CCSP Deliverable D555
Turku / Parainen, 2016

Evelina Koivisto
Rickard Erlund
Ron Zevenhoven
Mats Fagerholm

Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation

Original FP5 Description of Work title:
Report on diopside carbonation tests with the different process routes

ccsp
Carbon Capture and Storage Program

CLIC Innovation Oy
ETELÄRANTA 10
P.O. BOX 10
FI-00131 HELSINKI
FINLAND
www.clicinnovation.fi

CLIC Innovation Oy
Carbon Capture and Storage Program (CCSP)
Deliverable D555

Evelina Koivisto, Åbo Akademi University
Rickard Erlund, Åbo Akademi University
Ron Zevenhoven, Åbo Akademi University
Mats Fagerholm, Nordkalk Corporation, Parainen

Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation

Original FP5 Description of Work title:
Report on diopside carbonation tests with the different process routes

Report Title: Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation

Original FP5 Description of Work title:
Report on diopside carbonation tests with the different process routes

Key words: mineral carbonation, silicate raw materials, lime kiln application

Abstract:

As a follow-up of deliverable D548 *Process for upgrading diopside-based rock for lime kiln gas CO_2 carbonation,* this report addresses the characterization of four Finnish magnesium silicate - type rocks. The aim is identify a rock that has suitable properties 1) from a viewpoint of extraction of magnesium, Mg, to be carbonated and 2) reasonable proximity to an industrial-scale lime kiln. Implicitely, the lime kiln would be a kiln operated by Nordkalk in Finland, and preferably a side-material from Nordkalk's quarry operation would be used as the Mg-source.

After D548 showed that a (pre-concentrated) diopside material from the (Nordkalk) limestone quarry at Parainen had a low content of Mg that also was difficult to extract, the work was extended to an Mg-hornblende material from near Suomusjärvi, and a serpentinite from near Vammala. Results were again compared to results obtained with the overburden rock from the (currently closed) nickel mine at Hitura. The results are reported here as two journal papers submitted to *Minerals Engineering*, addressing (part 1) solid/solid extraction and (part 2) aqueous solution extraction of primarily Mg, but also reporting on Ca, Fe and a few other elements.

The results show that similar to the Parainen diopside also the Suomusjärvi (Salittu) Mg-hornblende gave very small amount of extractable and extracted Mg. The Vammala serpentinite gave good results although less good than what can be obtained with the Hitura serpentinite. It can be concluded that two preferable routes to proceed are 1) Hitura rock used at Nordkalk's lime kiln at SSAB, Raahe, or 2) Vammala rock used at Nordkalk's lime kiln at Parainen, in both cases involving a transport distance of ~140 km.

NOTE. After these findings Nordkalk re-assessed the objectives: only rock that can be obtained from Nordkalk's quarries in Finland are acceptable as raw material for Mg (or Ca) carbonation. Thus, forthcoming deliverable D557 *Updated cost evaluation including a feasible pilot plant design, final project summary report* will include identifying a suitable raw material from Nordkalk's quarry operation side-streams.

Turku / Parainen, February 2016

Table of contents

1. Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation - Part 1: Thermal solid/solid extraction ....1-1 — 1-15
submitted to Hydrometallurgy, February 2016

2. Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation - Part 2: Aqueous solution extraction.....2-1 — 2-18
submitted to Hydrometallurgy, February 2016

The locations of the rocks used in the study

Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation - Part 1: Thermal solid/solid extraction

Evelina Koivisto[a]; Rickard Erlund[a]; Mats Fagerholm[b]; Ron Zevenhoven[a]*

[a]Thermal and Flow Engineering Laboratory, Åbo Akademi University, Piispankatu 8, FI-20500 Turku, FINLAND
[b]Nordkalk Oy Ab, Skräbbölentie 18, FI-21600 Parainen, FINLAND
**Corresponding author, E-mail address: ekoivist@abo.fi*

Abstract:

The only option for carbon capture and storage (CCS) in Finland is mineral carbonation, which has been extensively researched at ÅA. Finding suitable minerals for mineral carbonation in different regions of Finland will keep transportation of either CO_2 or the actual mineral at a lowest possible level. Four different rocks from different regions in Finland have been compared with respect to composition and possibility to extract magnesium. This paper presents experiments applying thermal solid/solid extraction. It was found that a mixture of ammonium sulphate (AS) and ammonium bisulphate (ABS) could extract a significant part of magnesium compared to tests using only AS or ABS. Serpentinite rock is also the best option for magnesium extraction while diopside and magnesiohornblende are much less reactive. Continuous mixing during the experiment in a rotary tube and adding some water to the solid/solid mixture gives better extraction results. The binding capacities of CO_2 in the serpetinites with respect to the magnesium extractions achieved in this study are 240 kg CO_2/ton rock (Serp-A) and 207 kg CO_2/ton rock (Serp-B).

Keywords:

Amfibole, Ammonium bisulphate, Ammonium sulphate, ÅA route, Diopside, Magnesium silicate, Mineral carbonation, Pyroxene, Serpentinite

1. Introduction and Background

Finland's annual emission allocations are based on the reduction obligation of 16 % of the emission levels of 2005 by the year 2020 (Official Statictics of Finland, 2014). According to VTT (2012) it should also be possible to cover 85-100% of the Finnish energy use without emissions of carbon dioxide (CO_2) by 2050. This puts demands on technologies for carbon capture and storage (CCS) as well as increased energy efficiency. The only option for CCS within Finland's borders is mineral carbonation, which has been intensively researched at Åbo Akademi University (ÅA) (Fagerlund, 2012, Nduagu, 2012, Romão, 2015, Sjöblom and Eklund, 2014). Starting with an extraction reaction of mainly magnesium from silicate rock it becomes possible to sequester CO_2 through the overall (exothermic) reaction (Nduagu et al., 2012);

$$Mg_3Si_2O_5(OH)_4(s)+3CO_2(g)\rightarrow 3MgCO_3(s)+2SiO_2(s)+2H_2O(l),\ \Delta H= -64\ kJ/mol\ CO_2 \qquad (R1)$$

One mineral found to be suitable for mineral carbonation via the ÅA route is serpentinite. One of the studied serpentinites is originating from the Hitura ultramafic complex located in the central part of Finland. The complex consists of mainly porous serpentinites found to be reactive enough to be suitable to use in the ÅA route. This rock will be presented further here together with

another serpentinite rock from the Vammala region as well as a diopside and a magnesiohornblende, all from southern parts of Finland. The locations of the different rocks are shown in Figure 1. An issue for mineral carbonation is to find suitable minerals in different regions of Finland, preferably as close to large CO_2 emitting sources as possible. This part 1 focuses on possible suitable mineral reserves found in the regions of Hitura, Vammala, Salittu and Parainen and the extraction of magnesium from these rocks by thermal solid/solid extraction. Part 2 (Erlund et al., 2016) focuses on aqueous solution leaching methods (Sanna et al., 2014, Styles et al., 2013, Zhao et al., 2015) of the same rocks.

Figure 1. Locations of the rocks used in this study.

2. Material and Methods

2.1. Materials

Four different rocks have been studied. One is the also earlier studied mine overburden from the Hitura nickel mine consisting mainly of serpentine-rich rock and magnetite (Serp-A), (Nduagu et al., 2012, Romão, 2015). Earlier tests resulted in extractions of magnesium of up to 70% (Nduagu, 2012, Romão et al., 2013). This serpentinite from the now closed Hitura nickel mine was chosen since a possibility could be to apply CO_2 sequestration by mineral carbonation to a lime kiln located at a steel making plant in Raahe. The distance between Raahe and Hitura nickel mine is approximately 140 km. The Hitura nickel mine was closed in June 2013 as a result of the low nickel price. The dimension of the ultramafic complex is about 0.3 x 1.3 km (Belvedere Resources, 2016).

Rock from close to the Vammala mine was earlier studied by Mäkelä (2011) and Zevenhoven et al. (2012). Both suggest that more studies of the rock should be done in order to optimize the

extraction of magnesium. The rock used in this study (Serp-B) is, however, originating directly from the mine. A benefit with this rock type is the location close to CO_2 emitting sources located in southern part of Finland. The distance between Vammala and a lime kiln in Parainen, for example, is also approximately 140 km.

A concentrated diopside rich fraction of the wall rock of a lime stone quarry was also studied (diopside). The rock was concentrated using density separation. Diopside has a density higher than 3.3 g/cm^3, which was a higher density than the rest of the rock. However, it should be mentioned that the diopside rich fraction only corresponded to 10% of the whole wall rock sample. The benefit of being able to carbonate this rock would be the short (zero) distance from the CO_2 emitting source (i. e. the lime kiln) and for the company to utilize mined side rock. Lu et al. (2011) and Frost and Beard (2007) mention the option for a reaction with diopside in an acidic environment, resulting in serpentinite as product. This was tested more thoroughly in part 2 of this paper (Erlund et al., 2016). Diopside belongs to the pyroxene group with silicon-oxygen tetrahedral chains. In the diopside rich fraction - obtained after the density separation of the wall rock from the limestone quarry - approximately half of the magnesium is substituted by iron. Thus, twice the amount of diopside would be required for the same amount of magnesium extraction compared to pure diopside. The pyroxene with magnesium substituted by iron is known as hedenbergite ($CaFeSi_2O_6$) and the Mg-Fe substitution giving the diopside-hedenbergite series also results in changes in the Si-O chain configuration (Deer et al., 1992).

The Salittu open pit is processing peridotite, a rock type mainly containing olivine and/or pyroxene (Länsi-Suomen ympäristölupavirasto, 2009). Olivine is known to be another suitable mineral besides serpentinite for mineral carbonation (IPCC, 2005). The Salittu mine is also located in southern part of Finland. However, no pyroxene nor olivine were found at all in the rock used in this study (Mg-Horn) when looking at the X-ray Diffraction analyses (XRD) in Table 1. Plagioclase and amphibole seems to dominate in the rock samples used here.

Table 1 shows XRD results for the rock types studied while Table 2 presents the X-Ray Fluorescence (XRF) analyses of the same particle size fractions. The diopside and the Mg-Horn contain much less magnesium than Serp-A and Serp-B. The diopside contains quite a lot of Ca and could with respect to that be used instead of Mg to bind CO_2. This requires that the Ca is not already bound to carbonates, however, which could be released as CO_2 when treated.

Table 1. XRD analyses of samples from the four different rock types used with particle size 63-125 µm. The values are given in %-wt.

Compound	Hitura Serp-A	Vammala Serp-B	Parainen Diopside	Salittu Mg-Horn
Serpentines $(Mg, Fe)_3Si_2O_5(OH)_4$	70-80	60-70	-	<5
Magnetite Fe_3O_4	15-20	10-15	-	-
Diopside-Hedenbergite $MgCaSi_2O_6$	-	-	90-95	<5
Plagioclase $(Na, Ca)(Si, Al)_4O_8$	-	-	< 5	30-40
Amphibole (Magnesiohornblende) $Ca_2[Mg_4(Al, Fe)]Si_7AlO_{22}(OH)_2$	-	< 5	-	30-40
Quartz SiO_2	-	-	-	15-20
Chlorite $(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2 \cdot (Mg, Fe)_3(OH)_6$	< 5	10-15	-	-
Calcite $CaCO_3$	< 5	-	-	-
Cordierite $Mg_2Al_4Si_5O_{18}$	-	-	< 5	-
Annite $KFe_3AlSi_3O_{10}(OH,F)_2$	-	< 5	-	-
Dolomite $CaMg(CO_3)_2$	-	< 5	-	-

Table 2. XRF analyses of samples from the four different rock types used with particle size 63-125 µm. All values are given as %-wt. The rest consists of elements hard to detect (for example Cl).

Compound	Hitura Serp-A	Vammala Serp-B	Parainen Diopside	Salittu Mg-Horn
CaO	0.4	0.45	23.8	10.9
SiO_2	35.5	35.3	49.9	48.7
TiO_2	0.04	0.15	1.2	0.85
NiO	0.35	0.27	0.02	0.018
Al_2O_3	0.45	2.7	2.9	14.7
Fe_2O_3	14.6	16.3	14.2	12.1
MgO	35.1	31.0	6.6	8.7
K_2O	0.02	0.08	0.29	0.67
Na_2O	<0.01	0.08	0.34	1.9
MnO	0.12	0.21	0.16	0.22
CuO	0.10	0.11	0.03	0.024
Cr_2O_3	0.38	1.2	<0.01	0.057
P_2O_5	0.01	0.02	0.09	0.18
S-Eltra	0.42	0.87	-	0.08
LOI 1000 ^oC	12.0	11.4	0.18	0.63
Rest	0.5	-0.17	0.3	0.2

Comparison of the binding capacities between the rocks and contents of valuable minerals in the context of mineral carbonation (Mg, Ca) are presented below, showing that the contributions of interesting ("carbonatable") elements are comparable in all rock types tested (Figure 2). Serp-A and Serp-B offer the possibility to bind a significant amount of CO_2 to magnesium while, theoretically, the diopside has some potential to bind CO_2 to calcium (Figure 2). Mg-Horn is quite low in both magnesium and calcium which in turn will result in the largest amount of rock needed per sequestered tonne of CO_2 in comparison with the other rock types (right figure in Figure 2). The sum of binding capacity of Mg and Ca in the rocks is, however, still comparable and in the same range for all rock types.

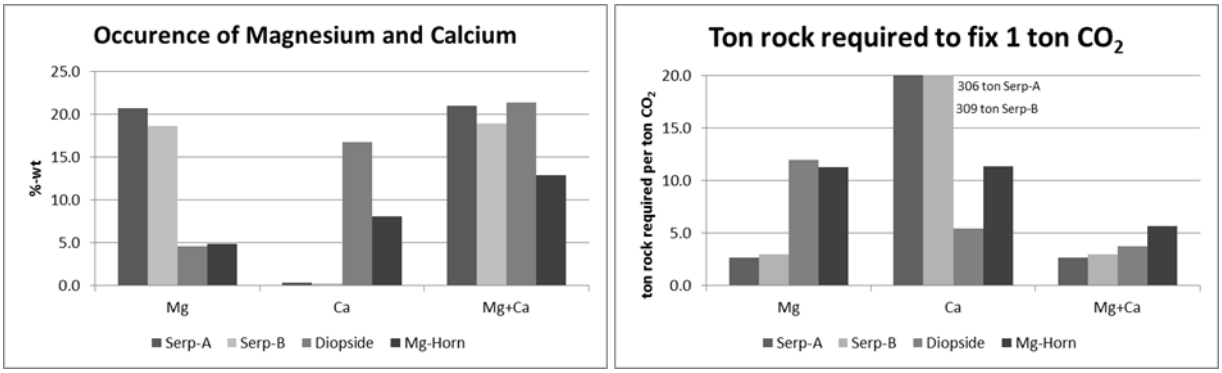


Figure 2. Left: Contribution of Mg and Ca in the rock types tested. Sums of the two elements in all rock types are given, Right: Ton required of the different rock types tested binding one ton of CO_2. The sums of binding capacity of both Mg and Ca are also shown.

2.2. Methods

Tests presented in this paper are mainly based on the procedure of the so called ÅA route (Figure 3). Preferably serpentinite (or other Mg-containing silicate rock) will initially be heated in a thermal solid/solid reaction together with ammonium sulphate. Intermediate, water-soluble products of mainly magnesium and iron sulphates (and double salts with the NH_4^+ ion) will form upon this treatment. Dissolution in water makes it thereafter possible to precipitate magnesium hydroxide ($Mg(OH)_2$) with the addition of ammonia (NH_3 (g)/(aq)) at pH 10-12. NH_3 is also generated as vapour during the thermal solid/solid reaction and could be directly used in the subsequent step to adjust pH. Finally, $Mg(OH)_2$ is carbonated by flue gas in a pressurised fluidised bed reactor (left image, Figure 3), (Fagerlund, 2012). Iron is often present in the studied minerals and has the advantage to precipitate as iron(oxy)hydroxides (FeOOH, $Fe(OH)_2$, $Fe(OH)_3$) at pH 8-10, which makes it possible to separate (through filtering) an iron precipitate before the actual magnesium precipitation and separation is done. This paper will focus on the extraction step, i.e. the thermal solid/solid step which is the initial step of the ÅA route.

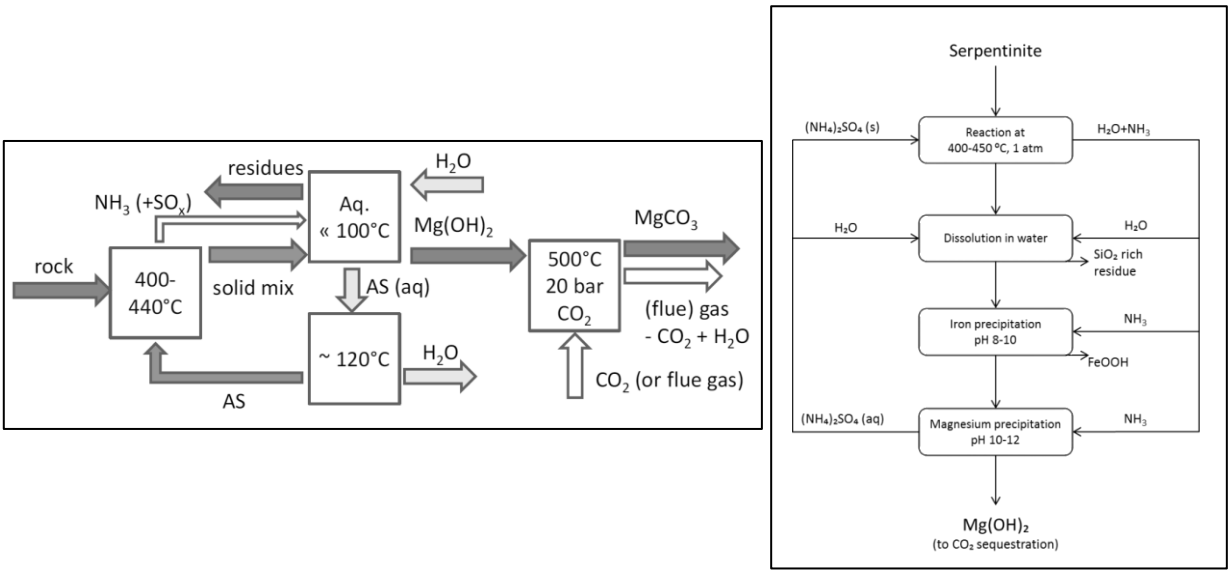


Figure 3. Left: A schematic illustration of the ÅA mineral carbonation route with gas/solid carbonation. AS: ammonium sulphate. Right: A more detailed scheme of the first stages of the ÅA route.

Two alternative processes to the ÅA route are the alternative ÅA route that involves wet carbonation of dissolved $MgSO_4$ and the UK route (AS replaced with ammonium bisulphate (ABS)) (Figure 4), (Wang and Maroto-Valer, 2011, Åbacka, 2013, Zevenhoven et al., 2015). Some experiments (number 5,6,7,9 and 10 in Table 3) were, as a result of these optional process routes, also run with (some) ABS instead of AS. A drawback, however, is that both these wet carbonation process routes will result in hydro magnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) formation which will require five magnesium atoms for every four carbon dioxide molecules captured. Note that in both routes a pre-separation (capture) of CO_2 may be omitted. Also, regenerating AS to form ABS is very energy intensive (Romão, 2015).

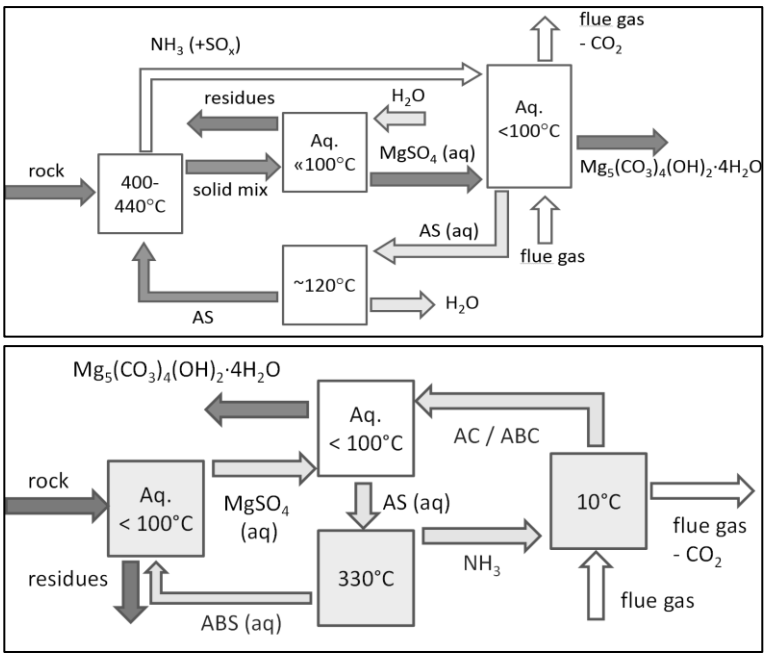


Figure 4. Above: Process scheme of the wet carbonation route with a carbonation step taking place in an aqueous solution. Below: UK route. AS as in the ÅA route is replaced by ABS and regenerated at a temperature of 330 °C.

A rotary tube (max capacity ~100 g) and a chamber furnace were used for the experiments (Figure 5). The rotary tube is rotating with an angle of 315 degrees. The rotation speed was equal for all experiments. Ceramic crucibles were used in the chamber furnace. The set temperature was reached before the samples were inserted in the furnaces and cooling took place with opened hood (rotary tube) or outside the furnace (chamber furnace). AS and/or ABS and optionally also water were mixed with the powdered rock. Experimental parameters for the set of different experiments in this study are given in Table 3. Particle size of the powdered was typically 63-125 µm for tests run in the chamber furnace and 125-250 µm for tests run in the rotary tube.

Figure 5. Rotary tube (above) and chamber furnace (below).

Table 3. Experimental parameters for the different types of tests. The tests beginning with WET (number 5 and 9) used also 2 ml of water mixed to the solids before the test was run. Test number 7 used 15 ml of water.

Test no.	Code	Reagent	Stoichiometric factor of reagent	Particle size (µm)	Mineral (g)	Furnace	T (°C)	t (min)	Dilution (ml)
1	ÅA-400/60	AS	1.15	125-250	40	Rotary	400	60	500
2	ÅA-440/60	AS	1.15	125-250	40	Rotary	440	60	500
3	ÅA-440/30	AS	1.15	63-125	40	Rotary	440	30	500
4	AS-440/30	AS	1.15	63-125	25	Chamber	440	30	315
5	WET-ABS	ABS	1.15	63-125	25	Chamber	440	60	315
6	DRY-ABS	ABS	1.15	63-125	25	Chamber	440	60	315
7	UK-90/3	ABS	1.15	125-250	40	Rotary	90	180	500
8	ÅA-440/60-1.5	AS	1.50	63-125	25	Chamber	440	60	315
9	WET-AS/ABS	AS+ABS	1.15	63-125	25	Chamber	440	60	315
10	DRY-AS/ABS	AS+ABS	1.15	63-125	25	Chamber	440	60	315

After cooling, the material was dissolved in distilled water and stirred for 20 minutes before insoluble material was filtered off. The solutions obtained were sent for atomic absorption spectroscopy (AAS) analyses where the amounts of magnesium and iron (calcium and aluminium

were also analysed for some samples). A few samples were also analysed with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP).

3. Results and Discussion

Extraction results of magnesium and iron (also calcium and aluminium for the rocks containing >2 %-wt of these elements) from the different tests are presented in Table 4. The Mg-Horn and the diopside fraction did not give significant extractions of magnesium. The content of magnesium in the rock was low already to start with. The extraction values for diopside are given for the concentrated (density separated) fraction which was 10% of the total mass of side rock of a lime stone quarry. This fraction together with the Mg-Horn will not be discussed any further since they do not possess the required characteristics to be suitable to use in the context of carbon capture and storage by mineralization (CCSM) and the ÅA route. Various input minerals for the ÅA route were earlier analysed by Sjöblom and Eklund (2014), concluding that only minerals with 17-27 %-wt. Mg and >2.5 %-wt. crystal water released Mg efficiently (>40 %). It seems that the single tetrahedral silica chain in pyroxenes causes these minerals to be resistant to extraction whereas the crystal water of e.g. serpentine introduces more chemical instability into the structure (Sjöblom and Eklund, 2014). This reasoning is consistent with the findings in this study.

The binding capacities of CO_2 with respect to the best Mg extractions reached in Serp-A and Serp-B in this work are 240 and 207 kg CO_2/ton rock, respectively. The same values for diopside and Mg-Horn are 3 and 7.4 kg CO_2/ton rock, respectively.

Table 4. Extraction results of Mg, Fe, Ca and/or Al from the Serp-A, Serp-B, diopside and Mg-Horn rocks. Numbers are given in % extracted.

		Serp-A		Serp-B			Diopside			Mg-Horn			
No	Code	Mg extr.	Fe extr.	Mg extr	Fe extr.	Al extr.	Mg extr.	Ca extr.	Fe extr.	Mg extr.	Ca extr.	Fe extr.	Al extr.
1	ÅA-400/60	28.9	20.2	16.4	21.1	-	-	-	-	4.4	2.7	5.8	2.7
2	ÅA-440/60	43.4	30.9	33.6	32.5	-	0.1	3.1	0.2	4.4	2.9	1.4	0.6
3	ÅA-440/30	37.6	24.5	22.7	27.2	20.0	-	-	-	-	-	-	-
4	AS-440/60	36.4	25.8	24.4	26.0	19.0	-	-	-	-	-	-	-
5	WET-ABS	64.0	40.3	61.7	25.3	23.3	1.2	4.5	1.8	8.4	6.8	3.2	3.1
6	DRY-ABS	55.8	38.4	54.2	24.2	-	1.7	4.6	2.1	7.3	6.4	3.5	3.0
7	UK-90/3	41.9	17.6	45.0	32.7	0.1	3.6	4.3	4.1	7.0	4.9	8.0	5.9
8	ÅA-440/60-1.5	-	-	26.6	25.4	16.9	-	-	-	-	-	-	-
9	WET-AS/ABS	-	-	52.3	47.5	24.8	-	-	-	-	-	-	-
10	DRY-AS/ABS	-	-	49.8	43.2	23.6	-	-	-	-	-	-	-

3.1. The difference in extraction of Serp-A and Serp-B

Serp-A was found to be more reactive than Serp-B in the tests where only AS was used. Extraction of magnesium, on the other hand, was achieved to more or less the same extent independent of

whether Serp-A or Serp-B was used with ABS as fluxing salt. Using a mixture of 50% AS+ 50% ABS together with Serp-B gave almost as good extraction as for the tests using only ABS (Table 4).

3.2. The impact of furnace type

Comparing magnesium extractions in test number 2 (Serp-A: 43.4%, Serp-B: 33.6%) and test number 4 (Serp-A: 36.4%, Serp-B: 24.4%, Table 4), where the parameters are similar except type of furnace used, it becomes clear that the rotary tube (test 2) gives slightly better extraction of magnesium but also iron. A reason for this could be that mixing the material continuously creates better contact between the AS and the rock.

3.3. The impact of increasing reaction time

Nduagu et al. (2014) suggests that reaction times >30 minutes would be preferable to achieve as efficient extraction as possible. Most tests were run for 60 minutes in this study. Looking at test number 2 (60 min) and 3 (30 min) in Table 4 where the only parameter changing is time, it becomes visible that the longer reaction time will increase extractions of both magnesium (from 22.7 to 33.6 %) and iron (from 27.2 to 32.5 %).

3.4. The impact of lowered temperature and increasing reaction time

Test number 7 in Table 4 refers to a test run at much lower temperature (90°C), but with longer reaction time (3h) than in the other tests. The idea behind this was adopted from Sanna et al., (2014). 100% ABS was used and 15 ml of water was also added to the material mix before it was inserted to the furnace. Magnesium extractions of 41.9% (Serp-A) and 45 % (Serp-B) were obtained. It seems possible to extract magnesium also by applying longer time but lower temperature. Erlund et al. (2016) report more results from leaching in aqueous ABS solutions at similar temperature and time scale.

3.5. The impact of excess AS

Test number 8 (Table 4) was done after recommendations according to Nduagu et al. (2014), who stated that an excess amount of ammonium sulphate (1.5 times the stoichiometric amount needed as reported in R2) should be used in order to obtain a more quantitative magnesium recovery. R2 is giving the stoichiometric reaction of the extraction reaction with serpentine and AS and R3 gives the possible reaction using excess amount of AS.

$$Mg_3Si_2O_5(OH)_4(s) + 3(NH_4)_2SO_4(s) \rightarrow 3MgSO_4(s) + 2SiO_2(s) + 5H_2O(g) + 6NH_3(g) \quad (R2)$$

$$Mg_3Si_2O_5(OH)_4(s) + 4.5(NH_4)_2SO_4(s) \rightarrow 1.5(NH_3)_2Mg_2(SO_4)_3(g) + 2SiO_2(s) + 5H_2O(g) + 6NH_3(g) \quad (R3)$$

Synthetic efremovite ($(NH_4)_2Mg_2(SO_4)_3$) could according to Nduagu et al. (2014) be the dominating extracted phase in R3. Only quite modest levels of magnesium extraction (<60%) were achieved with stoichiometric amounts of AS and $MgSO_4$ as product (R2). Thus Nduagu et al. (2014) and more recently Highfield et al. (2015) suggest that a 50% excess amount of AS is needed to reach full extraction in the case where efremovite is formed as intermediate.

However, no remarkably better extraction of the Serp-B rock was achieved by increasing the amount of AS to 1.5 times the theoretical need instead of 1.15 as in the rest of the experiments. 26.6 % of its magnesium was extracted from Serp-B, compared with the test with 1.15 times the theoretical amount of AS needed giving a magnesium extraction of 24.4 %.

3.6. The impact of using a mixture of AS, ABS and water as fluxing agent

Tests number 9 and 10 in Table 4 gave Mg extractions of 52.3 and 49.8 %, respectively. Mixtures of 50% AS + 50% ABS were used and a 2 ml of distilled water was also added to the mixture in test number 9. The extractions compared to test 4 (only AS) and tests number 5 and 6 (only ABS) shows that the iron extraction became better using a mixture (Figure 6). The magnesium extraction on the other hand becomes a bit lower using a mixture (compared to tests using only ABS) but more tests could be done to further explain this. Part 2 of this paper (Erlund et al., 2016) and Romão et al. (2015) also report that replacing some of the AS with ABS could make the extraction more efficient. Using a mixture instead of only ABS could make the necessary regeneration of AS to ABS somewhat easier.

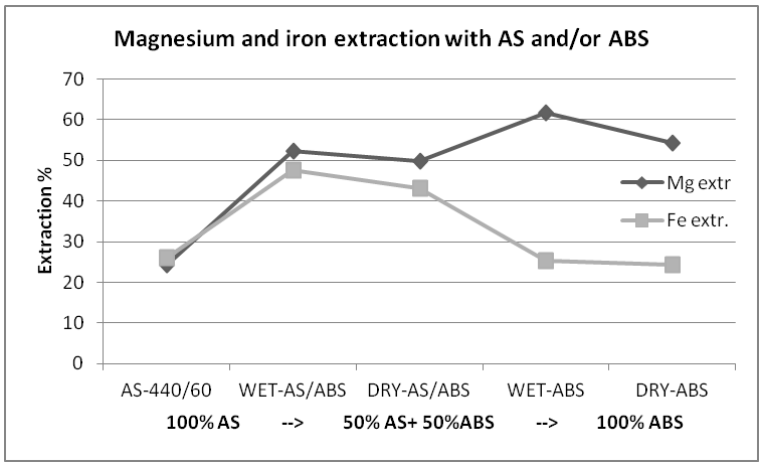


Figure 6. Extraction of magnesium and iron from Serp-B in the presence of different amounts of AS and ABS.

The decomposition of AS at 400 ^{o}C was reported earlier (Dixon, 1944, Halstead, 1970) as reactions (R4-R6). It could be seen that ABS will form upon heating of AS according to these reactions. This could partly explain the fact that ABS will be more reactive than AS since AS first will decompose to some extent (R4, R5) to ABS before a third intermediate, ammonium pyrosulphate ($(NH_4)_2S_2O_7$, APS) is formed (R6) which could contribute to the reaction with serpentinite according to (R7). The serpentinite and flux reaction chemistry was also studied more in detail by Highfield et al. (2012, 2015) and Nduagu et al. (2014).

$$2(NH_4)_2SO_4(s) \rightarrow (NH_4)_2S_2O_7(s)+2NH_3(g)+H_2O(g) \quad (R4)$$

$$2(NH_4)_2SO_4(s) \leftrightarrow 2NH_4HSO_4(s)+2NH_3(g) \quad (R5)$$

$$2NH_4HSO_4(s) \leftrightarrow 2(NH_4)_2S_2O_7(s)+H_2O(g) \quad (R6)$$

$$Mg_3Si_2O_5(OH)_4+1.5(NH_4)_2S_2O_7 \rightarrow MgSO_4+2SiO_2+3NH_3+3.5H_2O \quad (R7)$$

Water makes the extraction of magnesium more efficient (Romão, 2015). This could be seen from experiments number 5 vs. 6 and 9 vs. 10 in Table 4. Water could contribute to (capillary) forces between the particles giving better contact. Addition of water will also contribute to a larger amount of NH_3, NH_4^+ and SO_4^{2-} being soluble which in turn will result in less evaporation and sublimation.

3.7. Comparison of AAS and ICP analyses

Aqueous samples from tests number 8-10 were analysed both with AAS and ICP. Significant differences were found between these two analysis methods. The difference in magnesium extraction calculated based on this is shown in Table 5. The AAS analyses values are about 0.8 times the values of the ICP analyses. The difference in the case where 50% AS+50% ABS together with a small amount of water was used was 52.3 % (AAS) vs. 65 % (ICP). Sample for tests 1-7, however, were analysed with AAS only, as reported in Table 4.

Table 5. Difference between AAS and ICP analyses results of magnesium extractions. The values are given in %.

No	Code	Mg extr.(%, AAS)	Mg extr.(%, ICP)	Ratio AAS/ICP
8	ÅA-440/60-1.5	26.6	33.5	0.79
9	DRY-AS/ABS	49.8	60.2	0.83
10	WET-AS/ABS	52.3	65.0	0.80

4. Conclusions

Four different magnesium silicate rocks originating from different regions in Finland were tested for CO_2 sequestration potential. Two of these- both being serpentinites- could be seen as an option for CCSM while the diopside and Mg-Horn did not give a significant extraction of elements for subsequent carbonation. Serp-A is most reactive and Serp-B could give similar extraction levels depending of the amounts/ratios of AS and ABS used. The binding capacities of CO_2 with respect to the Mg extraction obtained with Serp-A and Serp-B in this work are 240 and 207 kg CO_2/ton rock, respectively. Water seems to enhance the kinetics and a mixture of AS and ABS could offer better extractions but still to keep the regeneration of AS back to ABS after the extraction and dissolution steps as simple as possible. Future work in this field should address the optimization of water usage and the regeneration of AS/ABS if the ÅA route is modified towards using AS/ABS mixtures. More tests could also be done in order to optimize the AS/ABS ratio. Adding excess AS (ratio Serp/AS=1/1.5) to a test using Serp-B did not show any better extraction compared to a test using only 1.15 times the stoichiometric amount of AS. Analyses methods should be further compared in order to find the most suitable analysis method for the work presented in this study.

Acknowledgement

This work was funded by CLIC Oy CCSP project (2011-2016) and Nordkalk Corporation. The authors acknowledge Thomas Nyberg and Synnöve Hollsten from Nordkalk for the extensive AAS, XRF and XRD analyses done. Sten Lindholm at ÅA is acknowledged for the ICP analyses.

Nomenclature

Abbreviations

ÅA	Åbo Akademi University
AAS	Atomic Absorption Spectroscopy
ABS	Ammonium bisulphate
APS	Ammonium pyrosulphate
AS	Ammonium sulphate
CCSM	Carbon Capture and Storage by Mineralisation
CCS	Carbon Capture and Storage
ICP(-AES)	Inductively Coupled Plasma Atomic Emission Spectroscopy
Mg-Horn	Magnesiohornblende from Salittu region in Finland
Serp-A	Serpentinite from Hitura nickel mine in Finland
Serp-B	Serpentinite from Vammala region in Finland

Chemical Compounds

CO_2	Carbon dioxide
$CaSO_4$	Calcium sulphate
$CaSO_4 \cdot 2H_2O$	Gypsum
$FeCaSi_2O_6$	Hedenbergite
Fe_3O_4, $FeO \cdot Fe_2O_3$	Magnetite
$Fe(OH)_2$	Iron(II)hydroxide, Ferrous hydroxide
$Fe(OH)_3$	Iron(III)hydroxide, Ferric hydroxide
$FeSO_4$	Iron (II) sulphate, Ferrous sulphate
$MgCO_3$	Magnesium carbonate
$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	Hydro magnesite
$MgCaSi_2O_6$	Diopside
$MgSO_4$	Magnesium sulphate
$MgSi_2O_5(OH)_4$	Serpentine
NH_4HSO_4	Ammonium bisulphate, ABS
$(NH_4)_2Mg_2(SO_4)_3$	Synthetic efremovite
$(NH_4)_2SO_4$	Ammonium sulphate, AS
$(NH_4)_2S_2O_7$	Ammonium pyrosulphate, APS

References

BELVEDERE RESOURCES. 2016. *Hitura Mill and Nickel Mine*. Available at: http://www.belvedere-resources.com/operations/nickel-properties/hitura/ [Accessed: January 14, 2016]

DEER, W. A., HOWIE, R. A. and ZUSSMAN, J. 1992. *An Introduction to the Rock-Forming Minerals – Chain Silicates. Vol 2,* 143-155.

DIXON, P. 1944. *Formation of Sulphamic Acid during the Thermal Decomposition of Ammonium Sulphate.* Nature, 154, 706

ERLUND, R., KOIVISTO, E., FAGERHOLM, M. and ZEVENHOVEN, R. 2016. *Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation- Part 2: Aqueous solution extraction*. To be submitted.

FAGERLUND, J. 2012. *Carbonation of $Mg(OH)_2$ in a pressurised bed for CO_2 sequestration*. Dr. Thesis. Åbo Akademi University, Turku, Finland. Available at: http://urn.fi/URN:NBN:fi-fe201311267415

FROST, B. R. and BEARD, J. S. 2007. *On Silica Activity and Serpentinization*. Journal of Petrology 48(7), 1351-1368

HALSTEAD, W. 1970. *Thermal decomposition of ammonium sulphate*. Journal of Applied Chemistry 20(4), 129-132

HIGHFIELD, J., LIM, H., FAGERLUND, J. and ZEVENHOVEN, R. 2012. *Activation of serpentine for CO_2 mineralization by flux extraction of soluble magnesium salts using ammonium sulfate*. RSC Advances 2, 6535-6541

HIGHFIELD, J., ÅBACKA, J., CHEN, J., NDUAGU, E., ZEVENHOVEN, R. 2015. *Overview of the ÅAU/ICES Collaboration in Ex-Situ CO_2 Mineralization*. Presented (poster) at the 13th International Conference on Carbon Dioxide Utilization (ICCDU2015), Singapore

IPCC. 2005. *Mineral carbonation and industrial uses of carbon dioxide*. Special Report on Carbon dioxide Capture and Storage: Chapter 7. Cambridge University Press, UK

LU, H-Y., LIN C-K., LIN, W., LIOU, T-S., CHEN, W-F. and CHANG, P-Y. 2011. *A natural analogue for CO_2 mineral sequestration in Miocene basalt in the Kuanhsi-Chutung area, Northwestern Taiwan*. International Journal of Greenhouse Gas Control 5, 1329-1338

LÄNSI-SUOMEN YMPÄRISTÖLUPAVIRASTO (South-West Finland Environmental Permission Agency). 2009. *Permission Decision. In Finnish: Lupapäästös*. Nro 106/2009/2 Dnro LSY-2008-Y-341, Helsinki, Finland

MÄKELÄ, M. 2011. *Carbon dioxide sequestration as mineral carbonation in Southern Finland. In Finnish: Hiilidioxidin sitominen mineraalikarbonaatiolla Etelä-Suomessa*. Master's Thesis. University of Turku, Turku, Finland.

NDUAGU, E., BJÖRKLÖF, T., FAGERLUND, J., WÄRNÅ, J. and ZEVENHOVEN, R. 2012. *Production of magnesium hydroxide from magnesium silicate for the purpose of CO_2 mineralisation-Part 1: application to Finnish Serpentinite.* Minerals Engineering 30, 75–86.

NDUAGU, E. 2012. *Production of $Mg(OH)_2$ from Mg-silicate rock for CO_2 sequestration*. Dr. Thesis. Åbo Akademi University, Turku, Finland. Available at: http://urn.fi/URN:NBN:fi-fe201311117327

NDUAGU, E., HIGHFIELD, J., CHEN, J and ZEVENHOVEN, R. 2014. *Mechanisms of serpentine–ammonium sulfate reactions: towards higher efficiencies in flux recovery and Mg extraction for CO_2 mineral sequestration*. RSC Advances 4, 64494–64505

OFFICIAL STATISTICS OF FINLAND. 2015. *Finland's greenhouse gas emissions continue to decrease*. Available at: http://www.stat.fi/til/khki/2014/khki_2014_2015-05-22_tie_001_en.html [Accessed: February 2, 2016]

ROMÃO, I. S., GANDO-FERREIRA, L. M. and ZEVENHOVEN, R. 2013. *Combined extraction of metals and production of $Mg(OH)_2$ for CO_2 sequestration from nickel mine ore and overburden.* Minerals Engineering 53, 167-170.

ROMÃO, I. S., GANDO-FERREIRA, L. M. and ZEVENHOVEN, R. 2015. *Separation of valuable metals extracted from serpentinite during the production of $Mg(OH)_2$ for CO_2 sequestration*. Minerals Engineering 77, 25-33

ROMÃO, I. S. 2015. *Production of magnesium carbonates from serpentinites for CO_2 mineral sequestration- optimisation towards industrial application*. Dr. Tech. Åbo Akademi University/University of Coimbra, Turku/Coimbra, Finland/Portugal. Available at: http://urn.fi/URN:ISBN:978‐952‐12‐3329‐6

SANNA, A., LACINSKA, A., STYLES, M. and MAROTO-VALER, M. M. 2014. *Silicate rock dissolution by ammonium bisulphate for pH swing mineral CO_2 sequestration.* Fuel Processing Technology *120, 128–135*

SJÖBLOM, S. and EKLUND, O. 2014. *Suitability of Finnish mine waste (rocks and tailings) for Mineral Carbonation.* PROCEEDINGS of ECOS 2014 – 27th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. Turku, Finland, paper 244

STYLES, M. T., SANNA, A., LACINSKA, A. M., NADEN, J. and MAROTO-VALER, M. 2013. *The variation in composition of ultramafic rocks and the effect on their suitability for carbon dioxide sequestration by mineralization following acid leaching*. Greenhouse gases science and technology 4, 440-451

VTT. 2012. *Low Carbon Finland 2050*. Available at: http://www.vttresearch.com/Documents/2012_V2.pdf [Accessed: January 21, 2016]

WANG, X. and MAROTO-VALER, M. M., 2011. *Dissolution of serpentine using recyclable ammonium salts for CO_2 mineral carbonation*. Fuel 90(3), 1229-1237

ZEVENHOVEN, R, FAGERLUND, J, BJÖRKLÖF, T, MÄKELÄ, M and EKLUND, O. 2012. *Carbon dioxide mineralisation and integration with flue gas desulphurisation applied to a modern coal-fired power plant*. PROCEEDINGS of ECOS 2012– 25th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. Perugia, Italy, paper 179

ZEVENHOVEN, R., SLOTTE, M., ÅBACKA, J. and HIGHFIELD, J. 2015. *A comparison of CO_2 mineral carbonation processes involving a dry or wet carbonation step*. ENERGY - The International Journal (Special edition for ECOS'2015) – submitted (October 2015)

ZHAO, Q., LIU, C., JIANG, M., SAXÉN, H. and ZEVENHOVEN, R. 2015. *Preparation of magnesium hydroxide from serpentinite by sulphuric acid leaching for CO_2 mineral carbonation*. Minerals Engineering 79, 116-124

ÅBACKA, J. 2013. *Low Temperature Carbonation of Magnesium Hydroxide and Sulfate*. M.Sc. Thesis. Thermal and Flow Engineering Laboratory, Åbo Akademi University, Turku, Finland.

Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation - Part 2: Aqueous solution extraction

Rickard Erlund[a]; Evelina Koivisto[a]; Mats Fagerholm[b]; Ron Zevenhoven[a]*

[a]Thermal and Flow Engineering Laboratory, Åbo Akademi University, Piispankatu 8, FI-20500 Turku, FINLAND
[b]Nordkalk Corporation, Skräbbölevägen 18, FI-21600 Pargas, FINLAND

**Corresponding author, E-mail address: rerlund@abo.fi*

Abstract:

Extraction of magnesium from minerals serpentinite, amphibolite and diopside for mineral carbonation in Finland are compared. In this part two of the study, the extraction in an aqueous solution reactor is the main focus, using solvents as ammonium bisulphate (ABS), ammonium sulphate (AS) and hydrochloric acid. The advantage using a mixture of ABS and AS as solvent is analysed. A process suggested containing an aqueous solution extraction reactor is compared to a mineral carbonation process with a thermal solid/solid extraction step. Extracted elements, mainly magnesium, are measured with atomic absorption spectroscopy (AAS). The two serpentines tested in the study showed sufficient reactivity required for an efficient carbonation process, while for the two other minerals reactivity were insufficient. The best extraction results obtained of the two serpentines give a binding capacity of CO_2 is 292 and 260 kg CO_2/ton rock. Reactivity with a minimal amount of water, and recirculation and regenerating solvent salts is analysed.

Keywords:

CCSM, CSM, CO_2 Sequestration, Mineral Carbonation, Ammonium Salts, Serpentine, Diopside, Amphibole, Magnesium extraction

1. Introduction

The worldwide increasing risks of climate change and the demand of decreasing CO_2-emissions forces society to find technological solutions. Besides several forms of renewable energy, carbon caption and storage by mineralisation (CCSM) can contribute to decreasing of CO_2-emissions. Overburden rock is piling up and suitable minerals can be used for carbonation, which of the product can be used as building materials etc. Studies showed that serpentine is a favourable mineral for magnesium extraction in a solid/solid process followed by gas/solid carbonation of $Mg(OH)_2$ for carbon caption and storage (Nduagu et al. 2012a, Fagerlund et al. 2012, Romão et al. 2013). A suitable Serpentine within Finland was found in the overburden at the Hitura nickel mine (Nduagu et al. 2012a). The location of the mine is in western central Finland, a 500 km distance to southern Finland where most of the industrial CO_2 is emitted, for example a lime kiln at Parainen. The long distance between the mineral deposit and the lime kiln site results an unacceptable CO_2-penalty for mineral transportation. However, a lime kiln at steelmaking plant in Raahe is located 140 km.

In this study CCSM suitability of magnesium rich minerals from the southern part of Finland will be adressed. In Part 1 the minerals were tested following the process scheme according to the solid/solid extraction reaction that is part of the so-called ÅA-route. The demand of waste heat for

a 400-440 °C reaction temperature during the magnesium extraction, available on a lime kiln, is not always available where the carbon capture is to be applied. Leaching the magnesium in aqueous solution temperature of 70-90°C could be sufficient and the process would be more widely applicable. However, still water has to be heated which requires energy. The suitability of the Mg-rich minerals from southern Finland and the serpentinite from Hitura for aqueous solution extraction is reported in this paper. Moreover, the solid/solid extraction is compared to the aqueous solution extractions for three other rock types. One of the tested minerals is a serpentinite similar to the rock from Hitura, apart from a small fraction of chlorite. The two others are a magnesio-hornblende and a diopside, containing less magnesium than the serpentinites.

The Mg-rich diopside tested was from the limestone quarry next to a lime kiln at Parainen. The short transport distance would minimize the CO_2-penalty generated from the transportation compared to the other rocks. According to Hsueh-Yu Lu et al., serpentine can be obtained from diopside by leaching calcium in acidic aqueous solution (Lu et al., 2011).

$$3\ CaMgSi_2O_6 + 6H^+ \rightarrow Mg_3Si_2O_5(OH)_4 + 3Ca^{2+} + H_2O + 4SiO_2 \qquad \text{(R1)}$$

Diopside Serpentine

However, some authors (Sanna et al., 2014) state that pyroxenes are chemically very stable. Experimental results with a diopside-containing pyroxene reacting with aqueous ammonium bisulphate (ABS, NH_4HSO_4) resulted into a Mg-extraction of only 30 % after 3 hours, while a 70 % Mg-extraction was obtained using olivine ($(Mg,Fe)_2SiO_4$) rock (Sanna et. al., 2014). Also, from lizardite-type serpentinite more than 85 % of the magnesium was extracted after 3 hours. Interestingly, two thirds of the magnesium was already extracted after approximately 5 minutes (Styles et al., 2014).

Studies of magnesium containing rock for carbon capture have shown that quarries in southern Finland contain possibly suitable minerals and serpentine-containing rock located in Vammala was selected for further testing. The mineral from the Vammala quarry is a serpentinite, at a location 140 km from a lime kiln and 85 km east of the Meri-Pori coal-fired power plant (Zevenhoven 2012 et al.). Mg-rich olivine mineral from a quarry in Salittu in southern Finland was selected as well (Länsi-Suomen ympäristölupavirasto, 2009). The location of the quarry is favourable, considering the 100 km distance to a lime kiln and close to other CO_2 emitting industries. The locations of the mineral deposits are shown in Figure 1.

Leaching experiments with diopside and amphibolite containing minerals from South Africa using a solution as 2 M H_2SO_4 show that extraction of Mg can be accomplished (Meyer et. al. 2014). According to Styles et al. (2014), Teir et al. (2007a), serpentines are the most favourable mineral for wet extraction. Compared to olivine the extraction kinetics are favourable (Styles et al. 2014). Other studies have shown that serpentines are a hundred times more widely available in nature than olivine (Hemmati et al. 2014).

Figure 1 – The locations of the rocks used in the study.

2. Experiments

2.1. Materials

Table 1 represents the chemical composition of the minerals tested and Table 2 shows the fractions of the minerals estimated using X-Ray Fluorence (XRF) and X-Ray Diffraction (XRD). The diopside used in the experiments was a 10% fraction enriched from Mg-rich overburden from the lime quarry at Parainen. A concentration ("enrichment") of the diopside was performed by the Geological Survey of Finland (GTK) based on flotation separation of different density fractions. The concentrated, diopside-rich fraction has a density below 3300 kg/m^3. XRD of the diopside showed that almost half of the diopside actually was hedenbergite, where the diopside magnesium is substituted with iron (Deer et al, 1992).

XRF and XRD analysis of the Mg-rich stone from the Salittu quarry did not reveal olivine. However, it contains a 30-40% fraction of a magnesio-hornblende (Mg-Horn), belonging to the amphibolite group, which gives a total 8.7% of MgO in the rock. Another large fraction is a plagioclase 30-40% which explains the high content of calcium and aluminium. Extraction of calcium from plagioclase is insufficient, making it unsuitable for CCSM purposes (Wei et al. 2009). Another considerable fraction, 15-20%, is quartz, containing no useful elements for CCSM, simply resulting in a burden for the process if not a valuable product can be obtained from it.

The stones from Vammala and Hitura are serpentinite overburden rock from nickel mines. Table 1 shows that the chemical compositions of the rocks are very similar apart from the higher content of aluminium in the Vammala stone while containing slightly less MgO. However, the serpentinites MgO content is about four times larger compared to the other rock. This results in a theoretical carbon capture and storage requirement of 375 kgCO_2/tonne Serp-A and 338 kgCO_2/tonnes Serp-B (Koivisto et al. 2016). Table 2 shows that both serpentinites contains mainly serpentine and magnetite. These fractions are slightly larger for the Hitura stone, while Vammala also contains 10-15% chlorite. Extraction of magnesium from chlorite and talc schist is more efficient compared to serpentines, unfortunately the chlorite has a lower magnesium content than serpentine (Sjöblom and Eklund, 2014).

Table 1. Chemical compositions of the minerals tested, based on XRF analysis. Unit: %-wt. LOI stands for ignition loss.

Compound	Hitura Serp-A	Vammala Serp-B	Parainen Diopside	Salittu Mg-Horn
CaO	0.4	0.45	23.8	10.9
SiO_2	35.5	35.3	49.9	48.7
TiO_2	0.04	0.15	1.2	0.85
NiO	0.35	0.27	0.02	0.018
Al_2O_3	0.45	2.7	2.9	14.7
Fe_2O_3	14.6	16.3	14.2	12.1
MgO	35.1	31.0	6.6	8.7
K_2O	0.02	0.08	0.29	0.67
Na_2O	<0.01	0.08	0.34	1.9
MnO	0.12	0.21	0.16	0.22
CuO	0.10	0.11	0.03	0.024
Cr_2O_3	0.38	1.2	<0.01	0.057
P_2O_5	0.01	0.02	0.09	0.18
S-Eltra	0.42	0.87	-	0.08
LOI 1000 °C	12.0	11.4	0.18	0.63
Rest	0.5	-0.17	0.3	0.2

2.2. Methods

The experiments of comparing the minerals were done by leaching in water solution containing three different additives for mapping the solubility of primarily magnesium. Also iron was measured, while also calcium and aluminium were measured, due to high content, for the tests with diopside and Mg-horn. For leaching in a more neutral (pH 5,5) solution ammonium sulphate was used, which was used as flux salt in the solid/solid extraction used by several authors (Nduagu et al. 2012a, Romão et al. 2013, Koivisto et al. 2016). The two other additives chosen, ammonium bisulphate, NH_4HSO_4 (ABS) and hydrochloric acid (HCl), were for leaching tests in acidic solutions. Moreover, some experiments were done with oxalic, acetic, formic and citric acid, resulting in insufficient extraction. These are not considered further.

Table 2. Mineralogy of the various minerals of the 63-125µm fraction. Unit: %-wt. Estimated on basis of XRD analysis and the chemical composition.

Mineral	Hitura Serp-A	Vammala Serp-B	Parainen Diopside	Salittu Mg-Horn
Serpentines $(Mg, Fe)_3Si_2O_5(OH)_4$	70-80	60-70	-	<5
Magnetite Fe_3O_4	15-20	10-15	-	-
Diopside-Hedenbergite $MgCaSi_2O_6$	-	-	90-95	<5
Plagioclase $(Na, Ca)(Si, Al)_4O_8$	-	-	< 5	30-40
Amphibole (Magnesiohornblende) $Ca_2[Mg_4(Al, Fe)]Si_7AlO_{22}(OH)_2$	-	< 5	-	30-40
Quartz SiO_2	-	-	-	15-20
Chlorite $(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2 \cdot (Mg, Fe)_3(OH)_6$	< 5	10-15	-	-
Calcite $CaCO_3$	< 5	-	-	-
Cordierite $Mg_2Al_4Si_5O_{18}$	-	-	< 5	-
Annite $KFe_3AlSi_3O_{10}(OH,F)_2$	-	< 5	-	-
Dolomite $CaMg(CO_3)_2$	-	< 5	-	-

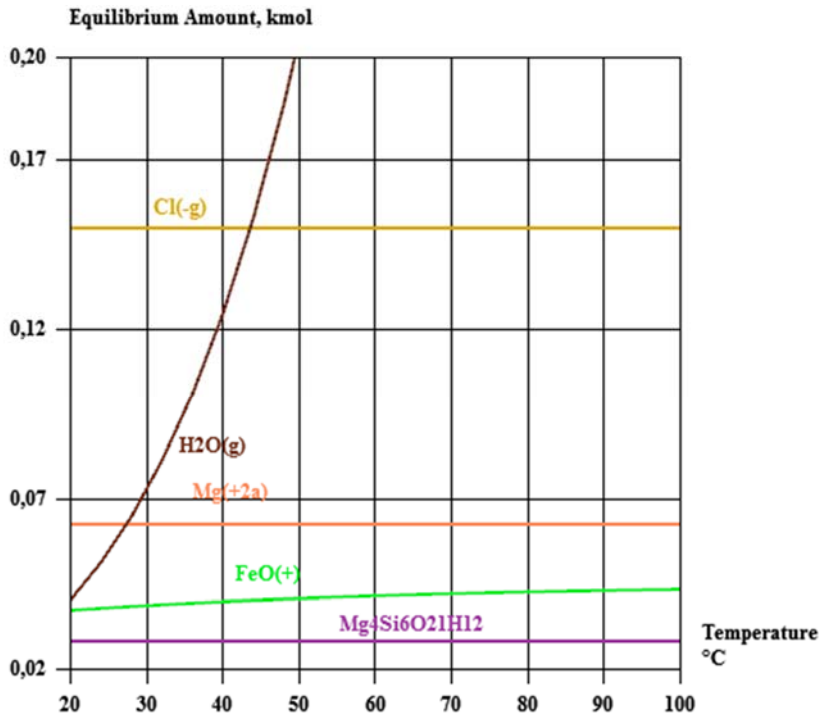


Figure 2 - The results of Gibbs energy minimization with HCl reacting with water, Serpentine and magnetite from temperatures between 20°C and 100°C (HSC 8, 2014).

Studies by others have shown that leaching magnesium from serpentine with 1M HCl results in >80% Mg-extraction after 2 hours (Hemmati et al. 2014). Even stronger solutions of 2M HCl at 70°C, can leach 100% of the magnesium in 1 hour. (Teir et. al. 2007b) However, the regeneration of HCl after precipitation of magnesium hydroxide or magnesium carbonate at pH 10 is expensive and requires large amounts of energy. Due to this regeneration problem a lower concentration of 0.15M HCl was chosen for the experiments. To avoid excess HCl the molar ratio between Cl^- and extracted elements of serpentines Fe^{2+} and Mg^{2+} was chosen close to 1. However, the same concentrations of HCl results in excess Cl^- in relation to the extractable elements (Mg^{2+}, Fe^{2+}, Ca^{2+}, Al^{3+}) of diopside and Mg-Horn.

The equilibrium of the reaction of serpentine and HCl was estimated using Gibbs energy minimization software HSC Chemistry 8 (HSC 8, 2014). Reactants 0.085 moles serpentine, 0.015 moles magnetite, 0.15 moles HCl and 2 moles water were taken as input. The results are shown in Figure 2, from which it is clear that not all of the magnesium will be extracted to Mg^{2+} at equilibrium. A sealed 0.5 litres conical flask was used as the reactor with rapid magnetic stirring. The experiments were done at room temperature (25 °C) considering that the equilibrium of Mg^{2+} shown in Figure 2 is constant between 20 °C and 100 °C. The starting concentration for the tests with AS and ABS are chosen to match the experiments in the Styles et al. (2014) studies, where several minerals magnesium extraction is tested in a 0.4l 1.4M salt solution, giving an opportunity for comparison of the minerals (Styles et al. 2014). To ensure complete stirring and the best contact between the solution and the mineral particles in the experiments a low 25g/litre solid/liquid ratio was used

combined with magnetic stirring at rapid speed. AS gives a relatively neutral pH 5.5 measured in the reactor with a 1.4M solution, while ABS is acidic with pH 0.93 for the same concentration.

Equilibrium calculations (HSC 8, 2014) for both cases are shown in Figure 3. Reactants used were 0.85 moles serpentine, 0.15 moles magnetite, 1.4 moles of ammonium salt and 5 moles water. The product of the reaction for later carbonation is magnesium sulphate. The left graph in Figure 3 shows that the higher the temperature, the higher the concentrations of $MgSO_4$ at equilibrium when AS is used. A temperature over 40°C is needed for significant amounts of $MgSO_4$. Shown in the right graph of Figure 3 it is the similar case with ABS, showing that already at 25°C significant amounts of $MgSO_4$ are produced. For the experiments a temperature of 70°C is used ensuring the higher $MgSO_4$ concentration at theoretical equilibrium. A heated bath was added to the reactor keeping the temperature stable during the experiments reported below.

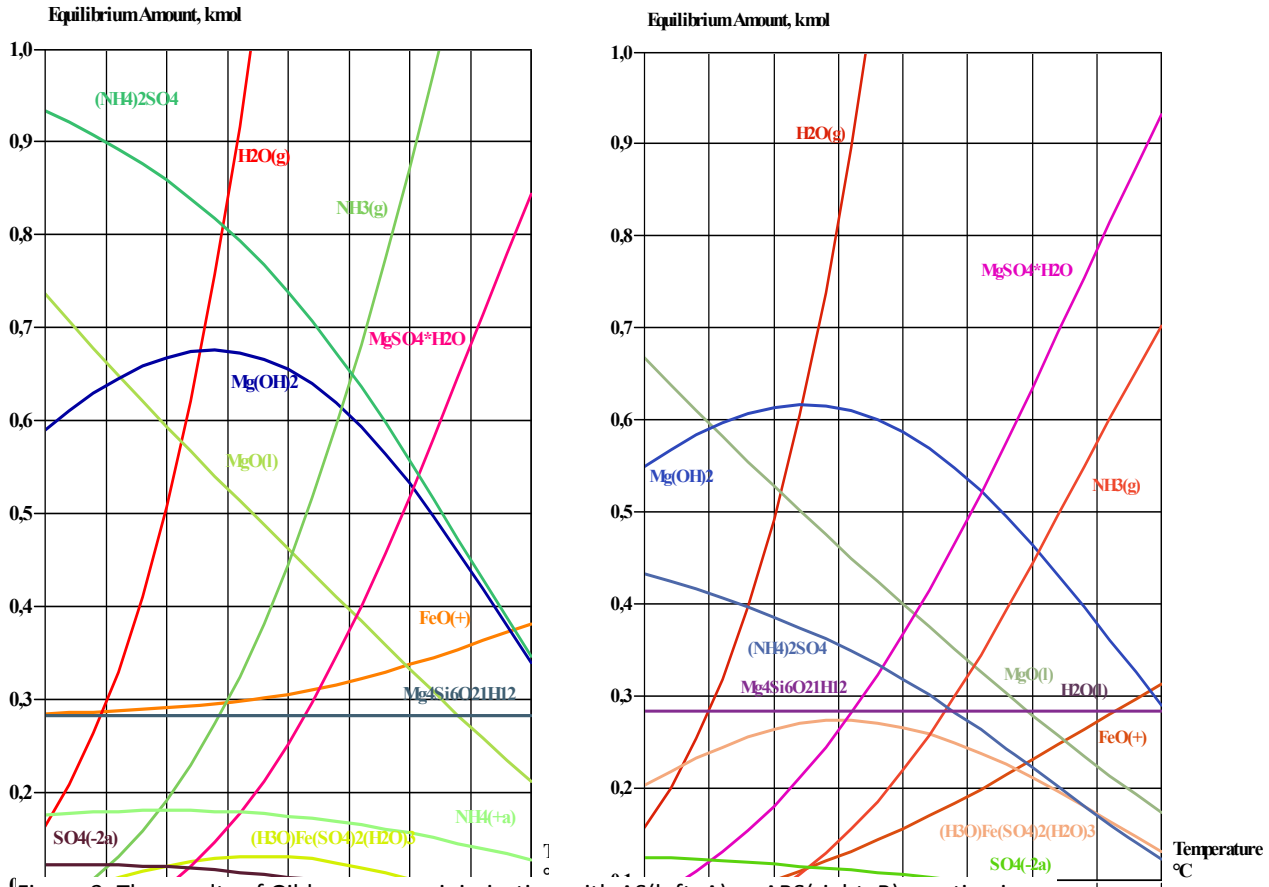


Figure 3. The results of Gibbs energy minimization with AS(left, A) or ABS(right ,B) reacting in water with serpentine and magnetite at temperatures between 20°C and 100°C. (HSC 8, 2014)

Recirculating ABS in a continuous process requires energy, as it is formed from AS, shown in reaction R2 in Table 3 (Romão 2014). The energy is required for the sublimation of ammonia at 330°C taking place (simulated using HSC 8, 2014). The ammonia can be used to give the alkaline solution needed in the carbonation of the $MgSO_4$ where hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) is precipitated. Ammonia added to sulphate ions and ABS will form AS (R5), which can be recirculated and used for generating ABS.

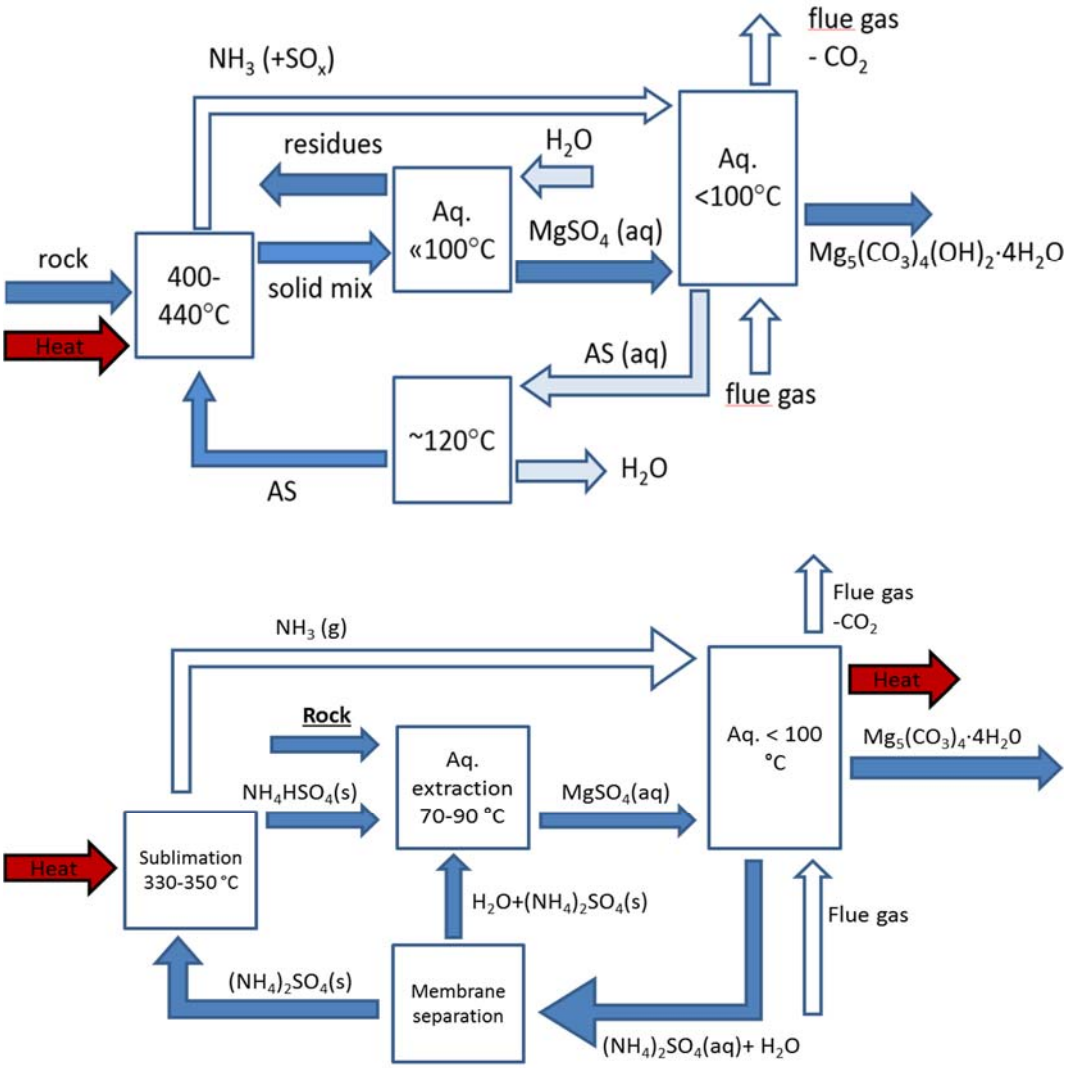


Figure 4. A(Above). The process scheme of the process with thermal solid/solid extraction studied in Part one of this paper (Koivisto et al. 2016). B(Below). Process scheme with aqueous leaching of magnesium.

Table 3 – Reactions in the process shown in Figure 4B

$(NH_4)_2SO_4 \rightleftharpoons NH_3(g)+NH_4HSO_4$	(R2)
$NH_4HSO_4 \rightleftharpoons NH_4^+ + HSO_4^-$	(R3)
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	(R4)
$NH_4OH(l) + NH_4HSO_4 \rightleftharpoons (NH_4)_2SO_4 + H_2O$	(R5)
$5MgSO_4 (s) + 10H_2O (l) + 10NH_3 (g) + 4CO_2 (g) \rightleftharpoons Mg_5(OH)_2(CO3)_4 \cdot 4H_2O (s) + 5(NH_4)_2SO_4 (aq)$	(R6)

In Figure 4B, a process is proposed where only a part of the AS forms ABS by sublimation of ammonia. This will decrease the energy needed for reaction R2, while a part of the AS can be sent directly to the extraction reactor. Substituting AS with ABS will increase the pH-value as is shown in

Figure 5. Decreasing the amount of ABS results in less dissociation of its anion HSO_4^- as in reaction R4, which is considered a weak acid.

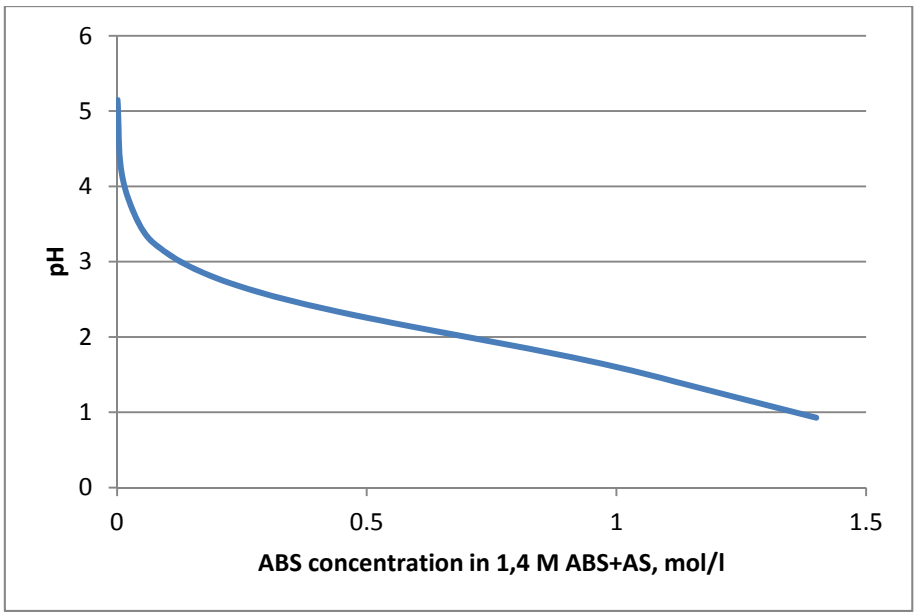


Figure 5. pH of a solution with a certain amount of ABS with ABS+AS being 1,4M mol/l at 25 °C.

By testing 1,4M solutions of various ratios of AS and ABS from 1:1 to 1:3 with Serp-A and 1:1 to 1:7 with Serp-B, the impact of less ABS in the solution could be assessed. Sustaining a sufficiently acidic environment for the extraction of magnesium from serpentinite without compromising the extraction achieved is the goal of the process in Figure 4B.

The earlier mentioned mineral carbonation process with magnesium extraction in a thermal solid/solid reactor as tested in part 1 of this paper (Koivisto et al. 2016) is shown in Figure 4A. At the 400-440 °C the extraction of magnesium is accomplished with AS. The high temperature forces some NH_3 to evaporate from salt in the reactor, while in the liquid/solid process shown in Figure 4B, the NH_3 is evaporated while regenerating ABS from AS at 330 °C. As mentioned above, the ABS lowers the pH in the solution to levels necessary for the extraction of magnesium from serpentinite. Less material has to be heated and to a lower temperature (330 °C) in the liquid/solid process compared to the solid/solid process (400-440 °C). However, considerable amounts of water have to be heated to 70-90 °C in the liquid/solid process which gives an energy penalty compared to the solid/solid that is unattractive if no low temperature waste heat is available.

In the solid/solid process the use of water is limited by the solubility of $MgSO_4$ and AS, which both are highly soluble in water. Concerning the liquid/solid process, the extraction efficiency of higher concentrations of ammonium salts and serpentinite have to be tested to minimize the water usage. In both processes shown in Figure 4, the $MgSO_4$ reacts with H_2O, NH_3 and CO_2 from the flue gas in a pH value around 10 as in R6. The product in is hydromagnesite ($Mg_5(OH)_2(CO_3)_4{\cdot}4H_2O$) as in R6 or nesquehonite ($MgCO_3{\cdot}3H_2O$), depending on the temperature (Zevenhoven et al. 2015).

2. Results and Discussion

2.1. Leaching in HCl solution

The concentration of the extracted magnesium in the leaching solution is measured after 1, 2, 3 and in some cases 5 hours using AAS. Leaching experiments with 0.5 l 0.15 M HCl were done at 25 °C according to the procedure described in the experimental part. After 5 hours 1.4% of magnesium was extracted from the diopside and 6.4 % from of the Mg-Horn. These figures are simply not sufficient for mineral carbonation. The extraction levels for the two serpentinites are completely different, being 43.5 % for Serp-A and 17.8 % for Serp-B after 5 hours. Considering that both contain large amounts of the same mineral the difference is surprising. However, the leaching results for the serpentinites in such low concentrations of the additive are promising.

2.2. Ammonium bisulphate

The best extraction results were obtained with 1.4 M ABS as solvent, except with the diopside. The pH 0.93 solution was slightly weaker compared to pH 0.81 for the 0.15 M HCl solution, but the bisulphate behaving as weak acid, buffers the H^+ concentration when H^+ ions are consumed in the leaching reaction. The extraction from Mg-horn is slightly better and for the diopside less compared to HCl. However, the extractions from serpentinites in ABS solution are considerably better compared to leaching with a HCl solution. Presumably the fully dissociated HCl reacting with the serpentinite lowers the H^+ concentration while the reactivity decreases as a result of the rising pH. The decrease of H^+-ion in the buffering 1.4 M ABS solution is considerably less. Also, the higher temperature of 70 °C in the ABS leaching tests compared to 25 °C, using HCl, has an impact on the reactivity. In this case, the extraction of Mg from both serpentines after 3 hours is 77 %. After one and 2 hours the Serp-B is slightly less extracted than Serp-A, indicating that the kinetics of Serp-B is slower while the Serp-A appears to reach equilibrium earlier considering the matching results after 3 hours. The extraction figures of the serpentinites are only slightly lower than the Scottish serpentinites tested at higher temperature of (100 °C) in Styles et al. (2014) work. The behaviour of the Finnish serpentinites at 70°C is more similar to the olivine tested from Minelco, Norway (Styles et al., 2014). However, Mg extraction from olivine from Åheim, Norway, tested with thermal solid/solid process at ÅA was under 10%. A higher amount of iron in a serpentinite lowers the reactivity along with specific surface and porosity (Nduagu et. al. 2012b). The Scottish serpentinite contains 92.3 % lizardite while the Serp-A contained 70-80 % and Serp-B 60-70 % lizardite, respectively besides a fraction of 10-15 % iron-containing magnetite (Styles et al., 2014).

2.3. Ammonium sulphate

Despite the fact that HSC chemistry 8 suggests (in Figure 3A) that large amounts of Mg^{2+} and $MgSO_4$ would be extracted from serpentinite at temperatures over 40°C with AS in equilibrium as ABS the extraction from both serpentinites is only 3-5% after 5 hours. The results are shown in Figure 6C. These results indicate that the extraction kinetics are very slow in a less acidic environment of pH 5.5. Thus, it can be stated that serpentinites are not reactive at pH 5.5. Again the Serp-A gave a slightly better extraction than Serp-B. Extraction of Mg from Mg-horn and the diopside are under 1 %. According to Nduagu aqueous leaching with AS extracted 0.3-0.5% magnesium after 1 hour (Nduagu 2008).

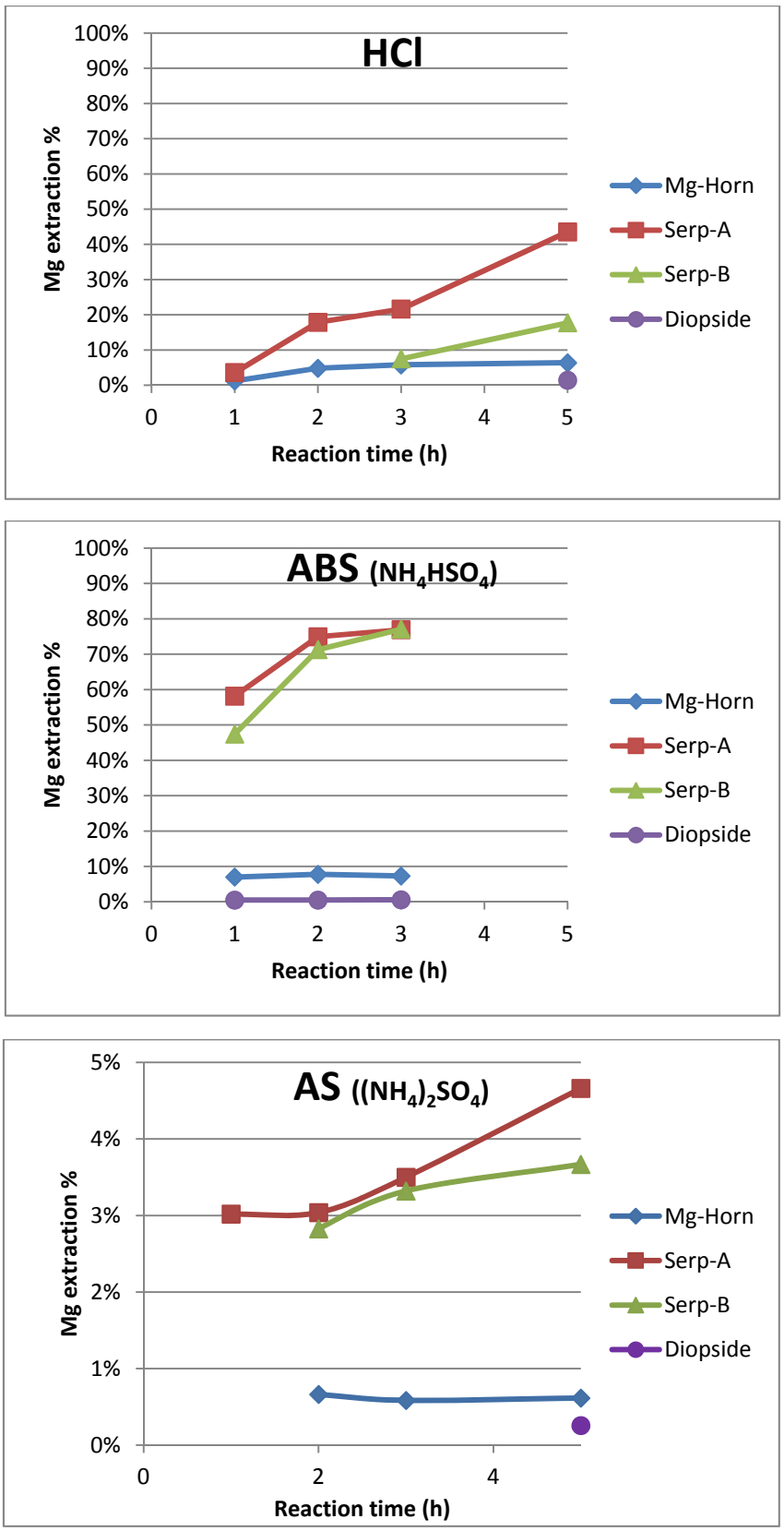
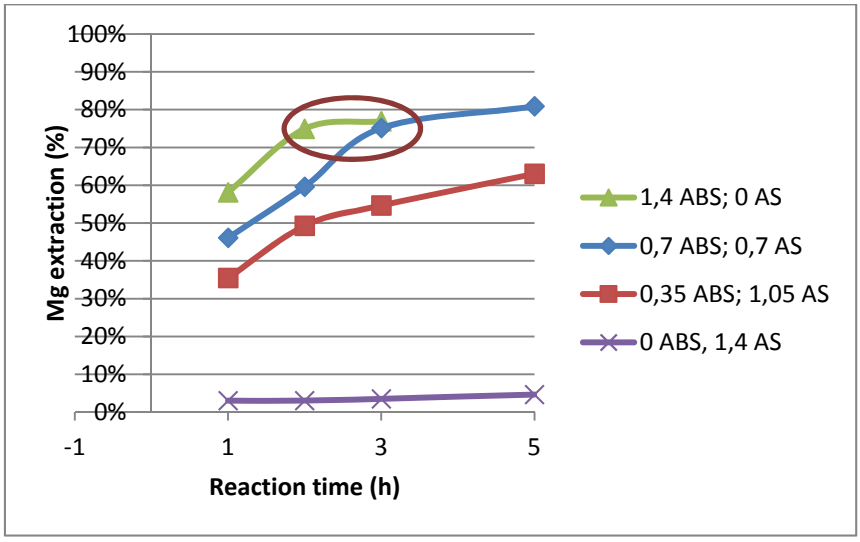


Figure 6. A (Above): Magnesium extraction of the minerals tested in 0,5l 0,15M HCl at 25°C with a fraction of 125-250µm. B(centre) and C(below):Magnesium extraction of the minerals tested in 0,4l 1,4M ABS(B) and AS(C) solution at 70°C with a fraction of 63-125µm.

2.4. Mixture of AS and ABS as solvent

It was attempted to find the critical pH to obtain an efficient extraction of Mg while using minimal amounts of ABS (requiring heat for regeneration). This was tested by substituting the AS with ABS for various pH values for both serpentines. The results are shown in the graphs in Figure 7. Already a 1:7 mole/mole ABS to AS ratio gives an extraction 4 times that when using pure AS with Serp-B. The extraction with a 1:3 ABS to AS ratio is also considerably slower than with pure ABS. After 5 hours of extraction the Serp-A gives an Mg extraction of 63 %, but only about 50 % after a more preferable 2-3 hours. However, Serp-B reaches extraction figures under 40 % after 5 hours and after 3 hours the extraction is less than half that obtained with pure ABS. The difference in behaviour testing 0.35 M ABS and 1.05 M AS with these rocks is comparable with the earlier mentioned tests with 0.15 M HCl. It can be assumed that a decrease of the H^+ concentration, affects reactivity negatively of Serp-B more than Serp-A. A considerably more acidic solution with 1:1 ratio of ABS and AS shows that only 62% of the magnesium is extracted after 5 hours and 57 % after 3 hours.



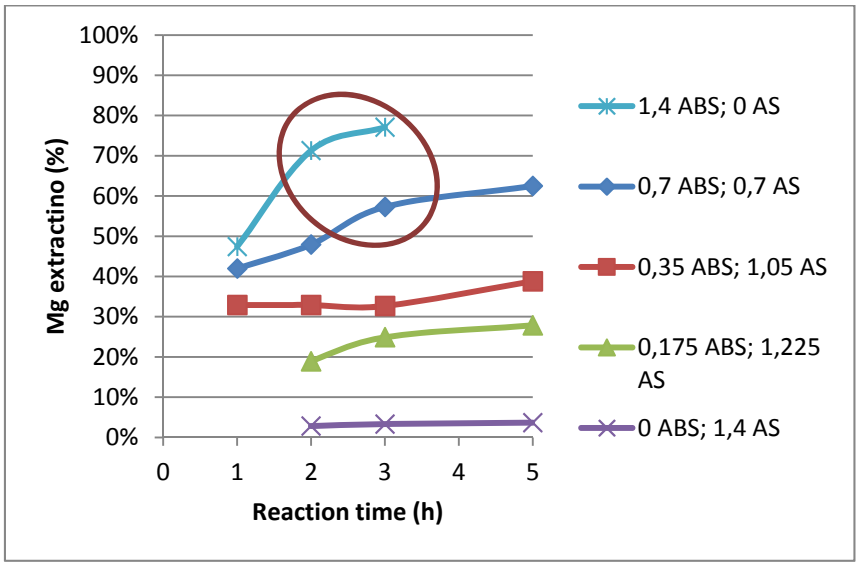


Figure 7. Extraction of magnesium in 0,4 l 1,4 M Ammonium salt with various amounts of AS substituted with ABS. Above (A): Serp-A, Below (B): Serp-B. The most optimal results are circled.

The concentration of the anion of ABS, bisulphate, considered to be a weak acid, in a ratio to the moles Mg^{2+} and Fe^{2+} against Mg-extraction is plotted in Figure 8. The Serp-A reaches 75 % Mg-extraction between a HSO_4^-/(Mg+Fe) ratio of 3 to 6, while Serp-B requires a ratio of 6. From the relation of 0-3 HSO_4^-/(Mg+Fe) the Serp-A is more reactive than Serp-B. Substituting ABS with AS for Serp-B would not be effective in the process suggested if only a part of the AS is generated to ABS. However, the 1:1 ratio is affecting the extraction after 1 and 2 hours for Serp-A, while the extraction after 3 hours is similar to what is obtained with pure ABS as solvent after 2-3 hours. The energy used for the sublimation of NH_3 at high temperature 330 °C and generation of ABS can be reduced with a longer reaction time or possibly higher reaction temperature for better kinetics. Depending on how much energy is needed for the ABS recovery in total, the optimal ABS to AS ratio using Serp-A is between 1:1 and 1:3.

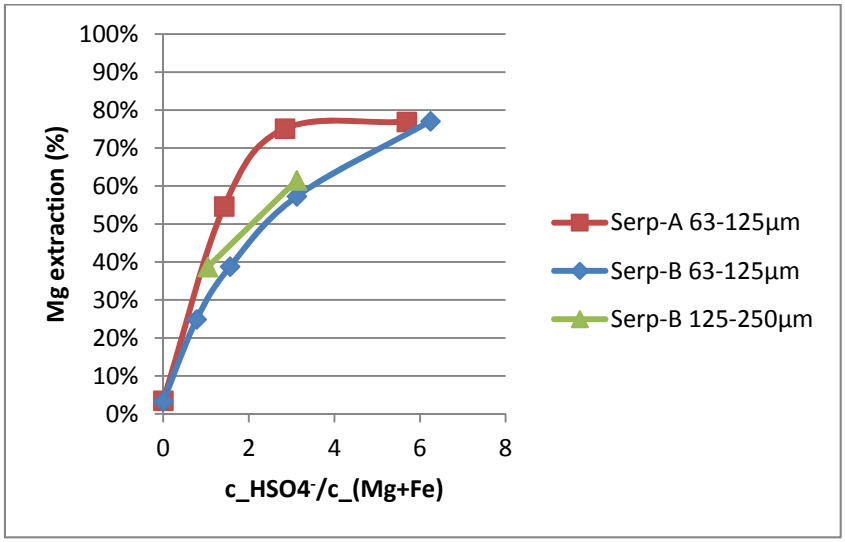


Figure 8 – The relation between $HSO4^-$ and Mg respectively Fe in serpentine against Mg extraction. Results of leaching tests with 0,4l 0-1,4M ABS and 0-1,4M AS at 70°C at 3 hours.

2.5. Particle size

Various particle sizes were tested in a 1.4 M ABS solution to monitor its impact on reactivity. The hardness of pure serpentine is between 2 and 5 on Mohs scale, considered a soft mineral, resulting in a rather low energy use for milling (minerals.net 2016). According to Sanna et al., grinding a serpentinite to a particle size less than 300 µm, the fraction under 75 µm will be 40 % of the mass (Sanna et al. 2013). Similar behaviour was found in this study, where 99 % of the Serp-B was grinded to a size under 250 µm resulting in 37 % of the mass having a particle size of <63 µm. Considering that about 37 % of the particles are under 63 µm with grinding energy targeting 125-250 µm, the reactivity of 38-63 µm, 63-125 µm and 125-250 µm was tested. The results are shown in Figure 9, where 3 hours leaching of the fraction 38-63 µm resulted in 86 % extraction of the magnesium, 9 % better than for the fraction 63-125 µm and 21 % better compared to fraction 125-250 µm. The efficiency of the process can considerably improve when making use of this. Future work, concerning process efficiency should further study this effect and determine the reactivity of the smaller fractions using mixtures of AS and ABS.

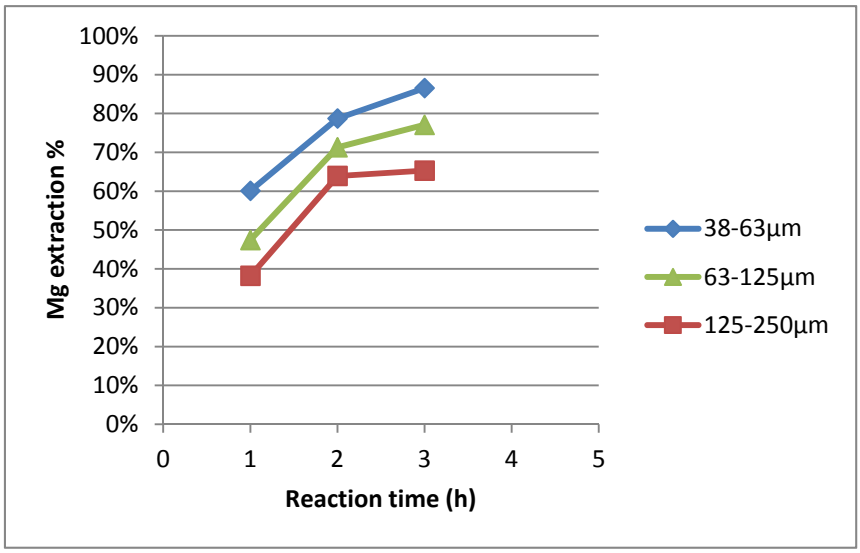


Figure 9 – Magnesium extraction in 0.4l 1.4 M ABS solution at 70 °C with fractions of various particle sizes of Serp-B rock.

Table 4 - A comparison of the specifications and the results between thermal solid/solid and aqueous liquid/solid leaching.

Extraction method	**Thermal Solid/Solid**	**Aqueous Liquid/Solid Leaching**
Sublimation of NH_3	High temperature (440 °C) required in the reactor.	Generation of ABS from AS at 330 °C. Only half of the AS has to be heated.
Heating of water masses	Absence of water in the reactor. Less energy used for heating (440 °C)	Water and the reactants are heated to the reaction temperature of 70-90 °C
Reactivity and results	Reaction time 60 min, typically 60-65 % Mg-extraction of serpentinite.	Reaction time 120-180 min, typically 75 % Mg-extraction of serpentinite.
Total use of water in the process	Water needs to dissolve the produced $MgSO_4$, which is highly soluble.	For 25-50 g rock, 1litres of water is used.
External/Waste energy	High temperature external heat is needed (extraction temp. 440 °C),	Less high temperature external heat (330 °C) is needed, only a part of the AS forms ABS. Low temperature external heat needed (extraction temp. 70-90 °C)
Use of solvent.	1.15 to 1.5 stoichiometry of solvent salt is needed compare to the extracted elements of serpentine.	A molar ratio >3 of solvent salt compared to the extracted elements of serpentine.

2.6. Comparison of thermal solid/solid and aqueous liquid/solid extraction.

All rocks tested gave more or less similar results using both thermal solid/solid or aqueous solution extraction methods. Results obtained showed aqueous extraction of 75-80% magnesium extraction of the serpentinites, compared to 60-64% using thermal solid/solid extraction as in Part one of this paper (Koivisto et. al. 2016). However, it must be mentioned that the reaction time is 1-1.5 times longer using the aqueous extraction method. A comparison between the methods is shown in Table 4.

3. Conclusions

The extraction of Mg from four Mg-rich types of rock in an aqueous solution reactor was analysed with ABS, AS and HCl as solvent. Mixtures of ABS and AS were used for analysing the advantages of using less energy consuming acidic salt while obtaining sufficient extraction figures.

Magnesium extraction for Mg-Horn and diopside is insufficient in all of the cases. However, it is attractive and sufficient to extract magnesium from the serpentinites tested in an acidic solution. Using 0.15M HCl as solvent resulted in magnesium extraction of 17-41% 125-250µm of the serpentinites, not sufficient for a CCSM process. As stronger HCl solution for better extraction is not an option, considering that the recovery of HCl is not attractive. Up to 75-80 % of its magnesium can be extracted from serpentinite of the fraction 63-125 µm in 1.4 M ABS, and the Serp-A reaches the final result faster than Serp-B. Compared to the thermal solid/solid reactor used for the work in Part 1 of this paper the reactivity is clearly better, with 60-65% of the magnesium extracted from the serpentinites (Koivisto et al. 2016). Saving energy by substituting partly the acidic salt ABS with AS, Serp-A was clearly the more Mg-releasing compared to Serp-B. The best extraction results obtained have a binding capacity of CO_2 is 292 kg CO_2/ton Serp-A and 260 CO_2/ton Serp-B.

The Serp-A is the preferable rock to use, while its location in Hitura, western central Finland, is not ideal apart from the lime kiln at a steelmaking plant at a 140 km distance. The Serp-B location, in southern Finland, near population and industry dense areas is more preferable. For mineral carbonation in southern Finland, the transportation can counterbalance the better reactivity concerning Serp-A if it is compared to Serp-B.

Acknowledgement

This work was funded by CLIC Oy CCSP project (2011-2016) and Nordkalk Corporation. The authors acknowledge Thomas Nyberg and Synnöve Hollsten from Nordkalk for the extensive AAS, XRF and XRD analyses done.

Nomenclature

Abbreviations

CCSM	Carbon capture storage by mineralisation
Serp-A	Hitura serpentinite
Serp-B	Vammala serpentinite
Mg-Horn.	Magnesio-hornblende from Salittu
XRD	X-Ray Diffraction
XRF	X-Ray Fluorence

Chemical Compounds

AS	Ammonium sulphate
ABS	Ammonium bisulphate
HCl	Hydrochloric acid
MgO	Magnesium oxide
$Mg(OH)_2$	Magnesium hydroxide
$MgSO_4$	Magnesium sulphate
$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$	Hydromagnesite
NH_3	Ammonia
HSO_4^-	Bisulphate

References

Deer, W. A., Howie, R. A., Zussman, J. 1992. An Introduction to the Rock-Forming Minerals – Chain Silicates pp. 143-155.

Fagerlund, J., Highfield J., Zevenhoven, R. 2012. Kinetics studies on wet and dry gas–solid carbonation of MgO and $Mg(OH)_2$ for CO_2 sequestration, RSC Advances, 2012, 2, 10380-10393

Hemmati, A., Shayegan, J., Bu., J. Yeo. T.Y., Sharratt, P., 2014, Process optimization for mineral carbonation in aqueous phase. International Journal of Mineral Processing 130, 20-27

HSC Chemistry version 8.1.1. 2014. Outokumpu Research. Pori, Finland.

Koivisto, E,. Erlund, R., Zevenhoven, R. 2016. Extraction of magnesium from four Finnish magnesium silicate rocks for CO_2 mineralisation - Part 1: Thermal solid/solid extraction. Mineral Engineering, to be submitted.

Lu, H-Y., Lin C-K., Lin, W., Liou, T-S., Chen, W-F., Chang, P-Y. 2011. A natural analogue for CO_2 mineral sequestration in Miocene basalt in the Kuanhsi-Chutung area, Northwestern Taiwan. International Journal of Greenhouse Gas Control 5, 1329- 1338.

Länsi-Suomen lupapäätös ympäristölupavirasto(South-western Finland Environmental Permission Agency). 2009. Lupapäästös. Nro 106/2009/2 Dnro LSY-2008-Y-341. Accessed: Helsinki, Finland.

Meyer N.A., Vögeli, J.U., Becker, M., Broadhurst, J.L., Reid, D.L., Franzidis, J.P. 2014. Mineral carbonation of PGM mine tailings for CO_2 storage in South Africa: A case study, Minerals Engineering 59, 45–51

Minerals.net 2016. http://www.minerals.net/mineral/Serpentine.aspx [cited 21.1.2016]

Nduagu, E. 2008. Mineral carbonation: preparation of magnesium hydroxide [$Mg(OH)_2$] from serpentinite rock Master's Thesis. Åbo Akademi University, Turku, Finland.

Nduagu, E., Björklöf, T., Fagerlund, J., Zevenhoven, R. 2012a. Production of reactive magnesium from magnesium silicate for the purpose of CO_2 mineralization. Part 1: Application to Finnish serpentinite. Minerals Engineering 30, 75–86.

Nduagu, E., Björklöf, T., Fagerlund, J., Mäkelä, E., Salonen, J., Geerlings, H., Zevenhoven, R. 2012b. Production of magnesium hydroxide from magnesium silicate for the purpose of CO_2 mineralization –Part 2: Mg extraction modeling and application to different Mg silicate rocks. Minerals Engineering 30, 87-94.

Romão, I., Eriksson, M., Nduagu, E., Fagerlund, J., Gando-Ferreira, L.M., Zevenhoven, R. 2012. Carbon dioxide storage by mineralization applied to a lime kiln. PROCEEDINGS of ECOS 2012 – 25th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. Perugia, Italy, paper 226

Romão, I.S., Slotte, M., Gando-Ferreira, L.M., Zevenhoven, R. 2014. CO_2 sequestration with magnesium silicates—Exergetic performance assessment. Chemical Engineering Research and Design, 92, 12, 3072–3082

Sanna, A., Wang, X., Lacinska, A., Styles, M., Paulson, T., Maroto-Valer, M. 2013. Enhancing Mg extraction from lizardite-rich Serpentine for CO_2 mineral sequestration. Minerals Engineering 49, 135–144

Sanna, A., Lacinska, A., Styles, M., Maroto-Valer, M., M. 2014. Silicate rock dissolution by ammonium bisulphate for pH swing mineral CO_2 sequestration. Fuel Processing Technology, 120, 128–135

Sjöblom, S., Eklund, O. 2014. Suitability of Finnish mine waste (rocks and tailings) for Mineral Carbonation. PROCEEDINGS of ECOS 2014 – 27th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. Turku, Finland, paper 244

Styles, M. T., Sanna, A., Lacinska, A. M., Naden, J., Maroto-Valer, M. 2014. The variation in composition of ultramafic suitability for carbon dioxide sequestration by mineralization following acid leaching. Greenhouse gases: Science and technology, 4, 4, 440-451

Teir, S., Kuusik, R., Fogelholm, C.J., Zevenhoven, R. 2007a. Production of magnesium carbonates from Serpentinite for long-term storage of CO_2. International Journal of Mineral Processing, 85, 1–15

Teir S, Eloneva S, Fogelholm CJ and Zevenhoven R. 2007b. Dissolution of natural Serpentinite in mineral and organic acids. Fuel Processing Technology 83, 1–2, 36–46.

Wei, L., Hu, H., Chen., Q., Tan, J. 2009. Effects of mechanical activation on the HCl leaching behavior of plagioclase, ilmenite and their mixtures, Hydrometallurgy, 99, 1-2, 39-44.

Zevenhoven, R., Fagerlund, J., Björklöv, T., Mäkelä, M., Eklund, O. 2012. Carbon dioxide mineralization and integration with flue gas desulphurisation applied to a modern coal-fired power plant. PROCEEDINGS of ECOS 2012– 25th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems. Perugia, Italy, paper 179

Zevenhoven, R., Slotte, M., Åbacka, J., Highfield, J. 2015. A comparison of CO_2 mineral carbonation processes involving a dry or wet carbonation step. ENERGY - The International Journal (Special edition for ECOS'2015) – submitted (October 2015)