphs of calcium carbonate (the ratio of these depends on other reacting conditions, studied by [Santos et al. \(2012\)](#)). As the reaction progresses, carbonate diffraction peaks become predominant while brucite peaks shrink, indicating solubilisation back into magnesium chloride. If the reaction is halted prior to completion, the product will contain brucite; this is undesirable as it signifies loss of additive and low product purity. When the reaction is completed, only the diffraction patterns of calcium carbonates can be seen, meaning that magnesium chloride has been fully regenerated.

Key to these reaction steps are the greater solubility of CaCl_2 over MgCl_2 , and the lower solubility of CaCO_3 over Mg-carbonates ([Hu et al., 2008](#)). This mechanism prevents the formation of Mg-carbonates in the product, thus ensuring high CaCO_3 product purity and additive regeneration. Concurrent precipitation of Ca- and

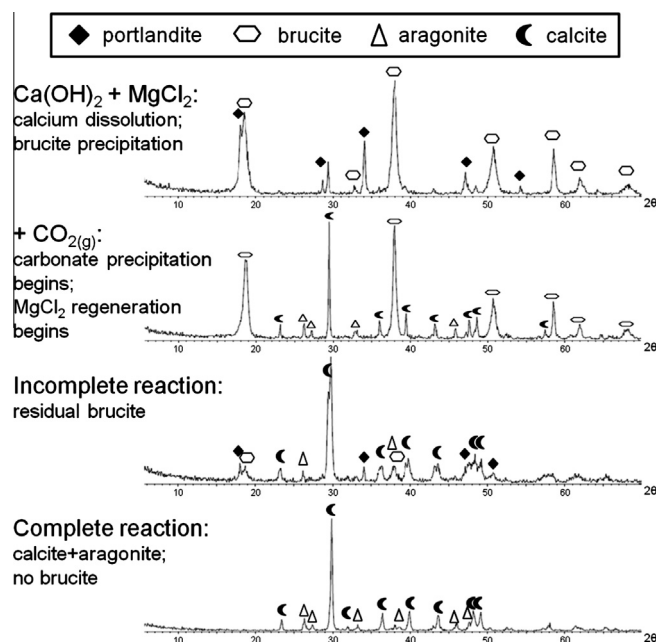


Fig. 1. Self-regenerative cycle of MgCl_2 as applied during carbonation of $\text{Ca}(\text{OH})_2$; adapted from [Ceulemans \(2011\)](#).

Mg-carbonates is also prevented since it would imply the formation of HCl in solution, unless this was neutralized with, for example, ammonia (NH_3) ([Ferrini et al., 2009](#)). As such, this self-regenerative mechanism also enables the re-utilization of the magnesium chloride-rich solution in further carbonation cycles without the need for purification or re-crystallization ([Ma et al., 2011](#); [Santos et al., 2012](#)). One constraint of this approach, however, is that it is applicable only to direct carbonation systems, as the leached solids, containing the precipitated $\text{Mg}(\text{OH})_2$, cannot be separated from the Ca-rich solution prior to carbonation. Besides leaching of CaO, MgCl_2 also has the potential to leach calcium from siliceous materials, as it is a known contributor to cement and concrete corrosion exposed to saline waters ([Kurdowski and Duszak, 1995](#)).

Based on these findings, the present work aims to study the calcium leaching efficiency of MgCl_2 for a variety of alkaline materials useful for mineral carbonation, with particular emphasis in accessing the ability of MgCl_2 to leach calcium from Ca-silicate, Ca-ferrite, Ca-sulphate and Ca-aluminate rich materials. Furthermore, this study also investigates the effect of MgCl_2 on the mineral carbonation kinetics and conversion. For this purpose, the methodology utilized in another of our studies, reported in [Santos et al. \(2013a\)](#), wherein both mechanical mixing and sonication were utilized for the carbonation of stainless steel slags, is herein adopted. In that study, the application of ultrasound was successfully shown to intensify the mineral carbonation reaction, via the reduction in particle size and the removal of passivating layers (residual silica and mainly calcitic precipitates), thus increasing the specific surface area and exposing the unreacted particle core to the reactive medium.

Here, it is theorized that by combining MgCl_2 with ultrasound during the carbonation of silicate-rich and microstructurally heterogeneous alkaline materials, the precipitated carbonate layer will become enriched in aragonite. This effect can have implications on the morphology and on the packing density of carbonate layer, given the different crystal shapes formed by each polymorph: rhombohedral and scalenohedral for calcite, and acicular (needle-like) for aragonite ([Santos et al., 2012](#)). In turn, the porosity/permeability of the passivating layer may improve, and it may become more fragile to abrasion/attrition (caused by inter-particles

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