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Development of an attrition-leaching hybrid process for direct aqueous mineral carbonation

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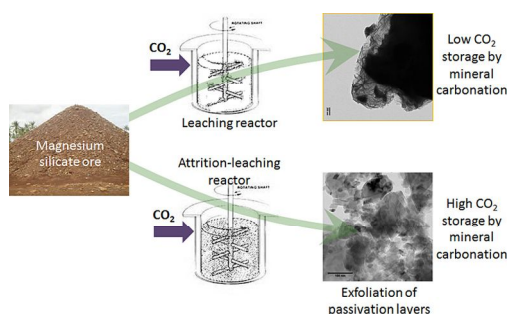
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HIGHLIGHTS

- Attrition leaching, a new hybrid process for direct aqueous mineral carbonation.
- Hybrid process yields continuous mechanical exfoliation of passivation layer.
- Proven synergy between mechanical exfoliation and mineral carbonation.
- Hybrid process yields up to 80% carbonation in 24 h.
- Robustness of the hybrid process towards variations in ore type.

GRAPHICAL ABSTRACT



Keywords:

Direct aqueous mineral carbonation
Magnesium silicates
Attrition
Leaching
Stirred bead mill

ABSTRACT

Mineral carbonation is the single most eligible companion solution to geosequestration for mitigation of anthropic CO₂ emissions on a large scale. Amongst its possible pathways, direct aqueous mineral carbonation stands out as one of the most promising ones. The originality of the present work lies in the transposition of the concomitant exfoliation/mineralisation concept, which was first proposed by the mineral carbonation research group from the Arizona State University in early 2000s, inside a dedicated attrition environment, more specifically inside a stirred bead mill. Experimental results and analyses bring definite proofs about the possibility and synergy of concomitant exfoliation and mineralisation. Given high carbonation yield for olivine and serpentinised ores (up to 35% in 5 h and 80% in 24 h in water, and 70% in 5 h with inorganic additives) and the capacity of stirred mills to process mining size throughputs, this work leads to real perspectives for developing large scale robust solutions for direct aqueous mineral carbonation.

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1. Introduction

1.1. Generalities about mineral carbonation

Alongside geological storage, a number of complementary CO₂ mitigation solutions have been proposed and investigated, particularly since the mid-nineties. Mineral carbonation, which consists in binding CO₂ as chemically inert mineral carbonate, has been identified as one such solution for two decades already [1,2]. This process, which is about accelerating the otherwise slowly naturally occurring silicate weathering process [3], produces carbonates and other products that are environmentally benign under ambient conditions, hence it offers CO₂ storage permanency. Because carbonatable materials, mainly magnesium silicates, are plentiful on Earth, often outcropping, mineral carbonation is acknowledged as a medium to large scale solution for CO₂ sequestration. Acceptability from land use and other competitive interests, food security in particular, does not appear to be a prohibitive issue considering the widespread and geolocalisation of carbonatable minerals. Industrial Mg- or Ca-bearing wastes [4], such as slags [5], red mud [6], mining wastes [7,8], fly ash [9] and desalination brines [10] also offer early opportunities for mineral carbonation; however alkaline industrial wastes represent an annual sequestration potential less than 1% of the worldwide emissions [11]. Therefore natural carbonatable minerals represent the only sensible target for development and deployment of mineral carbonation.

Long relegated to the immature or “niche” category, mineral carbonation is now accepted as an eligible companion solution to geosequestration for CO₂ mitigation, and is currently met with actual pilot-scale demonstration projects, like the GreenMag-Newcastle program [12,13].

1.2. The direct aqueous mineral carbonation process: state-of-the-art and issues

Amongst the various mineral carbonation routes that are being investigated [14], direct aqueous mineral carbonation is possibly the most promising one. Pioneering studies from Albany Research Center (now NETL-Albany) reported carbonation yields as high as 78% in 30 min for serpentine particles with inorganic additives [15]. However their process suffers strong energy penalties due to the prior dehydration of the serpentine materials at 600–650 °C, the fineness of the feed particle size distribution (d_{50} less than 10 μm [16]), and the severe operating conditions (155 °C

and total CO₂ pressure of 185 atm). Further work from Arizona State University team [17–19] not only aimed at reducing these penalties, but also focused on local reaction mechanisms, bringing evidence of the formation of amorphous silica-rich passivation layers on the surface of Mg-bearing silicates during carbonation. Such mechanism has been recognised for a long time however, during natural weathering under oxidizing conditions [20]. Still, both the formation mechanisms of amorphous silica layers [21,22] and their transport properties [23] remain the subject of some controversy. The nature of the passivation layer depends on many factors, including the structure and the chemical composition of the substrate particles [24], the density of the mineral phase that makes up the passivation layer, and the temperature of carbonation. As an illustration, Fig. 1 from our previous work [25] shows the products obtained from –100 μm olivine particles, carbonated in water only, i.e. without additives. An operating temperature of 180 °C led to the formation of a covering silica iron oxide-rich layer some 20–30 nm thick, totally impervious, against that of a micrometer thick phyllosilicate layer at 120 °C. The nano-thick layer passivated the silicate surface resulting in no measurable carbonate formation, whereas the micron-thick one, possibly less impervious and/or covering, gave a few percent carbonation yield in 24 h. Such complexity casts serious doubts about the possibility of developing robust chemistry-based solutions, given the great many variety of ore types to be processed and the sensitivity of passivation layers to mild changes in operating conditions.

What springs to mind is to attack the problem from a different direction, moving away from trying to adapt the chemistry to the ore. It is also important to note that chemical solutions often imply consumption of additives, which are not always recyclable and often synonymous with added costs and potential environmental impacts.

1.3. Introduction to the hybrid aqueous mineral carbonation process

McKelvy et al. also attempted to deliberately exfoliate the passivation layer mechanically [18], as an alternative to depassivation using chemical additives. Their implementation consisted in (i) applying sonication to the particles and (ii) adding quartz particles of the same size as the reactive olivine particles to promote physical abrasion of the passivation layer. Tests were carried out in a stirred reactor, at 185 °C and 150 bar of CO₂ with the ARC standard 1 M NaCl + 0.64 M NaHCO₃ solution. If sonication (20 kHz, 600–1500 W), performed at mid-experiment, did not lead to any signif-

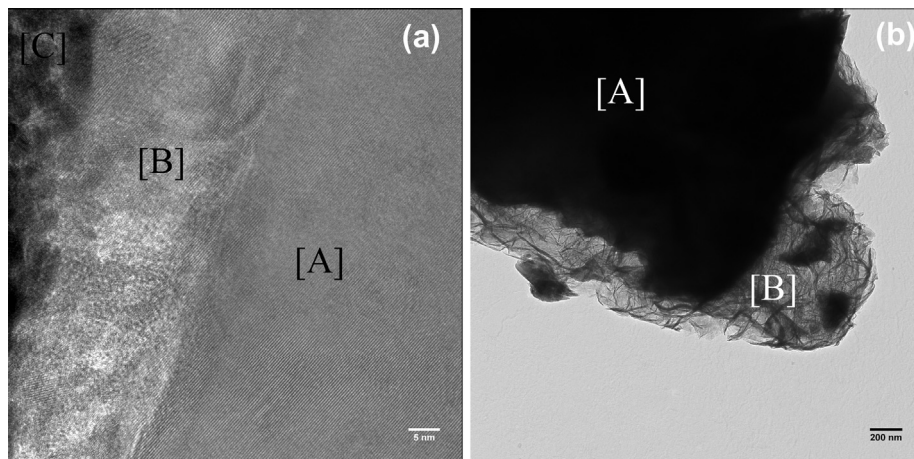


Fig. 1. Examples of silica-rich passivation layers forming at the olivine particle surface during direct aqueous mineral carbonation caption (Bodénan et al. [28]). (a) TEM image zooming on the cross-section of the olivine particle surface after 24 h at 120 °C (slurry solid concentration: 3 g L⁻¹; PCO₂: 20 bar): [A] residual olivine, [B] layer made of iron oxide and silica, [C] traces of gold from surface metal deposition for making of the thin section by FIB. Scale indicator = 5 nm. (b) TEM image of olivine particle surface after 95 h at 180 °C (slurry solid concentration: 90 g L⁻¹; PCO₂: 20 bar): [A] residual olivine, [B] magnesium phyllosilicate layer. Scale indicator = 200 nm.

icant improvement, addition of abrasive particles into the carbonation reactor yielded promising results. After 1 h, they obtained a rise in extent of carbonation from 68% without abrasive to 84% for a feed bearing 60 wt% abrasive particles. Using more than 60 wt% silica particles led to a drop in extent of carbonation, which they interpreted as silica self-abrasion reducing its effectiveness as an olivine exfoliation agent. They also confirmed that this exfoliation was effective over a range of temperatures and pressures.

Similarly, Park and Fan [26–29] tested ultrasounds, acoustic and internal grinding to remove the diffusion limiting silica layer, whose hindering effect they reported in their 2003 work [26]. However they were interested in a pH-swing process instead of direct aqueous carbonation, so they applied different grinding media for the dissolution phase that was carried out in a fluidized bed reactor under ambient conditions. They concluded that glass beads were the most effective at refreshing passivated serpentine surfaces and that combination of internal grinding and Mg-leaching solvent yielded rapid serpentine dissolution. Their approach also differed from that of ASU regarding the size of the grinding media, as they used 2–5 mm beads to exfoliate $-75\ \mu\text{m}$ serpentine particles. They argued that the ASU's results were simply due to particle size reduction, whereas their technological choice would meet the intended objective of refreshing surfaces rather than creating new unpassivated surfaces through particle fracture. Actually, the fact that the ARC/ASU test work led to $2\ \mu\text{m}$ particles in the end product [30] must be, at least partly due to their conducting exfoliation and mineralisation concomitantly, which Park and Fan did not achieve given the nature of the pH-swing process. The technological soundness of Park and Fan's fluidized bed solution is also difficult to assess, if one takes the sheer quantity of material to be processed.

Be as it may, there is evidence from the existing literature that mechanical exfoliation of passivating layers is one avenue which, if successful, would confer mineral carbonation a desirable robustness with respect to the variability of ore type and operating conditions. The present work took the position that ASU's results were mitigated by the fact that they did not implement the coupled exfoliation/mineralisation concept in efficient enough an exfoliation environment. In our earlier contribution [25], we have summarised the excellent carbonation yields that were obtained by operating the direct aqueous mineral carbonation process inside a dedicated attrition environment, more specifically inside a stirred bead mill.

The present paper serves to give a full and detailed account of the process itself, which involves coupling attrition and leaching for mineral carbonation, and discusses the driving mechanisms. Such an innovative hybrid process is referred to as “attrition-leaching”, whereby leaching of the ore is carried out inside an

attrition mill for the purpose of continuous elimination of leached passivation layers. The work brings definite proofs about the synergy of concomitant mechanical exfoliation and mineralisation. Included in the present paper is a preliminary life cycle assessment analysis of this innovative process, with implication for process optimisation. Given the capacity of stirred bead mills to process mining size throughputs, this work opens real perspectives for developing large scale robust solutions for direct aqueous mineral carbonation.

The authors point out that the value of such a process extends beyond that of mineral carbonation, in that it could find applications in hydrometallurgical treatment of ores and wastes, for which leaching is recurrently hampered by surface passivation issues.

2. Materials and methods

2.1. Experimental rationale and set-up

Stirred bead mills, of which a number of commercial versions can be found [31] have a number of attributes which make them particularly suited for exfoliation purpose in the context of direct aqueous mineral carbonation. These include [31, 32,33]:

- scalability from small scale (a few litres) experiments, through tip speed or grinding media stress intensity;
- engineering maturity for large scale continuous operations, with typical feed flow rates set points about $200\ \text{m}^3\ \text{h}^{-1}$ for large units in operation, at high slurry density. Typical slurry solid concentration used in this work is $90\ \text{g}\ \text{L}^{-1}$ or about 9 wt%, but this type of equipment can operate in the field at 40 wt% and higher;
- energy efficiency for particle abrasion with $-100\ \mu\text{m}$ feed typically, but with possibility to extend to coarser feed, say $-2\ \text{mm}$;
- possibility to use low cost natural grinding medium, such as silica, with the interesting possibility of autogenous grinding mode;
- feasibility of modifying existing designs to sustain the pressure and temperature conditions demanded by direct aqueous mineral carbonation through material selection, and to allow continuous CO_2 gas injection and dispersion.

In the context of this work, a 300 mL stirred autoclave reactor was modified and used as a high pressure high temperature stirred bead mill. Photographs of the set-up are given in Fig. 2. The set-up permitted conducting direct aqueous mineral carbonation experiments in batch mode, under controlled temperature and pressure conditions, with and without concomitant attrition depending on

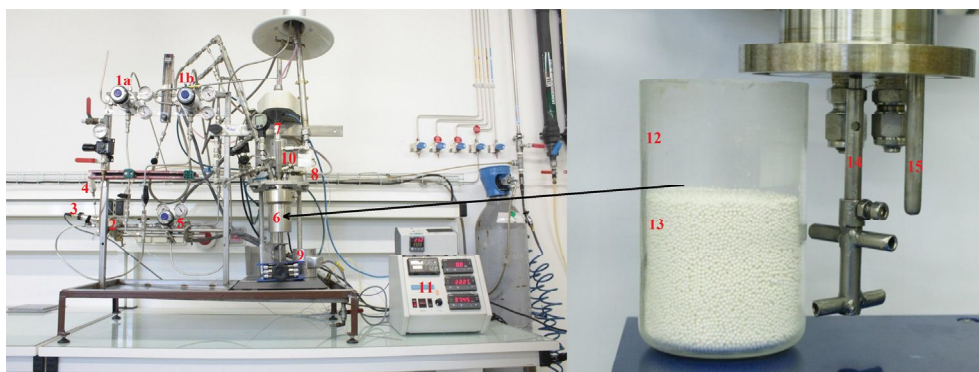


Fig. 2. Overview of the attrition-leaching set-up and close-up view of the attrition chamber with alumina beads. 1 gas line equipped with pressure regulation valve (a N_2 , b CO_2), 2 gas reservoir, 3 pressure transducer, 4 Pt-100 probe, 5 pressure regulation valve, 6 300 mL Hastelloy reactor, 7 pressure transducer, 8 Pt-100 probe, 9 furnace, 10 magnetic drive, 11 control and monitoring panel, 12 glass inner jacket, 13 grinding media, 14 attrition/gas dispersion stirrer, 15 thermowell.

Table 1
Chemical composition of the five ores selected for this work (Bodénan et al. [28]).

	Olivine (wt%)	Harzburgite Hz1 (wt%)	Harzburgite Hz2 (wt%)	Lherzolite (wt%)	Wehrlite (wt%)
SiO ₂	42.2	40	39.3	46.3	44.6
MgO	46.4	41.1	40.4	30.8	32.0
Fe ₂ O ₃	9.8	7.8	7.3	7.6	7.5
Al ₂ O ₃	0.5	0.6	1.3	4.0	3.7
CaO	0.2	0.6	0.9	5.0	4.9
MnO	0.1	0.12	0.1	0.15	0.14
Na ₂ O	0.2	<0.2	<0.2	<0.2	<0.2
K ₂ O	0.02	<0.05	<0.05	<0.05	<0.05
TiO ₂	0.008	<0.05	<0.05	<0.05	<0.05
Total C	0.04	0.11	0.10	0.12	<0.1
Loss on ignition at 1000 °C	0.1	9.1	10.4	5.7	6.2

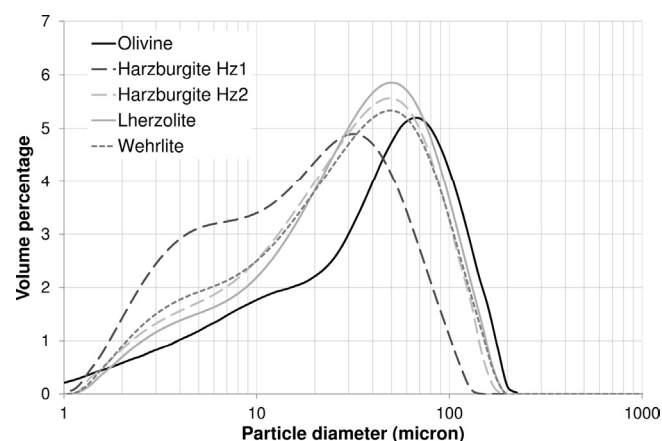


Fig. 3. Particle size distribution of the five materials, measured by laser granulometry (Mastersizer 2000).

whether grinding media would be used. The CO₂ pressure inside the reactor was regulated using a CO₂ ballast tank and gas pressure regulator, and instantaneous CO₂ consumption by the liquid–solid suspension was monitored by recording temperature and pressure inside the ballast. Slurry temperature was monitored and PID controlled.

When operating in hybrid attrition-leaching mode, the stirred reactor was filled with 30 vol.% of 1.3 mm diameter alumina beads. Nominal test conditions used 90 g L⁻¹ suspensions with ~100 microns feed material. Different ores were tested during this work, whose characteristics are reported in Table 1. The mechanical stirrer was rotated at moderate speed (800 rpm) to promote attrition grinding. Dispersion of CO₂ was achieved by feeding the gas through the stirrer hollow tubing for efficient gas–liquid mass transfer. A glass jacket, shown on the right handside of Fig. 2, was used to prevent reactor wear.

2.2. Materials

Five materials were used in this study. The first one, referred to as olivine, is produced by Magnolithe GmbH (Austria) and is mainly forsteritic olivine. The value of this particular mineral is that it has undergone heating at 1000 °C; hence it no longer contains structural water, which simplifies estimation of formed carbonates by thermogravimetric analysis (TGA). The other four materials are natural peridotites, with two harzburgites and wehrlite from New-Caledonia, and lherzolite from the French Pyrenees. Table 1 gives the chemical composition of these materials. Their mineralogical characteristics can be found in Bodénan et al. [25].

The ores were dry ground in a jar mill, which was operated to produce ~100 µm feed material for mineral carbonation testing. The size distribution of these resulting materials is given in Fig. 3.

2.3. Experimental protocols

For the sake of this study, three distinct experimental protocols were used.

– *Reference mode*: This protocol produces the reference carbonation performance against which the other protocols are gauged. The slurry, consisting of ultra-pure water (or inorganic additive solution) and the investigated material, was prepared in a glass jar. After the jar was placed inside the autoclave, the reactor was purged several times with nitrogen under stirring to remove oxygen both from headspace and in solution. The ballast was filled with CO₂ to about 45 bar, enough to ensure full carbonation of the material in the operating

conditions. Data acquisition was then started, with a sampling frequency of 1 Hz. The slurry was heated under stirring up to the set temperature (120 °C or 180 °C), which was reached after about half an hour. Subsequently, the stirring was stopped and CO₂ was introduced into the reactor so that to reach a partial pressure of 20 bar (accounting for partial pressures of nitrogen and water vapour at the considered temperature). Note that this pressure value was mainly chosen for comparison purposes with the open literature [18,34,35]. After stabilization of pressure and temperature in the ballast and in the reactor (after about 1 min), the stirring was started again (800 rpm) and the system was let on reacting for 24 h to highlight the differences in between this mode and the two-step mode, which both yield fast initial carbonation kinetics due to the fineness of the resulting particle size distribution. Nevertheless the monitoring of instantaneous gas consumption gave access to the whole reaction kinetics. At the end of the reaction, the acquisition was stopped and the slurry was cooled down to 60 °C (still under stirring). Pressure was released and the slurry was transferred into a 1 L beaker and weighed. The reactor internals were thoroughly cleaned with osmosed water to recover stuck solid particles. The rinse solution was weighed and put into the beaker. The resulting slurry was passed through a 0.2 µm micropore filter. The filtrate was analysed by ICP-AES and the solid was oven dried at 70 °C during 24 h before weighing and analysis.

– *Two-step mode*: 300 g of alumina or zirconia beads (1.3 and 1 mm diameter, respectively), ultra-pure water and the investigated material were introduced in the glass jar, which was placed inside the autoclave. The reactor was purged several times with nitrogen while stirring to remove oxygen both from the headspace and the solution. The stirring speed was set to 800 rpm and the attrition step was pursued during 24 h at room temperature, the reactor being immersed into a thermostated bath to prevent temperature rise due to the friction of the grinding media. Thereafter the reactor content was transferred into a 1 L beaker. The reactor internals were carefully cleaned with ultra-pure water to recover stuck solid particles. The mixture of slurry and grinding media was passed through a 0.8 mm sieve to separate the millimetre beads from the fine slurry. The beads were thoroughly rinsed with ultra-pure water to recover more solid. The diluted slurry was centrifuged at 200g and 25 °C for 15 min. After centrifugation, the clear supernatant was removed, the wet solid was reintroduced in the glass jar and water was added so that to almost match the previous slurry concentration. The glass jar was placed in the reactor

and the carbonation step was then performed as described for the reference mode. After filtration, the solid product was also analysed for particle size distribution.

- *Hybrid attrition-leaching mode*: The reaction proceeded as described in the reference protocol, except that the grinding media was introduced in the glass jar along with the reactant suspension. After 24 h of carbonation under attrition, the fine slurry was separated from the millimetre beads as described for the two-step mode (using a 0.8 mm sieve and a careful rinse of the beads, all contents being weighed at each step). The resulting slurry was passed through a 0.2 μm micropore filter and analysed for liquid and solid phases.

2.4. Extent of carbonation

The extent of carbonation is defined as the fraction of Mg and Ca from the initial feed material which is included into solid carbonates. The amount of solid carbonates formed by mineralisation is calculated by measuring the carbon content of the treated ores, accounting for the presence of carbonate in the initial ore (however negligible in most cases, see Table 1). Thermogravimetry analyses were also performed to confirm these results, but not retained for final calculations, as residual silicates (with the exception of olivine) contain structural water which is released within the same temperature range as formed carbonates (300–600 °C).

From the final amount of carbonates, the evolution of the carbonation yield can be backtracked all the way to the very start of the process from the instantaneous CO_2 consumption record, including the reactor headspace filling stage. It is then checked that this starting point matches with the beginning of steady pressure inside the reactor. Instantaneous carbonation yield is estimated by application of the Peng–Robinson state equation, using the temperature and pressure measured inside the CO_2 ballast tank that feeds the system.

CO_2 dissolution and precipitation of carbonates can occur simultaneously at the start of the application of CO_2 to the system, making identification of the initial carbonation kinetics difficult. As expected, this difficulty was highest when using finely ground particles in two-step processing mode, the high initial particle surface area yielding very fast initial dissolution and carbonation kinetics.

2.5. Water analyses and characterisation of solid phase

After filtration of the entire reaction product using a 0.2 μm micropore filter, the liquid phase was analysed on an Ultima 2 ICP-AES spectrometer (Horiba Jobin Yvon) to determine the amount of dissolved elements (Mg, Si, Fe).

Carbon content of the solid product was measured on a Perkin Elmer 2400 CHNS elemental analyser, using about 2 mg of powder. For carbonation yields higher than 5%, elemental analyses were replicated three or four times using separate samplings and showed less than 5% relative variation.

Thermograms were obtained on a Q600 apparatus (TA Instruments).

Apart from carbon and thermogravimetric analyses, the solid phase was characterised by scanning electron microscopy (SEM), using a Zeiss Ultra 55 FEG microscope operated at 10 kV and a working distance of 7.5 mm, and equipped with an energy dispersive X-ray (EDX) system from Bruker. Transmission electron microscopy (TEM) was also performed either on powders dispersed on carbon film or on thin sections prepared by a focused ion beam (FIB), using a Jeol FEG 2100F operated at 200 kV and equipped with an energy dispersive X-ray system from Jeol. Laser granulometry was used to determine particle size distribution: the measurement was made in wet mode on Mastersizer 2000

apparatus (Malvern Instruments), using a Hydro 2000S dispersion unit (stirring at 1750 rpm).

3. Results and analysis

3.1. Benchmarking process performance

As with any process development, it is always necessary to rate the performance obtained under given process conditions against a reference or a set of objectives. Here, we predicted the change in extent of carbonation with time as if the material remained unpassivated throughout the test, i.e. through a shrinking particle model which used a dissolution rate law established for fresh ore surface [36]. This gave the best achievable kinetics for olivine carbonation under given operating conditions. As the process is controlled by the chemical reactions that occur at the particle surface, the actual particle size distribution of the olivine feed has to be accounted for. The particle size analysis, measured by laser diffraction, was first converted from a volume distribution to an areal distribution. This distribution was then divided into 20 size classes, each class contributing 5% of the areal distribution. Each size class was entered into the geochemical code Chess [37] as a distinct material, albeit with the same thermodynamic properties (from CTD database entry forsterite Mg_2SiO_4) but with distinct specific surface area. This modelling approach was used to predict the lixiviation kinetics with good precision [38].

The example from Fig. 4 compares the measured reference experiment with no grinding medium and the best achievable performance for a 90 g L^{-1} suspension of olivine in water, at a temperature of 180 °C and a CO_2 partial pressure of 20 bar.

The most striking feature shown in Fig. 4 is the magnitude of the gap between the actual measured extent of carbonation (reference mode), which implies some passivation of the olivine surface, and the prediction without passivation. The sheer size of this gap demonstrates that overcoming the passivation problem is pivotal for development of the aqueous mineral carbonation process. Moreover, Fig. 4 indicates that, if no passivation phenomena occurred, 100% carbonation of olivine could be achieved with such grain sizes, using pure water as a solvent – i.e. without any additives – in about 5 h.

3.2. Robustness of the hybrid exfoliation/mineralisation process

The five materials selected for this work were tested using the hybrid attrition-leaching protocol. Tests were carried out at

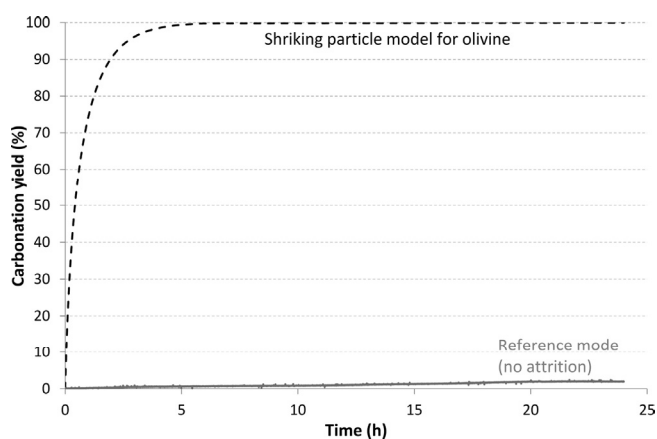


Fig. 4. Comparison between the best possible carbonation performance attainable, i.e. without surface passivation, and the reference mode performance (olivine 90 g L^{-1} , 180 °C, 20 bar of CO_2) (Bodéan et al. [28]).

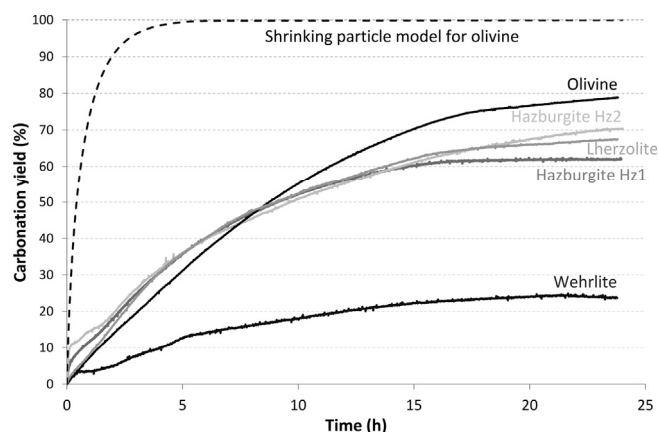


Fig. 5. Demonstration of the robustness of the hybrid mineral carbonation process, showing the hybrid process performance for all five materials investigated and the best achievable performance for olivine (90 g L^{-1} , $180 \text{ }^\circ\text{C}$ and 20 bar of CO_2) (Bodénan et al. [28]).

$180 \text{ }^\circ\text{C}$, 20 bar of CO_2 and 90 g L^{-1} . Fig. 5 shows the hybrid process performance for all five materials, along with the best achievable performance for olivine given as reference. The results with olivine undergoing the hybrid process show that this protocol is able to bridge a significant portion of the gap between the performance measured without attrition and the best achievable performance, keeping in mind that the process itself is not optimised. Table 2 gives the final carbonation extents for all five materials, with and without hybrid exfoliation.

Lherzolite and harzburgite, which all contain a high amount of serpentinised materials, gave carbonation performance close to that of olivine. Of the five materials tested, only wehrlite yielded significantly lower carbonation extent, albeit significantly higher than that obtained without any grinding.

Emphasising that the test conditions were not optimized in any way with respect to solid concentration, attrition rate, bead size distribution or bead volume fraction, not to mention that the converted autoclave is not an actual attrition bead mill, the results that were obtained demonstrate the potential of the hybrid attrition-leaching process, and its robustness with respect to variations in used materials to be processed. This latter feature is critical given the expectation that mineral carbonation should be able to process different materials equally. Material insensitivity cannot possibly be achieved reliably by any chemically based process.

In the liquid phase, only traces of iron were detected. Average extraction yields of silicon and magnesium in solution reached about 1.5% for both two-step and hybrid modes. In the reference experiments (without attrition), similar concentrations of Si were obtained, but significantly less Mg (less than half) as the result of the ore passivation. Note that for the 90 g L^{-1} olivine slurry, the shrinking particle model predicts that, after 24 h, 2.1% of the initial Si content would be in solution, Mg being completely converted into solid carbonate.

Table 2

Carbonation yield* after 24 h for the five ores selected (90 g L^{-1}), for the three test protocols at $T = 180 \text{ }^\circ\text{C}$, $\text{PCO}_2 = 20 \text{ bar}$, and with alumina grinding beads unless otherwise specified.

	Reference mode (no grinding media)	Two-step mode	Hybrid mode
Olivine (Magnolite)	2.0% (CO_2 consumption)	46.7% (38.0% with ZrO_2)	78.8% (repetition: 76.7%)
Harzburgite Hz1	7.8% (CO_2 consumption)	35.8% with ZrO_2	62.1%
Harzburgite Hz2	6.3%	34.0% with ZrO_2	70.4%
Lherzolite	0.6% (CO_2 consumption)	45.8%	67.5%
Wehrlite	non detectable	17.2% with ZrO_2 (repetition: 19.2%)	23.7%

* Calculated from C analysis of solids (unless otherwise mentioned).

3.3. Synergy between attrition grinding exfoliation and mineralisation processes

One important question about the hybrid process concerns the nature and extent of the synergy between the exfoliation and mineralisation mechanisms. Table 2, which shows that carbonation yield with the hybrid process is consistently higher than with the two-step process, proves the synergy between the two processes, hence their actual hybridisation.

Fig. 6 shows the carbonation yield curves with both processing modes for olivine, harzburgite, and lherzolite samples. The two-step mode yields consistently faster mineralisation kinetics at the start of the mineralisation step. This is explained by the finer particle size distribution from the first attrition only step of the two-step mode, as shown in Fig. 7. However, the hybrid mode mineralisation kinetics always exceeds that of the two-step within a few hours, giving 20% or more additional carbonation yield after 24 h.

These measurements prove that there is an actual synergy between attrition grinding and mineralisation processes. This result rejects the argument put forward by Park and Fan that the effect observed by the ARC was due to particle size only.

Additional understanding was sought at the local particle scale, starting with the particle size distribution. Fig. 7 shows the size distribution of the different products for olivine sample. The similarity of PSD obtained at the end of the hybrid process and prior to carbonation in the two-step process confirms the previous statement. Nonetheless one part of the gap reduction between the experimental results and the theoretical ones must be attributed to size reduction.

Size distributions of final products are also similar in mean diameter, with a measured d_{50} value of $7.0 \text{ }\mu\text{m}$ and $4.2 \text{ }\mu\text{m}$ for two-step and hybrid protocols respectively. The fineness of the final product is clearly dictated by the conditions used for the attrition grinding process, as reflected by the convergence between the product size distributions, notwithstanding the right tail of the two-step process product. However, analysis of the particles themselves shows radically different reaction products.

Fig. 8 displays characteristic features of the two-step and hybrid product particles.

The reaction product from the two-step mode is composed of large magnesite particles, which account for the mode to the right of the particle size distribution in Fig. 7, and unreacted olivine cores surrounded by the same passivating phyllosilicate layer found in experiments without attrition (cf. Fig. 1b). Note that this phyllosilicate may include chemical elements coming from the grinding media, explaining the slight differences between the carbonation kinetics observed when using alumina or zirconia beads (cf. Fig. 6a).

This reaction product is to be expected from a purely fine grinding effect. Indeed, the large particles of magnesite were allowed to grow to large sizes during the 24 h mineralisation only with the two-step protocol. Passivation of fine particles produced by the 24 h attrition grinding phase did occur, but the fineness of the feed

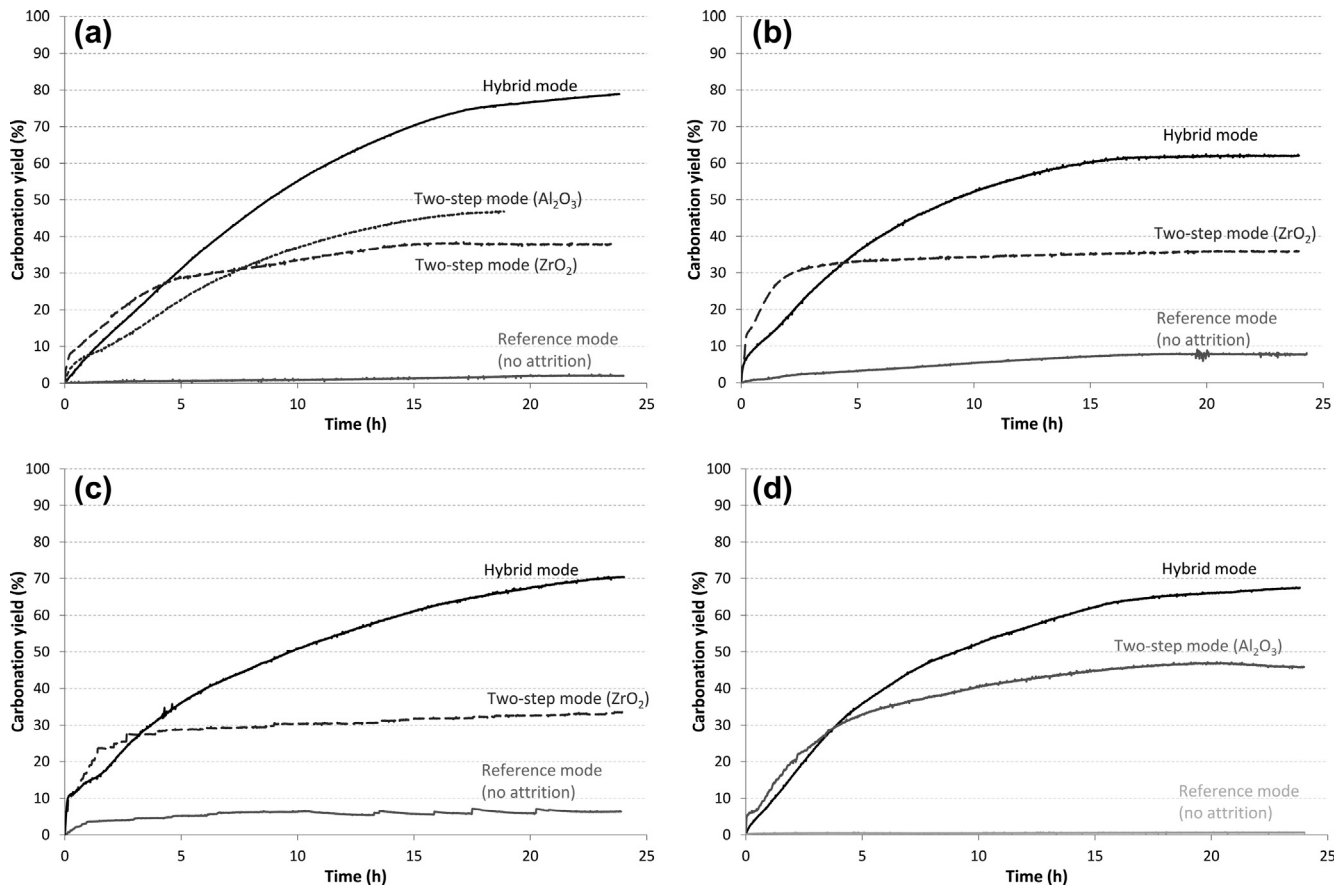


Fig. 6. Carbonation yield curves for the reference, two-step and hybrid processes (slurry concentration = 90 g L^{-1} , $T = 180 \text{ }^\circ\text{C}$, $\text{PCO}_2 = 20 \text{ bar}$, grinding bead type given in brackets for two-step mode): (a) olivine; (b) harzburgite Hz1; (c) harzburgite Hz2; (d) lherzolite.

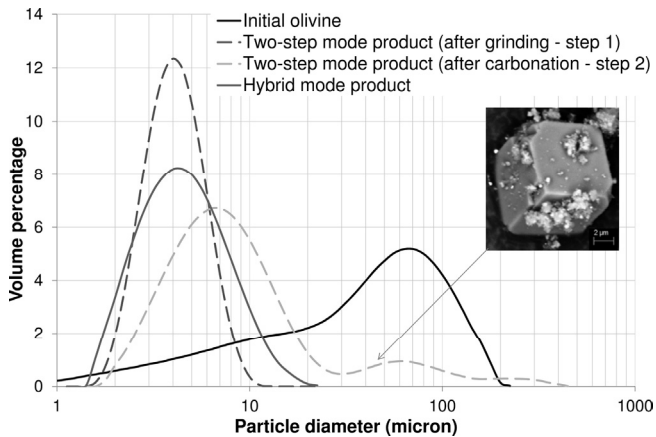


Fig. 7. Particle size distribution of the feed and reaction products for the olivine sample (90 g L^{-1} , $180 \text{ }^\circ\text{C}$ and 20 bar of CO_2 , alumina grinding beads); insert is an example of large magnesite particles obtained in two-step mode.

particles to the mineralisation step, with a d_{50} of $3.8 \text{ }\mu\text{m}$, yielded the measured increase in carbonation.

The hybrid product particles, with d_{50} about $4 \text{ }\mu\text{m}$ (see Fig. 7), are actually aggregates that are constituted of particles a few tens of nanometers in size. These aggregates contain carbonates, amorphous silica particles or silicate particles with very low magnesium content and alumina fragments from grinding bead wear.

A significant observation from Fig. 8b is the absence of a fibrous phyllosilicate layer covering residual olivine grains and that was

invariably observed with the two-step process. This confirms, at the particle scale, the actual synergy between exfoliation and reaction in the hybrid process. Indeed, this shows that the hybrid process successfully prevents the formation of the passivation layers whose formation controls the performance of the direct aqueous mineral carbonation. We also note the scarcity of residual olivine particles in the hybrid process, because olivine has reacted almost fully thanks to the continuous elimination of passivation layers, leaving behind amorphous silica containing traces of magnesium and aluminum.

4. Discussion

The results and analyses presented in the previous section have demonstrated the soundness of the hybrid mineral carbonation process, defined previously as the conduction of direct aqueous mineral carbonation under attrition conditions. The operating conditions tested within this work were chosen by analogy with those of typical stirred bead mills, which are proven units dedicated to attrition. However, for the purpose of the hybrid process under consideration, the margin for performance improvement is expected to be significant.

Assessment of the potential of the hybrid process is discussed hereafter from both life cycle analysis and process viewpoints. One issue of importance concerning the hybrid mineral carbonation process concerns its technical feasibility for large scale operations. Large scale stirred bead mills being a mature technology, as reflected by their current popularity in the metalliferous mining sector, the feasibility of the hybrid mineral carbonation process is deemed very much achievable. Nonetheless, large scale stirred

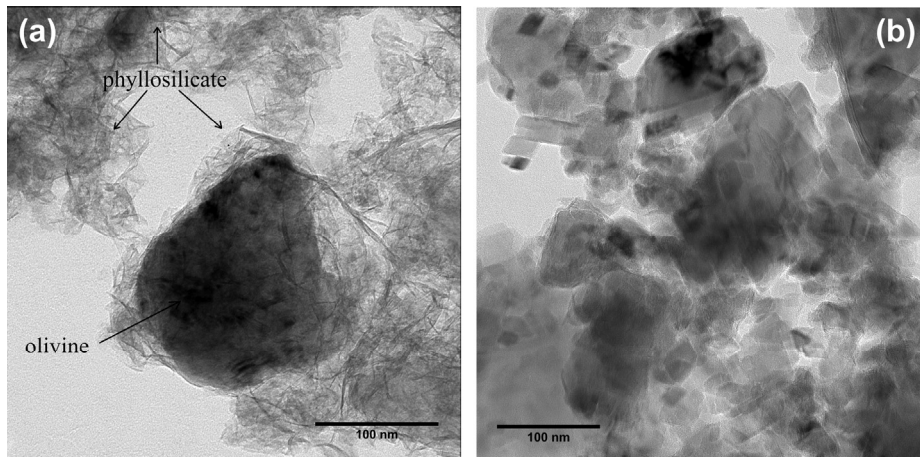


Fig. 8. TEM images of reaction products (olivine 90 g L^{-1} , $180 \text{ }^\circ\text{C}$, 20 bar of CO_2): (a) from two-step mode (24 h of reaction following 24 h of attrition under ambient conditions) showing phyllosilicate layer covering residual olivine particle; (b) from hybrid leaching-attrition mode (24 h) showing magnesite particles of tens of nanometers.

bead mills capable of operating under pressures and temperatures demanded by the mineralisation process are not yet commercialised, and existing machinery will have to be adapted to meet the requirements of the hybrid mineral carbonation process. The necessary adaptations however, which concern liner and agitation internals, gas dispersion and solid dynamic classification are all technically feasible. The scalability of such attrition grinding mills from models a few litres in volume, which simplifies considerably operating conditions determination and sizing of large scale systems, is a major asset for industrialisation of the hybrid mineral carbonation process.

4.1. Preliminary LCA analysis of the hybrid aqueous mineral carbonation process

The experimental results presented in this paper were used to perform an LCA analysis of the hybrid process, in an attempt to assess its environmental performance. To this end, the following functional unit was used to produce 1 MWh of electrical energy with a coal power plant. This analysis was performed to position the environmental ranking of the hybrid process against two scenarios for the functional unit selected, namely without CO_2 capture, with CO_2 capture and geosequestration, and with CO_2 capture and ex-situ mineral carbonation using the hybrid process, and to identify possible means of improving the environmental footprint of the hybrid process.

For the hybrid process, the following process parameters were accounted for in the analysis:

- The mass fraction of Mg (+Ca) in the ore, and the extent of conversion of Mg (+Ca) obtained at the end of the hybrid process, defined as the molar fraction converted to carbonates - MgCO_3 (and CaCO_3). Both parameters yield the amount of ore necessary to store one ton of CO_2 . Under the most favourable conditions of the hybrid process, it was estimated that 2.47 tons of olivine were necessary to store 1 ton of CO_2 .
- The slurry solid concentration. This variable was used to determine the energy necessary to heat up the water, relative to the amount of processed ore.
- The initial PSD of the ore, as extracted, and the PSD of the ore after crushing and grinding before it is used in the hybrid process. This information yielded estimation of the energy used for comminution using Bond's formula, using a realistic Bond work index value of 13 kWh/t .

- The PSD of the material at the end of the hybrid process. This parameter was used to assess the amount of energy expended by the mechanical exfoliation process.
- The slurry temperature and the efficiency of the heat exchanger used to recycle the water through the process. This information gave the energy necessary for heating up the water, the CO_2 and the ore. The heat capacity of Mg_2SiO_4 was used in the calculations.
- The CO_2 pressure. As the hybrid process was operated at a CO_2 partial pressure of 20 bar , the LCA analysis considered a transport of CO_2 through a 380 mm diameter pipeline at a pressure of 20 bar . A distance of 300 km was assumed between the source CO_2 (power station and MEA CO_2 capture plant) and the mineral carbonation plant, which eliminated the need for additional compression stages along the pipeline to compensate for head loss. The energy required to pressurize the CO_2 to the operating pressure of the hybrid process, namely 20 bar , was also accounted for in the analysis.

The following environmental indicators were used to quantify the environmental performance of the hybrid process:

- related to resource consumption: *natural resource depletion* and *non-renewable primary energy consumption*,
- related to global warming: *climate change*,
- related to air pollution: *terrestrial acidification* and *photochemical oxidation*.

These indicators were deemed most reliable and relevant for the purpose of the work.

Results reported here for the hybrid process were those obtained with the olivine ore under the following operating conditions:

- The ore was assumed to be crushed from 1 cm to 1 mm , then dry-milled from 1 mm to $100 \text{ }\mu\text{m}$.
- Notwithstanding the marginal effect of solids concentration in the range $90\text{--}250 \text{ g L}^{-1}$ on reaction rate and carbonation yield (cf. Section 4.2.), the latter was set to the best value measured in this study (about 79%), corresponding to olivine processing at $180 \text{ }^\circ\text{C}$ under 20 bar of CO_2 .
- Solids concentration was set to 250 g L^{-1} .

These conditions, particularly with respect to the solids concentration, are favourable in terms of water and energy usage.

Table 3 gives the overall LCA analysis results for the hybrid process, giving the overall impacts, and the relative weight of the coal power station, CO₂ capture, CO₂ transport and hybrid process.

While the analysis shows that CO₂ transport has a negligible impact on the overall process impact, it indicates that the hybrid process has an environmental impact comparable to that of the coal power station plus CO₂ capture system on those LCA criteria not associated with resource consumption. For criteria associated with resource consumption, the hybrid process has an environmental impact comparable with the CO₂ capture process used to produce pure CO₂ stream from the power station exhaust gases. The CO₂ capture is included in the LCA analysis as the experiments reported here with the hybrid process were carried out using pure CO₂. The impact indicator values show that the hybrid process should be tested using dilute CO₂, which could possibly yield a lesser dependency on CO₂ capture, hence a reduced overall environmental impact.

Table 4 compares the overall LCA results for the functional unit:

- without CO₂ capture
- with CO₂ capture and geological storage
- with CO₂ capture and the hybrid process.

The positive effect of capture and storage, whether geological or by mineralisation, on the climate change indicator confirms that both solutions meet their objective of reducing the net greenhouse gas emissions. Both CO₂ mitigation options however have negative impacts on most of the other LCA indicators selected, the hybrid process having at least twice the impact of the geological storage scenario. The impact of the hybrid process would possibly be further reduced through a number of levers, including the use of dilute CO₂ gas streams, and the beneficiation of reaction products, possibly in the construction sector.

4.2. Process optimization

There are a number of possibilities for optimizing the hybrid process to be explored further, following the guidelines set by the preceding LCA analysis. Complementary experiments were performed to test the scope for reducing temperature and increasing slurry solid concentration, bearing in mind that both these operating conditions can be changed.

Stirred bead mills can be operated at high solid concentration, say 40 wt% and more with metalliferous ores. Fig. 9 shows the variation in performance of the hybrid mineralisation process with the

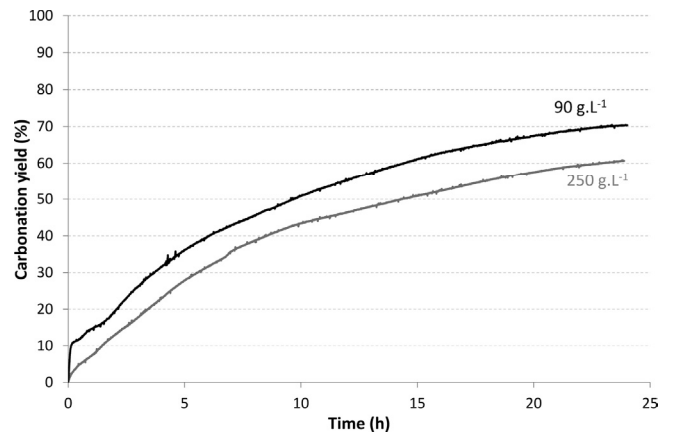


Fig. 9. Hybrid mineralisation process performance for harzburgite Hz2 at 90 g L⁻¹ and 250 g L⁻¹ (180 °C and 20 bar of CO₂).

harzburgite sample Hz2 between 90 g L⁻¹ and 250 g L⁻¹. After 24 h, these conditions gave a carbonation yield of 70.4% and 60.7%, respectively, recalling that the relative uncertainty in final carbon contents related to material inhomogeneity is less than 5% (cf. Section 2.5.). The reduction in performance with the highest solids concentration in the test is deemed related to the difficulty of our stirred bead mill set-up, which is a modified autoclave, to provide efficient agitation considering the mechanical limitations of the stirring mechanism.

Considering that the process used the same operating conditions in both cases, this result suggests that the hybrid mineralisation process can potentially be operated at the highest slurry concentration accepted by industrial stirred bead mills. As shown in the LCA analysis, this is an important practical issue, since going from 9 wt% to 40 wt% solids means that water required for the process is reduced by more than 30%, and so the energy required to maintain the slurry temperature at that required by the mineralisation process.

Considering the nature of the passivation layer and its associated transport properties [39], a temperature of 180 °C appears to be about the ideal temperature. Nonetheless, the hybrid mineralisation process, by nature, circumvents the passivation layer issue. The question is about its overall efficiency in relation with the properties of the passivation layers. Providing this question with answers is premature, development work is required using

Table 3
LCA results for the CO₂ mitigation scenario using the hybrid process.

Environmental impact indicators	Units	Total	Coal power station	MEA CO ₂ capture	Pipeline transport of CO ₂	Hybrid process
Natural resource depletion	kg Sb eq.	12	55.39%	25.63%	0.05%	19.01%
Non-renewable primary energy consumption	Primary MJ	20,942	47.70%	22.01%	0.06%	30.23%
Climate change	kg CO ₂ eq.	608	151.60%	-102.8%	0.14%	51.17%
Terrestrial acidification	kg SO ₂ eq.	2.5	65.23%	-17.10%	0.16%	51.91%
Photochemical oxidation	kg NMVOC eq.	1.99	48.99%	17.98%	0.30%	32.73%

Table 4
Selected LCA criteria for the three selected scenarios.

Environmental impact indicators	Units	Without CO ₂ capture	With CO ₂ capture and geological storage (%)	With CO ₂ capture and the hybrid process (%)
Natural resource depletion	kg Sb eq.	6.7	+46	+79
Non-renewable primary energy consumption	Primary MJ	9990	+47	+110
Climate change	kg CO ₂ eq.	923	-68	-34
Terrestrial acidification	kg SO ₂ eq.	1.64	-26	+52
Photochemical oxidation	kg NMVOC eq.	0.973	+38	+105

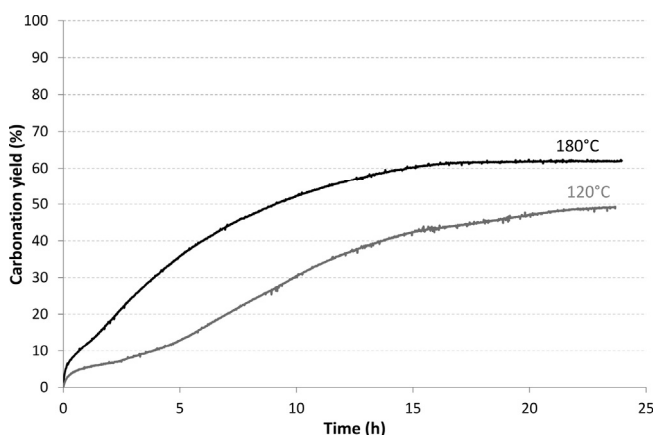


Fig. 10. Hybrid mineralisation process performance for 90 g L^{-1} Hz1 slurry at 180°C and 120°C (20 bar of CO_2).

industrially designed stirred bead mills. Notwithstanding, Fig. 10 shows the variation in performance of the hybrid mineralisation process with the harzburgite Hz1 sample at 180°C and 120°C . After 24 h, these conditions gave carbonation yields of 62.1% and 49.2%, respectively.

Whether the drop in performance is associated with a greater difficulty of the attrition grinding process to exfoliate the passivation layer that forms at 120°C , it is premature to say; however it is possible. At any rate, the conversion of the harzburgite sample at 120°C is significant, and additional research is necessary to determine the best operating temperature from an overall process performance analysis.

As discussed previously, there is significant scope for enhancing the performance of the hybrid mineralisation process over those reported in this work, which already stand amongst the best ones measured to date. For instance use of the $1 \text{ M NaCl} + 0.64 \text{ M NaHCO}_3$ solution (cf. Section 1.2.) instead of water still improves the carbonation yield which reaches 70% within 5 h (87% in 24 h) in the case of 90 g L^{-1} olivine slurry at 180°C .

Besides all the positive attributes of this technology which have been discussed earlier, important performance gains are expected from operating the hybrid mineralisation process in a continuous mode, for which closed and open loop configuration should be tested.

5. Conclusions

As one of the most promising solution to CO_2 mitigation, mineral carbonation remains an important area of research and development. In this paper, an innovative process is proposed for aqueous mineral carbonation. The proposed solution is referred to as hybrid process as it merges the aqueous mineral carbonation reactions with a continuous attrition process carried out in a stirred bead mill. The attrition process permits continuous exfoliation of passivation layers that form during the leaching of magnesium silicates, and hence overcomes the most important limiting factor for development of an efficient aqueous mineral carbonation process. It is found that the process shows marginal sensitivity to ore type and operating conditions, contrary to chemical-based processes whose performance is highly dependent on the nature of the ore and the geochemistry of the reactive system. Careful analyses of reaction products reveal that there is an actual synergy between the mechanical exfoliation of the reactive particle and mineral carbonation processes. Without optimization of the process conditions, the hybrid process consistently yields high carbonation yields for serpentinised ores with reasonable kinetics. Through

the hybrid process, all the reactive ore is consumed, leaving a mixture of fine particles of innocuous carbonate and siliceous particles.

It is argued that the margin for improvement of this process is significant. Indeed, a number of operating conditions can be modified, with a strong likelihood of producing improved performance. Using an actual stirred bead mill in a continuous circuit, as opposed to the autoclave used in batch mode in this work, will provide more efficient conditions for attrition and mineralisation reactions. The capacity of stirred mills to process mining scale throughputs, and their ease of scale-up are very important assets of the proposed hybrid mineralisation process for industrial scale applications. A number of other conditions can be investigated, all of which can contribute to improving the performance of the proposed process, in terms of kinetics and net energy consumption. These include, without specific order, lowering the partial pressure of CO_2 , operating with diluted flue gases instead of pure CO_2 , optimizing the attrition conditions, such as operating the stirred mill in semi or complete autogenous mode, reducing the net energy balance of the process by reducing the amount of process water through increasing the solid concentration, and lowering the operating temperature.

This process is not without pending questions however, the main one concerning the handling and beneficiation of the reaction products. As found experimentally, the process produces a suspension bearing fine carbonate and siliceous particles with a mean size around $5 \mu\text{m}$. These ca. $5 \mu\text{m}$ aggregates are themselves constituted of tens of nanometers sized individual grains. Product handling demands a dewatering step for process water recovery. Centrifugal tests used for product characterisation have indicated that the particles have good settling properties, hence solid-liquid separation is not deemed to be an issue. The beneficiation of the product however is very much an open question. Physical separation of carbonate and siliceous particles seems unlikely, so that beneficiation should target the product mixture as a whole. The chemical content of the product could make it eligible for making magnesium cements, however dedicated research is necessary to test the possibilities of beneficiating the hybrid process products in the construction sector.

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