



Review article

Developments in mineral carbonation for Carbon sequestration



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ABSTRACT

Mineral technology has attracted significant attention in recent decades. Mineral carbonation technology is being used for permanent sequestration of CO₂ (greenhouse gas). Temperature programmed desorption studies showed interaction of CO₂ with Mg indicating possibility of using natural feedstocks for mineral carbonation. Soaking is effective to increase yields of heat-activated materials. This review covers the latest developments in mineral carbonation technology. In this review, development in carbonation of natural minerals, effect of soaking on raw and heat-activated dunite, increasing reactivity of minerals, thermal activation, carbonations of waste materials, increasing efficiency of carbonation process and pilot plants on mineral carbonation are discussed. Developments in carbonation processes (single-stage carbonation, two-stage carbonation, acid dissolution, pH swing process) and pre-process and concurrent grinding are elaborated. This review also highlights future research required in mineral carbonation technology.

1. Introduction

Global burning of fossil fuel cause GHGs (greenhouse gases) emissions. These emissions affect climate causing extreme weather patterns [1]. Fossil fuels and industrial processes are principal contributor to these emissions [2]. Particularly, steel industry is major CO₂ emission source with 5 % of global release [3] and cement industry is responsible for 8 % of global release [4]. Developing new processes for energy-efficient CO₂ capture is mandatory to mitigate global warming [5]. Developing viable strategies for tackling climate change is important to avoid the worst environmental impacts and its perturbation by anthropogenic sources. Different technologies investigated for CO₂ mitigation are mineral carbonation, geological storage, oceanic storage and chemicals production [6]. Aqueous mineral carbonation can permanently remove CO₂ from the atmosphere because it has been considered as geologically stable [7]. It's important to capture CO₂ and use it as a commercial product [8].

CCS is very common in academic research, industry projects and pilot projects and there are more than twenty CCS facilities which

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are operational [9,10]. To form thermodynamically stable carbonates, mineral carbonation (MC) is the best strategy for sequestering CO₂ that reacts magnesium silicates with CO₂. It has been an active area since the mid-1990s of greenhouse gas mitigation research. The most sustainable and safest way to sequester CO₂ is via mineral carbonation [11,12].

Seifritz proposed mineral carbonation that reacts CO₂ with silicate rocks [13]. MC occurs naturally which consumes CO₂ and use ultramafic minerals to produce stable carbonate with silica. However, carbon may be sequestered through geological storage [14]. Long term CO₂ sequestration is desired to form thermodynamically stable carbonate product. Several natural minerals rich in Mg and Ca in the form of silicates are being used for the fixation of CO₂ such as serpentine, pyroxene, olivine, amphiboles and wollastonite [15–18].

This review will cover developments in carbonation of natural minerals, effect of soaking on raw and heat-activated dunite, silanol nests formation, increasing reactivity of minerals, two-stage carbonation, developments in thermal activation, developments in carbonation of waste materials, increasing efficiency of carbonation process and pilot plants on mineral carbonation.

2. Development in carbonation of natural minerals

It has always appealed to carbonate minerals without any pretreatment such as grinding and thermal activation. For this purpose, it's important to study how natural minerals interact with CO₂. Temperature programmed desorption (TPD) experiments are usually performed to see how much CO₂ can be attached with Mg. It has been reported that dunite has highest CO₂ uptake among mafic and ultramafic rocks [19]. However, dunite which is heat-activated and dunite which is heat-transformed are not tested through TPD experiments especially sub 75 µm fractions rather than fine particles generated through ball milling. TPD experiments were performed to gain insight into the available magnesium atoms in raw dunite, dunite which is heat-activated and dunite which is heat-transformed. CO₂ ion current from various dunite samples is shown in Fig. 1. Integration of the CO₂ evolution curve was 28.9, 22.2 and 4.63 for dunite which is heat-activated (630 °C, 4 h), raw dunite and dunite which is heat-transformed (800 °C, 3 h) respectively. These results show high magnesium sights for interaction with CO₂ in dunite which is heat-activated (630 °C, 4 h), followed by raw dunite and dunite which is heat-transformed (800 °C, 3 h). These results further confirm that material rich with amorphous magnesium silicates has high magnesium sights for interaction with CO₂ and that's why has higher magnesite yields [20]. Maxima occurs at 368 °C for raw dunite as compared to 181 °C for dunite which is heat-activated (630 °C, 4 h) and 155 °C for dunite which is heat-transformed (800 °C, 3 h). These results show that magnesium interaction with CO₂ was strongest for raw dunite followed by dunite which is heat-activated (630 °C, 4 h) and dunite which is heat-transformed (800 °C, 3 h). Rigopoulos et al. has observed that ball milling in presence of ethanol increase CO₂ capture capacity of pyroxenites by 41 times (rise in CO₂ uptake from 3.8 µmol g⁻¹ to 155.6 µmol g⁻¹) [21]. It has been also observed that ball milling for 12 h duration using 50 % ethanol increased CO₂ uptake capacity by a factor of 6.9 (40.1 µmol g⁻¹ to 278.1 µmol g⁻¹) [22]. In another study CO₂ uptake capacity increase by a factor of 4.5 has been reported compared to unground sample [23]. Main challenge with this process is ball milling energy consumption and cost of ethanol. Further research is required to search for low-cost solvents which serve the purpose.

Natural minerals like basalt and peridotite are also being used for in-situ and ex-situ mineral carbonation. Ayub et al. have studied the potential of using basalt of Central Belt of Malaysia for mineral carbonation and investigated that Fe, Ca and Mg present in the basalt can react with CO₂ and makes various carbonates [24]. XRD analysis indicated presence of pyroxene and olivine which are reactive minerals for mineralization. Mesfin et al. have studied dissolution of basaltic glass and labradorite using aqueous NaCl, KCl, CaCl₂, and MgCl₂ for in-situ mineral carbonation [25]. They investigated basaltic glass and Ca-rich plagioclase for subsurface carbon storage and observed increase in dissolution by increasing pH and adding Ca to aqueous phase. Rahmani et al. have investigated brucite derived from peridotite for aqueous mineral carbonation [26]. They observed 99 % Mg conversion to MgCO₃ between 150 °C and 175 °C.

Carbonation products and by-products of natural minerals serve various purposes. Carbonation products such as MgCO₃ and CaCO₃ can be used as paint filler (CaCO₃), paper filler (CaCO₃), aggregate (CaCO₃), cement ingredient (CaO + CO₂), acid reducer and fertilizer

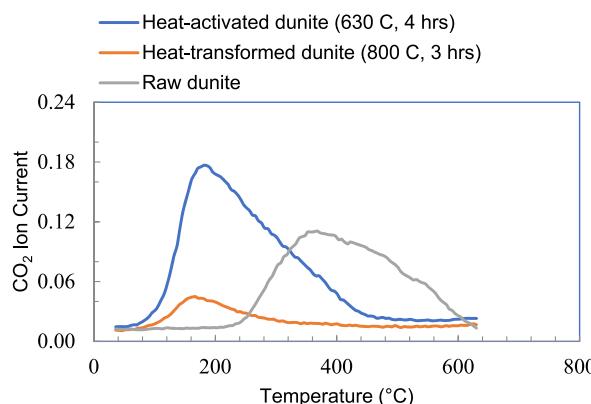


Fig. 1. CO₂ ion current from TPD of raw dunite, heat-activated dunite and heat-transformed dunite.

formation [27]. Construction industry is a major sector for utilization of carbonation products as alternate building materials and cement and concrete production [27]. Mineral carbonation products and feed can be used as pozzolanic cement replacements [28] and to produce silica enriched residue for applications in cement industry [29]. Peridotite and slag is used to produce cement, paper and rubber [30]. MC products may be employed to produce cement, concrete, mortars, aggregates or specialty products based on magnesium and calcium for applications such as paints and polymers and specialty products for thermal energy storage, CO₂ transport medium or to produce silica, metals or metalloids [31]. Carbon dioxide is being used to cure cementitious materials. Carbonation of cement occurs naturally from atmospheric CO₂ [32]. Carbonation products and feedstock as well can be used as a pozzolanic cement substitute [28]. Silica can be extracted from carbonation materials through nitric acid dissolution and is useable as a pozzolanic material in cement manufacturing [29]. CO₂ and carbonation process has been used in increasing strength of various cementitious materials [33,34].

3. Effect of soaking on raw dunite and heat-activated dunite

3.1. Raw dunite soaking

Raw dunite 15 wt% solids slurry (30 g mineral in 170 g distilled water) was soaked to study effect of soaking on magnesite yield. Dunite feed sample, 15 % dunite slurry sample after 1 day and after 1 week were dried in the oven at 110 °C for 24 h prior to measure the BET surface area. For BET measurement, vacuum degassing was done overnight and then sample tubes are put in the machine to measure the BET surface areas. BET surface area increased slightly. BET surface area of initial dunite sample is 3.7 m²/g, 4.8 m²/g (1 day soaking), 5.3 m²/g (1 week soaking). Fifteen days dunite soaked and one-month dunite soaked samples were carbonated and magnesite yield of these samples is compared with non-soaked dunite carbonated sample (Fig. 2 a). As no significant increase in BET surface area with soaking was observed, magnesite yields are also not higher for soaked samples.

3.2. Heat-activated dunite soaking

One month soaking was performed for dunite which is heat-activated at 630 °C for 4 h. This dunite is then carbonated at 130 bar, 185 °C using 0.64 M NaHCO₃. Magnesite yields increased for soaked dunite (Fig. 2 right). XRD was done for carbonated sample of heat-activated dunite (630 °C, 4 h) after one month soaking. Peak intensity for magnesite peaks was increasing while olivine is decreasing (Fig. 3) [35].

3.3. Silanol nests formation (*in-Situ* FTIR results)

Formation of silanol nests have been reported in literature [20]. It is important to study whether these nests form during heat-activation or during the aqueous mineral carbonation process. For this study, self-supporting wafer using raw dunite was prepared. This wafer was heated till 500 °C in *in-situ* FTIR (Bruker) with temperature ramp of 5 °C/min and spectrum are obtained after every 10 °C. Spectrum at room temperature and with 100 °C temperature rise is shown in Fig. 4 (overlaid) and Fig. 5 (stacked). These results (especially spectrum at 500 °C) show that broad hump attributed to silanol nests does not form during heat-activation process.

Water vapor was adsorbed on activated dunite at 80 °C for 30 min. Then desorption was performed till 500 °C with ramp of 5 °C/min and spectrum obtained after every 10 °C. These results (all spectrum) show that broad hump due to silanol nests form between 3200 and 3500 wavenumbers. This hump due to silanol nests is supposed to form due to reaction of water vapor with the activated dunite (Fig. 6). This finding is very important as formation of silanol nests hinders carbonation process and reduces process efficiency

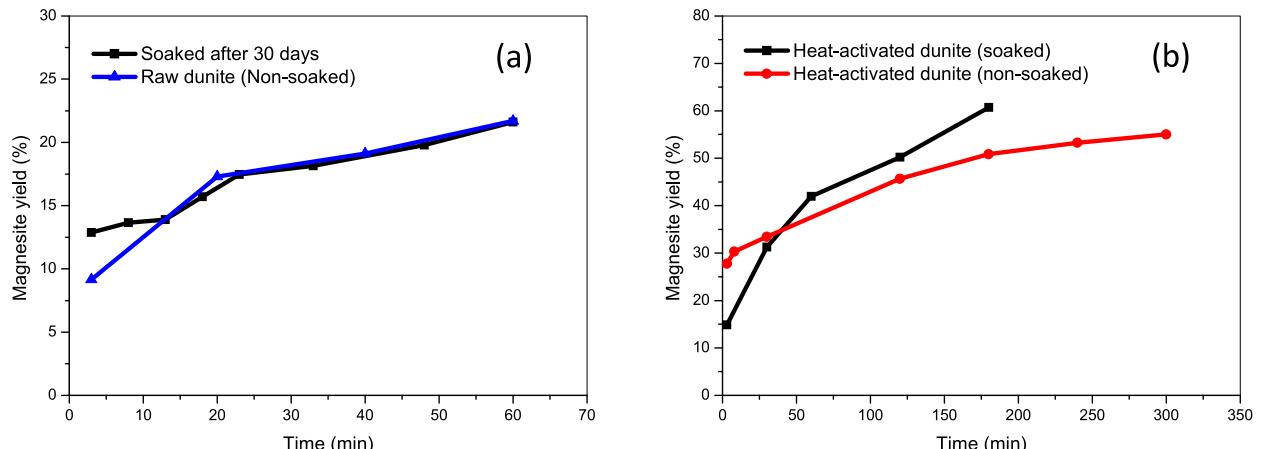


Fig. 2. Magnesite yields for soaked and non-soaked dunite (a), Yields for soaked and non-soaked dunite which is heat-activated (b).

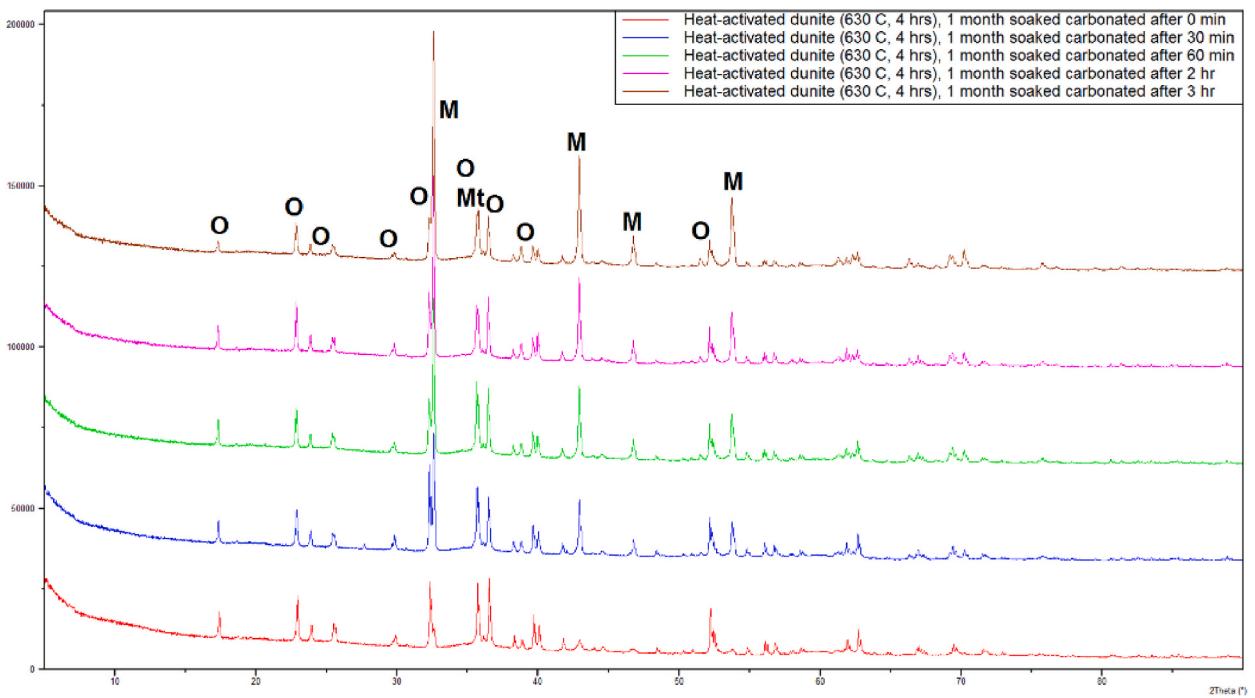


Fig. 3. XRD analysis of carbonated heat-activated dunite (630°C , 4 h) which was soaked for a month, M = Magnesite, O=Olivine, Mt = Magnetite.

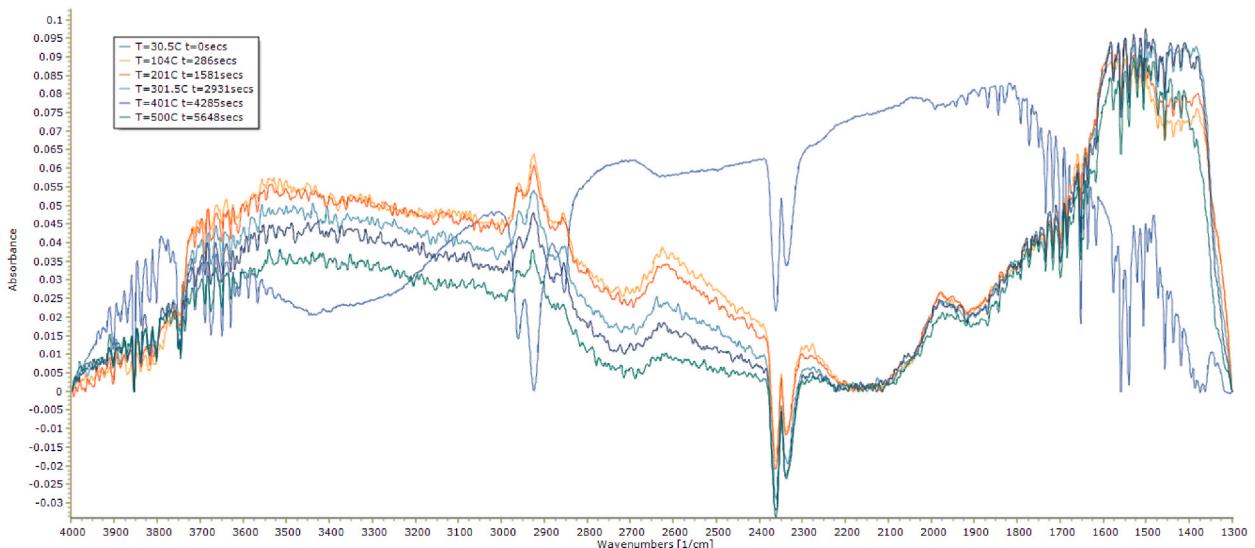


Fig. 4. Overlayed spectrum with 100°C temperature increase.

and magnesite yields [36]. This finding suggests that minimum water should be used during carbonation process or developing mineral carbonation process employing solvents which does not form silanol nests.

4. Increasing efficiency of carbonation process

Carbonic anhydrase especially bovine carbonic anhydrase may resolve rate limitation through enzyme-catalyzed CO_2 hydration and resulted an increase in brucite carbonation of 240 % [37]. Carbonic anhydrase works as a catalyst and enhance reaction kinetics and absorption yields [38]. Carbonic anhydrase or Scenedesmus alga spontaneously precipitate solutions [39]. Two geochemical treatments such as reaction with partially saturated flue gas having 10 % CO_2 and heap leaching with dilute sulfuric acid has been reported to double the amount of CO_2 stored [40]. Separate dissolution and precipitation concept has been introduced which increases

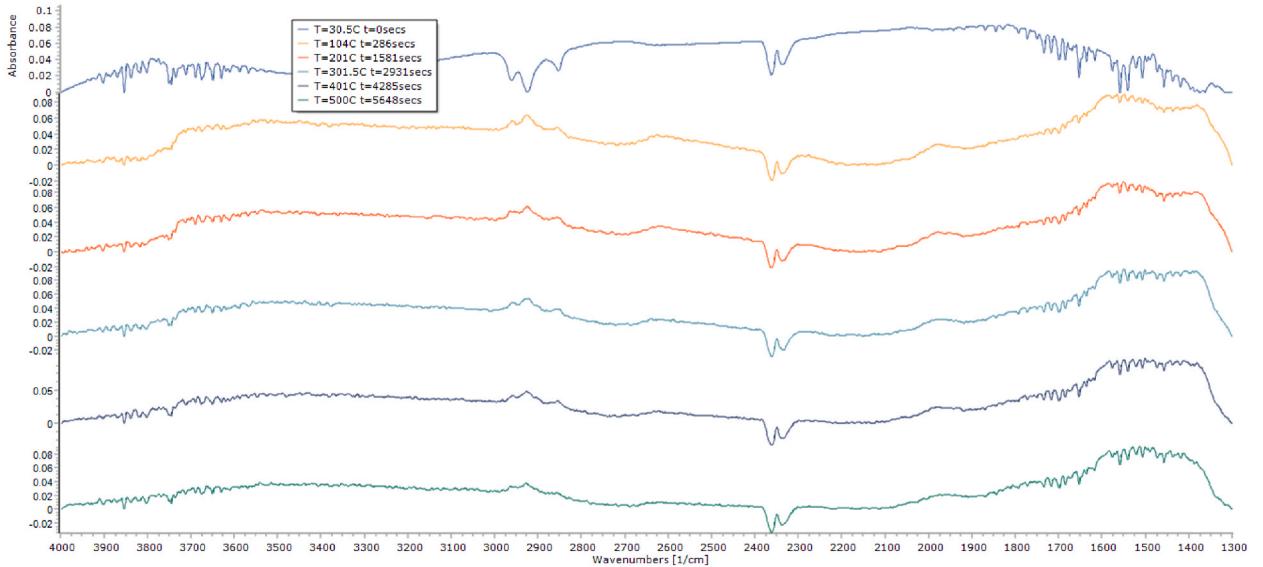


Fig. 5. Stacked spectrum with 100 °C temperature increase.

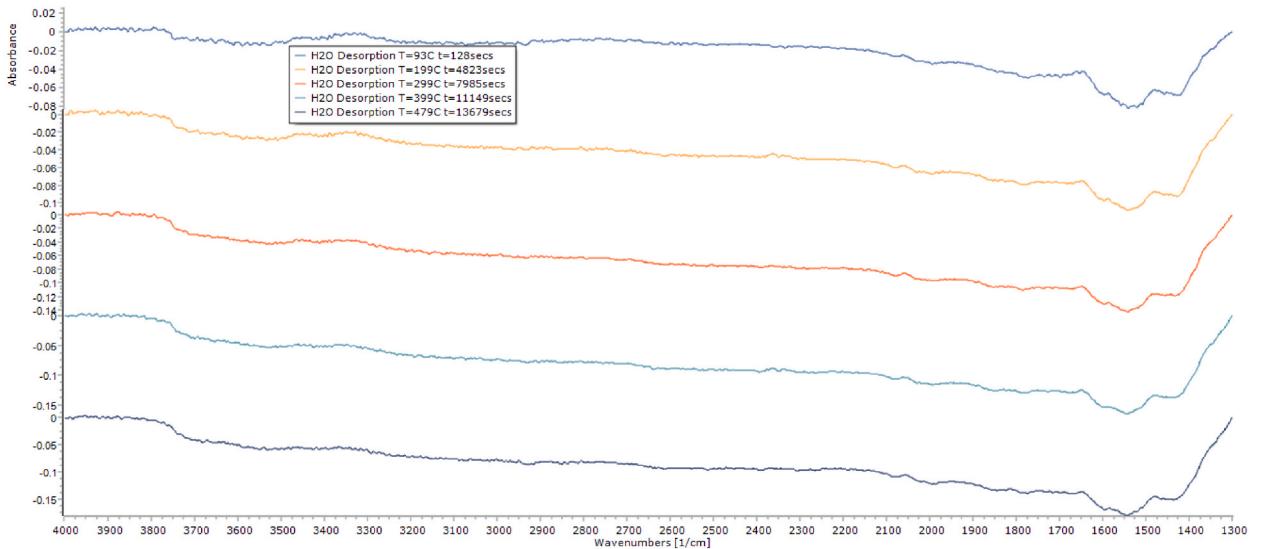


Fig. 6. Spectrum for desorption step with 100 °C temperature rise.

yields at lower pressures [41,42]. Ball-milling and additives use has accelerated mineral carbonation reactions thus increasing carbonation of 5 and 15.7 % for silicates and hydroxides respectively [43]. Mineralization rate increases with increase in temperature, reaction time, pressure, revolutions per minute, pH, use of additives, using grinding media and reducing feed particle size. Increase in temperature till 185 °C has increased olivine yield which also facilitate magnesite precipitation [44]. Decrease in yield (62 %–49 %) occurred for harzburgite when temperature was reduced from 180 to 120 °C [45]. Increase in pressure increases CO₂ solubility which accelerates mineralization rate [44]. Particle size reduction increase surface area which results in higher yields e.g. 100 % yield was observed using sub 10 µm particles of olivine [46]. Using additives, proton exchange reactions occur fast which enhance mineralization rate [47]. Grinding media addition during reaction removes silica rich passivating layers thus increasing mineralization rate [48–51].

4.1. Developments in seeding

Although the formation of magnesite is favored by thermodynamically, a limiting factor has been the slow rate of precipitation. The conversion efficiency could be improved using seeding materials by implementing heterogenous nucleation. Seeding provide

heterogeneous nucleus sites and activated carbon and alumina are preferred [52]. Moreover, seeding prevent spontaneous nucleation in metastable solutions [53].

4.2. Developments in minerals recovery

Minerals are recovered through mineral carbonation using waste ash to recover mineral because waste ashes contain calcium ions [54]. A new process for the simultaneous CO₂ mineralization and recovery of aluminum as NH₄Al (SO₄) .12H₂O was proposed under the guidance of roasting reaction thermodynamics and phase diagram of the MgSO₄–Al₂(SO₄)₃–(NH₄)₂SO₄–H₂O system [55].

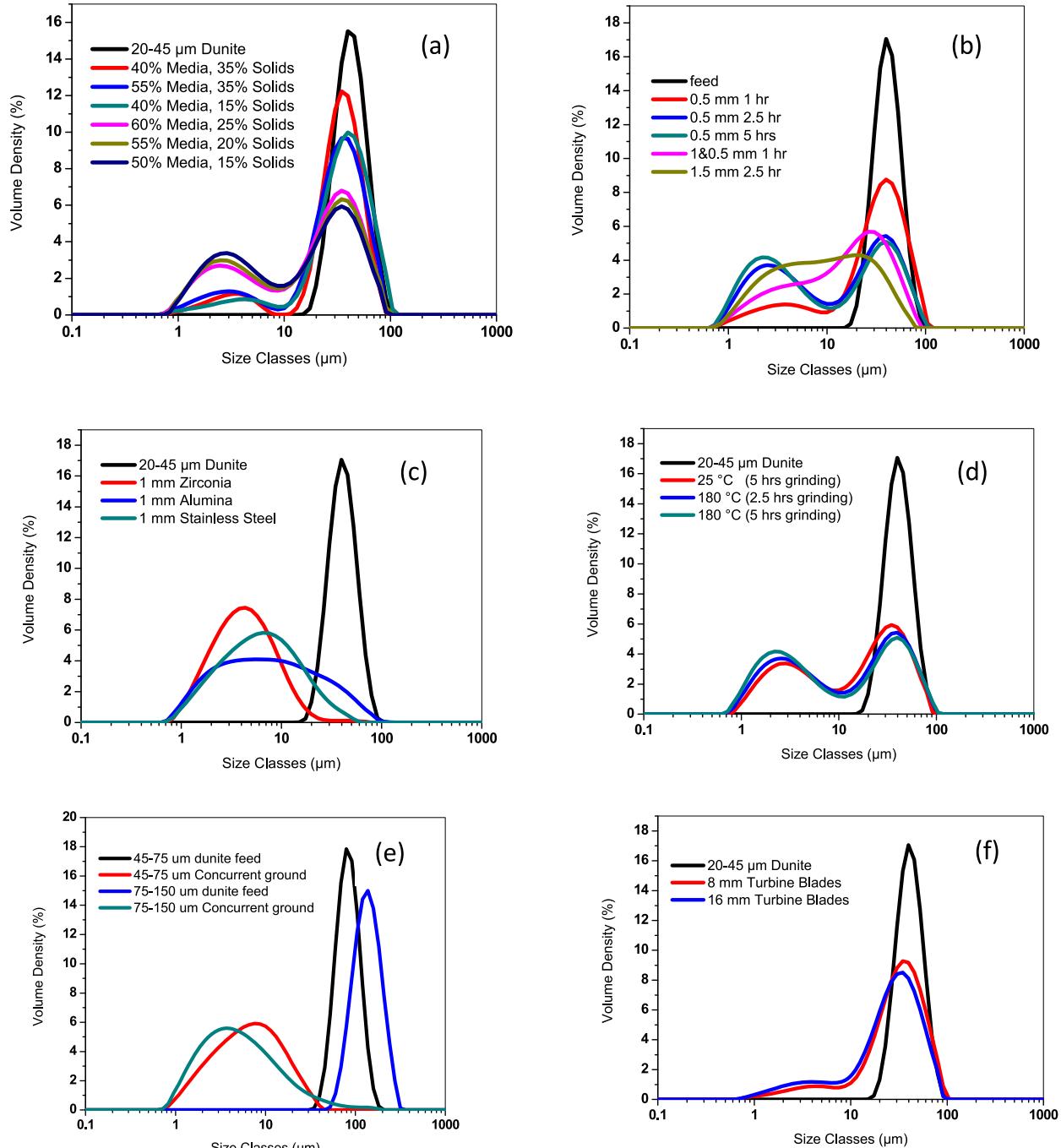


Fig. 7. Grinding without carbonation, different media and solids concentrations (a), different media size and time (b), different media types having same volume (c), different temperature and grinding time (d), different particle fractions (e), different blades size (f) (Modified from Refs. [48,66]).

4.3. Formation of silica-rich layers

Silica-rich layers formation occurs during carbonation reactions and these layers retards leaching of the magnesium from inner core of the feedstocks thus limiting magnesite yields or magnesium extractions. This process occurs during single stage [51] as well as during two-stage carbonation [49]. It has been also observed that passivation layer does not form under specific condition studied here [56]. Pokrovsky and Schott have extensively studied the formation of silica-rich layers and found that they are usually 10–20 Å (angstrom) thick having layered structure [57–60]. These layers retard mineral carbonation process and may constitute of a secondary product [61].

4.4. Developments in grinding (both pre-process grinding and concurrent grinding)

4.4.1. Grinding without carbonation

Grinding is important to break silica-rich layers. It is vital to study grinding separately from carbonation to optimize the process and for simplicity to find best conditions. Different media (zirconia) and solids concentrations are tested through grinding without carbonation in a Parr reactor of 300 ml [62,63]. It is observed that 50 wt% media and 15 wt% solids are optimum concentrations for carbonation (Fig. 7 a) and was used in further experiments. This is same as observed for stirred bead mills [64,65]. When different sizes of the media were tested for different time intervals it has been observed that 2.5 h grinding time is optimum (Fig. 7 b). Different media have different densities which can affect the quantity of media for any experiment, hence, zirconia, stainless steel and alumina were tested having equal media volume of 10 cm³ (for 2.5 h) (Fig. 7 c). Zirconia media proved best followed by stainless steel and alumina. Regarding optimum temperature of grinding and time, 180 °C temperature for 2.5 h was best compared to 5 h grinding at 25 °C or 5 h grinding at 180 °C (Fig. 7 d). These findings were using 20–45 µm dunite batch. It has been observed that 1 mm zirconia also ground 45–75 µm dunite and 75–150 µm dunite fractions (Fig. 7 e). This proves that larger fractions can be ground using same conditions found optimum for 20–45 µm dunite. Different turbine blades length was investigated, and 16 mm blades were slightly better compared to 8 mm blades however, pertaining to energy considerations 8 mm blades were chosen best and used for carbonation studies (Fig. 7 f). Regarding different blades shapes, pitched turbine blades are best [62].

Conclusion of these studies indicate that 50 wt% media, 15 wt% solids, zirconia media, 1 mm size, 2.5 h grinding, 180 °C temperature, 8 mm blades length and pitched turbine blades are best for grinding of the rock (fine particle size distribution, Fig. 7) and particle grinding and attrition during carbonation directly corresponds to magnesite yield. Basic mechanism for grinding is that one layer of media is present at reactor base while the other falling particles on this layer grind the rock or mineral particles trapped between these two and this grinding also removes forming silica-rich layers due to Mg and Si leaching from the rocks and minerals. This action is best observed for 50 wt% media and 15 wt% solids and fine particle size distribution is observed (Fig. 7) and thus these conditions are chosen for carbonation.

4.4.2. Concurrent grinding during carbonation

Single-stage carbonation is operated at high temperature and pressure which operate using minerals (lizardite, olivine, and antigorite) and rocks (dunite, harzburgite) [67]. Rashid et al. has employed concurrent grinding during single stage carbonation for various feedstocks and their fractions such as dunite, olivine and lizardite without heat-activating these minerals and rocks [51]. Dunite reactivity is greater than olivine and lizardite (Fig. 8). Six times higher yields were obtained for dunite and olivine during concurrent grinding carbonation compared to reference experiments. Grinding media is not used in reference experiments which served as control while in concurrent grinding experiments, 50 wt% media was used which introduces attrition and enhanced leaching

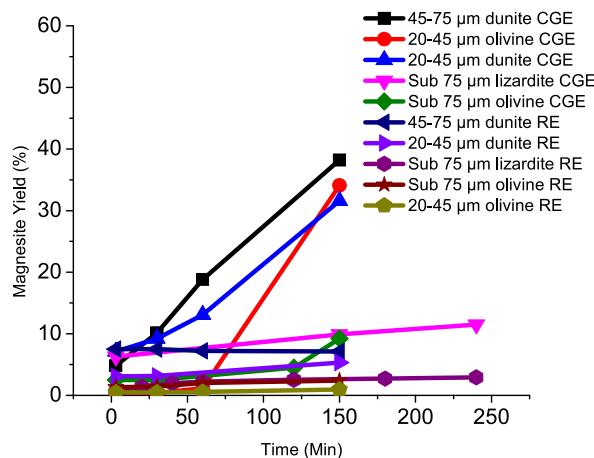


Fig. 8. Single stage carbonation yields with concurrent grinding (1 mm zirconia) and without concurrent grinding (reference experiments) (modified from Refs. [51,66]), Reaction conditions are 180 °C temperature, 130 bar and 15 % solids and 50 wt% media for concurrent grinding experiments, CGE= Concurrent grinding experiment, RE = Reference experiment.

during carbonation thus providing new surfaces for carbonation reactions with simultaneous removal of silica rich layers. Park et al. has ground the solids containing silica-rich layers and was able to extract further magnesium from those solids [68]. Chizmeshya et al. employed quartz particles as a grinding media during carbonation and obtained higher magnesite yields [44]. Julcour et al. and Bodenan et al. developed concurrent grinding technique for various feedstocks and introduced various modes of operation such as single step and two-step concurrent grinding carbonation [45,69]. Julcour et al. obtained many times higher magnesite yields during 24 h carbonation [45] however, carbonation time, media and solids concentrations were not optimum and performance difference between medias are not evaluated.

Some studies focused on pre-process grinding i.e. grinding to fine/ultrafine size prior to carbonation. Jiajie and Hitch research group have also performed pre-process grinding studies on carbonation especially for waste materials [56,70–74]. They employed mine waste to reduce cost and wet milling to activate waste and obtained even higher yields than pure olivine [75]. They observed increase in surface area and yields with grinding process. Jiajie et al. also highlights that 120 min milling was effective in increasing surface area, inducing crystallinity and amorphization [71]. They also observed increase in yield for mine waste containing olivine and serpentine [70]. They also observed that olivine transforms to serpentine during milling. They have identified milling limit for crystallite size [72]. They have discussed effect of mechanical activation on various magnesium silicates [74]. Eikeland et al. has observed 100 % magnesite yield when sub 10 μm olivine was carbonated for 4 h [46]. This finding indicates that pre-process grinding in stirred ball mills to obtain sub-10- μm particles may follow carbonation to devise a commercial scale mineral carbonation process.

4.4.3. Two-stage carbonation

The two-stage carbonation is a two-step process. During the first step mineral is dissolved and precipitation of nesquehonite/magnesite/calcite occurs during the second step.

4.4.3.1. Open (bubbling) system against closed system. Closed system experiment used back pressure regulator at 3 bar, 45 °C with 2 wt % solids and samples are collected at 1 min, 30 min, 1 h, 2 h and 4 h. Open system experiment was performed with mass flow controller at 3 bar, 45 °C with 2 wt% solids and samples are collected at 1 min, 30 min, 1 h, 2 h and 4 h. Both systems provide similar Mg extraction (Fig. 9). Similar PSD was observed (Fig. 9 and Table 1). These findings suggest that a two-stage process may be carried out in a close system or open system and obtained yields will be same as well as PSD. This experiment shows that close system which is simpler and more convenient can be adopted for two stage process compared to tedious open system that's emits CO₂ in vicinity of experiment. Further detail of these systems is discussed elsewhere [66].

Nesquehonite formation observed in 60 % media concurrent ground sample after dissolution in a two-stage process (Fig. 10). This finding indicates that during dissolution nesquehonite may precipitate although it is expected that it will not precipitate in line with dissolution conditions. This precipitation may decrease the Mg extraction during dissolution phase.

4.4.3.2. Effect of soaking on concurrent grinding during two stage process. Experiments were done with lizardite which is heat-activated but non-soaked and lizardite which is heat-activated but soaked for a week. Experiments occurred under similar conditions i.e., 3 bar, 45 °C, 2 wt% solids and using 60 wt% 1 mm zirconia. Soaking does not affect Mg extraction (Fig. 11). Eighty four percent Mg extraction occurred in 4 h. This is in contrast with heat-activated dunite as its soaking has increased yields during single-stage carbonation. PSD for feed, soaked and non-soaked lizardite is reported in Table 2 which shows that soaking reduced particle size distribution as particles dissolved during soaking.

4.4.3.3. Wear and tear during concurrent grinding. After dozens of concurrent grinding experiments, change in liner color has been observed (Fig. 12). 1 % HCl solution was used to dissolve the red layer formed around the periphery and solution was analyzed by ICP-

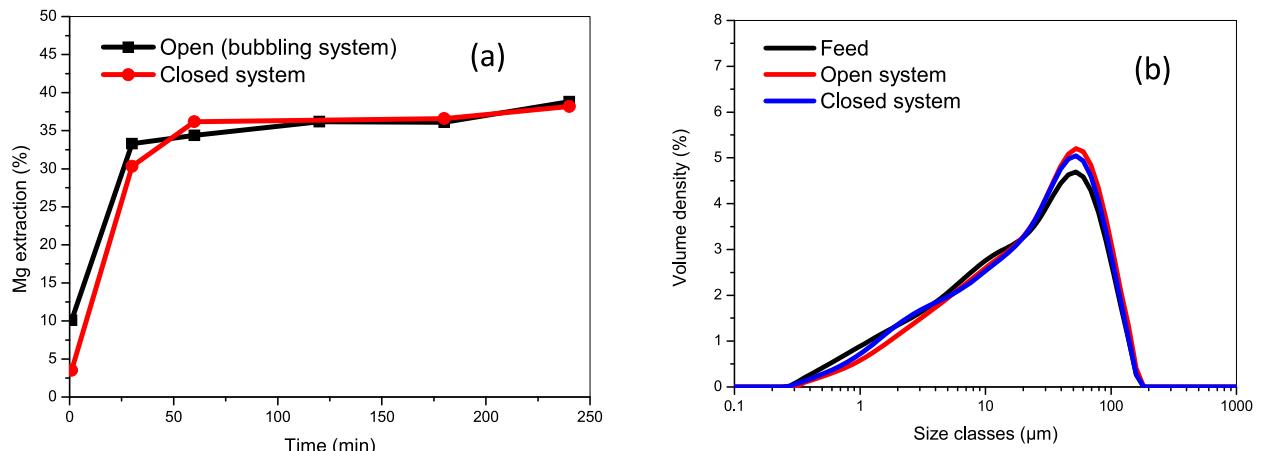


Fig. 9. Mg extraction for open system and closed system (a), PSD analysis for open system against closed system (b).

Table 1
PSD analysis for open (bubbling) system against closed system.

	d_{10} μm	d_{50} μm	d_{90} μm
Sub 75 μm heat-activated lizardite feed	1.9	20	76
Open (bubbling) system	2.7	25	80
Closed system	2.2	23	77

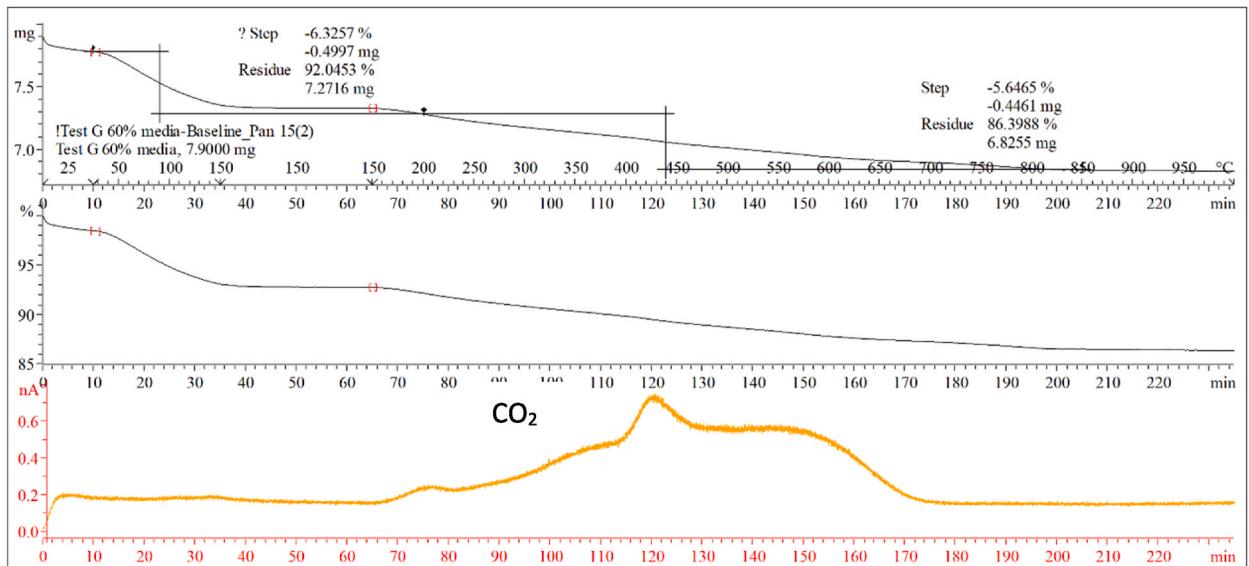


Fig. 10. TGA-MS analysis of 60 % media concurrent ground sample during dissolution.

OES. Elements detected are Fe, Mg, K, Ca. Presence of Fe indicate this layer has been formed due to leaching of the iron present in liner material. This wear and tear may cause trouble in devising a commercial mineral carbonation process employing concurrent grinding technique. Media can still be used; however, frequent inspections of the liner's internals will be required or even its replacement. One other option may be using pre-process grinding in stirred mills followed by carbonation or concurrent carbonation using less quantity of media to disengage secondary products (silica, magnesite) formed during carbonation.

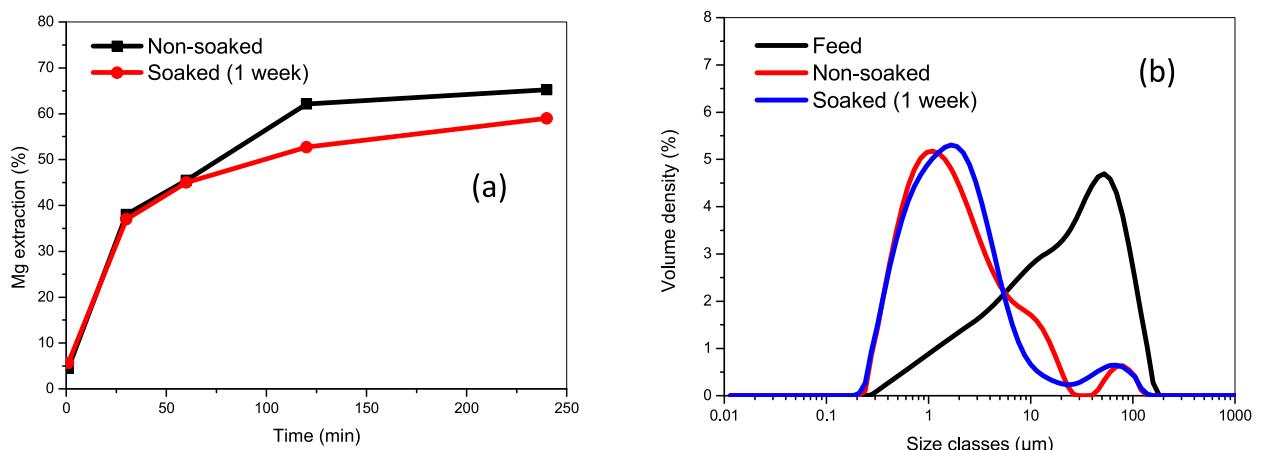


Fig. 11. Comparison of Mg extraction for soaked (1 week) and non-soaked experiments. Experiments performed at 3 bar, 45 °C, 2 wt% solids and using 60 wt% 1 mm zirconia media (a), PSD for, Feed, Soaked and Non-Soaked samples (b).

Table 2
PSD for, Feed, Soaked and Non-Soaked samples.

	d_{10} μm	d_{50} μm	d_{90} μm
Sub 75 μm heat-activated lizardite feed	1.9	20	76
Non soaked	0.46	1.5	9.2
Soaked (1 week)	0.46	1.5	6.7



Fig. 12. Liner wear and tear during concurrent grinding inside reactor.

5. Developments in thermal activation

Thermal activation refers to dehydroxylation of serpentine minerals (lizardite, antigorite) or partially serpentinized rocks (dunite, harzburgite) due to which hydroxyl groups release as water vapors. The optimum temperature for lizardite is 635 °C [76]. Intermediate phases formed during dehydroxylation has been found to be more reactive [77]. Any heat-activated material may be carbonated through single-stage process, two-stage process, pH swing process or dissolved in acidic solution referred to as acid dissolution. Various researchers have studied the heat-activation of dunite [29,78], lizardite [42,79–83], antigorite [28,84–86] and harzburgite [69]. Increase in yield during single-stage carbonation has been observed with thermal activation for various materials e.g. dunite [20], lizardite [79] and antigorite [28]. It has been observed that hydromagnesite formation occurs during mineral preheating phase inside batch reaction in absence of CO₂ [79] and CO₂ being supplied from additive (sodium bicarbonate).

Heat-activated lizardite has been dissolved in a two-stage process employing concurrent grinding [49]. Fig. 13 shows Mg extractions for reference experiment, concurrent ground first and second run using dry-residue recycle, continuous 4 h concurrent ground, long 12 h run, effect of sampling, Mg extractions for first and second run using wet-residue recycle and Mg extractions first and second run using grinding aids. Concurrent ground runs have almost double Mg extractions compared to reference experiments. Reference experiments have no grinding media added, hence Mg leaching into the solution leaves behind silica rich layers which stop further leaching of Mg and retards Mg extraction which is undesired for a continuous process. Addition of grinding media facilitates creation of new surfaces through continuous removal of silica rich layers and expose new surfaces to the aqueous solution thus enabling higher Mg extractions and leach Mg from inner part of the heat-activated minerals. Long 12 h run has shown highest Mg extractions but take considerable time of grinding and Mg extraction rise is less after 6 h. It has been reported that optimum media concentration for two-stage dissolution is 60 wt% [49]. Werner et al. used heat-activated lizardite with 1.5 mm zirconia media to grind it in a two-step process involving two dissolution reactors and a precipitator [42]. They observed an increase in yields with concurrent grinding due to silica rich layers removal. Zarandi et al. has observed nesquehonite transformation into hydromagnesite and dypingite with prolonged wetting and drying cycles [87]. Oliver et al. has observed that small nitrogen bubbles and carbonic anhydrase increase degassing rates as well as production of nesquehonite [39].

Acid dissolution in a buffer solution for sub 75 μm dunite which is heat-activated, sub 75 μm dunite which is heat-transformed, sub 75 μm raw dunite, sub 75 μm dunite from twin sister mountain and sub 20 μm dunite which is heat-transformed and 20–45 μm dunite which is heat-transformed are shown in Fig. 14 [50]. Sub 75 μm showed highest magnesium, silicon and iron extractions followed by dunite which is heat-transformed, raw dunite and dunite from twin sister mountain. Smaller particle size promotes dissolution as indicated with higher dissolution for sub 20 μm dunite which is heat-transformed compared to sub 75 μm dunite which is heat-transformed and 20–45 μm dunite which is heat-transformed. Mg/Si ratio (Fig. 14 c) is highest for heat-activated dunite. Heat-activated dunite has congruent dissolution similar to heat-activated lizardite [82]. Forsterite rich materials (dunite from twin

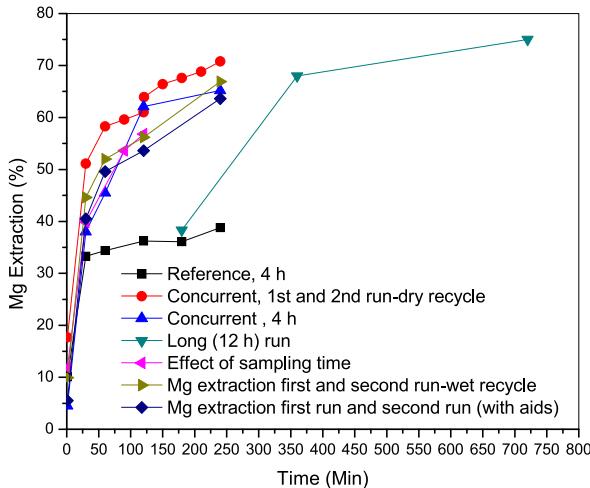


Fig. 13. Two stage dissolution using sub 75 μm heat-activated lizardite, all dissolutions performed using 2 wt% solids and 60 wt% 1 mm zirconia media at 45 $^{\circ}\text{C}$ and 3 bar, reference experiment is without using grinding media (modified from Refs. [49,66]).

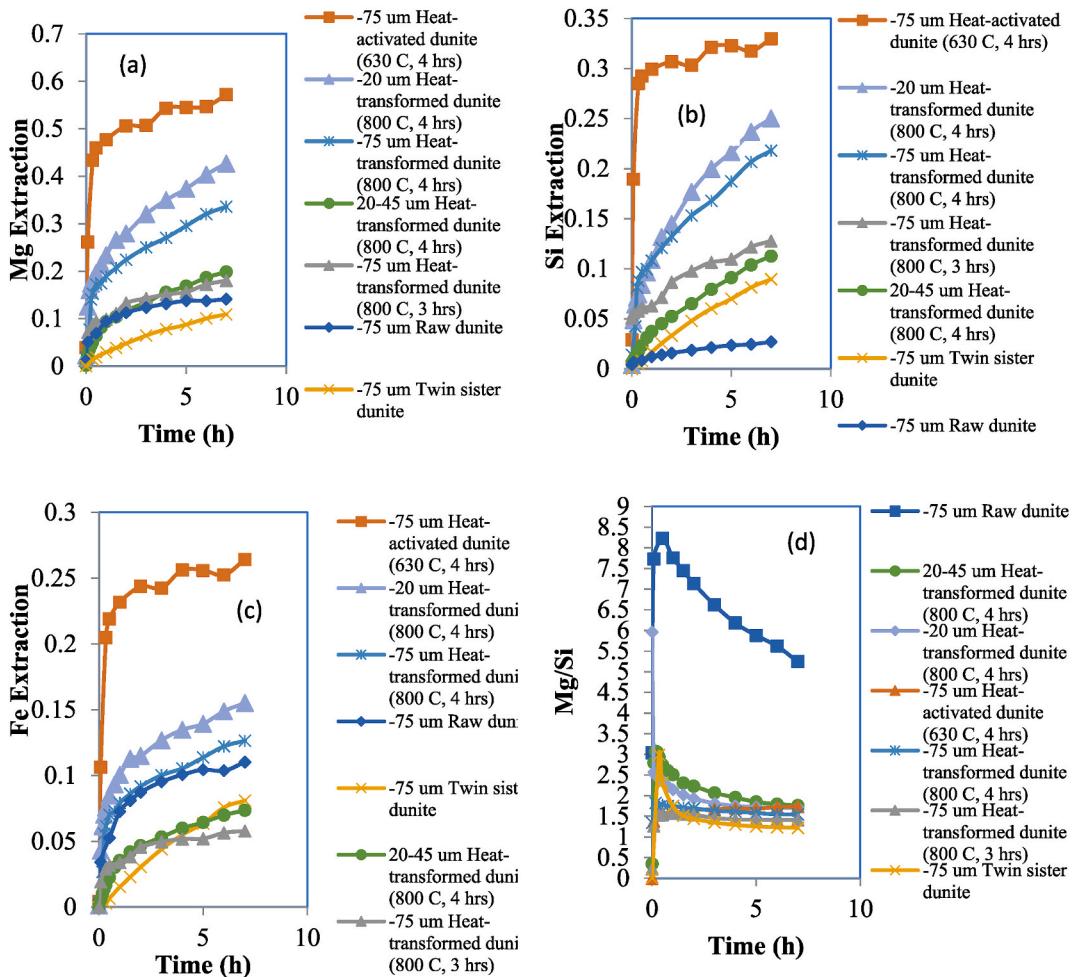


Fig. 14. Acid dissolution in a buffer solution for heat-activated dunite, heat-transformed dunite, raw dunite and twin sister dunite and various fractions of heat-transformed dunite, Mg extractions (a), Si extractions (b), Fe extractions (c), Mg/Si ratio (d) (modified from Refs. [50,66]).

sister mountain and dunite which is heat-transformed) showed incongruent dissolution which is typically reported in literature [57, 88]. Employing multi-stage dissolution with solids regrinding, almost 80 % Mg extraction has been achieved from heat-activated lizardite [29].

pH swing process is presented in Fig. 15 pH swing process which occur through indirect carbonation has two steps; (1) magnesium and calcium extraction under acidic conditions (2) the carbonation under alkaline conditions. This is most studied process with many acid and base additives [89]. pH swing process may be divided into four steps such as acid dissolution, purification, carbonation and recovery [90]. Optimum conditions for Mg extraction from waste tailings is reported as 70 C, 4 M HCl and 69 μm particle size [90]. Main challenge associated with pH swing process is recovery of the chemicals being used in the process. Magnesium bisulphate has been employed to extract 95 % Mg after 3 h dissolution [91] and increase process efficiency and reduce process cost.

6. Developments in carbonation of waste materials

Various studies have used waste materials for carbonation thus reducing waste and avoiding mining cost for minerals and rocks. These studies are presented in Table 3.

7. Pilot plants and commercial processes on mineral carbonation

Various universities and industries have developed pilot scale carbonation reactors to study mineral carbonation on a large scale which is first step to develop a commercial process for mineral carbonation. It has been observed that there is no significant difference in magnesite yields obtained in a 600 ml reactor compared to yields in a 30 L pilot scale reactor [108]. Table 4 highlights various pilot plants used for mineral carbonation. Further development in pilot plants is required to devise a commercial scale mineral carbonation process.

Conclusions and recommendations

TPD studies showed interaction of CO_2 with Mg indicating possibility of using natural feedstocks for mineral carbonation. Grinding with 50 wt% ethanol has been proven effective in converting feedstocks into nanometer size. Soaking is effective to increase yields of heat-activated materials, however, further research is required to make it feasible for raw feedstock with heat-activation. Silanol nests formation during carbonation hinders magnesite yields thus requiring solvents which do not result silanol nests. Six times higher magnesite yields have been achieved using concurrent grinding in a single stage carbonation while two times Mg extraction is obtained in two-stage dissolution using concurrent grinding. However, steel slags, alkaline wastes and coal fly ash have been not subjected to concurrent grinding. Best conditions for single stage carbonation are 50 wt% media, 15 wt% solids, zirconia media, 1 mm size, 2.5 h grinding, 180 °C temperature, 8 mm blades length and pitched turbine blades which can equally be used for carbonation of slags, wastes and fly ashes. 60 wt% media is optimum for two-stage dissolution. Wear and tear during concurrent grinding may damage the reactor internals or inside liners and requires frequent monitoring. Thermal activation increased yields and Mg extractions regardless of the carbonation process. Seeding can increase carbonation yields. CO_2 can be used in curing cementitious materials and increasing their mechanical strengths. By-products utilization and minerals recovery can reduce the process cost of mineral carbonation.

Recommendations to overcome associated challenges are listed below.

- Determination of the suitable additive for mineral carbonation.
- Suitable process determination and its cost effectiveness for different approaches of carbon sequestration.
- Development of robust pilot plant designed with economic viability and carbonated mineral product should be marketable.

CRediT authorship contribution statement

Muhammad Imran Rashid: Conceptualization, Data curation, Methodology, Writing – original draft. **Zahida Yaqoob:** Data curation, Formal analysis, Writing – review & editing. **M.A. Mujtaba:** Formal analysis, Software, Writing – review & editing. **H. Fayaz:** Funding acquisition, Writing – review & editing. **C Ahamed Saleel:** Funding acquisition, Writing – review & editing.

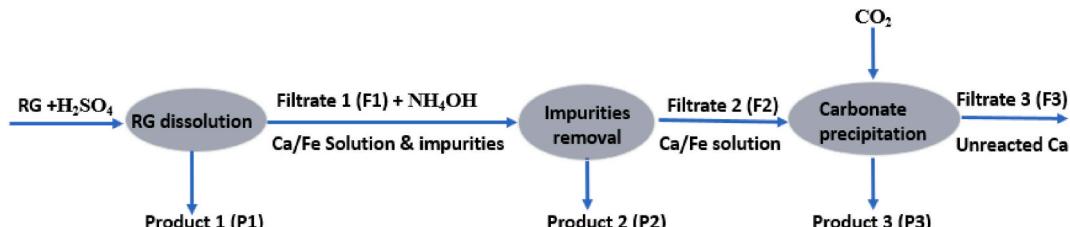


Fig. 15. pH swing process.

Table 3
Carbonation of various waste materials and related findings.

Waste materials	Carbonation conditions	Findings	Reference
Pulp and paper industry waste	2 h dissolution, 30 °C Carbonation at 30 °C and 30 bar	79.4 % and 73.2 % extraction efficiency with nitric acid and acetic acid. 74 % carbonation efficiency	[92]
Serpentinites, tailings, waste rock	2 h reaction	4 M HCl, 70 °C and 69 µm were optimal conditions for Mg extraction	[90]
Air lime mortars	Quarry waste 20 h ball milling in 50 % ethanol solvent	Addition of milled quarry waste increased carbonation depth and compressive strength	[93]
Fly ash from municipal waste gasification	CO ₂ at 50 kpa fed for carbonation	ashes could absorb upto 23.7 % CO ₂ . Heavy metals were immobilized	[94]
Portland-cement based	<300 µm material HNO ₃ , NaOH solutions for pH = 3-13	Carbonation affects pH thus reducing release of hydroxide and increasing release of carbonate	[95]
Cementitious materials	Aging under N ₂ , air and 2 % CO ₂	CO ₂ reduced chromium leaching	[96]
Cast stone	90 days aging under N ₂	High humidity increased reaction extent. Carbonation increased drying rate of caste stone.	[97]
Ternary cement	Grinding in planetary ball mill with 0.4 % propylene glycol	Increase in C–H content ratio increased carbonation	[98]
Sulfur waste & metallurgical residue	Solid waste dried at 105 °C for 24 h	Ettringite, C–S–H gels and portlandite increased solid wastes strength	[99]
Waste cement powder	Atmospheric conditions and 4 ammonium salts used	Carbonation efficiency is highest with ammonium acetate and ammonium nitrate	[100]
Oil shale mine waste	Ambient temperature pressure	Carbonation efficiency >89 % and is optimal at 2.5 % pulp density. CO ₂ uptake capacity is 80 wt%	[101]
Magnesia cement and construction wastes	Crushing in jaw crusher and sieving through 2 mm sieve	Unconfined compressive strength increased 218.1 % with concentrated bacteria which also increased brittleness	[102]
Blast furnace slag	Grinding in ball mill, 180 days curing under CO ₂	Sodium carbonate incorporation increase carbonation resistance	[103]
Construction and demolition waste	Carbonation in 3 % CO ₂	Mechanical properties and durability decreased with addition of recycled aggregate	[104]
Waste concrete	90 days curing followed by drying at 60 °C for 24 h	650 °C treatment compared to 400 °C resulted in higher CO ₂ uptake and compressive strength	[105]
Blast furnace slag	Slag conversion into respective sulphates	Ti and Al metals recovered. 82 % Ca and 84 % Mg transformation into carbonates	[106]
Blast furnace slag	Roasting followed by leaching	85 % titanium and 84.6 % aluminum recovered	[107]

Table 4
Pilot plants on mineral carbonation.

Pilot Plant	Capacity	Raw Materials	Reaction Conditions (Temperature, pressure)	Yield	References
Newcastle, Australia	30 L	Lizardite	150 °C, 150 bar	43 %	[108]
Quebec, Canada	237 kg CO ₂ /t (18.7 L reactor)	Mine tailings	1.3 bar, 40 °C	0.8 g CO ₂ , g residue ⁻¹	[109,110]
Abo Akademi, Finland	187 kg CO ₂ /h	Serpentine	500 °C, 20–30 bar	90 %	[111]
Universidad de Sevilla, Spain	–	ceramic brick composed of quartz, diopside, wollastonite, orthoclase and anhydrite	0.5 bar, 25 °C 5–12 month	23 wt% CO ₂ captured	[112]
Rome, Italy	7.79 dm ³	Steel slag	25–37 °C, atmospheric pressure	4–6 wt% CO ₂ captures	[113]

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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