

CO₂ SEQUESTRATION BY MAGNESIUM SILICATE MINERAL CARBONATION IN FINLAND

Ron Zevenhoven and Jens Kohlmann

Helsinki University of Technology, Lab. for Energy Engineering and Environmental Protection
PO Box 4400, FIN-02015 Espoo, Finland. ron.zevenhoven@hut.fi, jens.kohlmann@hut.fi

Abstract

Fixation of CO₂ from fossil fuel combustion in the form of solid carbonates appears to be a realistic option for the capture and storage of this greenhouse gas. Vast amounts of magnesium silicate minerals exist worldwide that may be carbonated, with magnesium carbonate as stable and environmentally harmless product. Also in Finland magnesium silicate resources exist that could support Finnish commitments under the Kyoto Protocol. This paper describes the option of CO₂ sequestration with magnesium silicates in Finland. Addressed are mineral resources, mineral quality and the mineral carbonation process, including some experimental results on magnesium silicate carbonation kinetics.

Introduction

Finland currently generates ~55% of its heat and power from fossil fuels (~50% when peat is excluded). This is illustrated by Table 1, which applies to the region around Helsinki, accounting for ~14 % of the Finnish CO₂ emissions from fossil fuel-fired power plants (~11% when peat is excluded). Although Finland is slowly shifting its fuel consumption to renewable fuels like wood and waste-derived fuels, economic growth is asking for more base-load energy, which can be covered only by additional nuclear power or increased use of carbon-based fuel (fossil and non-fossil). This will give increased CO₂ emissions in the near future, making it difficult to fulfil Finland's commitments considering CO₂ emissions put down in international agreements.

Table 1: Power plants in Helsinki: fuel consumption and CO₂ emissions in 1999 [1].

Power plant	Power			Fuel consumption and emission per year			
	Electricity [MW]	District heat [MW]	hard coal [kt]	heavy fuel oil [kt]	light fuel oil [kt]	gas [Nm ³]	CO ₂ emission [kt]
Hanasaari B	227	364	350.9	3.744	-	-	862
Salmisaari	160	270 + 170	383.9	2.774	0.001	-	943
Vuosaari A	160	160	-	-	0.031	169.5 · 10 ⁶	342
Vuosaari B	480	420	-	-	0.024	595.6 · 10 ⁶	1202

The problem could be partly solved by CO₂ sequestration, *i.e.* the removal of CO₂ from flue gases followed by long-term storage. The only option for Finland appears to be mineral carbonation, because Finland doesn't have deep oceans or exhausted oil or gas fields, and improved forestry, biofixation and the utilization of CO₂ do not have enough capacity.

For mineral carbonation the use of magnesium based silicates, $x\text{MgO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$ is favoured because they are worldwide available in huge amounts, as illustrated by Figure 1. These natural resources may be capable of binding all fossil fuel-bound carbon [2,3]. Magnesium silicates can be divided into several subgroups. The largest quantities are olivine, $(\text{Mg,Fe})\text{SiO}_4$, forsterite, Mg_2SiO_4 , and serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. Some other suitable minerals exist in smaller amounts.

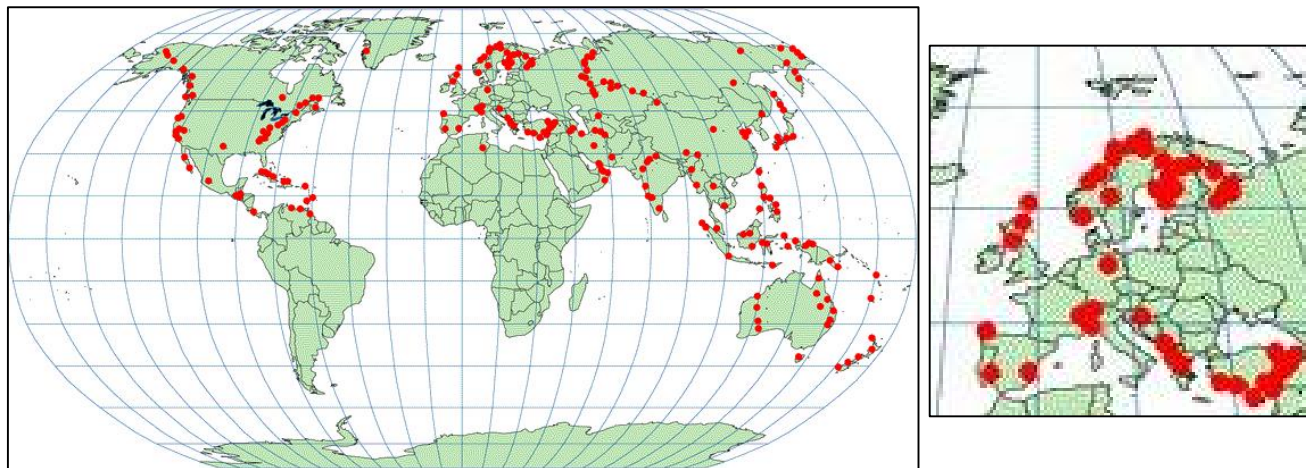
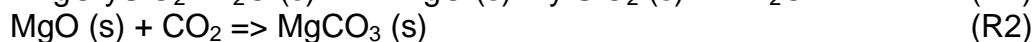
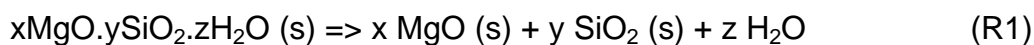


Figure 1 Distribution of magnesium silicate mineral deposits worldwide (*left*) and in Europe (*right*), indicating significant resources in Finland (taken from [2])

The chemistry for this CO_2 fixation can be summarised as



The overall carbonation reaction ($\text{R1}+\text{R2}$) is exothermal: the heat effect is +64 kJ/mol and +90 kJ/mol MgCO_3 , for serpentine and olivine/forsterite, respectively. Large-scale flue gas CO_2 sequestration as mineral carbonates will, however, require enormous amounts of mineral. For a typical power plant, the mass flows of fuel and carbonated mineral will be of the same order of magnitude: 1 kg of CO_2 may require 2 kg of serpentine for disposal.

At a few laboratories researchers are looking for technical solutions to perform the carbonization of magnesium with carbon dioxide on a large scale. Most important results are reported from the USA, *i.e.* National Energy Research Laboratory at Los Alamos (NM), Albany Research Center at Albany (OR) and Arizona State University at Tempe (AZ) [2-6]. Two problems must be solved to make this approach more attractive, as also concluded in a recent feasibility study from the UK [7]:

- 1) extracting the reactive component MgO from the mineral (reaction R1), reducing the mass streams that have to be handled at the power plant, and
- 2) speeding-up the kinetics of reaction (R2), which has to take place at temperatures below 300-400°C (and at elevated pressures).

Whilst the research in the USA is concentrating increasingly on wet methods, using aqueous solutions, the research started in August 2000 at Helsinki University of Technology (still) aims at dry methods. First results are reported here.

Magnesium silicate resources in Finland

Magnesium silicates are often a base component of ore which is mined to produce metals like nickel or gold. The silicates usually exist in mixtures of different silicates [8]. In Finland there are many mining activities, mainly mining for metals (nickel, copper), although also talc and limestone is mined. There are 15 major active mines in Finland of which 9 are found in areas with rich magnesium silicate deposits (see Figure 2). For example, at the Hitura mine in northern Finland 720000 tons of ore are mined per year, containing 3500 tons of nickel. 4 - 5% of the ore is pure serpentine or serpentinite, which is a mixture of mainly serpentine, talc and sand [9].

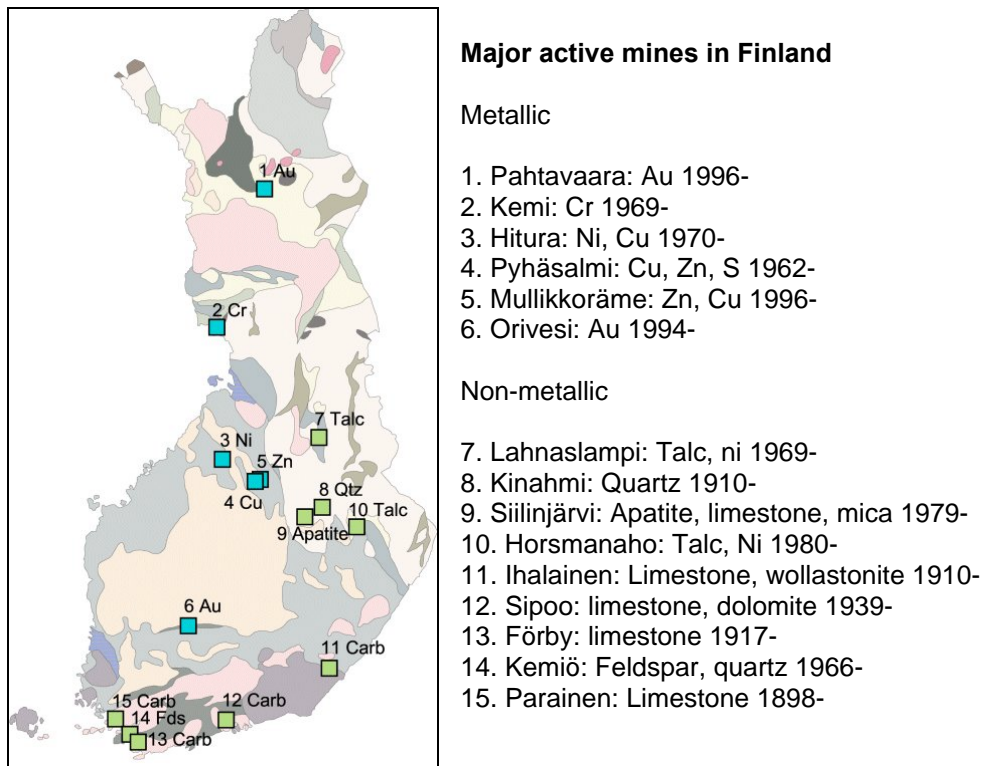


Figure 2: Major active mines in Finland [10]

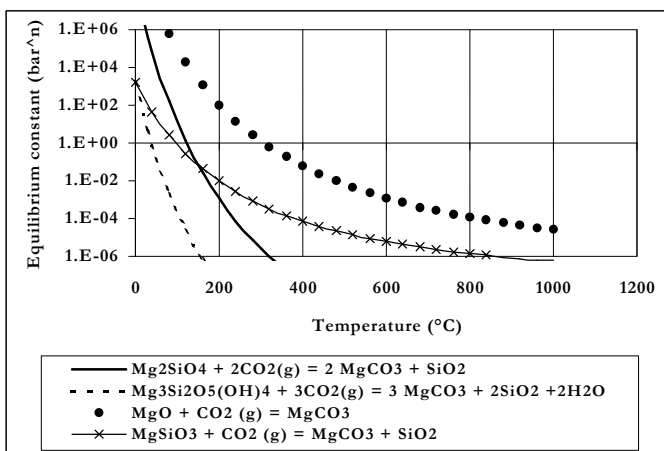


Figure 3 Thermodynamic equilibrium constant for carbonation of MgO, MgSiO_3 , olivine and serpentine [11]

Magnesium silicate carbonation

The thermodynamics of magnesium silicate carbonation (R1 and R2) shows that, depending on the partial pressure of CO_2 , temperatures of the order 200-400°C are preferable – see Figure 3. Moreover, the process will benefit from elevated pressures. (A value for the equilibrium constant $\gg 1$ favours chemical reaction to the right-hand side. This says, however, nothing about chemical reaction kinetics).

Data on the chemical reaction rate of magnesium silicate carbonation is scarce.

The team from the USA reported reaction rates such as 40-50% conversion after 24 h at 150-250°C, 85-125 bar, with olivine particles of 75-100 µm, in 1998 [4,5]. More recent achievements report 65% conversion after 1 hour, mainly as a result of careful control of solution chemistry [5,6].

To get some indication of the quality and reactivity of Finnish magnesium carbonates, a few experiments were conducted using a serpentine that was mined near Kittilä north of Rovaniemi, Finland. Chemical analysis showed that this mineral is quite pure, the contents of Mg and Si being 99.9% and 89.1%, respectively, of the theoretical value for serpentine. However, the mineral contains also 4.4 %-wt carbonate (carbon bound as CO₃).

Fine powdered samples (average particle size approx. 50 µm) were carbonated in a pressurised thermogravimetric analyser (PTGA). At 200°C no detectable carbonation was measured after 3 hours, at 1 bar in N₂/CO₂ 85 /15 %-vol and in N₂/CO₂/H₂O 80/15/5 %-vol, nor at 15 bar in a N₂/CO₂ 85/15 %-vol gas mixture. The final CO₃ content of the samples was approx. 4.3 %-wt, from which it can be concluded that nothing had happened to the samples.

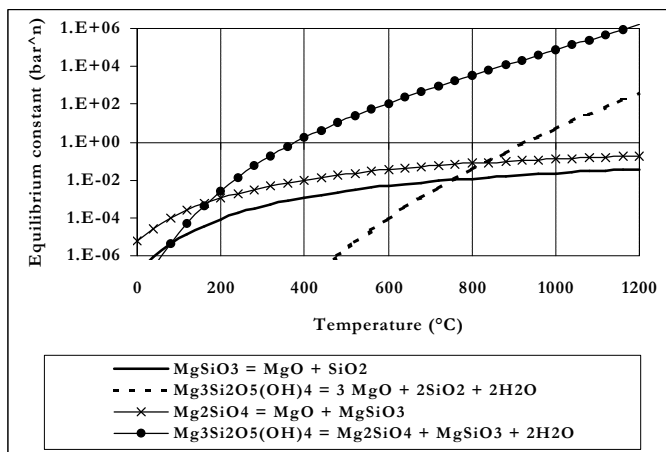


Figure 4 Thermodynamic equilibrium constant for the decomposition of magnesium silicates [11]

A second set of tests aimed at “setting free” the active component MgO from the mineral at elevated temperature, followed by carbonation at lower temperatures. As illustrated by the thermodynamic equilibrium calculations given in Figure 4, MgO may be separated from serpentine at temperatures above 900°C. Higher temperatures are needed for olivine. For a large scale pulverised coal-fired power plant one approach could be to inject serpentine into the upper furnace, where the temperature is sufficient to release MgO, followed by carbonation of the MgO (reaction R2) at lower temperatures downstream.

For this purpose a serpentine sample was heated rapidly to 1000°C, followed by cooling at a lower rate to 200°C, in the PTGA in a N₂/CO₂ 85/15 %-vol gas atmosphere. The results shown in Figure 5 (corrected for buoyancy effects) show a mass loss during heat-up which corresponds to ~110% of the water bound in the serpentine. Apparently this is due to the release of CO₂ present in the serpentine mineral as carbonate, probably MgCO₃ (see above). During the cool-down stage an increase of sample mass is seen until the temperature has decreased to ~400°C, corresponding to almost 3% uptake of CO₂ by MgO. Surprisingly, the mass of the sample appears to decrease again when lowering the temperature further to 200°C. The mass fraction of carbon bound as CO₃ in the final product is ~0.5 %-wt *i.e.* lower than in the starting material. Repeating this experiment at 15 bar resulted in a final CO₃ content of ~0.8%-wt. Clearly, more work is needed to obtain a better understanding of the processes taking place during these tests. This includes a more detailed analysis of the magnesium silicate minerals, also in order to get insight into the (possibly catalytic) effects of contaminations.

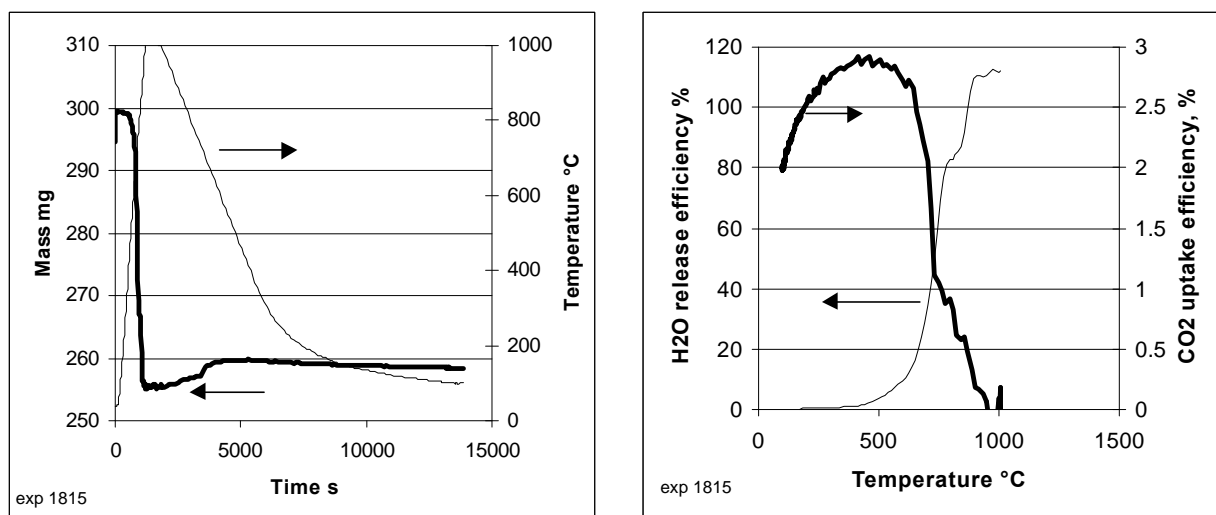


Figure 5 Heat-up and cool down of a powdered serpentine sample in a N_2/CO_2 85/15 %-vol gas atmosphere, showing mass and temperature vs. time (*left*) and the release of water during heat-up and uptake of carbon dioxide during cool-down (*right*) [11]

Conclusions / Future work

From the Finnish point of view mineral sequestration seems to be the most suitable if not the only possibility to reduce the CO_2 emissions, especially if Finland doesn't shift its energy policy towards nuclear power. A reduction of about 5% CO_2 emissions would be enough to decrease CO_2 to the level agreed upon in Kyoto in 1997. In Finland the required mineral seems to be available in sufficient amounts for such a reduction to be obtained by mineral carbonation.

At a mineral carbonation efficiency of 100% for each ton of CO_2 , 2.18 tons of mineral serpentine would be required. To capture the CO_2 released by the Salmisaari power plant at least 2 Mt serpentine would be required per year. A 5 % reduction in CO_2 emissions for all Finland would require a quantity of 6.11 Mt serpentine per year. Every ton of carbon dioxide would result in 0.66 tons of quartz and 1.92 tons of magnesium carbonate: 1 ton of serpentine produces 1.2 tons of solid reaction products. These should, preferably, be returned to the mine, if not the CO_2 itself is transported to the mineral deposit by pipeline.

The material is already produced as a side product at several mines, but increased mining would be required. The mining of magnesium silicates could also improve the efficiency of the metal production. Some sort of integration of metal ore processing and magnesium silicate treatment to give magnesium oxide, MgO would be highly beneficial, also from an process economy point of view. At this point magnesium silicate is still a side product of metal mining but as soon as a valuable use for the mineral is discovered, its price will certainly increase. This will be reflected directly by the costs of electricity and heating.

In the experiments of this study only the direct carbonization of a rather pure mineral serpentine has been tested. Isothermal tests at 200°C give no change in the mineral's carbonate content, whilst heating to 1000°C followed by cooling to 200°C shows a low, if any, level of carbonation.

If direct carbonation is possible with Finnish magnesium silicate minerals it will certainly need a catalyst to reach reasonable conversions within a realistic timeframe.

Future work will continue along these lines within the Finnish national research programme CLIMTECH (1999-2000). The three major objectives of the participation of Helsinki University of Technology are

- 1) optimisation of the chemistry of direct, dry, magnesium silicate mineral carbonation, addressing process conditions, flue gas composition and the use of catalysts
- 2) more detailed mapping of Finland's magnesium silicate mineral resources and the quality of these minerals, and reviewing the aspects of carbonated mineral disposal
- 3) economic aspects of CO₂ sequestration by mineral carbonation, considering the type and size of fossil fuel-fired power plant and whether to transport mineral or CO₂

Acknowledgements

This first study was funded by Ekokem Oy support funding ("apurahoitus") 2000. The work is currently continuing under the Finnish national research programme Climtech (1999-2002) and receives support from IVO Foundation as well.

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This paper was accepted, in this form, for oral presentation at R'02 Recovery Recycling Re-integration, Geneva, Switzerland, February 12-15, 2002 (<http://www.R02.org>)