CO₂ mineralisation of brines with regenerative hydrotalcites in a cyclical process

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Abstract

CO₂ mineralisation is a process that can store the CO₂ as a solid mineral permanently, to mitigate carbon emissions. Brines rich in alkaline earth metals present an attractive opportunity to trap CO₂ in the form of insoluble carbonates. Moreover, this can be accomplished, as shown in this work, using flue gas concentrations of CO₂ and at near-ambient temperatures, eliminating the need for energy-intensive CO₂ capture step and heating of dilute aqueous solutions. The conventional alkaline substances to neutralise the solution, such as sodium hydroxide or amines, are costly, and the processes required to regenerate them (e.g. distillation or electrolysis) are energy intensive, which hinders the feasibility of this CO₂ sequestration approach. We herein developed a process to remove chloride anions from alkaline brines by ion exchange, using lamellar structured materials, namely hydrotalcites (HT). These HT, which are layered double hydroxides prepared by co-precipitation method, release hydroxyl groups in exchange for chloride, sufficiently raising the pH of brines to enable the precipitation of carbonates during CO₂ mineralisation. Several calcined-HT were synthesized using different ratios of magnesium and aluminium content, and various reaction temperatures and solid-to-liquid ratios were investigated for chloride removal. Moreover, the HT materials are recyclable for multiple usage by taking advantage of the HT's 'memory effect' property. Gaseous CO₂ and Na₂CO₃ solution were tested as the recharging agents, to replace the chloride anions from the spent HT interlayers and intercalate with HCO₃⁻ or CO₃²⁻, followed by a calcination process to produce the reusable calcined-HT. Several reaction cycles were conducted to evaluate the reusable property. It was found that the chloride removal efficiency remains over 70% after five cycles, and calcium utilisation efficiency of the brine carbonation process can surpass 90%. This unique cyclical closed-loop HT process thus presents a more cost- and energy-effective approach to brine carbonation than previous studies. In addition, the produced carbonates are of sufficient quality for a variety of applications that can further reduce the process cost of this type of CO₂ sequestration.

Keywords: Layered double hydroxide; carbon capture and sequestration; regenerative additive; dechlorination; alkaline brines; precipitated calcium carbonate.

1. Introduction

As the global economies and population continue to grow and prosper, and greenhouse gas emissions continue unabated, we are facing the challenge to tackle climate issues. The term climate change has now turned to climate emergency, and human beings are approaching to so-called tipping point [1], beyond which irreversible climate and environmental changes can occur. The fossil fuels we use for power generation, transportation and housing, constitute the most significant contributors to greenhouse gas emissions. Around the world, governments are active in releasing new regulations to restrict carbon emissions or to add carbon taxes to slow down the emissions, and many have set the goal to be net zero by 2050 [2]. To achieve this goal, renewable and clean energy, such as wind and solar, should be exploited to generate electricity or develop hydrogen energy, and energy efficiency should be improved to cut down the demand for energy. Carbon capture, utilisation and storage (CCUS) plays a crucial role in helping industrial plants to mitigate emissions. Carbon capture involves the use of separation processes to concentrate the CO₂ for latter storage, sequestration or utilization. CO₂ utilisation is attractive as it generates revenue to enable CO₂ capture, and refers to converting CO₂ to produce fuels, polymers, chemicals, food and construction materials [3].

Converting CO₂ to carbonates through mineralisation is a significantly important approach due to its huge processing capacity compared to other technologies, and also its ability, with the right feedstock and process, to accomplish capture, sequestration and utilization simultaneously [4]. Mineralisation processes transform gaseous CO₂, in its pure or impure form (i.e. using flue gases directly), into solid carbonates by reaction with alkaline earth metals, and this reaction is favoured by thermodynamics: it is spontaneous and exothermic. However, the challenge is to develop CO₂ mineralisation technologies that are fast enough to meet emissions rates from large point sources and to keep reactor sizes reasonably small, and that are cost-effective and energy-efficient enough to result in net-CO₂ sequestration that is economically viable. For example, Mg(OH)₂ can be extracted from serpentinite and then be used for CO₂ mineralisation, however, this is energy intensive according to life cycle assessment calculations because the process demands elevated temperatures for extraction and mineralisation [5]. In comparison, calcium carbonates more readily form due to its lower Gibbs free energy, and finds wider range of applications, such as in paper, paint and pigments [6].

Brines are concentrated seawater, such as the concentrate produced by desalination plants, and contain high concentrations of Ca²⁺ and Mg²⁺ already in dissolved state, and thus ready to react with CO₂. This advantage over the carbonation of solid minerals, coupled with huge amount of brines across the world, make this a potential feed stock for mineralisation processes. In our previous study, we aimed to convert these cations into solid carbonates to

fix CO₂ [7, 8]. Basic substances were demanded to balance the solution acidification that results from CO₂ injection (and carbonic acid dissociation, accelerated with nickel nanoparticles as catalysts for hydration reaction [9, 10]) coupled with alkaline earth metal precipitation and chloride ions accumulation. Therefore, NaOH and MEA solutions were tested, and they both performed well in brine carbonation processes, which were optimized by adjusting the operational conditions. However, these solutions can only be used once, and would require energy intensive regeneration via distillation or electrolysis for further reuse. In the present research, an alternative approach is developed to replace these base solutions and to use the materials that can be easily regenerated and recycled, to cut down the cost and energy demand. This approach uses a class of materials known as hydrotalcites (HT).

HT compounds are magnesium aluminium hydroxycarbonates, referring to the form $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-}_{x/n}) \cdot mH_2O$, which are composed of double layered hydroxides, with interlayers containing anions or water molecules [11]. The structure of this compounds is similar to brucite (Mg(OH)₂), comprising octahedra of Mg²⁺ cross-linked by OH⁻, and each sheet is stacked to form the three-dimensional structure [12]. The key feature of HT is that they are formed by sheets that are positively charged with the interlayer occupied by different anions to neutralise the charge, and H₂O molecules filling the interlayer space. Preparation method is classified into the following main categories: precipitation method [13, 14], preparation with anions rather than carbonates, hydrothermal treatment [15], anionic exchange method, urea hydrolysis method, among others [16]. HT have ion exchange property that can remove various anions from aqueous solutions [17]. The interlayers ions can be replaced by other anions depending on the following order [11]: CO₃²⁻ > SO₄²⁻ > OH⁻ > F⁻ > Cl⁻ > Br⁻ > NO₃⁻ > I⁻. This ion exchange property is governed by the ionic radii and the Gibbs free energy of reaction [18]. Given the high affinity of CO₃²⁻ for HT, CO₃²⁻ is used as intercalated anion for the sample preparation in this research. In fact, HT are potential candidates to capture CO₂ in liquid phase from the ambient atmosphere [19].

Another useful property of HT is their ‘memory effect’ [16]. This refers to ability of HT to be reconstructed via reacting with stronger anions in solution, and subsequently undergoing calcination process. The calcination process of regenerated HT is accompanied by an increase in surface area, as the released CO₂ and H₂O can expand the surface of interlayers. This can thus be implemented to regenerate the materials after anions removal process. [16] According to the selectivity sequence of anions, carbonate anions are significantly favoured by the interlayers, therefore carbonate anions can replace any other anions in the solution, including chloride as relevant for brines. The regeneration of spent HT-Cl can also be implemented with thermal treatment by heating the samples to 550-800 °C, to release hydrochloric acid [20]. However, higher calcination temperatures, over 600 °C, can lead to

loss of ion exchange capacity because the layered hydroxide decomposes to MgO and MgAl_2O_4 [21]. HT finds applications in various fields due to its unique properties, such as: flame retardant in industry; antacid or stabilizer in medicinal pharmaceuticals [22]; absorbent or catalyst and catalyst support [16, 23]. In terms of HT application in salt solutions, Dindi et al. [24] investigated a method to capture CO_2 using desalination brine, by producing NaHCO_3 and HCl with the use of HT for ion exchange. The process resulted in concentration reductions of 70% for Cl^- and 20% for Na^+ in the brine, and 6 cycles of thermal regeneration was tested, with slow degradation observed due to spinel formation. Kameda et al. [25] tested ion removal from CaCl_2 solution using calcined-HT, and found that it was capable of simultaneously removing Ca^{2+} (up to 93%) and Cl^- (up to 98%) from the solution; Cl^- by ion exchange with CO_3^{2-} , and Ca^{2+} by supersaturation and precipitation from solution as $\text{Ca}(\text{OH})_2$.

In this study, artificial brines are implemented to undergo the chloride removal process with calcined-HT, thereby producing alkaline solution to proceed through CO_2 mineralisation reaction. Calcined magnesium and aluminium oxides with different Mg/Al molar ratios were prepared by thermal composition of synthetic hydrotalcite prepared via co-precipitation method, and optimal operational conditions were evaluated to achieve highest chloride removal efficiency. The CO_2 mineral sequestration were carried out in a batch reactor, using simulated flue gas (12 vol% CO_2) and near-ambient temperature (30 $^\circ\text{C}$). In addition, HT was regenerated with two different approaches to investigate the feasibility to recycle this material based on its memory effect. The crystal structure of mineral samples before and after different steps of process were characterised to assess stability and degradation.

2. Experiment and method

2.1 Materials preparation

Magnesium nitrate hexahydrate and aluminium nitrate nonahydrate from Fisher Scientific, and calcium chloride dihydrate ($\geq 99\%$), sodium carbonate ($\geq 99.99\%$) and sodium hydroxide ($\geq 97\%$) from Sigma-Aldrich, were used as acquired. The HT were prepared via standard co-precipitation method [11, 26]. In a five-necked jacketed beaker, 500 mL 0.2 M Na_2CO_3 solution was placed and kept at 40 $^\circ\text{C}$ with circulated warm water. Then, a volume of 500 mL mixed solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3 M or 0.4 M) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1M), prepared with the molar ratios of 3 or 4, was slowly injected into the flask using a peristaltic pump (323 series from Watson-Marlow Pumps) set at a very low flow rate. The pH value of the reacting solution was continuously monitored and kept at 10 ± 0.1 via controlling the pumping rate of 1 M NaOH solution, based on the isoelectric point theory that CO_2 absorption is favoured when the

preparation pH value is equal to, or higher than 10 [27]. The slurry mixture was stirred vigorously to assure the pH of local portions of the solution is similar to that of the bulk. Stirring lasted for two hours, after which the obtained precipitates were filtered and washed with deionised water until the filtrate was neutral. Then the precipitates were dried at 60 °C for 24 hours to obtain the synthesized HT. It is known that the crystallinity and morphology of HT can be improved via further aging process or with thermal treatment [28]. Since we aimed to produce regenerative materials with Cl removal function, it made sense to select a route with short processing time. Thus, calcined-HT (CHT) obtained from synthesized HT by heating at 500 °C for 2 hours in standard atmosphere.

The produced CHT were characterised by N₂ absorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). The specific surface area and porosity data were determined by N₂ absorption using JW-BK200 from JWGB Sci. & Tech. The samples were first degassed at 300 °C for over 3 hrs under vacuum, the specific surface area was analysed by Brunauer-Emmett-Teller (BET) method, and porous volume and pore size distribution were obtained from N₂ desorption isotherms by Barrett-Joyner-Halenda (BJH) method. XRD data were collected and analysed using X'Pert Pro Multipurpose from Panalytical, and diffractograms were collected using Cu radiation at scanning speed of 1.3 °/min and step width of 0.02°. TGA data was collected under N₂ with the heating rates at 10 °C/min using Mettler Toledo TGA 2. The morphological and elemental analyses of samples and precipitates were conducted using a JEOL JSM-5600LV SEM-EDX.

2.2 Chloride removal process

Artificial brine was prepared with CaCl₂ at a concentration of 0.020 M, thus containing 1600 ppm Cl⁻. To more closely simulate desalination brine, some tests were also conducted using solution containing both 0.020 M CaCl₂ and 0.60 M NaCl. Chloride removal performance was conducted using CHT prepared using two Mg/Al molar ratios (3 and 4), under two temperatures (40 °C and 60 °C) and three solid/liquid ratios (0.010 g·mL⁻¹ to 0.020 g·mL⁻¹). Different removal temperatures were tested to determine the optimal reaction temperature. Another key parameter that influences the removal efficiency is the solid/liquid ratio, which refers to the ratio of CHT to brines. All experiments were performed with constant removal reaction time, 2 hours under magnetic stirring, as it was investigated that this time length is sufficient for the reaction to reach equilibrium in this study.

The concentration of Ca²⁺ in the equilibrated solutions was measured by ICP-OES using Vista MPX from Varian Inc., and concentration of Cl⁻ was measured with ISC-1000 Ion Chromatography System from Thermal Scientific based at Newcastle University. The chloride

removal efficiency is calculated via Eq. (1), where $C_{Cl^{-}(\text{outcome})}$ and $C_{Cl^{-}(\text{initial})}$ represent the concentration of chloride after reaction and initial condition, respectively. The solids recovered after equilibrium are termed HT-Cl, being hydrotalcite containing chloride in its interlayer.

$$\text{Chloride removal efficiency(\%)} = \left(1 - C_{Cl^{-}(\text{outcome})} / C_{Cl^{-}(\text{initial})}\right) \cdot 100 \quad (1)$$

2.3 HT-Cl regeneration via ion exchange method

The regeneration method is based on the theory of ion exchange, due to carbonate/bicarbonate ions being more susceptible to attaching to the interlayers of HT compared to the other mono- or divalent anions [11, 29]. Two scenarios to release chloride from HT-Cl in aqueous solution were tested in this work: (i) using gaseous CO_2 injection, and (ii) adding Na_2CO_3 to the solution.

In the first scenario, we add HT-Cl sample to DI water and inject pure gaseous CO_2 to produce carbonate/bicarbonate ions (ratio between two species depends on the solution pH), thus releasing chloride from the interlayers of HT. Solid to liquid ratio used was $0.025 \text{ g}\cdot\text{mL}^{-1}$ and the gas flow rate was 160 mL/min , which was injected into the solution intermittently to ensure the pH value did not decrease sharply (CO_2 injection stopped when the pH value reduction was over 3.0 compared to initial pH value). The total duration CO_2 of injection depended on the solution volume, with a target time of $0.07 \text{ min}\cdot\text{mL}^{-1}$, after which solutions were magnetically stirred until equilibration. In the second scenario, HT-Cl samples were added to $0.1 \text{ M Na}_2\text{CO}_3$ solution at a solid to liquid ratio of $0.025 \text{ g}\cdot\text{mL}^{-1}$, and magnetically stirred until equilibration. Both of these two experimental scenarios were conducted at room temperature (20°C) and the solutions were stirred for 2 hours to allow for equilibration. After, the solids were recovered by filtration, and dried to achieve carbonate or bicarbonate bonding within the regenerated HT. The calcination process was undertaken at 500°C for 2 hours to obtain regenerated CHT. Several cycles of Cl^{-} removal experiment and regeneration process were applied to each synthesized HT to determine regeneration efficiency. This is expressed according to Eq. (2), which compares the molar amount (M) of chloride was recovered in the regeneration step of the current cycle to the preceding Cl^{-} removal amount in the same cycle. Values lower than 100% suggest irreversible binding or entrapment of Cl^{-} within the HT structure.

$$\text{Regeneration efficiency(\%)} = \left(M_{Cl^{-}(\text{recovered, current cycle})} / M_{Cl^{-}(\text{removed, current cycle})}\right) \cdot 100 \quad (2)$$

2.4 CO₂ uptake

The dechlorinated brine solutions were used to fix CO₂ by precipitating carbonates, either for permanent storage or for utilization in place of natural carbonates. To simulate an industrial implementation without the need for pre-carbonation CO₂ capture, the CO₂ absorption was performed with 12 vol% CO₂ simulated flue gas, and the temperature used was 30°C, to avoid the need for heating in an industrial implementation. Both CO₂ capture and heating of aqueous solutions are energy-intensive processes, and thus have a significant effect on the net CO₂ sequestration of a mineral carbonation process. As such, the present process aims at minimizing energy requirements and maximizing net CO₂ sequestration. The experiments were conducted with 200 mL screwed reactor with three ports on the cap to fix the pH probe, thermocouple and bubble generator. Flue gas was bubbled into the solutions obtained from Cl⁻ removal step, and the pH was monitored in real-time to terminate the process and the pH was 8 in this study when high calcium conversion efficiency is achieved and before further acidification leads to carbonate re-dissolution. The solution was magnetically stirred at the rate of 500 rpm throughout the process. The final Ca²⁺ concentration, post-carbonation, was measured with ICP-OES, and calcium conversion efficiency (CCE) was calculated according to Eq. (3). The carbonate precipitates were filtered and dried prior to characterization.

$$\text{Ca}^{2+} \text{ conversion efficiency}(\%) = \left(1 - C_{\text{Ca}^{2+}(\text{outcome})} / C_{\text{Ca}^{2+}(\text{initial})}\right) \cdot 100 \quad (3)$$

3. Results and Discussions

3.1 Characterisation

The XRD diffractograms of calcined and not-calcined HT, prepared with different ratios of Mg/Al, are shown in Fig. 1. The samples before calcination are well crystallised and layered materials, attributing to magnesium aluminium hydroxycarbonate, while they turn to amorphous phases and less crystallised materials after calcination. The poorly crystallised condition is due to the disorder of the interlayers and lack of symmetry of the structures. The crystallinity increased with the higher Mg/Al ratio of 4. The interatomic distance of the d₀₀₃ layer, which represents the basal spacing of two host layers [29], also became shorter with higher Mg/Al ratio. The same trend was also obtained for d₀₀₆. The characteristic diffraction peaks for such HT material appear at 2θ values of 11.02°, 23.55°, 34.84°, 39.03°, 46.29°, 60.96° and 62.26° [30]. After calcination process, the structure of hydrotalcite was collapsed and converted to a mixture of oxides of magnesium and aluminium.

Fig. 1. XRD patterns of hydrotalcites and calcined hydrotalcites with different Mg/Al ratios.

The morphologies of these samples were characterised by SEM/EDX. The rosette-shaped hydrotalcite, produced under pH value of 10, is shown in Fig. 2, with the layered structure visible. The porous sponge-like morphology still maintains after calcination, which means that the micro-scale layered structure is not affected by thermal decomposition as much as the atomic-scale crystalline structure.

Fig. 2. SEM images of samples: (a) hydrotalcite (Mg/Al at 4); (b) calcined hydrotalcite (Mg/Al at 4); (c) calcined hydrotalcite (Mg/Al at 3)

According to semi-quantitative EDX analysis of elemental composition, the Mg/Al atomic ratio for samples prepared at 3 and 4 are 3.02 and 3.51, respectively. The Mg/Al ratios of the final products are thus close to the values used in the original stoichiometries.

The TG and DTA curves for HT samples prepared with Mg/Al ratio of 4, and before calcination, are shown in Fig. 3. There are three main endothermic weight loss peaks appearing, which represent the loss of weakly bonded interlayer water molecules up to around 220°C for the first weight loss peak, and the loss of chemically bonded hydroxyl and carbonate/bicarbonate

interlayer anions occurring, from 300 to 600 °C, for the second (major) and third (minor) peaks [31]. It has been reported that extrinsic water placed in the multilayers on the surface of samples is lost at 60 °C, while the intrinsic water starts to be lost above 150 °C [32]. It has also been reported that most of the CO₂ release occurs before 500 °C, with 20-30% remaining and being released at 600 °C and 900 °C [33]. However, high temperature CO₂ release is accompanied by migration of Al ions in the calcined material, and thus loss of structure [33]. As such, and given the TGA results obtained, all the prepared HT samples were calcined at constant temperature of 500 °C to produce CHT. By weighting the synthesized HT samples before and after calcination process, there was around 41-43% weight loss, which agrees with the weight loss observed in the TGA, and can thus be mainly assigned to the release of CO₃²⁻/HCO₃⁻ and OH groups as H₂O_(g) and CO_{2(g)}, respectively.

Fig. 3. TG-DTA diagram for synthesized hydrotalcite (Mg/Al = 4) before calcination.

3.2 Cl removal process

The ion exchange ability of the CHT prepared is evaluated with the artificial brine to investigate the effect of Mg/Al ratio at different temperatures and solid/liquid ratios. The effect of temperature on Cl⁻ removal was first investigated under 40°C and 60°C with different Mg to Al ratios with a fixed solid to liquid ratio of 0.014 g·mL⁻¹; this value was selected to attempt to check the temperature effect slightly outside the optimal condition, and the results are illustrated in Table 1. The results indicate that higher temperature can lead to higher Cl⁻ removal efficiencies at both Mg/Al ratios, which means that higher temperature can help Cl⁻ ions penetrate the interlayers and attach to the hydrotalcite. Ahmed and Gasser [34] reported thermodynamic data on the adsorption process of layered double hydroxides, and attributed higher adsorption at higher reaction temperatures to a more negative Gibbs free energy change, which is in agreement with the behaviour of endothermic processes at higher

temperatures. Based on these results and reasoning, 60°C was applied in the subsequent experiments.

Table 1. Chloride removal efficiency with different synthesised CHT using S/L of 0.014 g·mL⁻¹.

Mg/Al ratio	Reaction temperature at 40°C	Reaction temperature at 60°C
3	83.1%	87.5%
4	85.3%	88.9%

Solid to liquid ratios ranging from 0.010 to 0.020 g·mL⁻¹ were tested with different CHT samples, and results are shown in Fig. 4. These S/L ratios are approximately varied from 0.6 to 1.2 times the stoichiometric amount needed for 0.040 M Cl⁻ solution. As expected, higher removal efficiencies can be achieved by increasing the CHT mass, and the efficiencies obtained closely correspond to stoichiometry, except at the highest dosage where the efficiency comes close to, but does not reach 100%. At low S/L ratio, all the active sites are relatively fully exposed for adsorption, but the availability of higher energy sites decreases with higher particle concentration due to competition [35]. Moreover, the CHT prepared with greater Mg/Al ratio showed slightly better Cl⁻ removal performance. The Mg/Al ratio affects the number of basic sites, according to the research of Nakatuska et al. [36], and basic sites increase with the Mg/Al ratio. MgO content contributes with two types of basic sites, O₂⁻ and OH⁻, on the surface, whereas Al₂O₃ does not contribute to strong basic sites on the surface [37].

Fig. 4. Cl⁻ removal efficiency with CHTs under different ratios.

The BET specific surface area, N₂ adsorption and desorption isotherms, and pore size distribution were analysed at 77K, and data is shown in Fig. 5 and Table 2. The specific surface area expanded after calcination, since the CO₂ release between layers can enlarge the pores of samples. The specific surface area of the sample with Mg/Al ratio at 4 is greater than that at 3, as is its average pore size. The larger pore size of in the mesoporous region and greater specific surface area contributes to the observed higher Cl⁻ removal efficiency. After the Cl⁻ removal experiment, the specific surface area reduced, attributing to the Cl⁻ ions captured between the interlayers, and the average pore size after reaction became smaller compared to before reaction. It can be seen from Table 2 that the specific surface area and total pore volume of the reacted sample decreased even lower than that of the original pre-calcination HT.

Fig. 5. N₂ adsorption/desorption isotherms and pore size distribution of hydrotalcite (red, right) and calcined hydrotalcite (black, left).

Table 2 specific surface area and pore size distribution

Sample	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
Hydrotalcite (Mg/Al= 4)	39.3	0.299	13.67
CHT (Mg/Al=3)	181.4	0.971	12.03
CHT (Mg/Al=4)	191.7	0.858	14.16
CHT (Mg/Al=4) after Cl ⁻ removal reaction	12.4	0.078	9.28

As shown in Fig. 5, the sample post-calcination exhibits Type II and Type IV isotherm classification in combination with a H3 type hysteresis loop. In contrast, the sample pre-calcination exhibits Type I isotherm at relative pressure (P₀/P) lower than 0.5, and turns to Type II isotherm with higher relative pressure with Type H3 loop [38]. Fig. 5 also contains sub-

plots of the mesopore size distribution of these two samples, based on BJH calculation method using desorption isotherms. The calcined sample has a sharp peak at around 22nm, while the sample before calcination displayed a sharp peak at 4nm and broader mesopores distribution. This means that the thermal treatment promotes larger mesopore formation and influences the pore size distribution.

The XRD diffractograms of CHT before and after Cl^- removal reaction is shown in Fig. 6. The XRD pattern of the calcined material was restored to a crystalline structure corresponding to pre-calcination HT after the sample was exposed in the aqueous solution to Cl^- , which refers to the ‘memory effect’ property of HT [16]. This allows the samples to be regenerated for cyclical usage. Fig. 6 presents an SEM image of sample after Cl^- removal reaction, and it contains plate-like morphology reminiscent of fresh HT.

Fig. 6 XRD diffractograms of CHT before and after Cl^- removal reaction (left) and SEM image of sample after Cl^- removal reaction (right).

The effect of sodium chloride on the absorption process was also investigated, because of its high concentration in desalination brines. The experiment was carried out with the CHT sample with Mg/Al at 4, S/L at $0.020 \text{ g}\cdot\text{mL}^{-1}$, under 60°C , in solution with 0.020 M CaCl_2 and 0.60 M NaCl . In the presence 0.60 M NaCl solution, the total amount of chloride anion removal was 2327 ppm, which is greater than the amount of Cl^- (1600 ppm) contributed by the CaCl_2 content, and greater than the amount that the same sample under the same S/L ratio achieved in absence of NaCl (Fig. 4). This shows that CHT is capable of removing Cl^- that originates from Ca^{2+} as well as Na^+ , thus extending its applicability to various types of brine.

3.3 Cycle assessment and regeneration process

The possibility to regenerate and reuse hydrotalcite can significantly decrease the operational costs on the whole process. The crucial property of this material is the so called 'memory effect', which can benefit the regeneration process. TG/DTA analysis data for a spent sample (after chloride removal) is shown in Fig. 7. The two main peaks are similar to those in the HT before calcination, however, the first weight loss peak is shifted about 20 °C lower compared with the HT (Fig. 3). This can be explained by the interaction of chloride ions weakening the interlayer water [39].

Fig. 7 TG/DTA curves for spent HT sample after Cl⁻ removal reaction.

Based on the anion absorption sequence aforementioned, carbonate and bicarbonate anions were deployed to be ion exchangers. Thus, to test recyclability of CHT, five cycles of Cl⁻ removal and regeneration with gaseous CO₂ and Na₂CO₃ solution, followed by calcining to 500 °C for 2 hours, were used. The comparative results are presented in Fig. 8 and Fig. 9.

With the use of Na₂CO₃ solution for regeneration (Fig. 8), the Cl⁻ removal efficiency can be maintained above 80% under two S/L ratios tested, 0.015 and 0.020 g·mL⁻¹. It is concluded that regeneration with Na₂CO₃ is promising because of the relatively high pH of Na₂CO₃ solution, allowing the structure to be restored well during the regeneration process. The higher S/L ratio at 0.020 g·mL⁻¹ achieves higher Cl⁻ removal efficiency in the first cycle (98%), and with the increasing number of the experimental cycles the Cl⁻ removal efficiency gradually declines, but remains above 83% after five cycles. The Na₂CO₃ regeneration efficiency was not as high with S/L at 0.015 g·mL⁻¹. The reason is that more chloride anions are adsorbed per unit mass of HT, chloride anions occupy more space within the HT interlayers and block pores, which demands stronger ion exchange process to remove them.

Fig. 8 Recycling process performance with multiple Na₂CO₃ regeneration cycles of CHT under varying S/L ratios; chloride removal efficiencies (left axes) and Na₂CO₃ regeneration efficiencies (right axes).

The results for the use of CO₂ injection into the HT-Cl solution for regeneration are shown in Fig. 9. This method can save process cost, and thus energy, because no chemicals are used, and this source of CO₂ can be achieved from the calcination process, as the CO₂ can be used circulated. The Cl⁻ removal efficiency can be also kept above 90% up the third cycle under higher S/L, as in the case of Na₂CO₃; however, the efficiency of CO₂-regenerated CHT sharply decreases thereafter. Because the CO₂ was injected continuously into the regeneration solution, the pH value eventually became too low after several rounds of experiments. The pH value dropped below 7.0 in the third cycle regeneration, which led to the HT being exposed to acid condition that eventually degraded the structure of the layered double hydroxide. Under this scenario, some mesopores collapse due to the host layers being brucite-like Mg(OH)₂, which is basic and can be dissolved in acid circumstance [40]. This was confirmed from the BJH desorption pore size and pore volume, presented in Table 3. As a result, both Cl⁻ removal efficiency and CO₂ regeneration efficiency drastically decreased in the fourth cycle, and a fifth cycle was not run due to insufficient solids being recoverable from regeneration.

Fig. 9 Recycling process performance with multiple CO₂ regeneration cycles of CHT under varying S/L ratios; chloride removal efficiencies (left axes) and CO₂ regeneration efficiencies (right axes).

Table 3. Surface area and pore size distribution of regenerated CHT samples by CO₂ gas

CHT sample	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
Mg-Al-O Mg/Al=4	191.7	0.858	14.16
1 st regen by CO ₂	195.2	0.412	7.26
3 rd regen by CO ₂	190.9	0.391	5.36

It was found, based on EDX spectra analysis shown in Fig. S1 and Fig. S2 in the Supplementary Material, that there was significant amount of Cl⁻ ions remaining on the host layers of regenerated CHT after the fourth cycle: 0.47 wt.% and 0.13 wt.% respectively, for CO₂ and Na₂CO₃ regeneration processes. With the regeneration process not removing the Cl⁻ content entirely via ion exchange, the Cl⁻ removal efficiency in the next cycle decreased. In addition, that increase in Ca signal from EDX might be due to CaO, and CaO content of the regenerated HT increased over each cycle, given that 1.24 wt.% and 1.63 wt.% of Ca²⁺ was detected by SEM-EDX after the fourth cycle with CO₂ and Na₂CO₃ regeneration, respectively. Accumulation of CaO in the HT would lead to formation of CaCO₃ during the regeneration process, which then cannot be decomposed with the calcination temperature at 500°C, as this is below the decomposition temperature of calcium carbonates [41].

The XRD patterns of spent HT-Cl samples, having undergone various cycles of regeneration via the two approaches discussed are shown in Fig. 10. The main structural features of hydrotalcites are reconstructed well after each generation, however, the crystallinity degree of the samples decreased with the increasing regeneration cycles. A new peak appears at 29.4° 2θ, which can be assigned to calcite [42]. The intensity of this calcite peak is lower for the samples regenerated with gaseous CO₂ than for the samples regenerated with Na₂CO₃ solution, and in the latter case grow stronger with each passing cycle. In the case of Na₂CO₃

regeneration, the accumulation of calcite attached on the HT occurred due to the higher pH value of the solution during regeneration allowing for precipitation of calcium carbonate. The calcite peak disappeared in the fifth cycle with CO₂ regeneration due to the pH of the solution declining below 6.0 during CO₂ injection, which dissolves the accumulated carbonate back to the solution.

Fig. 10 XRD patterns of HT-CI collected after various cycles of regeneration using CO₂ (left) and Na₂CO₃ (right), after Cl⁻ removal reaction.

The calcite formation, accumulation, and eventual disappearance in the case of CO₂ injection, is also confirmed from the XRD patterns of CHT prior to Cl⁻ removal reaction, as shown in Fig. 11. The carbonate was not decomposed during calcination because the temperature is not sufficient. The two main broad peaks in Fig. 11 are assigned to periclase (MgO) [33], which forms from the heat treatment of the double layered hydroxide.

Fig. 11 XRD patterns of CHT collected after various cycles regeneration using CO₂ (left) and Na₂CO₃ (right), after calcination.

SEM images of HT samples after first and fourth regeneration cycle using gaseous CO₂ are shown in Fig. 12. It displayed that the structure is plate-like and there were rosette-shaped particles on the surface, but the higher order structure seen for the fresh HT (Fig. 2) degrades as cycles pass. This indicates that the regeneration process cannot fully reconstruct the original morphology of hydrotalcite, which gradually impacts the Cl⁻ removal performance previously presented.

Fig. 12 SEM images of HT sample after first regeneration (left) and fourth regeneration (right) using gaseous CO₂.

3.4 CO₂ uptake

CO₂ uptake performance of the dechlorinated brine was investigated using a batch reactor and simulated flue gas (12 vol% CO₂). Dechlorinated solution has suitable alkaline pH and contains Ca(OH)_{2(aq)}, thus readily reacting with CO₂ to produce CaCO₃, as a means of fixing the gaseous CO₂ as a stable solid for permanent storage. The pH values of dechlorinated solutions obtained after each of the five cycles of Cl⁻ removal, using regenerated CHT, was measured before the mineralisation process, and are shown in Table 4. There is a gradual declining trend in pH with the increasing cycles, due to the degradation of HT and its Cl⁻ removal ability, as previously presented. Yet, in all cases, the pH is sufficiently alkaline to allow for CaCO₃ precipitation. The Ca²⁺ concentration in the dechlorinated solutions, before and after mineralisation reaction, was measured by ICP-OES; from these data, CCE was calculated and these values are shown in Table 5.

Table 4. Initial pH values of dechlorination solutions obtained after several regeneration cycles and using two regeneration methods, S/L = 0.020 g·mL⁻¹.

Cycle No.	1	2	3	4	5
CO ₂ regen	12.4	12.1	12.1	11.8	11.6
Na ₂ CO ₃ regen	12.4	12.3	12.2	11.8	11.8

Table 5. CCE values post mineralisation using dechlorinated solution obtain after several regeneration cycles and using two regeneration methods, S/L = 0.020 g·mL⁻¹.

Cycle No.	1	2	3	4	5
CO ₂ regen	93.7%	93.8%	88.5%	82.3%	80.3%
Na ₂ CO ₃ regen	91.2%	89.8%	90.4%	85.1%	84.0%

The CCE values in Table 5 start just below 94% and decrease as the dechlorination performance degrades. The main reason for the CCE limitation under all conditions is that during mineralisation reaction, the pH of the solution drops as the reaction progresses, and once it reaches a value that is too low for CaCO₃ precipitation, its dissolution occurs (pH < 8.0, which according to the subsequent discussion is when dissolution of CaCO₃ starts). When the starting pH is lower, that limiting pH value is reached sooner, thus with a smaller fraction of Ca²⁺ having precipitated. The pH value plotted against time during a mineralisation reaction is shown in Fig. 13. This experiment was conducted using the dechlorination solution from the first cycle, thus its initial pH was highest at 12.4. The pH value at first gradually decreases, since sufficient OH⁻ ions buffer the formation of H⁺ ions from carbonic acid dissociation. Once most Ca²⁺ precipitates, the solution loses its ability to buffer the pH, and it dramatically decreases. In this experiment, CO₂ gas flow was shut down after 20 minutes, and it is seen that shortly thereafter the pH rebounded to around 8.0, due to degassing of excess CO₂ from the solution until equilibrium with precipitated CaCO₃ is reached. It is evident from this graph that it would make more sense to stop the mineralisation process, and immediately recover the precipitates, once the pH reached the limiting value for CaCO₃ precipitation (around 8.0) on the way down, just prior to the 20-minute mark, otherwise it is necessary to wait until past 80 minutes for CaCO₃ to re-precipitate. Therefore, the following several cycles of CO₂ mineralisation experiments were all stopped once the pH value reached 8.0 during CO₂ injection, and hence CaCO₃ approached equilibrium under the CO₂ partial pressure present (approx. 0.12 atm).

Fig. 13 pH variation during CO₂ mineralisation process of dechlorinated brine; CO₂ injection stops at 20 minutes, S/L = 0.020 g·mL⁻¹.

Fig. 14 TGA/DTA curves (left) and SEM image (right) of a mineralised CO₂ product.

Fig. 14 shows TG/DTA curves of one of the produced precipitated carbonates, and it can be assessed that there are two weight loss peaks, one very minor attributed to traces of Ca(OH)₂ and one major attributed to the main CaCO₃ phase, at the temperature ranges of 370-480°C and 780-840 °C, respectively [43]. The SEM image in Fig. 14 displays the morphology of the product, consisting of pure rhombohedral calcite crystals [44].

4. Process design to apply hydrotalcite in mineralisation process

In our previous research [7, 8], different alkaline substances were tested to allow for the brine carbonation process to proceed; however, their recovery and reutilization after one-time usage was not tested given difficulties in achieving this through distillation or electrolysis. In this

research, we propose the use of calcined hydrotalcite for dechlorination of brine (as opposed to buffering of pH). This layered double hydroxide is meant to replace the previous alkaline substances with the aim of recycled usage to reduce the operational process cost and energy demand, thus maximizing net CO₂ sequestration of the process. The schematic of the overall process is displayed in Fig.15 and consists of the following steps. First, input calcined hydrotalcite into the brine to implement the first round of Cl⁻ removal process and raise the pH of the solution sufficiently for CO₂ mineralisation reaction to subsequently occur. The spent HT-Cl material is filtered out and collected from the dechlorinated solution, and sent to be regenerated with gaseous CO₂ or Na₂CO₃ solution. Preferably, the CO₂ source for regeneration can be partially obtained from the calcination process of HT. Flue gas is introduced to the dechlorinated brine to conduct mineralisation reaction, producing solid carbonates that are filtered out and collected. The residual solution from mineralisation, now poor in Cl⁻ and in Ca²⁺, is used as the solution for the regeneration of spent HT-Cl. This solution following HT regeneration will gain Cl⁻, thus becoming acidic, so a low strength HCl solution is produced, and this can be used for industrial purposes. The regenerated HT is sent back to the calcination process, and CHT recycled back to the beginning of the flowsheet. The Cl⁻ removal efficiency and CO₂ mineralisation performance should be monitored at each cycle to determine the optimal time to replace recycled HT with fresh HT.

Fig.15 Schematic of the process.

hydroxide, which proceed under 500 °C to generate CHT. Eq. (5) shows the ion exchange reaction occurring in the brine, and the Gibbs free energy change of this reaction is negative according to several research studies [45-48]. This Gibbs free energy change decreases with higher temperature, which can explain why higher temperature can achieve higher chloride removal efficiency, and this related to the absorption of anions being an endothermic process [49, 50]. The standard molar Gibbs free energy of formation of hydrotalcite prepared by coprecipitation method can be calculated via Eq. (6) to be -949.62 kJ·mol⁻¹, using thermodynamic data obtained from databases [40, 51]. Using this value, it is possible to calculate the Gibbs free energy of reaction for the regeneration with CO₂ and with Na₂CO₃, in Eq. (6) and Eq. (7), as -40.90 kJ·mol⁻¹ and -49.35 kJ·mol⁻¹, respectively. As the Gibbs free energy change of the reactions of ion exchange and regeneration processes are all negative, all these reactions are confirmed to occur spontaneously, as experimentally verified.

$$\Delta_f G_m^\circ\{298.15\text{K}, \text{HT}\} = (1-x)\Delta_f G_m^\circ\{298.15\text{K}, \text{Mg}(\text{OH})_2\} + (x)\Delta_f G_m^\circ\{298.15\text{K}, \text{Al}(\text{OH})_3\} + (x/2)\Delta_f G_m^\circ\{298.15\text{K}, \text{CO}_3^{2-}\} \quad (6)$$

5. Conclusions

This study presented an alternative process to utilise earth alkaline cations of brines for CO₂ mineralisation based on the benefit of layered double hydroxides exchanging chloride ions to hydroxyl groups. Calcined hydrotalcite compounds (CHT) can be synthesised by coprecipitation reaction controlling the pH to be constant, followed by calcination process. This two-step process enhances the specific surface area, from 39 m²/g to 191 m²/g, needed for maximizing ion exchange capacity. The optimal, and therefore energy- and cost-effective conditions of CHT utilization, to achieve chloride removal of 98%, were found to be a solid-to-liquid ratio of 0.020 g·mL⁻¹ and a reaction temperature of 60 °C. The best performing CHT was prepared using a Mg/Al ratio of 4.

The morphology of CHT changed, and its specific surface area declined, after Cl⁻ removal process. Taking advantages of the 'memory effect' property of HT, two regeneration methods were tested and compared: one more acidic, using gaseous CO₂, and another more basic, using Na₂CO₃ solution. The results showed that the Cl⁻ removal efficiency gradually decreased with the increasing regeneration cycles, but the regenerated CHT could still achieve over 70%

and 85% Cl^- removal from brine after five cycles with CO_2 and Na_2CO_3 regeneration, respectively. Species irreversibly attached to the HT interlayers (carbonates and chloride) accumulated with every cycle, thus negatively affecting the Cl^- removal from brine and Cl^- recovery during regeneration, for both regeneration approaches, though to a lesser extent for Na_2CO_3 . For the CO_2 regeneration method, an additional detrimental effect reducing CHT performance was the acidic conditions present during regeneration, which irreversibly degraded the main structure of layered double hydroxide.

The dechlorinated brine, now containing $\text{Ca}(\text{OH})_{2(\text{aq})}$ in place of $\text{CaCl}_{2(\text{aq})}$, was found to be suitable for direct and rapid reaction with CO_2 at flue gas concentration (12 vol%). This enabled the mineralisation reaction to proceed to near completion, with the calcium conversion efficiency slightly declining with every subsequent cyclical experiment, from 93.7% to 80.3% with CO_2 regeneration and 91.2% to 84.0% with Na_2CO_3 regeneration. Pure precipitated calcium carbonate, rhombohedral calcite, was formed after carbonation reaction.

Compared to our previous studies on brine carbonation using NaOH and MEA as pH-buffering additives, the method of using the solid adsorbent HT can facilitate the regeneration process, likely reducing processing complexity, cost and energy demand. These engineering and economic analyses are intended in future piloting studies. Further study will also investigate strategies to improve the performance of gaseous CO_2 regeneration process, deemed preferable from cost and process integration perspectives, by buffering the pH during HT regeneration to avoid structure collapse and maintain high efficiency for more than five cycles.

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