

CO₂ emissions: mineral carbonation and Finnish pulp and paper industry (CO₂ Nordic Plus) and Use of serpentinites in energy and metal industry (ECOSERP)

Carl-Johan Fogelholm, Project leader, professor

Sanni Eloneva, Researcher

Helsinki University of Technology,
Dept. of Energy Technology,
Research group of Energy Technology and
Environmental Protection (ENY)
Sähkömiehentie 4 A, 02015 Espoo
Tel. +358 9 4511
Email: forename.surname@tkk.fi

Ron Zevenhoven, Project leader
Currently at Åbo Akademi,
Heat Engineering Laboratory
Biskopsgatan 8, 20500 Åbo
Tel. +358 2 215 3223
Email: ron.zevenhoven@abo.fi

Sebastian Teir, Researcher
Currently at VTT Technical Research
Centre of Finland
P.O. Box 1000, 02044 VTT
Tel. +358 40 487 8117
Email: sebastian.teir@vtt.fi

Tuulia Lepistö (former Raiski), Researcher
Currently at Energiamarkkinavirasto
(Energy Market Authority)
Lintulahdenkatu 10, 00150 Helsinki
Tel. +358 10 605 000

Jaakko Savolahti, Researcher
Currently at Pöyry Energy Oy
Tekniikantie 4 A, 02150 Espoo
Tel. +358 45 633 9379

Kari Pääkkönen, Area manager
Peter Sorjonen-Ward, Specialist researcher
Soile Aatos, Asko Kontinen & Tapiola Kuivasaari, Geologists
Geological Survey of Finland (GTK)
P.O. Box 1237, 70211 Kuopio
Tel. +358 20 550 11
Email: forename.surname@gtk.fi

Abstract

Mineral carbonation has been investigated at Helsinki University of Technology (TKK), laboratory of energy engineering and environmental protection since year 2000, since year 2005 also at Åbo Akademi (ÅA), heat engineering laboratory. Tekes – the Finnish Funding Agency for Technology and Innovation and the Finnish Recovery Boiler Committee funded through the ClimBus programme, in conjunction with the Nordic Energy Research Programme (2003–2006), the research regarding the application of *ex situ* mineral carbonation processes. One aspect was to verify the possible use of mineral carbonation for the separation, utilisation and long-term storage of carbon dioxide (CO₂) in the pulp and paper industry.

The Geological Survey of Finland (GTK) has been screening during 2004–2006 the location, quality and suitability of the Finnish processed serpentine and stoped serpentinite storage of mines and *in situ* serpentinite bodies of ultramafic rock formations for mineral carbonation of CO₂. Tekes and the GTK funded development work through the ClimBus technology programme on the utilisation of serpentine and serpentinite for CO₂ sequestration purposes, based on economical and environmental evaluation of mineral and mining processing operations. Also the options for other use of serpentine and serpentinite were evaluated.

The most promising magnesium- and calcium-based sources for carbonation are by-products of mining processes of ultramafic rocks (such as serpentinites and serpentine) and steelmaking slags. Carbonated minerals could possibly be used as paper coating materials (PCC), fillers or con-

struction materials. For magnesium carbonate new markets and applications must be developed.

Tiivistelmä

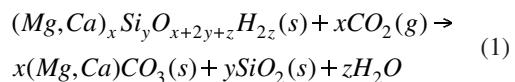
Teknillisen korkeakoulun Energiateknikan ja ympäristönsuojelun laboratorio on tutkinut mineraalikarbonaatiota mahdollisena hiilidioksidin loppusijoitusmenetelmänä vuodesta 2000 alkaen, ja tutkimus Åbo Akademian (ÅA) *Värmeteknik-* laboratoriassa on alkanut vuonna 2005. ClimBus-ohjelman kuuluvassa CO₂ Nordic Plus-projektissa, pohjoismaisen energiatutkimusohjelman rahoituksen ohella ja Tekesin ja Suomen soodakattilayhdystyksen rahoittamana ollut, on tutkittu mineraalikarbonoinnin soveltuutta maanpääälleseen teollisuusprosessiin ja paperi- ja massateollisuuden hiilidioksidin erotukseen, hyötykäyttöön ja loppusijoitukseen.

GTK on vuosina 2004–2006 kartoittanut mineraalikarbonaatioon mahdollisesti soveltuviin kotimaisten ultraemäksisten kivilajien ja mineraalien, pääasiassa serpentiniittikivien ja serpenttiinin, luonnollisia ja teollisia esiintymiä. Samassa yhteydessä on koottu tietoa serpenttiinin ja serpentiniitin muista hyötykäytöitä mahdollisuksista ja selvitetty mahdollisia muita käyttökohteita. Tekesin ja GTK:n rahoittamassa ECOSERP-projektissa kehitettiin myös serpenttiinien ja serpentiniittien hyödyntämistä edeltäviä yleisiä taloudellisia ja ympäristöllisiä arviontiperusteita olemassa olevien kaivannaisteollisten käytäntöjen pohjalta. ECOSERP-projekti on ClimBus-ohjelman kuuluvan CO₂ Nordic Plus -projektiin osaprojekti.

Lupaavimpia mineraalikarbonaatioon mahdollisesti soveltuivia kotimaisia magnesiumin ja kaliumin lähteitä ovat mm. teollisen prosessin läpi käyneet kaivannaisteollisuuden ultraemäksisten sivumateriaalien silikaattimineraalit (esim. serpenttiinirikastushiekka) ja metalliteollisuuden kuonat. Karboitouja mineraaleja on mahdollista käyttää mm. paperipinnoitteeksi (PCC), erilaisiksi täyteaineiksi, rakennusaineiden ja lannoitteiden raaka-aineeksi sekä ympäristökemikaaleiksi.

1 Background

The Kyoto protocol binds Finland as an EU member to reduce its greenhouse emissions to the level of 1990. The target set for Finland appears to be quite challenging since the production and utilization of power and heat is already remarkably efficient. The base industry in Finland is very energy-intensive, of which the pulp and paper industry is one of the most important industrial sectors. The pulp and paper industry also accounts for approximately 15% of the total carbon dioxide (CO₂) emissions fossil fuel usage in Finland. According to IPCC (2001), a combination of mitigation measures will be needed to achieve a stabilization of greenhouse gas concentration in the atmosphere, of which carbon dioxide capture and storage (CCS) is considered as one of the main options for reducing atmospheric emissions of CO₂ from human activities. From Finland's perspective CCS does not provide an easy answer to decreasing of CO₂ emissions, since there do not seem to exist suitable geological formations for sequestering CO₂. However, carbonation of Finnish magnesium silicates could provide a respectable reduction of CO₂ emissions in Finland, since Finland has a large abundance of mafic and ultramafic rocks, including serpentinites. Calcium- and magnesium-based silicates can react with CO₂ to form environmentally inert and stable carbonates (Goldberg *et al.* 2001):



Carbonation of silicate minerals has the highest capacity and longest storage time of CO₂ of the storage options currently known (Lackner 2003). However, this natural process is very slow, which means that the carbonation process must be accelerated considerably to be a viable large-scale storage method for captured CO₂. Several carbonation processes have been studied (Huijgen *et al.* 2003 and 2005), but they require energy (for crushing, grinding or preheating) and/or additives and are at their current development stage

considered too expensive as a CO₂. Therefore, research in the field of mineral carbonation focuses on developing an accelerated carbonation process that is also energy efficient.

2 Objectives

Mineral carbonation may become an important technology for long-term storage of CO₂ in Finland. In conjunction with the Nordic Energy Research project “Nordic CO₂ sequestration” (NoCO₂, 2003–2006), where Finland concentrated on mineral carbonation, this project more explicitly addressed Finland’s pulp and paper industry.

The project addressed three issues in common with NoCO₂:

- Mineral carbonation kinetics
- Lab-scale testing on mineral carbonation
- Design of a large-scale process for mineral carbonation and economic analysis.

The questions from the Finnish pulp and paper industry addressed in the work were:

- Desktop work on mapping the CO₂ emissions from Finnish pulp and paper industry
- Desktop work on mapping the options for CO₂ utilisation in Finnish pulp and paper industry
- Analysis of the link between mineral carbonation for long-term CO₂ storage and Finnish pulp and paper industry.

The geological survey part of the project addressed the optimal use of and benefits from the serpentine mineral and serpentinite rocks suitable for carbonation in their parallel project “Serpentine utilisation in energy and metal industries” (ECOSERP 2004–2006).

For TKK, one primary goal was the PhD thesis of Nordic post-graduate researcher Sebastian Teir (Teir 2008).

3 Project work programme

Duration of the project	Funding of the project
1.1.2003–30.6.2006	Total 154,500 €, of which Tekes funding 145,500 € (CO ₂ Nordic Plus)
1.1.2004–30.6.2006	Total 40,000 €, of which Tekes funding 22,000 € (ECOSERP)
Project partners	Helsinki University of Technology Geological Survey of Finland
Participating companies	The Finnish Recovery Boiler Committee
International co-operation	Nordic Energy Research

Mineral carbonation has been investigated at the Laboratory of Energy Engineering and Environmental Protection at Helsinki University of Technology (TKK) since year 2000, and since year 2005 also at Åbo Akademi University (ÅA), heat engineering laboratory. The research consists of both experimental and theoretical research. The chemical kinetics of gas-solid MgO and Mg(OH)₂ carbonation was studied using pressurized thermogravimetric analysis (PTGA). The thermodynamic equilibrium of carbonation systems was investigated using Outokumpu HSC and carbonation processes were modelled using Aspen Plus. Extraction and carbonation in aqueous carbonation processes were tested using atmospheric and pressurized batch reactors. Solution samples are analyzed using ICP-AES and AAS, while solid samples are studied using XRF and XRD. The carbonate content of carbonated samples was measured using standardised carbonate analysis methods.

International co-operation supported by this project has been fruitful and of a high standard. Ron Zevenhoven has been co-writing the chapter on

mineral carbonation and actively participating in the production of the IPCC Special report on CO₂ capture and storage, which was published last year by Cambridge University Press (Mazzotti et al. 2005). The 4th Minisymposium on Carbon Dioxide Capture and Storage was arranged by Zevenhoven, Teir, Eloneva, and Fogelholm at Dipoli, Espoo, and was considered a success both by arrangers and participants (from Finland, Sweden, Norway, Denmark, Estland, Latvia, Lithuania, Russia, and Germany). The conference held a high standard with speeches given by The Finnish Minister of Environment, Jan-Erik Enestam, and Jukka Leskelä of Finnish Energy Industries (TKK 2005).

4 Project results

4.1 Suitable raw materials

The most common Finnish magnesium-rich rocks are ultramafic intrusive or extrusive rocks, i.e. peridotites, dunites, hornblendites, pyroxenites and komatiites, and their metamorphic varieties, i.e. serpentinites, talc and asbestos rocks. Of these ultramafic rocks, the most interesting for CCS purposes are the serpentinites, because they consist mainly of serpentine (Table 1). Serpentines may contain about 40% of MgO (Deer et al. 1982). Millions of tons of poorly documented in situ or hoisted serpentinite or tailed serpentine

deposits situate mainly in central Finland. It has been estimated, according to the 1:100,000 scale geological mapping of Outokumpu-Kainuu ultramafic rock belt, that only in the Eastern Finland there are about 121 km² of serpentinites (Teir et al. 2006a).

In Finland ca. 25 Mt/a of mineral product would be required when converting serpentine to magnesite to achieve the Kyoto requirements. In theory, and conservatively estimating, the serpentinites of Outokumpu-Kainuu ultramafic rock belt could be sufficient for 200–300 years of CCS processing, if low-emission technologies are developed simultaneously (Teir et al. 2006a). The total amount of hoisted rock in Finnish mines was about 31 Mt in 2004, of which about 11 Mt was from ultramafic deposits in general. Some of the possibly suitable rocks for CO₂ capture are being constantly piled as barren rock or minerals dammed as tailings for waiting later use in the extractive industry (Figure 1). These minimum conditional resources of hoisted serpentine and serpentinite (33–39% MgO) in present Finnish Ni, Cr and talc mines (Hitura, Elijärvi, Horsmanaho and Lipasvaara) are about 29 Mt (Teir et al. 2006a), (Teir et al. 2004b). The Finnish industry produces also alkaline industrial residues, such as steelmaking slags, that could be carbonated for storage of CO₂ (Teir et al. 2005a,b).

Table 1. The mineral product mass of some common Finnish rock forming minerals needed for converting 10 Mt of CO₂ to carbonates.

Mineral or mineral group name	Approximate potential of a mineral to bind CO ₂ (kg/m ³) ¹	Mineral mass (Mt) needed to bind 10 Mt CO ₂
Olivine	2000	19
Pyroxene group	1300	27
Serpentine	1200	22
Amphibole group	1100	29
Talc	1100	25

1 According to (Xu et al. 2001)

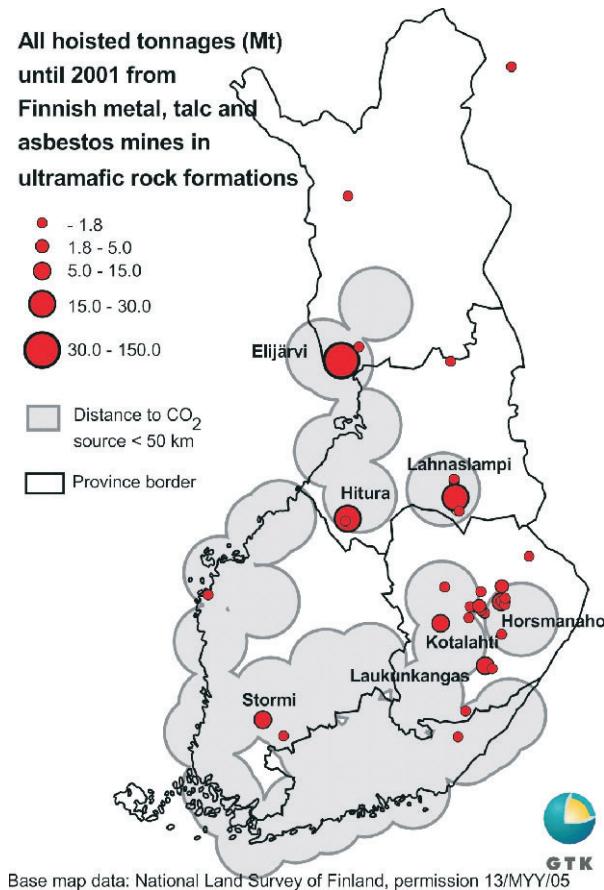


Figure 1. Possible sources of serpentine in Finland
(Teir et al. 2006a).

4.2 Finnish pulp and paper industry

The pulp and paper industry is one of the most important industrial sectors in Finland. Power and heat production is the most significant source of CO₂ emissions also in the forest industry (III). The forest industry covers almost all of its heat demand, and in many cases the mills deliver also district heat. Most of the energy used by the Finnish pulp and paper industry is generated from wood-based fuels such as black liquor and bark from pulp production processes. Approximately 15% of CO₂ emissions from the Finnish pulp and paper industry originate from the use of fossil fuels in processes other than power and heat generation, mainly in lime kilns and infrared dryers.

The lime kiln is a part of the chemical recovery system of a pulp mill. Lime sludge is the sludge of calcium carbonate (CaCO₃) formed during the preparation of white liquor in the chemical pulping process. The lime kiln is used to reburn calcium carbonate to form calcium oxide (CaO), which can be re-used in the pulping process. CO₂ is released in lime kilns from the calcination process, and from fossil fuel burned in the kiln. Calcium carbonate is also used to a large extent as a paper filler and coating material to provide opacity, high brightness, and improved printability. In Finland 700,000 tons/year of calcium carbonate is used for coating and 300,000 tons/year as a filler. Integrated pulp and paper mills use the lime

kiln stack gas CO_2 to manufacture precipitated calcium carbonate (PCC), which is synthetic calcium carbonate with a higher purity than natural calcium carbonate (limestone). In Finland the annual production is 400,000–500,000 tons of PCC, which consumes approximately 200,000 tons CO_2 . Although the PCC production process binds CO_2 more CO_2 is released when calcining limestone to produce calcium oxide required for the process (Teir et al. 2004b). If the calcium oxide required by the pulp and paper industry could be produced from a carbonate-free calcium silicate, a significant amount of CO_2 emissions could be prevented by utilizing the existing carbonation processes at the pulp and paper industry for long-term storage of CO_2 .

Alternative processes for producing PCC were compared to the current production chain. The results from the comparison by process modelling showed that a process using acetic acid could bind 0.34 t CO_2 per t CaCO_3 produced, while the current PCC production process chain (including calcination) emits 0.21 t CO_2 per t CaCO_3 produced (Teir et al. 2005c).

4.3 Gas-solid carbonation of magnesium hydroxide

The overall chemistry of MgO -based silicate mineral carbonation is exothermic, suggesting that a properly optimized carbonation process can be operated with a negative overall energy input requirement. When operating the carbonation as a gas-solid process at a sufficiently high temperature and a certain minimum degree of conversion, the high temperature heat that is generated can be used to drive mineral pre-heating and grinding of mineral or generate electricity for the power grid (Zevenhoven and Kavalaiskaite 2004). However, it has been shown that the direct gas – solid carbonation of magnesium silicates is too slow for any technological application, suggesting that a staged process that extracts or activates the MgO or Mg(OH)_2 in the mineral is necessary. In a process that combines an endothermic MgO or Mg(OH)_2 extraction step with an exothermic carbonation step the optimum temperatures for these steps will be different (Elo-leva 2004), and exergy analysis can be used to

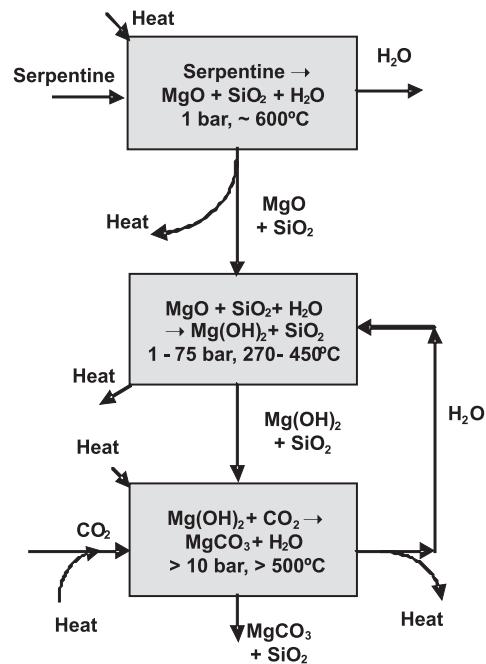


Figure 2. Process schematic for serpentine carbonation via MgO and Mg(OH)_2 production.

analyze the overall energy economy (Figure 2) (Zevenhoven et al. 2006c).

The chemical kinetics of MgO and Mg(OH)_2 carbonation was analyzed using pressurized thermogravimetric analysis (PTGA). Results from the tests based on wet chemical analysis of the samples before and after the test are collected in Table 1 and Table 2 for the tests with MgO (calcined Mg(OH)_2) and Mg(OH)_2 , respectively (Zevenhoven et al. 2006b).

Table 2. Results of conversion of MgO to MgCO_3 during cooling from 700 to 250 °C at 5 °C/min in 99 %‐vol CO_2 / 1 %‐vol H_2O , for various pressures.

Pressure bar	Conversion %
1	5.6
5	4.4
12	3.1
20	3.4
35	2.9

Table 3. Results of conversion of $\text{Mg}(\text{OH})_2$ to MgCO_3 after 6 h for various temperature/pressure combinations in 99 %-vol CO_2 / 1 %-vol H_2O .

Pressure bar	Temperature °C	Conversion %
1	370	6
12	460	19
35	495	50
35	510	46
35	525	44
35	540	43
40	510	60
40	525	37
40	540	40
45	525	44

The results in table 2 show that increased pressure levels reduce the degree of MgO carbonation that is obtained. This is contrary to what might be expected from the fact that the reaction $\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$ is thermodynamically limited by a minimum CO_2 partial pressure. Apparently the carbonation of MgO with CO_2 in the presence of small amounts of H_2O does not follow this general trend.

The results of the second test series (Table 3) do show the expected increased level of carbonation with increasing pressures and temperatures. Although for a given temperature a faster carbonation was obtained when pressure was increased, at a given pressure the carbonation rate appeared to decrease with temperature as a result of thermodynamic equilibrium limitations. XRD analysis of the resulting products confirmed a significant MgCO_3 content in the material.

4.4 Leaching and carbonation

The most efficient processes suggested for carbonation involve leaching or dissolution of silicates in a liquid media and precipitation of magnesium or calcium as carbonates or hydroxides (Huijgen et al. 2003 & 2005). Most of these processes have been considered too expensive as a CO_2 storage process, since they require energy (for crushing, grinding or preheating) and/or additives. Also, very little experimental data of these processes are available.

Serpentinite from the stockpile of the Hitura nickel mine of Outokumpu Mining Oy, Central Finland, was selected for the experimental study. A particle size fraction of 74–125 μm was sieved from a batch of ore and characterized using XRD, XRF and ICP-AES of dissolved samples. In order to test the dissolution properties of various acids (and NaOH) 1 g of serpentinite was dissolved in 50 ml separate aqueous solutions of HCl , H_2SO_4 , HNO_3 , CH_3COOH , and HCOOH at a room temperature under continuous stirring at 1,000 rpm.

The solutions were immediately filtered with 0.45 μm Pall GxF syringe filters 1 h after the addition of serpentinite. Experiments were performed with 1 M, 2 M, and 4 M concentrations of each acid (and NaOH). The temperature effect on leaching of magnesium from serpentinite was studied in more detail using aqueous solutions of HNO_3 .

The results from extracting magnesium from serpentinite in solutions of various acids and NaOH are shown in figure 3. All solutions tested dissolved relatively little silicon (0–3%). According to the results presented in figure 3 the solutions of H_2SO_4 were most efficient at extracting magnesium from serpentinite, followed by HCl , HNO_3 , HCOOH and CH_3COOH (listed in order of descending magnesium extraction efficiency). An aqueous solution of 1 M H_2SO_4 extracted 24% of the magnesium contained in serpentinite, while a solution of 1 M HCl extracted only 17%. Raising the concentration to 4 M improved the extraction

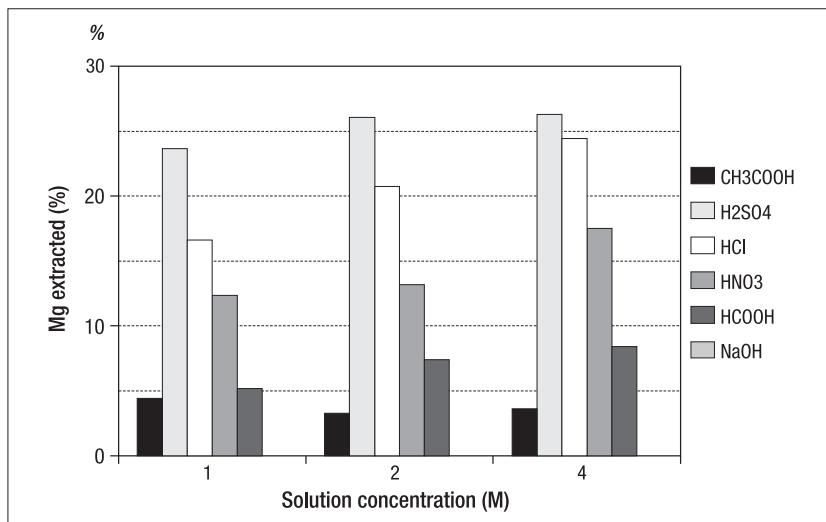


Figure 3. Relative mass of Mg extracted from serpentinite in various solutions (1 h, 20 °C).

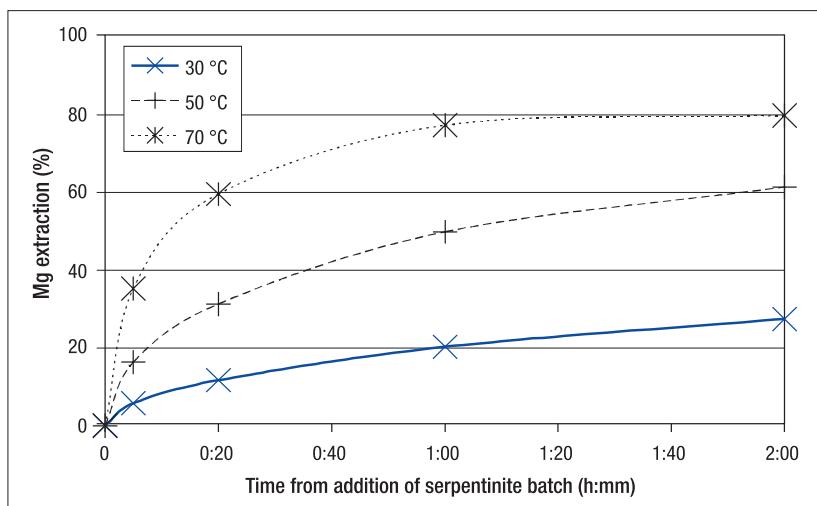


Figure 4. Relative mass of Mg extracted from 5 g serpentinite in solutions of 50 ml HNO₃ (65 wt-%) and 200 ml H₂O at 30 °C, 50 °C, and 70 °C.

to 24% for a solution of HCl, while a 4 M solution of H₂SO₄ extracted only 2 %-units more. Extraction at elevated temperatures in an aqueous solution of HNO₃ raises the extraction efficiency of magnesium (Figure 4) and iron from serpentinite significantly. Raising the temperature does not have a significant impact on Si extraction efficiency, but the rate of Si extraction is increased.

Precipitation of silica gel from the acidic solution seems to be promoted at higher temperatures, which also occurs when extracting calcium from calcium silicates in solutions of acetic acid at high solution temperatures (Teir et al. 2005a). Initial tests with precipitation of the solutions by addition of NaOH showed that CO₂ was fixed as magnesium oxide carbonate, Mg₃O(CO₃)₂.

5 Significance of results and future plans

The locations of already hoisted, piled or tailed ultramafic deposits are known, but their amount, mineralogy and mineral technical properties still need more clarification. The existing processing infrastructure and logistics make them easier to be considered as future raw material resources, than non-utilized in situ rock formations, if suitable industrial scale process technologies are developed for CCS purposes. Significant progress with gas-solid carbonation of magnesium oxide and magnesium hydroxide has been achieved and the process conditions for a three-stage process based on serpentine have been identified. Leaching and carbonation of silicate minerals could simultaneously extract valuable metals while providing a fast CO₂ sequestration process. However, more research is required to develop a sustainable carbonation process with reduced requirements of energy and/or additives. A potential new PCC production concept was discovered, that could produce a valuable product for the pulp and paper industry and fix CO₂ as carbonate simultaneously. This discovery led to a spin-off ClimBus project, SLAG2PCC (2005–2007), where the concept was being studied in detail, followed by SLAG2PCC Plus (2007–2009).

Currently the work on serpentinite carbonation for large-scale CO₂ storage in Finland continues primarily at Åbo Akademi (ÅA) where a high-pressure fluidised bed set-up for Mg(OH)₂ carbonation was built and taken into use for testing. This is part of Academy of Finland “Sustainable Energy” (SuSen) project “Carbonates in Energy Technology” (2008–2011), with Helsinki University of Technology (TKK) and the University of Turku as partners, and additional funding from KH Renlund Foundation. In parallel, ÅA works with international partners on the optimisation of the production of Mg(OH)₂ from serpentinite. Surprisingly, the Nordic Energy Research project did not continue after 2007 as carbon capture and storage is not addressed under the Nordic Energy Research project period 2007–2010.

6 Reports and publications (in chronological order)

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