

Ron Zevenhoven
Experience Nduagu
Inês S. Romão

Investigation of alternative-silicate raw materials for carbonation



CLEEN LTD
ETELÄRANTA 10
P.O. BOX 10
FI-00130 HELSINKI
FINLAND
www.cleen.fi

ISBN XXX-XX-XXXX-X
ISSN XXXX-XXXX



ccsp

Carbon Capture and Storage Program

CLEEN
Cluster for Energy and Environment

Åbo Akademi University
CCSP WP5.2, D513

Ron Zevenhoven
Experience Nduagu *
Inês S. Romão

Investigation of alternative-silicate raw materials for carbonation

* Currently Eyes High Postdoctoral Fellow
Department of Chemical and Petroleum Engineering,
University of Calgary, Canada



Åbo Akademi University
Turku, January 2014



Report Title: D513 - Investigation of alternative-silicate raw materials for carbonation

Key words: mineral carbonation, silicate raw materials

Abstract:

This report addresses Finnish magnesium-silicate resources for large-scale CO₂ mineral sequestration other than the Hitura nickel mine overburden rock that has been used in most assessments for application of the technology in Finland. Finding a rock suitable for application at Nordkalk's industrial-scale lime kiln in Parainen and available at low cost is the main motivation for this study.

A few assessments have been recently produced in cooperation with Åbo Akademi University, Geology and Mineralogy; besides summarizing these also experimental work on using (i.e. upgrading) diopside-type by-product / overburden from the limestone quarry at Parainen will be addressed.

The study is limited to rock from Finland since proximity to Parainen is a key feature.

It was found that processing of diopside-based by-product rock from the Parainen limestone quarry into more concentrated fractions has potential and deserves further study.

1 Introduction

This report addresses Finnish rock material resources that could be used as feedstock for CO₂ mineral sequestration in Finland, more specifically in south-west Finland at Nordkalk’s industrial-scale lime kiln at Parainen. Most R&D work on carbonation of magnesium silicate-based rock at ÅA, resulting in what is known as the “ÅA route”, was done on overburden rock from the nickel mine at Hitura of Belvedere Mining Oy. This material is a serpentinite (~87%-wt serpentine, ~13%-wt iron oxides).

The “ÅA route” is a staged process in which reactive magnesium in the form of magnesium hydroxide is produced from the rock, using ammonium sulphate (AS) as a flux salt (which is later recovered for re-use), followed by carbonation of the Mg(OH)₂ in a pressurized fluidized bed reactor. The recent ÅA PhD theses of Nduagu [1] and Fagerlund [2], and references therein summarise the development of increasingly fast and efficient Mg(OH)₂ production and carbonation, respectively. Figure 1 summarises the standard lay-out of the “ÅA-route”.

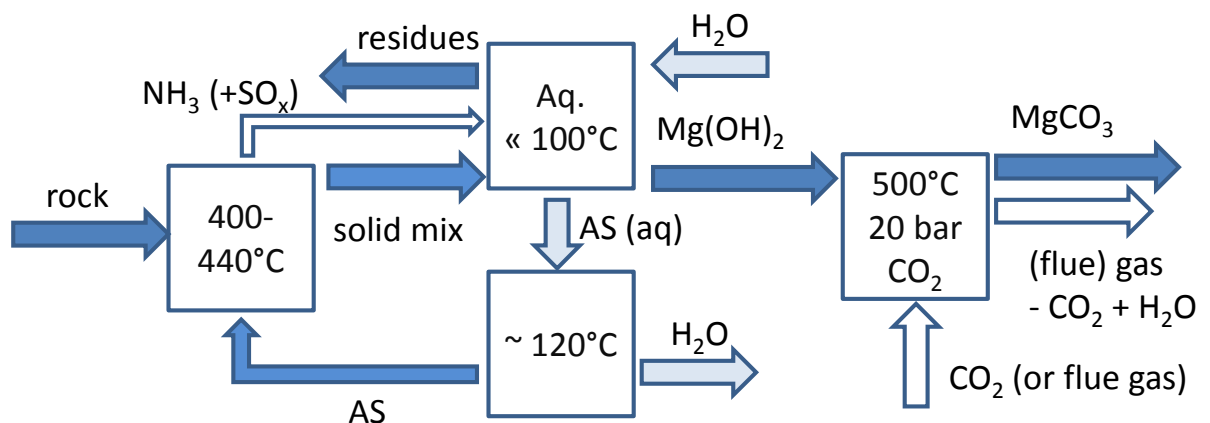


Figure 1 A schematic illustration of the “standard” ÅA mineral carbonation process with gas-solid carbonation

Current work by Romão [e.g. 4,5] and Slotte et al. [6,7] addresses the scale-up towards industrial scale, focusing on process integration, the use of Portuguese rock, and the operation on flue gas directly, avoiding a separate CO₂ capture step. For the standard ÅA route that operates at 20 bar CO₂ pressure this means compression of the complete process flue gas, and expansion of the product gas downstream the carbonation reactor.



(In an alternative process route¹ the carbonation takes place in aqueous solution, where the species that is carbonated is MgSO_4 [3]. Reaction with CO_2 in a (flue) gas stream - again, no CO_2 separation process step is needed - is made possible by the presence of NH_3 , obtained from the upstream rock/AS reaction, similar to the “standard” process. In this case, however different magnesium hydrocarbonates are obtained ($\text{MgCO}_3 \cdot x\text{H}_2\text{O}$, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$), depending on temperature and solution pH, and the (low temperature) carbonation reaction heat is not obtained in a useful form. The increased simplicity of the carbonation reactor is a significant advantage, however.)

While the studies on application in Finland more and more focus on the lime kiln at Parainen (producing significant amounts of waste heat that can be used for producing reactive magnesium from rock), these studies so far considered Hitura overburden serpentinite as the feedstock for most of the work. With a distance of more than 500 km from Hitura to Parainen, and with a lot of potentially suitable mineral being available in Finland, using an alternative Finnish rock material for application at Parainen would be very attractive.

Finland has large amounts of serpentine available. The suitability of any given mining site as a source of mineral for carbonation depends primarily on the magnesium (and calcium) contents of the rock. In addition, the distance from the CO_2 producer and total amount of rock, as well as possible nearby sources of waste heat are of importance.

International project cooperation has expanded the range of minerals that have been tested for CO_2 sequestration using ÅA’s method to serpentinites and olivines from Australia, Norway, Portugal [5] and Lithuania [8].

In this study, the potential of using Finnish rock from locations other than Hitura for the fixation of CO_2 will be assessed, focusing on use at Nordkalk’s lime kiln at Parainen. Some work involved the upgrading of diopside-based material from the limestone quarry at Parainen, which would make for a very attractive feedstock with negligible transport distances to the lime kiln.

2 Serpentinites from south-west Finland vs. Hitura rock

Several recent studies have addressed Finnish rock other than Hitura overburden, besides the actual nickel ore from that site [9]. Using data from the ÅA Geology & Mineralogy MSc thesis of Mäkelä [10] a series of rock deposits was analysed for application as feedstock for Meri Pori CO_2 . For example, Vammala is located at ~85 km east of Meri Pori.

¹ Developed in cooperation with A*Star/ICES in Singapore, project NEACAP (Novel low energy routes to activate minerals for large-scale carbonation to useful products), 2010-2014, as a Tekes/A*Star co-funded project. Final reporting to be completed in April 2014.

Table 1, taken from [11] and given also in Deliverable D504² lists the materials tested by Mäkelä. More detail is given in the Deliverable D504.

Table 1. Composition (as oxides) of the Finnish rocks for mineralisation as tested by Mäkelä [10]

Working names	MgO %-wt	CaO %-wt	*Fe ₂ O ₃ %-wt	SiO ₂ %-wt	Al ₂ O ₃ %-wt	Other %-wt
Hitura	36.2	0.5	14.4	24.8	<0.1	24.1
Vammala-1	19.2	9.0	15.4	45.0	3.5	7.9
Vammala-2	28.0	1.4	18.4	39.3	1.3	11.6
Satakunta olivine	5.5	8.7	15.3	46.9	16.1	7.5
Suomusjärvi-1	13.5	7.8	10.9	50.2	10.8	6.8
Suomusjärvi-2	20.9	8.3	11.9	44.3	7.0	7.6

The results as reported in [11] and Deliverable D504 show that the Vammala and Suomusjärvi materials are significantly less good than the Hitura material. Not only does the much lower Mg content dictate that much larger amounts of rock must be processed, also the fraction of the available Mg that was extracted and obtained as Mg(OH)₂ was of the order of ~25 % for Vammala material and as low as 14-21 % for rock from Suomusjärvi. This can be compared to extraction levels of 65-80 % for the Hitura overburden material.

3 Serpentinites from Northern Finland

Recently, the production of Mg(OH)₂ (for the purpose of CO₂ sequestration) from serpentinites from the Kuhmo region was assessed and reported as the ÅA Geology & Mineralogy BSc thesis of Aarnio [12].

It was shown that Mg(OH)₂ production levels of 80% and 70% were possible using two samples of so-called Kellojärvi serpentinites, that had Mg contents of 23% and 26%, respectively. In fact, a large part of the Mg was present in the rock as brucite, Mg(OH)₂. This makes the material an attractive feedstock for CO₂ mineral sequestration but at the same time also quite atypical. No numbers are reported for the amount of rock material that would be available. And, also for this rock the distance to Parainen of more than 700 km makes it an unattractive input material for use at Nordkalk's lime kiln.

Important is also the post-graduate work at ÅA Geology & Mineralogy of Sjöblöm, aiming

² Cleen CCSP Deliverable D504 A technology survey report on the feasibility of large-scale CO₂ mineralisation in Finland, August 2012



at finding uses for mining tailings and other by-products from Northern Finland. Materials were obtained from Talvivaara, Kevitsa, Pampalo and Mondo Minerals, besides rock from Hitura. Except for the Talvivaara material, the samples contain significant amounts magnesium-rich minerals olivine $(Mg,Fe)_2SiO_4$, pyroxene $Ca(Mg,Fe)Si_2O_6$ serpentine $(Mg,Fe)_3Si_2O_5(OH)_4$, talc $Mg_3Si_4O_{10}(OH)_2$ and chlorite $(Mg_5Al)(AlSi_3)O_{10}(OH)_8$. So far preliminary reporting [13] did not present results, but a next publication is forthcoming [14].

4 Diopside overburden rock from Parainen limestone quarry – first analysis

Already briefly addressed in the Deliverable D504 was the diopside-type material that is produced at the limestone quarry of Nordkalk at Parainen. The composition of this material is given in Table 2, taken from [4] and Deliverable D504. (The sample also contained ~ 0.9 %-wt sulphur.)

Table 2. Elemental and XRD analysis of the Parainen diopside sample.

Elemental Analysis (%)									Structural Analysis
CaO	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	Others	(XRD)
15.6	50.9	0.4	12.2	4.5	4.9	3.1	2.1	6.3	Hedenbergite, Orthoclase, Albite (Calcium), Muscovite, Clinocllore

It was attempted and reported by Romão et al. [4] to extract magnesium and calcium from the material using the solid-solid reaction with ammonium sulphate followed by precipitation using aqueous ammonia. The results were disappointing, as reported: extraction efficiencies were as low as 6-10% for Ca and 2-4% for Mg for the solid/solid reaction with AS at 400-500°C. (Also, note that only ¼ of the heat used for extracting species goes to extraction of Mg.)

While the main carbonate product would be $CaCO_3$ for which no pressurized carbonation reactor is needed, the amount of rock material to be processed (including crushing and grinding) would be 6x the amount of Hitura mine overburden, per ton of CO_2 sequestered.

Table 3 (taken from [4]) summarises a comparison of using Hitura serpentinite or the diopside-based quarry by-product in the ÅA process for CO₂ mineralisation.

Table 3 – Pros and cons of utilising serpentinite or diopside as raw materials in the ÅA CO₂ mineralisation process. (taken from [4])

	Serpentinite	Diopside
Availability	Must be purchased (500 km away)	Available at the plant site
Extraction temperature	~400 – 440 °C	≥ 500°C making the use of waste heat questionable.
Reactivity	Good reactivity (So far ~60 – 70 % of Mg extraction but 80% achieved using ammonium bisulphate, ABS)	Very low reactivity (<5% of Mg extraction)
Iron/Calcium/Aluminium by-product	Low content of Al hydroxides Suitable for the steel-making industry.	High content of Al making it unsuitable to the steel making industry. An extra carbonation step needed to carbonate the by-products coming from the first precipitation stage.
Mg(OH)₂ product	~0.5kgMg(OH) ₂ /kg of serpentinite processed (80% Mg extraction) Crushing energy is ~12% of the exergy input (as electricity): 0.19MJ/kgCO ₂ captured	~0.087 kgMg(OH) ₂ /kg of diopside processed (if 100% Mg extraction is achieved) To produce an equal amount of Mg(OH) ₂ (as when serpentine is used) it's necessary to process at least 5.75x more rock. Excessive energy consumption for milling the raw materials which escalates to 1.09MJ/tCO ₂ (~73% of the exergy input as electricity) In this case, the waste heat available from the limekiln will be insufficient to achieve an auto-thermal process while processing such amounts of rock in the solid/solid decomposition stage.
AS recovery	Final solution contains NH ₄ ⁺ , SO ₄ ²⁻ and water	Presence of alkali elements (Na ⁺ & K ⁺) in the remaining solution make the AS recovery and recycling problematic.

5 Diopside overburden rock from Parainen limestone quarry – attempts to upgrading

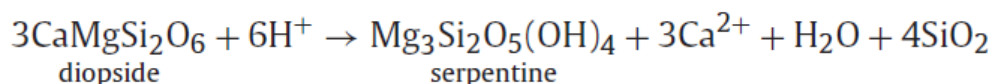


Figure 2 Diopside-based limestone quarry by-product rock from Parainen (size ~15 cm)

Figure 2 shows a diopside-based limestone quarry by-product rock from Parainen. Based on the composition data given in Table 2, the CO₂ binding capacity by the Ca and Mg in the rock is 260 kg CO₂ / ton rock.

As suggested in Deliverable D504, a more viable route to follow would be to try to improve the quality of the diopside material: the open literature reports that a low temperature dissolution reaction in an acidic environment may give a serpentine-forming reaction [15] that removes Ca and most of the SiO₂ from the diopside.

According to [15] diopside “... is readily dissolved in low-temperature environments according to the serpentine-forming reaction ..”, where the reaction referred to is



This was attempted for the processing of the Parainen diopside sample, aiming at converting 650 g diopside into 277g serpentine, 240 g SiO₂, 120 g dissolved Ca and water.

Pure acetic acid (molarity 17.5 M) was used for the tests, all tests were done at room temperature and atmospheric pressure. Based on XRF results, diopside constitutes only 71.4% of the material. A 100% serpentinization of this diopside-containing mineral would result in ~15% mass loss as Ca²⁺ and H₂O.

Powdered rock samples (particle size 75 - 125µm) were leached during 3 h or 20 h, without any mixing or stirring (5g and 20g samples in 20 ml acetic acid). The residue from leaching was washed with water, dried overnight at 120°C and weighed. The obtained solutions were analysed using ICP-OES.

The results are summarized in Table 4, showing that (based on Ca extraction into the solution) a conversion degree of ~10% can be obtained after 3 hours. At the same time

the dissolution of Mg is negligible.

Table 4 – Experimental results on converting diopside-based rock into more concentrated serpentine and dissolved calcium

Test #	Material mass (g)	Time (h)	Mass loss (g)	Ca % extracted	S % extracted	Mg, Na, Fe % extracted	Si, Al % extracted
1	20	3	0.32	10.7	1.0	0.15-0.26	< 0.03
2	20	3	0.30	9.8	1.5	0.15-0.26	< 0.03
3	5	20	0.21	3.0	3.8	0.19-0.70	< 0.03
4	5	20	0.19	3.1	3.0	0.19-0.70	< 0.03

Moreover, the following observations were made:

- Tests of 3 h performed better than the tests of 20 h. It appears that extracted elements recrystallize at long reaction times.
- Ca and S are almost selectively extracted as shown by ICP analysis.
- Measured total loss of material from the leaching process is comparatively higher in the 20 h tests than the 3 h tests.

Clearly, this effort has demonstrated potential, deserving follow-up R&D. The effect of temperature may be studied, while the separation of unreacted solid and SiO₂ from serpentine may present another challenge if not the whole solid mix can be sent through a carbonation reactor.

6 Conclusions

In this report a brief summary is given on results obtained with Finnish rock other than Hitura nickel mine overburden rock for the sequestration of CO₂, aiming at application at Nordkalk's lime kiln at Parainen.

Rocks tested by thesis workers at ÅA Geology & Mineralogy show significantly less good performance than the Hitura rock reference material.

Interesting results that deserve (and also will) receive follow-up as part of current Cleen CCSP activities involve the processing of diopside-based by-product rock from the Parainen limestone quarry into more concentrated fractions.

7 References

- [1] Nduagu, E., Production of $Mg(OH)_2$ from Mg-silicate rock for CO_2 mineral sequestration. PhD thesis, Åbo Akademi University, Turku Finland (2012) Available at: www.doria.fi/handle/10024/86170
- [2] Fagerlund, J., Carbonation of $Mg(OH)_2$ in a pressurised fluidised bed for CO_2 sequestration. PhD thesis, Åbo Akademi University, Turku Finland (2012) Available at: www.doria.fi/handle/10024/74477
- [3] Zevenhoven, R., Åbacka, J., Koivisto, E., Highfield, J. Two methods for direct flue gas decarbonation with serpentinite minerals (and some background on CO_2 capture, utilisation and storage) presented at: Riga Technical University, Latvia, 54th Int. Conf. "Environmental and Climate Technologies", Oct. 16, 2013
- [4] Romão, I., Eriksson, M., Nduagu, E., Fagerlund, J., Gando-Ferreira, L. M., Zevenhoven, R. Carbon dioxide storage by mineralisation applied to a pilot scale lime kiln. Proceedings of ECOS 2012 Perugia, Italy, June 2012, paper 226
- [5] Romão, I.S., Gando Ferreira, L.M., da Silva, M.M.V.G, Zevenhoven, R. CO_2 sequestration with serpentinite and metaperidotite from North-East Portugal. Applied Geochemistry *submitted* (December 2013)
- [6] Slotte, M., Zevenhoven, R. Total lime kiln gas compression for CO_2 mineral sequestration. Proc. of ECOS2013, July 15-19, 2013, Guilin, China, paper F005
- [7] Slotte, M., Romão, I., Zevenhoven, R. Challenges in process scale-up of serpentinite carbonation to pilot scale. ENERGY 62 (2013) 142-149
- [8] Stasiulaitiene, I., Vajegaite, V., Martuzevicius, D., Denafas, G., Sliupa, S., Fagerlund, J., Zevenhoven, R. Parameters affecting $Mg(OH)_2$ extraction from serpentinites in Lithuania for the purpose of CO_2 reduction by mineral carbonation. Environmental Progress & Sustainable Energy, *accepted / in press, available on-line* doi: 10.1002/ep.11792
- [9] Romão, I.S., Gando-Ferreira, L.M. and Zevenhoven, R. Combined extraction of metals and production of $Mg(OH)_2$ for CO_2 sequestration from nickel mine ore and overburden. Minerals Engineering 53 (2013) 167-170
- [10] [Mäkelä, M. Storing of carbon dioxide by mineral carbonation in Southern Finland (*in Finnish; Hiilidioksidin sitominen mineraal karbonaatiolla Etelä-Suomessa*) [MSc thesis]. Turku, Finland: University of Turku / Geology and Mineralogy; 2011.
- [11] 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
- [12] Aarnio, C. Production of $Mg(OH)_2$ from serpentinites from the Kuhmo greenstone belt (*in Swedish: Produktion av $Mg(OH)_2$ ur serpentiniten från Kuhmo grönstensbälte*). [BSc thesis]. Turku, Finland: Åbo Akademi University / Geology and Mineralogy; 2013.
- [13] Sjöblom, S., Eklund, O. Geological and mineralogical aspects on mineral carbonation of rocks and mine tailings. (extended abstract). Proc. of ACEME13, Leuven, Belgium, April 2013, 497-500
- [14] Sjöblom, S., Eklund, O. Geological and mineralogical aspects on mineral carbonation. Abstract accepted for ECOS2014, Turku, Finland, June 15-19, 2014
- [15] Hsueh-Yu Lu, et al. A natural analogue for CO_2 mineral sequestration in Miocene basalt in the Kuanhsi-Chutung area, Northwestern Taiwan. Int. J. of Greenhouse Gas Control 5 (2011) 1329-1338