Available online at www.sciencedirect.com

SciVerse ScienceDirect

Energy Procedia 37 (2013) 5945 – 5954

Energy Procedia

GHGT-11

Carbon storage by mineralisation (CSM): serpentinite rock carbonation via $Mg(OH)_2$ reaction intermediate without CO_2 pre-separation

Ron Zevenhoven[a*], Johan Fagerlund[a#], Experience Nduagu[a], Inês Romão[a], Bu Jie[b], James Highfield[b]

[a] *Abo Akademi University, Thermal and Flow Engineering Laboratory, 20500 Turku, Finland*
[b] *Institute of Chemical and Engineering Sciences (ICES), A-STAR, 627833 Singapore*
[#] *Currently at CITEC Oy Ab, 20740 Turku, Finland*

Abstract

CO_2 mineral sequestration, a.k.a. mineral carbonation offers an alternative to "conventional" CCS that involves underground storage of pressurised CO_2. It is being developed for locations that lack access to underground storage capacity for CO_2 and/or have access to suitable mineral resources, or for users that aim at marketable (hydro-) carbonate or otherwise useful solid product. The "Åbo Akademi route" of producing $Mg(OH)_2$ from serpentinite rock followed by gas-solid carbonation in a pressurised fluidised bed (PFB) has been further developed and optimized towards industrial demonstration. Recoverable ammonium sulphate salt is used as the fluxing agent for Mg extraction from rock. While $Mg(OH)_2$ production and its scale-up and subsequent carbonation are yet to be demonstrated beyond 78 and 65% efficiency, respectively, the carbonation reaction reaches an equilibrium already after 10-15 minutes. Process energy requirements are ~ 3 GJ (heat)/t CO_2 (similar to the capture stage of "conventional" CCS), while using ~ 3 t rock/ t CO_2, with separate streams of unreacted rock, FeOOH and $MgCO_3$ as main products. The scale-up activities involve defining reactor types and conditions for the $Mg(OH)_2$ production and the carbonation, respectively, using flue gas at ~500°C, 20 bar CO_2 partial pressure. This implies compression of a complete flue gas stream. It was shown that carbonation at a given (wet) CO_2 pressure gives results similar to when operating with diluted gas streams at higher pressures, at the same CO_2 partial pressure. Also simultaneous carbonation and sulphation of $Mg(OH)_2$ was found to be realizable. The beneficial role of increased yet reasonable levels of water vapour pressure is another research topic. While serpentinite-derived $Mg(OH)_2$ shows good reactivity the production of particle sizes suitable for bubbling PFB reactors is a complicating challenge.

Keywords: CO_2 mineral sequestration, serpentinite, staged processing via $Mg(OH)_2$, operation on flue gas

---

* Corresponding author. Tel.: +358-2-2153223; fax: +358-2-2154792. *E-mail address:* ron.zevenhoven@abo.fi.

doi:10.1016/j.egypro.2013.06.521

1. Background and Scope

CO_2 mineral sequestration, a.k.a. mineral carbonation offers an alternative to “conventional” CCS that involves underground storage of pressurised CO_2. An increasing number of routes is being patented and developed to larger scale for CO_2 mineralisation in regions where underground CO_2 storage is not possible or unattractive. The option to operate directly on flue gases (or CO_2-containing gases in general) is one important driver behind these developments [1]. Thus, carbon storage by mineralisation (CSM) circumvents the expensive (and, for oxygen-containing gases, complicating) CO_2 removal step from the CCS chain. Moreover, uses are being identified for the solid products and by-products of CO_2 mineralisation, e.g., the reclamation of land in countries such as Singapore [2].

A decade of work on CO_2 mineralisation in Finland has resulted in a process route that involves production of $Mg(OH)_2$ from serpentinite rock using recoverable ammonium sulphate (AS) salt, followed by carbonation of the $Mg(OH)_2$ in a pressurised fluidised bed at ~500°C, 20-30 bar CO_2 partial pressure. The motivation for gas-solid mineralisation is that it enables recovery of the heat released by the exothermic carbonation reaction in a useful form, in this case as pressurised steam. This heat would primarily be used for upstream production of $Mg(OH)_2$ from rock. The procedure is schematically depicted in Fig. 1.

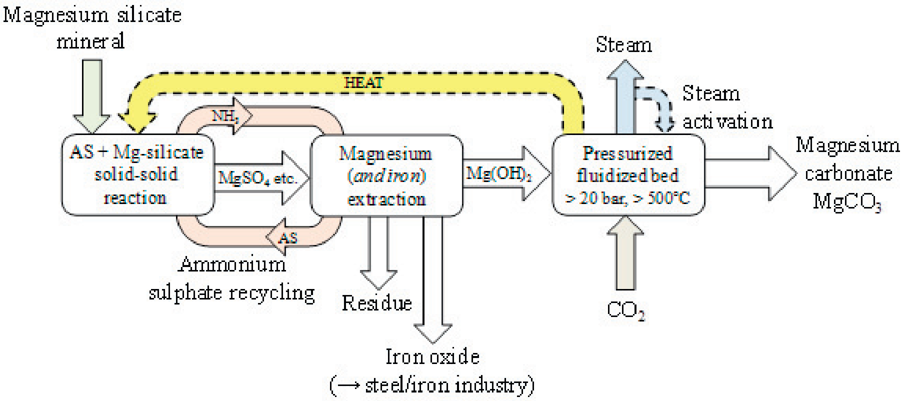

Fig. 1. The staged process route for magnesium silicate-based rock carbonation

A pressurised fluidised bed (PFB) test facility allowing for $Mg(OH)_2$ carbonation at temperatures and pressures up to 600°C, 100 bar has been used for more than a hundred tests. Gas-solid flow mechanics in an FB give good mixing and may prevent the build-up of a passivating product layer of carbonate by surface attrition. At the same time a procedure for the production of $Mg(OH)_2$ from magnesium silicate-based rock (primarily serpentinites) using ammonium sulphate is being optimised.

Earlier results were presented at GHGT-9 and GHGT-10, including a comparison of the use of Finnish and Lithuanian serpentinite [3-5]. That work showed that $Mg(OH)_2$ produced from serpentinites carbonated faster and to a higher carbonate content than a commercial, precipitated $Mg(OH)_2$ sample. ($Mg(OH)_2$ carbonates significantly faster than MgO, which in turn carbonates much faster than magnesium silicates.) As reported, a key factor is the specific surface area (SA) of the $Mg(OH)_2$; this is ~ 40 – 50 m^2/g for material produced from serpentinite rock using ammonium sulphate as a flux salt, *i.e.,* substantially higher than for a commercial material [~ 5 m^2/g] and with a proportionately higher porosity (0.24 vs. 0.024 cm^3/g [4]).

2. Progress since GHGT-10

Our work since GHGT-10, presented here, has progressed along five lines:

2.1 $Mg(OH)_2$ production from magnesium silicate-based rock

During a solid/solid reaction stage Mg is extracted from powdered rock using AS salt at 400-500°C followed by sequential precipitation of FeOOH (pH 8-9) and $Mg(OH)_2$ (pH 11.5) in an aqueous solution, raising the pH with NH_3 vapour released during the preceding solid/solid reaction. Improved understanding and efficiency of $Mg(OH)_2$ production from magnesium silicate rocks according to Nduagu *et al.* [6-7] was obtained, with achievable Mg extraction efficiencies of the order of 60-70 %. (The best result obtained so far is 78%, for Portuguese serpentinite, using ammonium bisulphate as the fluxing salt). An important reported finding was that the ammonium sulphate (AS) reactant salt decomposes to the key acidic ingredient, ammonium bisulphate (ABS), and ammonia vapour before reacting with the rock; at temperatures » 400°C ABS itself degrades and/or volatilizes, leading to deteriorating extraction efficiencies [8]. Fig. 2 summarises the closed-loop (for AS) process for $Mg(OH)_2$ production from suitable rock.

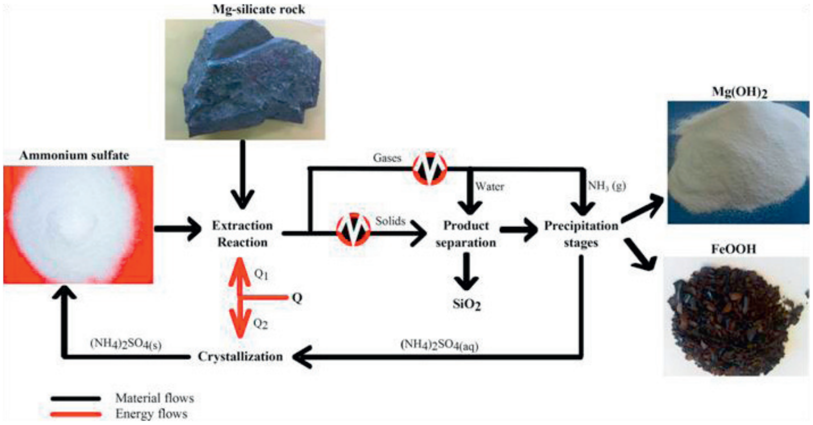

Fig. 2. Schematic of a closed loop process producing $Mg(OH)_2$ from magnesium silicate- based rock [9].

Starting with a layered powder solid/solid reaction system, rock processing time to $Mg(OH)_2$ would take 30 - 60 minutes at temperatures of 400 - 480°C, beyond which the extraction of Mg and Fe decrease [9]. Important for optimal processing is knowledge of the Fe/Mg ratio because the energetics of the process depend on what oxidized (Fe_xO_y) form iron is present in the rock: for a typical 10%-wt Fe the increased energy (heat) needs may be of the order of 50% [10]. (Maybe this can be accepted if marketable iron (hydroxyl-)oxides are produced for the iron- and steel industry.) No significant differences in carbonation behaviour are found between $Mg(OH)_2$ produced from different rock, however.

A problematic feature of this route to $Mg(OH)_2$ is that the average particle size of the produced material is of the order of 10 μm while 100 - 200 μm particles are best suited for the PFB reactor. Opting for a circulating PFB, instead of a bubbling PFB, does not avoid the problems of fluidising the fine and cohesive particles produced (Geldart type C). Efforts to crystallise larger particle sizes – with an SA ~50 m^2/g – is therefore part of ongoing work.

Most of our recent and current work involves scale-up for processing larger batches of material using a lab-scale rotary kiln furnace [11], and the extraction of Mg from olivines and “less attractive” rock that is available at or near large CO_2 point sources. For example, for the Finnish Meri-Pori coal-fired power plant (565 MWe) located on Finland’s west coast [†], it was recently reported that magnesium silicate rock located at mining sites ~85 km (to the East) from the power plant could allow for mineralisation of ~ 50 Mt/CO_2 [12]. A few other interesting rock deposits were found in South / South-west Finland, yet the more suitable (*i.e.* higher Mg-content) rock is found in central and northern Finland.

It is essential for the economic viability of the method that the AS salt is recovered for re-use, which here implies that aqueous AS is isolated as a (humid) solid. As an alternative to direct, evaporative crystallisation a method based on mechanical vapour recompression (MVR) can be used, reducing a significant heat penalty to a minor (compressor) power input penalty [9,13].

2.2 $Mg(OH)_2$ carbonation

Further optimisation of the $Mg(OH)_2$ carbonation efficiency in the PFB reactor is still ongoing. Although we are very satisfied with the rate of carbonation of $Mg(OH)_2$ particles with size of ~300 µm, reaching > 50 % within 5 minutes, at ~500°C, 20-30 bar CO_2 reported earlier [14-15], the final level of conversion to $MgCO_3$ must yet be brought closer to 100%. More recent results gave a conversion of ~65 at 540°C, 50 bar CO_2 pressure [16,17].

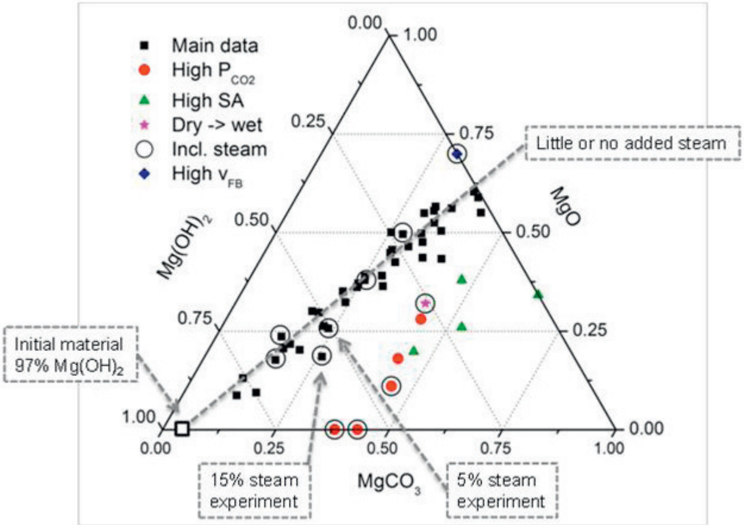

Figure 3. Ternary diagram of $Mg(OH)_2$ carbonation experiments performed using a PFB at various temperature and pressure conditions. The red dots represent experiments where steam was added to the CO_2 stream. High SA is $Mg(OH)_2$ produced from serpentinite, most other tests were on Dead Sea Periclase $Mg(OH)_2$ [16,17]

[†] This has been considered for a CCS demonstration that involved 1.2 Mt/y CO_2 capture and transport to Norway for underground sequestration, a project that was later cancelled.

Bringing down the time scale for carbonation of serpentinite from hours to minutes is an achievement in itself, but the experimental results so far show complex relations between particle size, particle texture (porosity and surface area), the fluidisation parameters, and carbonation temperature and CO_2 pressure.

A series of more than a hundred tests, mainly with a synthetic $Mg(OH)_2$ sample (Dead Sea Periclase, particle size 75 - 125 or 125 - 212 µm, internal surface ~5 m^2/g) gave carbonation conversion levels that, although rapidly attained (within 10 minutes), seldom exceeded 40%. See Figure 3 for the results obtained at 460 - 580°C, 10 - 75 bar. Clearly, the carbonation reaction is competing with undesirable calcination of $Mg(OH)_2$ to less reactive MgO. (XRD analysis also indicated the presence of $MgO{\cdot}2MgCO_3$ in the products under certain conditions.) [16,17]. As noted earlier, much better results were obtained using serpentinite-derived $Mg(OH)_2$ produced from Finnish, Lithuanian and other rock, giving porous, high surface area $Mg(OH)_2$ and, as a result, higher carbonation levels (which presumably are reached faster) – see the green triangle points in Fig. 3. The promoting effect of water (steam) is currently under intensive study [18]: in work soon to be published [19], commercial brucite and magnesia were completely carbonated in several hours (to magnesite) at temperatures as low as 150°C in 10 vol.% steam. However, the use of large amounts of steam may interfere with the final goal of large scale CO_2 sequestration in an energy-efficient way.

Carbonation process kinetics modelling revealed not only the effect of CO_2 and H_2O partial pressures for a given temperature on the final carbonation conversion (including also decreasing porosity into the model); it also confirmed that the carbonation of $Mg(OH)_2$ proceeds via MgO and an $MgO{*}H_2O$ reaction intermediate. A set of modelling results is given in Fig. 4.

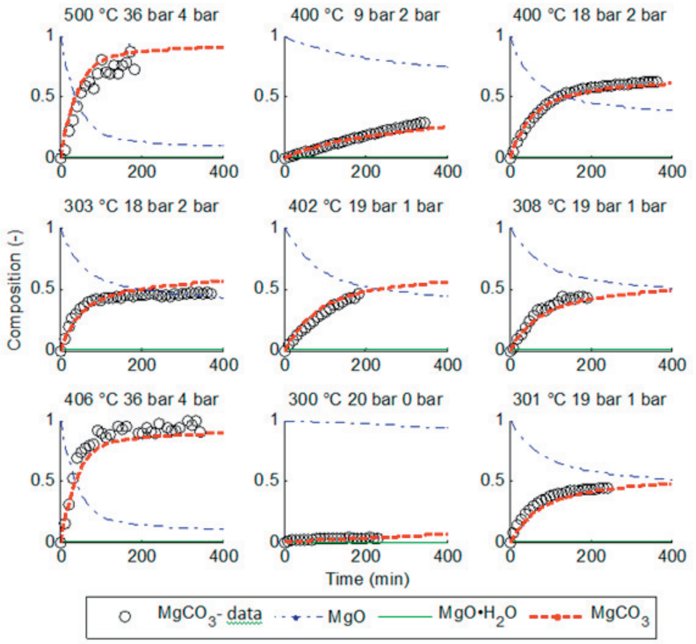

Fig. 4 Comparison between model and PTGA data for nine different experiments. The average conditions are given above each graph: temperature (°C), CO_2 pressure (bar) and H_2O pressure (bar) [16,17].

As noted above, the final choice between a bubbling or circulating PFB reactor is yet to be made for a large-scale application. (Fortunately, R&D activities on circulating PFB reactor design are being revived by FB equipment producers.)

2.3 Process energy use

Process energy efficiency assessment shows that the $Mg(OH)_2$ production, at ~400 °C, requires 3-4 times the heat that is generated by the (exothermic) $Mg(OH)_2$ carbonation at ~500 °C. This gives overall heat input requirements of 4-6 GJ/t CO_2, at 2.5-4 t rock/t CO_2 mineral requirements for Finnish serpentinite containing ~ 86% serpentine. Heat integration and optimisation by combined pinch analysis and Aspen plus simulations show that it can be reduced to ~3 GJ heat/t CO_2 at ~ 3 t rock/t CO_2 mineral input [20-21]. This is close to the heat demand in CO_2 capture based on amine scrubbing (from natural gas), noting that for the mineralisation process the energy input is primarily as ~ 400 °C heat, with only a few % as power for crushing and grinding of material.

As noted above, a significant part of the energy penalty results from the recovery of the AS salt for the Mg extraction. Mechanical vapour recompression (MVR) is being considered for that, as illustrated by Fig. 5. Potential energy savings of using MVR instead of evaporative crystallisation are of the order of 80 - 85% [10].

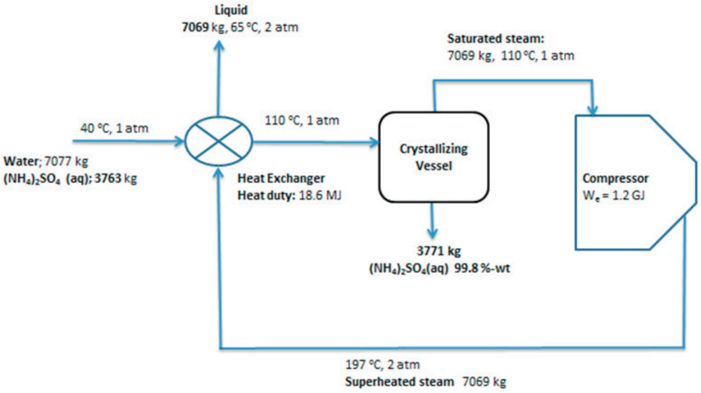

Fig. 5 Process flow diagram of mechanical vapour recompression (MVR) crystallization of AS salt (after [10])

2.4 Large-scale application

Two R&D projects that involve large-scale application of staged magnesium silicate carbonation processing are 1) at a lime kiln (production ~200 t/d) in Parainen, Finland [22] and 2) for natural gas-fired electricity production in Singapore, aiming at land reclamation with the solid products (with rock material imported from, for example, Australia) [23]. Importantly, for both cases, the CO_2 capture stage will be omitted: CSM will be applied to flue gases directly. (According to BASF a market for sorbents for CO_2 does not exist for CCS applications other than EOR/EGR [24].) For case 1) the CSM process can run without external heat input by making use of waste heat from the lime kiln, while for case 2) an LCA study was recently published [2], showing that only direct operation on the flue gas is a requirement for an economically attractive process.

For the lime kiln application, waste heat available from the kiln is enough to process 550 kg/hr of (Finnish Hitura) serpentinite with a capture potential of ~190 kg/hr of CO_2, for 80% of Mg extraction and 90% of $Mg(OH)_2$ carbonation. Even though the integration with flue gas allows for an auto-thermal process, a total of 0.71 MJ/kg CO_2 captured is needed, as an electrical input, for materials crushing/grinding and compression of gases. The energy penalty this gives on the district heating energy supply may be reduced by running this during low demand hours, for example during the summer. The mass flows for this case are given in Fig. 6. A further assessment is given in [25].

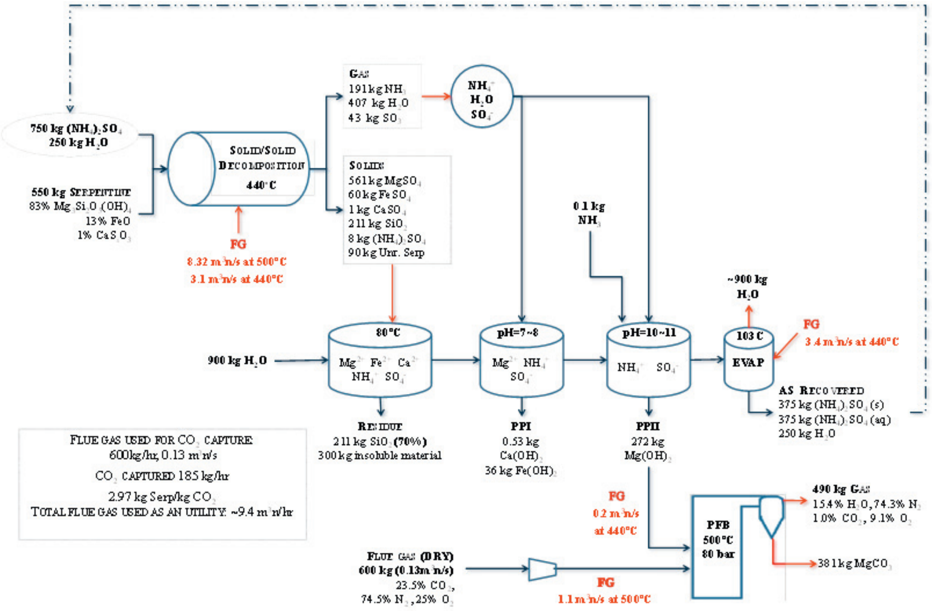

Fig. 6. Mass flows for 80% magnesium extraction and 90% $Mg(OH)_2$ carbonation using Hitura nickel mine serpentinite rock (kg values are for one hour operation) [22].

Important for economic viability is the implementation of carbonation on the flue gases directly, removing the somewhat problematic (for oxygen-containing gas streams) and (energy-) expensive CO_2 capture step from the CCS process train. A set of PFB carbonation experiments where CO_2 was mixed with nitrogen up to a certain CO_2 partial pressure was conducted for comparison with results from tests with the same undiluted CO_2 pressure.

Results (for Dead Sea Periclase) at 450-500°C are given in Fig. 7, showing that the results found for pure CO_2 of pressure $p_{100\%} = p_{CO2}$ aren't different from what is obtained with CO_2 partial pressure p_{CO2} equal to $p_{100\%}$, diluted with N_2 to $p_{total} = p_{CO2}/(\% \text{-vol } CO_2/100)$.

In an additional study (included in [12]), simultaneous removal of CO_2 and SO_2 from flue gases during $Mg(OH)_2$ carbonation is being assessed which, if successful, may make a separate unit flue gas desulphurisation (FGD) at power plants operating on sulphur-containing fuel obsolete. The results show that SO_2 indeed shows significant reactivity towards $Mg(OH)_2$.

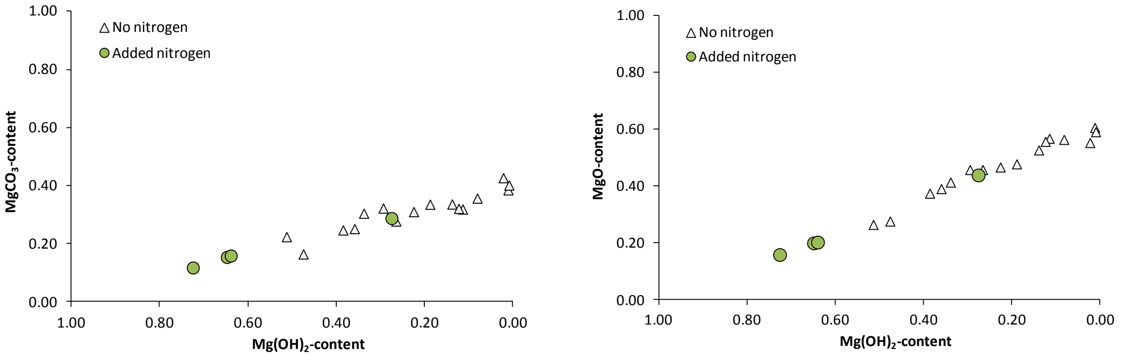

Fig. 7. Conversion of $Mg(OH)_2$ to $MgCO_3$ *(left)* and to MgO *(right)* in (wet) CO_2 or CO_2 diluted with N_2. Dead Sea Periclase $Mg(OH)_2$.

2.5 Alternative reaction intermediates for $Mg(OH)_2$

Finally, assessing the possibilities of operating with another reaction intermediate than $Mg(OH)_2$, for example $MgSO_4$, will be covered. Although the sulphate won't react with CO_2 directly, it can instead be contacted with an NH_3/CO_2 mixture, *i.e.* ammonium (bi-) carbonate, such as obtained in the "chilled ammonia" process for CO_2 scrubbing. Ongoing work shows that, in an aqueous solution (20-80°C), $MgSO_4$ does react with ammonium (bi-)carbonate but formation of different magnesium (hydro-) carbonates and hydrated sulphates is a complicating factor that compromises efficiency [26].

3. Conclusions

Progress made during the last two years (since GHGT-10) on the "Åbo Akademi route" for stepwise carbonation of serpentinite was summarised. While both the production of reactive magnesium as $Mg(OH)_2$ and its carbonation are yet to be further improved to > 90% for both process steps, developments are supported by scale-up of the method for application at an industrial scale lime kiln in Finland and possible use for land reclamation in Singapore. Operating on flue gases directly and energy efficiency are key feature of this CCS approach, where also the produced carbonate materials are considered to be of use and have market value. The obstacles the development work is facing are well defined, and the fact that serpentinite carbonation conversion times have been reduced to less than one hour is highly encouraging.

Acknowledgements

This work was supported by the Academy of Finland program "Sustainable Energy" (2008 – 2011) project "Carbonates in Energy Technology" (CarETech) and Tekes-Finland/A*Star-Singapore project "Novel Low Energy Routes to Activate Minerals for Large-scale Carbonation for Useful Products" (NEACAP) (2010-2013). Further support came from KH Renlund Foundation (2007 – 2010). Thomas Björklöf (currently with Neste Jacobs, Porvoo) and Martin Slotte of ÅA are acknowledged for discussions and other support.

References

[1] Zevenhoven, R, Fagerlund, J, Songok, JK, CO_2 mineral sequestration - developments towards large-scale application. *Greenhouse Gases: Science and Technology* 2011;1:48-57. doi: 10.1002/ghg3

[2] Khoo, HH, Sharatt, PN, Bu, J, Borgna, A, Yeo, TY, Highfield, J, Björklöf, TG, Zevenhoven, R Carbon capture and mineralization in Singapore: preliminary environmental impacts and costs via LCA. *Ind. & Eng. Chem. Res.* 2011;50:11350-11357 doi:10.1021/ie200592h

[3] Fagerlund, J, Teir, S, Nduagu, E, Zevenhoven, R. Carbonation of magnesium silicate mineral using a pressurized gas/solid process. (GHGT-9) *Energia Procedia* 2009;**1**: 4907-4914. doi: 10.1016/j.egypro.2009.02.321

[4] Fagerlund, J, Nduagu, E, Zevenhoven, R. Recent developments in the carbonation of serpentinite derived $Mg(OH)_2$ using a pressurized fluidized bed. (GHGT-10) *Energia Procedia* 2011;**4**:4993-4999. doi: 10.1016/j.egypro.2011.02.470

[5] Stasiulaitiene, I., Fagerlund, J, Nduagu, E, Denafas, G, Zevenhoven, R. Carbonation of serpentinite rock from Lithuania and Finland. (GHGT-10) *Energia Procedia* 2011;**4**: 2963-2970 doi: 10.1016/j.egypro.2011.02.205

[6] Nduagu E, Björklöf, T, Fagerlund, J, Wärnå, J, Geerlings, H, Zevenhoven, R Production of reactive magnesium from magnesium silicate for the purpose of CO_2 mineralization. Part 1. Application to Finnish serpentinite. *Miner. Engng.* 2012;**30**:75-86. doi:10.1016/j.mineng.2011.12.004

[7] Nduagu, E, Björklöf, T, Fagerlund, J, Mäkelä, E, Salonen, J, Geerlings, H, Zevenhoven, R. Production of reactive magnesium from magnesium silicate for the purpose of CO_2 mineralization. Part 2. Mg extraction modeling and application to different Mg silicate rocks *Miner. Engng.* 2012;**30**:87-94. doi:10.1016/j.mineng.2011.12.002

[8] Highfield, JG, Lim, HQ, Fagerlund, J, Zevenhoven, R. Activation of serpentine for CO_2 mineralization by flux extraction of soluble magnesium salts using ammonium sulphate. *RSC Advances* 2012;**2**: 6535-6541. doi: 10.1039/c2ra01347a

[9] Nduagu. E. *The production of $Mg(OH)_2$ from Mg-silicate rock for CO_2 mineral sequestration*. PhD thesis Åbo Akademi University, Turku Finland. (2012) *under review for forthcoming public defence*

[10] Nduagu E, Fagerlund, J, Zevenhoven, R. Contribution of iron to the energetics of CO_2 sequestration in Mg-silicates-based rock. *Energy Conv. & Manage.* 2012; **55**: 178-186. doi:10.1016/j.enconman.2011.10.023

[11] Nduagu, E, Romão, I, Fagerlund, J, Zevenhoven, R. Performance assessment of producing $Mg(OH)_2$ for CO_2 mineral sequestration. *Applied Energy* (2012) *submitted*

[12] Zevenhoven, R, Fagerlund, J, Björklöf, T, Mäkelä, M, Eklund, O. Carbon dioxide mineralisation and integration with flue gas desulphurisation applied to a modern coal-fired power plant. Proceedings of ECOS2012, Perugia, Italy, June 2012 - paper 179

[13] Björklöf, TG, *An energy efficiency study of carbon dioxide mineralization.* MSc thesis Åbo Akademi University, Turku Finland. (2010)

[14] Fagerlund, J, Nduagu, E, Romão, I, Zevenhoven, R., A stepwise process for carbon dioxide sequestration using magnesium silicates. *Front. Chem. Eng. China* 2010;**4**: 133-141 doi: 10.1007/s11705-009-0259-5

[15] Fagerlund, J, and Zevenhoven R. An experimental study of $Mg(OH)_2$ carbonation. *Int. J. Greenh. Gas Contr.* 2011;**4**:1406-1412 doi: 10.1016/j.ijggc.2011.05.039

[16] Fagerlund, J. *Carbonation of $Mg(OH)_2$ in a pressurised fluidised bed for CO_2 sequestration.* PhD thesis Åbo Akademi University, Turku Finland. ISBN 987-952-12-2707-3 (2012)

[17] Fagerlund J, Highfield J, Zevenhoven R. Kinetics studies on wet and dry gas-solid carbonation. *RSC Advances* 2012;**2**:10380-10393. doi: 10.1039/c2ra21428h

[18] Highfield, J, Bu, J, Fagerlund, J, Zevenhoven, R. The promoter effect of steam in gas-solid CO_2 mineralisation. ICCDU-XI, France, June 2011

[19] Highfield, JG, Chen, J, Bu, J, Haghighatlari, M, Fagerlund, J, Zevenhoven, R, *in preparation.*

[20] Fagerlund, J, Nduagu, E, Romão. I, Zevenhoven, R CO_2 fixation using magnesium silicate minerals. Part 1: Process description and performance *Energy* 2012;**41**:184-191. doi: 10.1016/j.energy.2011.08.032

[21] Romão, I, Nduagu, E, Fagerlund, J, M Gando-Ferreira, L, Zevenhoven, R CO_2 Fixation Using Magnesium Silicate Minerals. Part 2: Energy Efficiency and Integration with Iron-and Steelmaking *Energy* 2012;**41**:203-211. doi: 10.1016/j.energy.2011.08.026

[22] Romão, I, Eriksson, M, Nduagu, E, Fagerlund, J., Gando-Ferreira, L, Zevenhoven, R. Carbon dioxide storage by mineralisation applied to an industrial-scale lime kiln. Proceedings of ECOS2012, Perugia, Italy, June 2012 - paper 226

[23] Bai P, Bu J,Yeo TY, Sharratt P, Borgna, A, Khoo HH. Two birds with one stone: why CO_2 mineralization is attracting interest in Singapore. ICCDU-XI, June 2011, Dijon, France

[24] Katz, T, Clausen I. CO_2 capture from flue gases: existing options and perspectives. 4th EucheMs Chemistry Congr., August 2012, Prague, Czech Republic

[25] Slotte, M, Romão, I, Zevenhoven, R. Challenges in process scale-up of serpentinite carbonation to pilot scale" Proceedings of CPOTE12012, Sept 2012, Gliwice, Poland, paper 59

[26] Björklöf, T, Fagerlund, J, Zevenhoven, R. Novel Low Energy Routes to Activate Minerals for Large-scale Carbonation for Useful Products (NEACAP), project report Oct. 2010 – Sept. 2011, Åbo Akademi University, Turku Finland *(unpublished)* (21 pp.)