

Abstract

The cement industry contributes around 5-7% of man-made CO₂ emissions globally because of the Portland Cement (PC) production. Therefore, innovative reactive magnesia cement, with significant sustainable and technical advantages, has been proposed by blending reactive MgO and hydraulic binders in various proportions. MgO is currently produced from the calcination of magnesite (MgCO₃), emitting more CO₂ than the production of PC, or from seawater/brine which is also extremely energy intensive. Hence this research aims to investigate an innovative method to produce MgO from reject brine, a waste Mg source, through carbon sequestration, by its reaction with CO₂, to provide a comparable low carbon manufacturing process due to the recycling of CO₂. The produced deposits are then calcined to oxides with potential usage in construction industry. The entire system is a closed loop to achieve both environmental optimisation and good productivity. This research focuses on the chemical manufacturing process, integrated with material science knowledge and advancements, instead of concentrating purely on chemistry evaluations.

Six series of studies were conducted, utilising MgCl₂, CaCl₂, MgCl₂-CaCl₂, MgCl₂-CaCl₂-NaCl, and MgCl₂-CaCl₂-NaCl-KCl to react with CO₂ under alkaline conditions. The precipitates include hydrated magnesium carbonates, calcium carbonates and magnesian calcite. Generated carbonates were then calcined in a furnace to obtain MgO, CaO or dolime (CaO•MgO). All six series of carbonation processes were carried out under a controlled pH level, to study the constant pH's effect on the process and resulting precipitates. Other controllable factors include pH, temperature, initial concentration, stirring speed, and CO₂ flux rate.

In an individual-ion system, sodium distorts the hydrated magnesium carbonates (HMCs) formation with the production of hydromagnesite (HM), dypingite (D) and nesquehonite (N) mixture in the short time when the pH is above 10. However, ammonia shows nesquehonite only because of its good buffering capacity and evaporation properties, providing gradual phase transformation. Nesquehonite is needle-like in shape, produced at a relative low temperature, low carbonates and low pH level. Dissimilarly, hydromagnesite and dypingite are rosette-like, flower-like or accumulated sheet-like morphologies, produced in the presence of sodium when pH \geq 10 or more complex systems. In terms of calcium carbonates,

calcite (C) is rhombic in shape, considered as the most stable formation, produced at an ambient temperature. While vaterite (V) is spherical in shape, produced at a lower supersaturation, and aragonite (A) is arrow-like in shape, produced at a high temperature (60 to 80°C). Both vaterite and aragonite are metastable phases, and transfer into calcite finally in the ambient surroundings.

In a dual-ion system, the importance of parameters were investigated and ranked as pH > temperature > CO₂ infusion rate > stirring speed during the carbonation process. Magnesian calcite has four stages of formation: initial stage, intermediate stage, transitional stage and completed stage, dependent on magnesium incorporation within the precipitates. Regarding the mineralisation process, carbonates tend to aggregate into granules of the more abundant element of the initial reactants, such as when reactants are MgCl₂ > CaCl₂ in concentration. The formation mechanism from inner to outer layers of produced particles is magnesium calcium carbonates, calcium carbonates, and magnesium carbonates respectively. A higher calcined temperature requires a longer time to accomplish the oxides reactivity tests because of their reduced porosity and particle sizes. The decarbonation process happens at around 300-600°C for magnesium carbonates, and > 700°C for calcium carbonates. All three heating profiles 650°C, 800°C, and 1000°C are not adequate to fully breakdown the carbonates.

In a multiple-ion system, both sodium and potassium addition accelerate the magnesium participation, and sodium has a better performance than potassium in magnesium capture. Sodium addition increases the impurity level and extends the oxides' completion time in a reactivity test, while the potassium has the propensity to reduce this time.

In conclusion, the optimum parameters for the production of the carbonated precipitates are: 0.25MgCl₂ + 0.05CaCl₂ + 2.35NaCl + 0.05KCl, 700rpm stirring speed, 25°C room temperature, pH=10.5, and 500cm³/min CO₂ infusion rate. Reaction time is within a day. These parameters are chosen based on the sequestration level, particle performance morphology and the operational convenience. The optimum calcination parameters are at 800°C heating temperature with a 4h retention time.