

Report TKK-ENY-9

# Mineral carbonation for long-term storage of CO<sub>2</sub> from flue gases

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## Preface

This volume contains the two progress reports for the project "CO<sub>2</sub> long-term storage and utilisation in Finland", "*CO<sub>2</sub> loppusijoitus ja hyötykäyttö Suomessa*", as part of the Finnish National Research Programme CLIMTECH (1999-2002). The title of the sub-project at Helsinki University of Technology was "Mineral carbonation for long-term storage of CO<sub>2</sub> from flue gases"; the progress reports collected here cover the periods August – December 2001 and January - May 2002, respectively.

Our partner in this project was VTT Processes, Espoo; the work was financed by the Finnish Technology Agency Tekes and Nordkalk Oyj Abp, and received further support from Fortum Foundation.

The researchers at Helsinki University of Technology, Laboratory of Energy Engineering and Environmental Engineering were Jens Kohlmann and Dr. Ron Zevenhoven, with Prof. Carl-Johan Fogelholm as responsible supervisor. External researchers that participated in our part of the project were Dr. Arun B. Mukherjee from the University of Helsinki, Department for Limnology and Environmental Protection, and Mrs. Tiina Koljonen from VTT Processes, Espoo.

Hanne Siikavirta from Fortum Oy Power and Heat, Vantaa, and our other CLIMTECH colleagues are acknowledged for many useful discussions. Antero Moilanen and Jaana Korhonen from VTT Processes, Espoo, deserve many thanks for the PTGA work.

As of February 1, 2002, Jens Kohlmann is with Jaakko Pöyry Oy, Vantaa.

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## Publications

"The removal of CO<sub>2</sub> from flue gases using magnesium silicates, in Finland" Jens Kohlmann, Ron Zevenhoven. In: Proc. of the 11th Int. Conf. on Coal Science, San Francisco (CA), Sept. 30- Oct. 5, 2001 (CD-ROM)

"CO<sub>2</sub> storage by mineral carbonation in Finland (CO<sub>2</sub> lagring genom mineral karbonering i Finland)" Ron Zevenhoven, Jens Kohlmann, *invited lecture by Ron Zevenhoven*. In: Proc. of the Second Minisymposium on CO<sub>2</sub> Capture and Storage, Gothenburg (Sweden), October 26, 2001 pp. 13-18 (*available at <http://www.entek.chalmers.se/~anly/symp/symp2001.html>*)

"CO<sub>2</sub> sequestration by magnesium silicate mineral carbonation in Finland" Ron Zevenhoven, Jens Kohlmann. Proceedings of R'02 Recovery Recycling Re-integration, Geneva (Switzerland) February 12-15, 2002, paper 220 (CD-ROM)

"Direct dry mineral carbonation for CO<sub>2</sub> emissions reduction in Finland" Ron Zevenhoven, Jens Kohlmann, Arun B. Mukherjee. Proceedings of the 27th Int. Tech. Conf. on Coal Utilization and Fuel Systems, Clearwater (FL), March 4-7, 2002, pp. 743-745 (CD-ROM)

"Carbon dioxide emissions control by mineral carbonation: the option for Finland", Jens Kohlmann, Ron Zevenhoven, Arun B. Mukherjee. Proceedings of INFUB - 6th European Conference on Industrial Furnaces and Boilers, Vol. 2, Estoril (Portugal), April 2-5, 2002.

"CO<sub>2</sub> capture, storage and reuse potential in Finland", Tiina Koljonen, Hanne Siikavirta, Ron Zevenhoven, Ilkka Savolainen. Accepted for presentation at the 6<sup>th</sup> Int. Conf. on Greenhouse Gas Control Technologies (GHGT-6), Kyoto, Japan, September 30 – October 4, 2002

"Reaction kinetics of magnesium oxide-based mineral carbonation for CO<sub>2</sub> sequestration" Ron Zevenhoven, Jens Kohlmann. *under preparation, to be submitted to a technical journal*

## **Part 1 :**

# **Progress report August – December 2001**

**(report date January 15, 2001)**

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# 1. Introduction

## 1.1 Objectives and scope

Finland currently generates ~55% of its heat and power from fossil fuels (including peat). This is illustrated by Table 1, which applies to the region around Helsinki, accounting for ~14 % of the Finnish CO<sub>2</sub> emissions from fossil fuel (including peat) -fired power plants. Although Finland is slowly shifting its fuel consumption to renewable fuels like wood and waste-derived fuels there is still a legitimate demand 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 CO<sub>2</sub> emissions in the near future, making it difficult to fulfil Finland's commitments considering CO<sub>2</sub> emissions put down in international agreements. At present, global emissions of CO<sub>2</sub> are at levels above 19 gigatons per annum [2], which is the most significant quantity of greenhouse gases emissions to the atmosphere, responsible for approx. 60 % of the enhanced greenhouse effect.

Table 1: Power plants in Helsinki: fuel consumption and CO<sub>2</sub> 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 [10 <sup>6</sup> Nm <sup>3</sup> ]	CO <sub>2</sub> 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	342
Vuosaari B	480	420	-	-	0.024	595.6	1202

The problem could be partly solved by CO<sub>2</sub> sequestration, *i.e.* the removal of CO<sub>2</sub> 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 CO<sub>2</sub> do not have enough capacity.

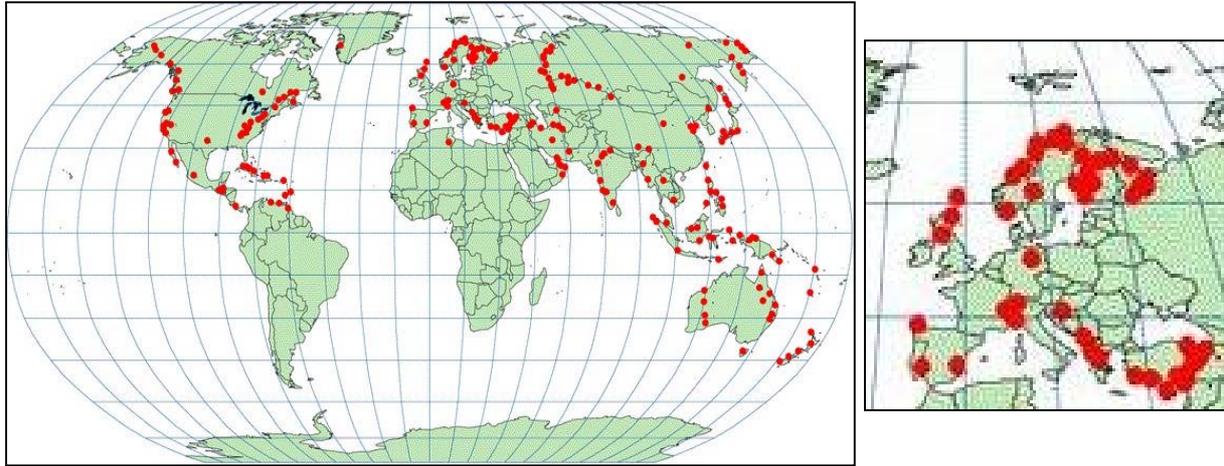


Figure 1 Distribution of magnesium silicate mineral deposits worldwide (*left*) and in Europe (*right*), indicating significant resources in Finland (pictures taken from [3])

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 available worldwide in huge amounts, as illustrated by Figure 1. In addition, it contains more reactive material per tonne of rock than for example calcium-based minerals due to the lower molecular weight of magnesium [2]. These natural resources may be capable of binding all fossil fuel-bound carbon [3,4]. Magnesium silicates can be divided into several subgroups. The largest quantities are olivine,  $(\text{Mg,Fe})\text{SiO}_4$ , and serpentine,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . Some other suitable minerals exist in smaller amounts.

The chemistry for this  $\text{CO}_2$  fixation can be summarised as



The overall carbonation reaction (R1+R2) is exothermal: the heat effect is +64 kJ/mol and +90 kJ/mol  $\text{MgCO}_3$ , for serpentine and olivine/forsterite, respectively. This may be compared with the heat of combustion of 394 kJ that is released in the formation of 1 mol of  $\text{CO}_2$ . Because these minerals are thermodynamically favoured,  $\text{SiO}_2$  and  $\text{MgO}$  are common in serpentinized *ultramafic* rocks (rocks rich in Fe and Mg) [5,6]. Large-scale flue gas  $\text{CO}_2$  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  $\text{CO}_2$  may require 2 kg of serpentine for disposal.

Only a few laboratories 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.* Los Alamos National Laboratory (NM), Albany Research Center at Albany (OR) and Arizona State University at Tempe (AZ) [3-4,7-9]. Whilst the research in the USA is concentrating increasingly on wet methods, using aqueous solutions, our research started in August 2000 at the Helsinki University of Technology (still) aims at dry methods. Two problems must be solved to make this approach more attractive, as also concluded in a recent feasibility study from the UK [10]:

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

The three major objectives of our studies at the Helsinki University of Technology, for which results are reported in the following chapters, are as follows:

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

## 1.2 Time table (August 2001)

	2001					2002						
	8	9	10	11	12	1	2	3	4	5	6	7
Kick-off meeting	x											
Reaction kinetic tests	x	x	x	x	x	x						
Catalytic influence tests				x	x	x	x	x	x			
Mineral resources			x	x	x	x						
End-product disposal		x	x	x	x	x	x					
Process plant lay-out						x	x	x				
Economic aspects						x	x	x				
Effect of power plant type						x	x	x				
27 <sup>th</sup> Clearwater Conference								x				
Helsinki U of T final report									x			
Climtech final report									x	x	x	

After the kick-off meeting at Fortum Oy, Vantaa, August 16, 2001 (present: RZ, JK, CJF, ABM), a progress meeting was held at VTT Energy, Espoo, December 10, 2001 (present: RZ and ABM) and a Climtech seminar was held at Espoo, December 13, 2001 (present: JK).

RZ presented the work in an invited lecture at the Second Minisymposium on CO<sub>2</sub> Capture and Storage, Gothenburg (Sweden), October 26, 2001.

Jens Kohlmann will switch to a position at Jaakko Pöyry Oy at Vantaa, as of February 1, 2002. However, he will complete his part of the project within the time schedule (*i.e.* before or in May 2002) and produce a lic. tech. thesis before the end of this year.

## 2. Part I : Optimisation of mineral carbonation chemistry

### 2.1 Magnesium oxide based mineral carbonation – earlier results

#### 2.1.1 Thermodynamics vs. kinetics

The thermodynamics of magnesium silicate carbonation (R1 and R2) shows that, depending on the partial pressure of CO<sub>2</sub>, temperatures of the order 200-400°C are preferable – see Figure 2. 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). As illustrated by the equilibrium calculations given in Figure 3, 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.

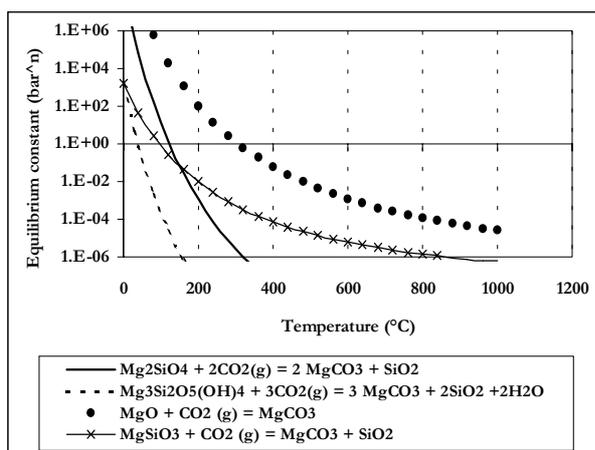


Figure 2 Thermodynamic equilibrium constant for carbonation of MgO, MgSiO<sub>3</sub>, olivine and serpentine [11]

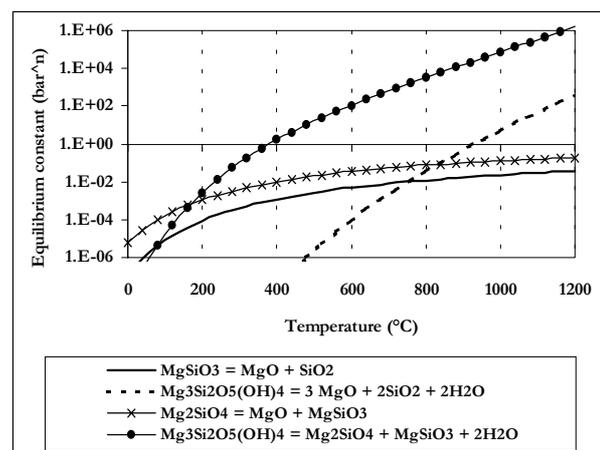


Figure 3 Thermodynamic equilibrium constant for the decomposition of magnesium silicates [11]

Data on the chemical reaction rate of the carbonation of magnesium-based minerals 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 [7,8]. More recent achievements using wet systems report 65% conversion after 1 hour, mainly as a result of careful control of solution chemistry [8,9].

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 – see Table 2. However, the mineral contains also 4.4 %-wt carbonate (carbon bound as CO<sub>3</sub>). Because of the amount of Mg in the mineral, it was assumed that this carbonate fraction is present as MgCO<sub>3</sub>, which implies that the “serpentine” is composed of 6.2 %-wt MgCO<sub>3</sub> and 93.8 %-wt Mg<sub>3</sub>Si<sub>2</sub>O<sub>9</sub>H<sub>4</sub>. Later, a calcium content of 0.69 %-wt was measured.

Table 2 Chemical analysis of the serpentine and magnesium hydroxide samples tested

%-wt, dry	Mg(OH) <sub>2</sub>	Mg	Si	CO <sub>3</sub>	Ca	MgO *	SiO <sub>2</sub> *	Other
Serpentine		26.3	18.1	4.41	0.69	43.6	38.7	12.6*, **
Mg(OH) <sub>2</sub>	99.7							0.3

\* Assuming all Mg as MgO, all Si as SiO<sub>2</sub> \*\* Pure serpentine contains ~ 13 %-wt bound H<sub>2</sub>O

### 2.1.2 Experiments with serpentine at constant temperature

Fine powdered samples (average particle size approx. 50 µm) were carbonated in a pressurised thermogravimetric analyser (PTGA) (*see Part 2 of this report for more details on the experimental procedure*). At 200°C no detectable carbonation was measured after 3 hours, at 1 bar in N<sub>2</sub>/CO<sub>2</sub> 85 /15 %-vol and in N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O 80/15/5 %-vol, nor at 15 bar in a N<sub>2</sub>/CO<sub>2</sub> 85/15 %-vol gas mixture. The final CO<sub>3</sub> content of the samples was approx. 4.3 %-wt, from which it can be concluded that nothing had happened to the samples.

### 2.1.3 Experiments with serpentine at increasing/decreasing temperature

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. For this purpose a serpentine sample was heated at 50 °C/min to

1000°C, followed (after 10 minutes) by cooling at 10°C/min to 200°C, in the PTGA in a N<sub>2</sub>/CO<sub>2</sub> 85/15 %-vol gas atmosphere.

The results shown in Figure 4 (corrected for buoyancy effects) show a mass loss during heat-up which corresponds to ~110% of the water and magnesium-bound carbonate in the serpentine. Apparently this is due to the release of bound CO<sub>2</sub> but other than MgCO<sub>3</sub> present in the serpentine mineral. Therefore, the serpentine was analysed for Ca as well, since CaCO<sub>3</sub> may be present as well. The analysis result of 0.69 %-wt Ca in the mineral does not explain the mass loss during heat-up. During the cool-down stage a sudden increase of sample mass is seen near 700°C, followed by a slow increase in CO<sub>2</sub> uptake by MgO up to approx. 0.8 % MgO conversion. The mass fraction of carbon bound as CO<sub>3</sub> in the final product was analysed to be 0.5 %-wt (which is lower than in the starting material.....).

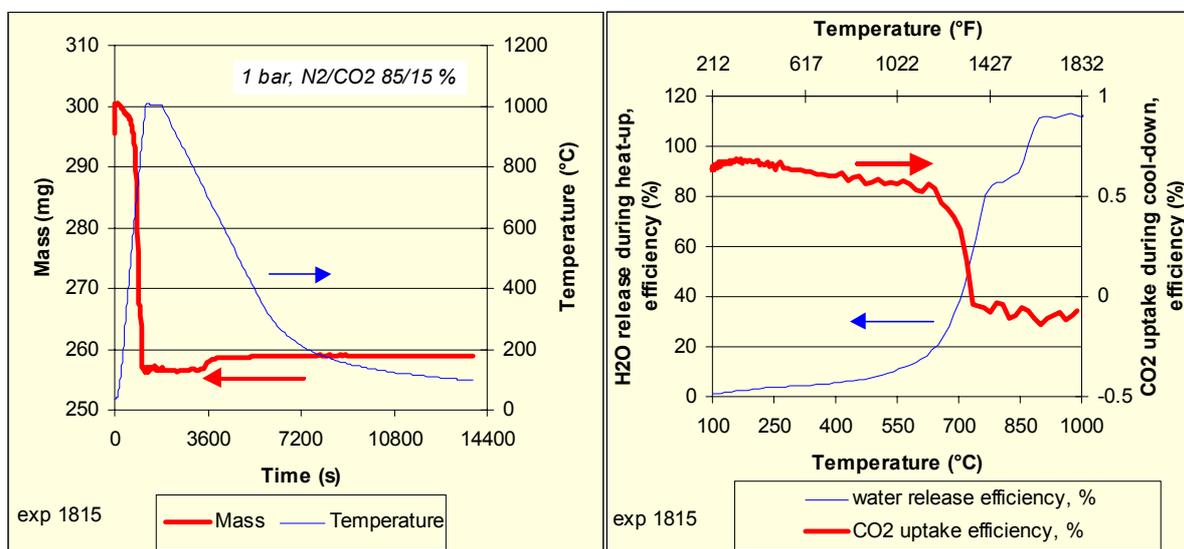


Figure 4 Heat-up and cool down of a powdered serpentine sample in a N<sub>2</sub>/CO<sub>2</sub> 85/15 %-vol gas atmosphere, showing mass and temperature vs. time (left) and the release of water during heat-up and uptake of carbon dioxide during cool-down (right)

Clearly, more work is needed to obtain a better understanding of the processes taking place during these tests (such as the sudden increase in CO<sub>2</sub> uptake at near 700°C in Figure 4 (right)). This includes especially a more detailed analysis of the magnesium silicate minerals, also in order to get insight into the (possibly catalytic) effects of contamination.

## 2.2 Magnesium oxide based mineral carbonation – new results

After the tests with the serpentine further tests were made with a 99.7 %-wt pure  $\text{Mg}(\text{OH})_2$  sample provided by Nordkalk Oyj Abp (average particle size approx. 20  $\mu\text{m}$ ) – see Table 2. Appendix 1 tabelises the experimental parameters for the tests described below.

### 2.2.1 Experiments with magnesium hydroxide at increasing/decreasing temperature 1: effect of other species mixed with the solid

A series of tests (tests # 1-4) was conducted with a rather pure  $\text{Mg}(\text{OH})_2$ . These tests involved heat up at 50  $^\circ\text{C}/\text{min}$  to 1000 $^\circ\text{C}$ , followed, after 10 minutes, by cooling at 10 $^\circ\text{C}/\text{min}$  to 100 $^\circ\text{C}$ , in a  $\text{N}_2/\text{CO}_2$  85/15 %-vol gas atmosphere, at 1 bar. Also, the  $\text{Mg}(\text{OH})_2$  was mixed with 1%-wt of  $\text{NaCl}$ ,  $\text{NaHCO}_3$  or  $\text{Al}_2\text{O}_3$ , respectively, as to investigate any catalytic effect of these. The results of the carbonation stage of the tests are summarised in Figure 5.

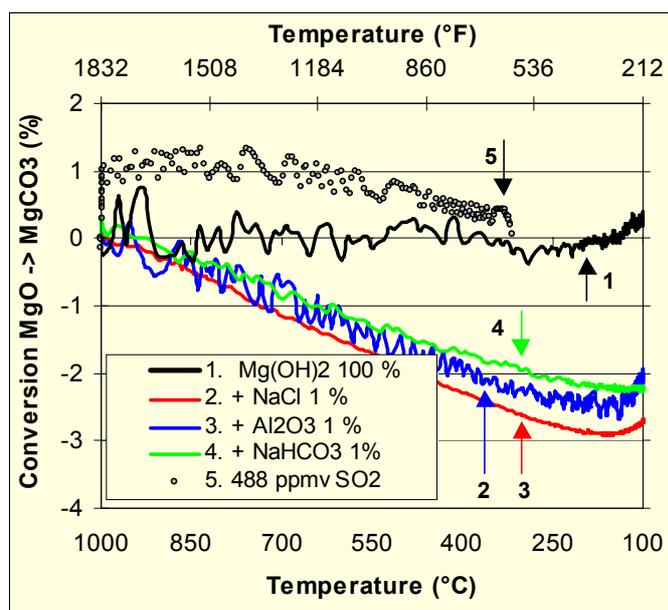


Figure 5 Efficiency of  $\text{MgO}$  carbonation starting with calcined  $\text{Mg}(\text{OH})_2$ , with 1 % of an added chemical, or with  $\text{SO}_2$  in the gas. Cooling rate 10 $^\circ\text{C}/\text{min}$ , 85/15 %/-%-v  $\text{N}_2/\text{CO}_2$ , 1 bar

A first finding was that the efficiency of the calcination of the  $\text{Mg}(\text{OH})_2$  to  $\text{MgO}$ , which reached almost 99 % for the test with pure  $\text{Mg}(\text{OH})_2$  at the end of the heat-up to 1000 $^\circ\text{C}$ , was not so high when other species were present. For a 99%-wt  $\text{Mg}(\text{OH})_2$  /1%-wt  $\text{NaCl}$  sample, the conversion efficiency of  $\text{Mg}(\text{OH})_2$  to  $\text{MgO}$  was reduced to 94 %, with 1 %-wt  $\text{Al}_2\text{O}_3$  to 90 % and with 1 %  $\text{NaHCO}_3$  to 94 %. It may be that the calcination reaction is slowed down by the presence of additional species, which may explain some of the results in Figure 5: apparently the calcination is still ongoing during the cool-down stage, giving a mass loss that exceeds the mass gain that would result from carbonation.

Some additional information was obtained with chemical equilibrium calculations (using the HSC-4 free energy minimisation software [12]), suggesting that the NaCl and NaHCO<sub>3</sub> may be completely volatilised and lost to the gas phase, whilst no such effect is to be expected with Al<sub>2</sub>O<sub>3</sub>. In all cases, MgO is the most stable Mg species.

In Figure 5, the result with pure Mg(OH)<sub>2</sub> shows oscillating behaviour with only at temperatures below 300°C a continuously increasing trend – all perfectly according to the thermodynamics for reaction (R2). The reason for the decreasing lines (until below 200°C) found when some NaCl, NaHCO<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> is mixed with the Mg(OH)<sub>2</sub> is totally unclear. This may be due to delayed calcination of the Mg(OH)<sub>2</sub>, *i.e.* this still continues when the temperature is decreasing again, since chemical equilibrium calculations do not indicate that species are formed that result in a mass decrease upon reaction with CO<sub>2</sub>.

### 2.2.2 Experiments with magnesium hydroxide at increasing/decreasing temperature 2: effect of gaseous compounds

One test (test #5) involved the effect of 500 ppm-vol SO<sub>2</sub> (to be exact: 488 ppm-vol) in the 85/15 %/% N<sub>2</sub>/CO<sub>2</sub> gas mixture on the reaction with Mg(OH)<sub>2</sub>. With the SO<sub>2</sub> present in the CO<sub>2</sub>/N<sub>2</sub> mixture, the conversion efficiency of Mg(OH)<sub>2</sub> to MgO was only 88 %. Again, thermodynamic calculations show that MgO is the most stable Mg species, with only traces of MgSO<sub>4</sub> in presence of SO<sub>2</sub>. As seen from the result that is included in Figure 5, with some SO<sub>2</sub> present in the gas a rapid increase to 1 % MgO carbonation is found which below 800°C starts to decrease again. This may be due to the presence of MgSO<sub>4</sub>, which apparently is carbonated to MgCO<sub>3</sub> more rapidly than MgO. Unfortunately, the SO<sub>2</sub> bottle was empty before the experiment could be completed at 200°C.

Four additional tests (tests #7, #9-11) were conducted with the Mg(OH)<sub>2</sub>, aiming at studying the effect of the presence of water and/or oxygen in the gas, besides carbon dioxides and nitrogen. These four tests involved heat up at 50 °C/min to 1000°C, followed, after 10 minutes, by cooling at 10°C/min to 200°C, at 1 bar, in a 1) an N<sub>2</sub>/CO<sub>2</sub> 85/15 %-vol gas atmosphere, 2) in N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O 80/15/5 %-vol, 3) in N<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> 80/15/5 %-vol, and 4) in N<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O/O<sub>2</sub> 75/15/5/5 %-vol. The results of the cooling, *i.e.*, carbonation stage, are given in Figure 6.

Despite the fluctuations in the PTGA signals, all cases show an increasing conversion of MgO to MgCO<sub>3</sub> at an increasing rate when the temperature sinks below approx. 300°C. With a gas containing CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O an unexpected sudden decrease in the sample mass is seen in the temperature range 750-500°C. A clear catalytic effect of water on the carbonation reaction is seen: in fact the highest MgO conversion was obtained with a gas containing CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O. A clear influence, if any, of the presence of oxygen, could not be deduced from these results.

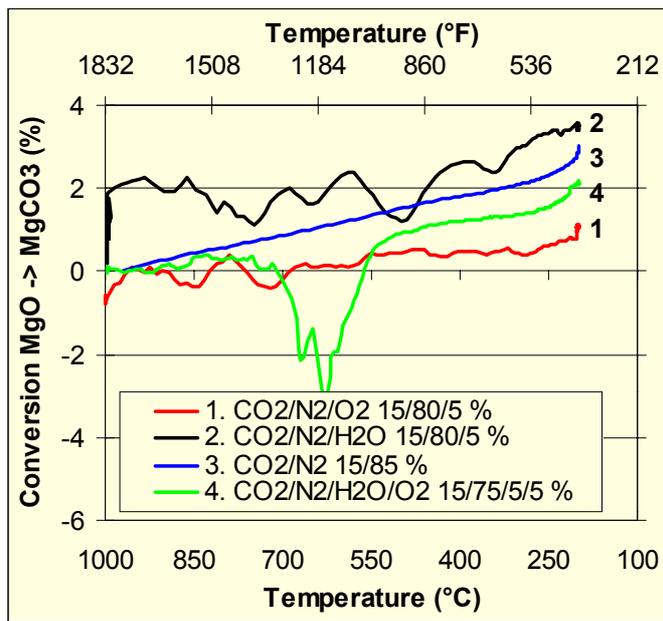


Figure 6 Efficiency of MgO carbonation starting with calcined Mg(OH)<sub>2</sub>, with H<sub>2</sub>O and/or O<sub>2</sub> in the gas, besides CO<sub>2</sub> and N<sub>2</sub>. Cooling rate 10°C/min, 1 bar.

For the rate of the carbonation reaction between MgO and CO<sub>2</sub> (R2) a simple kinetic model can be set up:

$$-\frac{dm_{MgO}}{dt} = k_+ m_{MgO} \cdot p_{CO_2} - k_- m_{MgCO_3} = m_{MgO, start} \frac{dX}{dt} \quad (1)$$

where m represents mass (kg), t is time (s), k<sub>+</sub> and k<sub>-</sub> are the kinetic rate constants for the forward and backwards reactions, respectively (units bar<sup>-1</sup>s<sup>-1</sup> and s<sup>-1</sup>, respectively), p<sub>CO<sub>2</sub></sub> is the partial pressure of CO<sub>2</sub> (bar) and X is the fractional conversion of MgO to MgCO<sub>3</sub> (-). It is noted that the equilibrium constant, K<sub>p</sub>, for reaction (R2) equals the ratio K<sub>p</sub> = k<sub>+</sub>/k<sub>-</sub> which can be modelled (with temperature T in K) as :

$$\ln K_p = 11839/T - 20,219 = - \ln p_{CO_2, equilibrium} \quad (2)$$

Using this, equation (1) can be rewritten into a function of forward rate constant  $k_+$ , related to the change of conversion  $X$  with temperature  $T$ ,  $dX/dT$ :

$$k_+ = \frac{\beta}{(1-X)p_{CO_2} - \frac{Z \cdot X}{K_p}} \frac{dX}{dT} = k_0 \cdot e^{-\frac{E_{act.}}{RT}} \quad (3)$$

where  $Z$  is the molar mass ratio  $M_{MgCO_3}/M_{MgO} = 2.0918$  and  $\beta$  is the heating (or cooling) rate (K/s). From this the Arrhenius constant parameters  $k_0$  and  $E_{act}$  may eventually be calculated.

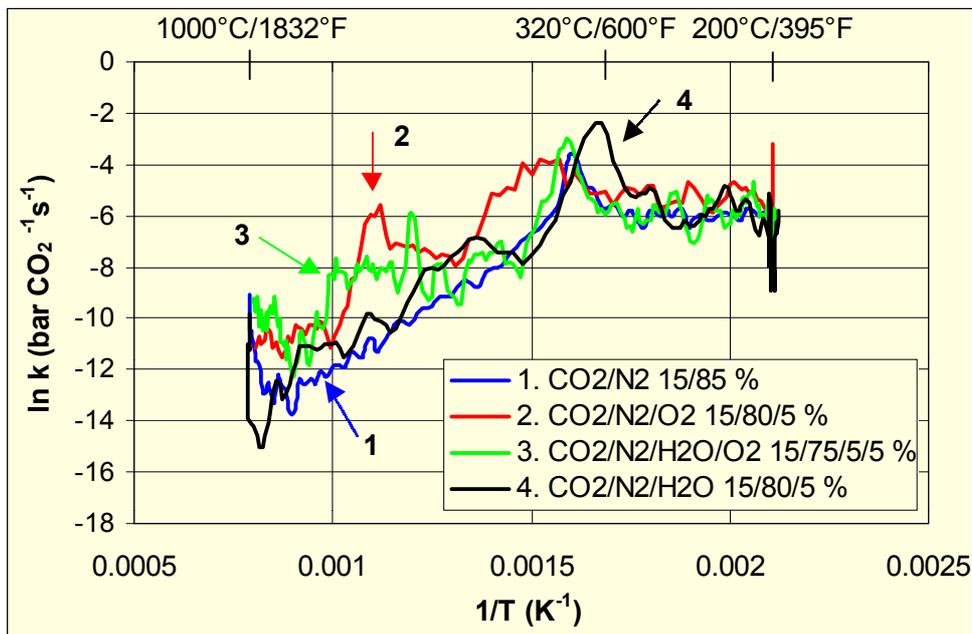


Figure 7 Rate constant for reaction  $\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$ , during cool-down (10 K/min) of MgO in various gas atmospheres, at 1 bar

Applying this procedure to the results shown in Figure 6 gives the rate constants as plotted in Figure 7. It is clearly seen that above about 350°C the rate decreases with increasing temperature as a result of unfavourable thermodynamics (*viz.* equation 2), whilst a rate that increases with temperature is seen for lower temperatures. This “turn-over” temperature may be the preferable temperature for mineral carbonation (for this sorbent material !) at 1 bar, and is slightly effected by the composition of the gas phase.

### 2.2.3 Experiments with magnesium hydroxide at increasing/decreasing temperature 3: effect of pressure

Besides the experiment with serpentine at 200°C/20 bar mentioned in section 2.1.2, both the serpentine and the Mg(OH)<sub>2</sub> samples were tested under heat-up (50 K/min, until 1000°C) followed by cool-down (10 K/min) conditions under pressurised conditions. The results of these tests are shown in Figure 8. Repeating the experiment shown in Figure 4, for serpentine, at 15 bar and analysing the solid residue afterwards showed a final CO<sub>3</sub> content of approx. 0.8 %-wt, which is higher than the 0.5 %-wt obtained at 1 bar. The experiment with Mg(OH)<sub>2</sub> (test #6) was made at 20 bar.

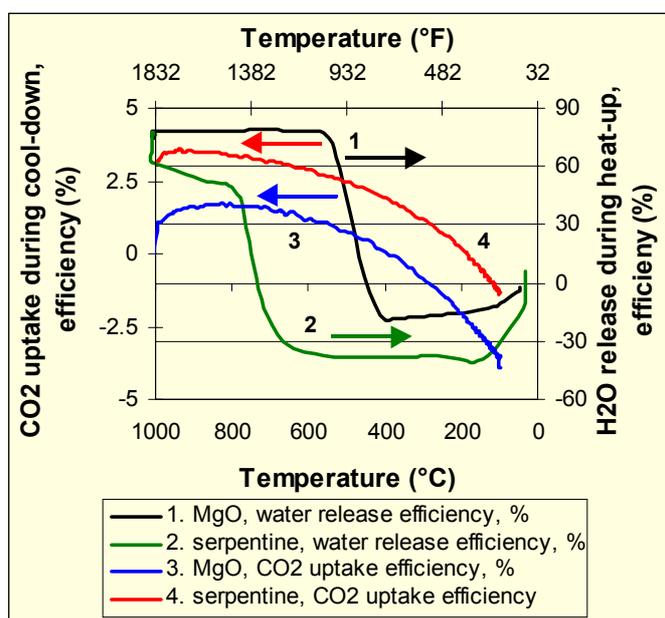


Figure 8 Heat-up and cool down of powdered serpentine and powdered Mg(OH)<sub>2</sub> samples in a N<sub>2</sub>/CO<sub>2</sub> 85/15 %/%-vol gas atmosphere, showing the release of water during heat-up (50 K/min) and, after 10 min. at 1000 °C, uptake of carbon dioxide during cool-down (10 K/min). Pressure 15 bar for serpentine, 20 bar for Mg(OH)<sub>2</sub>.

In Figure 8 a negative water release suggests that actually, until about 700°C a mass increase is taking place. What is really taking place may be mineral carbonation, although the 200°C/15 bar test with serpentine showed a negligible carbonation effect. Also, during the cool-down stage the mass of the sample continues to decrease, resulting in the curves shown for CO<sub>2</sub> uptake in Figure 8. Due to the unexpected outcome of the heat-up stage the composition of the sample at the beginning of the cool-down stage is largely unknown, which explains the shape and final values of the curves for CO<sub>2</sub> uptake.

As already noted above, more work and detailed analyses are needed here - additional tests are to be carried out during the second half of this project .

### 3. Part II : Mineral resources and quality; end-product disposal

#### 3.1 Magnesium oxide-based mineral resources and their quality

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 [13]. In Finland there are many mining activities, mainly mining for metals (nickel, copper), although also talc and limestone are mined. There are 15 major active mines in Finland of which 9 are found in areas with rich magnesium silicate deposits. 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 [14].

HITURA SERPENTINITE MASSIVES		9.10.2001
Location:	Site: Nivala town Map: Karvoskylä Sheet: 2344 05	
Size:	Hitura serpentinite massives (three separate massives): area m <sup>2</sup> 1 North Hitura 75000 (not exact figure) 2 Middle Hitura 65000 (not exact figure) 3 South Hitura 50000 (not exact figure) total 190000 (not exact figure)	
	Amount of the massives (to the depth of 500 m): m <sup>3</sup> total 95 000 000 (not exact figure)	
Mineralogy:	Mineralogy of the Hitura massives: Serpentine Main mineral Amphiboles Chlorites Talc Olivine Only accessory Sulphides (pyrrhotite, pentlandite, chalcopyrite, vallerite, mackinawite,...) Oxides (magnetite mainly) Cutting dykes: feldspars, quartz NOTE: Some asbestos form minerals are present.	
Mining:	The Hitura nickel mine, open pit and underground mine, is located only in the North Hitura massive. The mine area also covers the Middle Hitura massive and the main part of the South Hitura massive. In the tailing pond there is roughly 10 million tonnes serpentinite waste (not exact figure). In the stock pile there are roughly 4 million m <sup>3</sup> serpentinite rocks (not exact figure).	
Owner:	Outokumpu Mining Oy Hituran kaivos	

Figure 9 Description of the serpentine deposit at Hitura [17]

A mapping of so-called ultramafic mineral, *i.e.* magnesium oxide rich deposits in Finland, made by the Geological Survey of Finland is shown in Appendix 2 [15]. In the past no attempt has been made to evaluate ultramafic rocks in Finland as sources of magnesium for CO<sub>2</sub> sequestration. The map indicates widespread deposition of ultramafic rocks in the eastern and northern part of Finland. The quality, magnesium content in rocks for large scale industrial processing and its volume are still to be assessed. It is clear that the mineralogy

of ultramafic rocks is highly variable, depending on their geological + background. In Finland, the typical age of these deposits is approx. 1900 million years.

Assuming an average depth of the ultramafic rock beds of 50 m, each area of 1 km<sup>2</sup> marked in the map corresponds to 50 million m<sup>3</sup> of potentially useful deposit. This is a very rough estimation that should be used cautiously.

For CO<sub>2</sub> sequestration, the most important minerals are serpentine and olivine as they are rich in magnesium and readily soluble in hydrochloric acid [16]. Table 3 indicates mineral species and their chemical formulas associated in ultramafic rocks that are distributed around the world. It should be remembered that complex mineralogical condition of rocks (*i.e.* rocks exposed to high temperature and pressure during metamorphism) may have effect on kinetics and conditions of the sequestration process [16]. Olivine (the major pre-sepentinization mineral in dunite - a rock consisting of ≥ 90 vol % olivine) on the other hand, should behave uniquely in the CO<sub>2</sub> sequestration process. An important local “spot” such as the deposit of serpentinite at Hitura estimated at 100 million m<sup>3</sup> is unfortunately not shown in our map [17]. In other areas of Finland, deposit volume can not be estimated without the knowledge of geophysical data.

Large silicate minerals containing ultramafic rocks that are not easily reacted with industrial reagents should be avoided, whereas secondary carbonate mineral -containing rocks have no use as they have been sequestered by natural processes [16].

Table 3 Main mineralogy of serpentinite, peridotite and associated rocks [16]

Mineral group	Mineral species	Chemical formula	Rocks found in
Serpentine	Chrysotile	$Mg_3Si_2O_5(OH)_4$	Serpentinite; altered peridotite
Serpentine	Lizardite	$Mg_3Si_2O_5(OH)_4$	„
Serpentine	Antigorite	$Mg_3Si_2O_5(OH)_4$	High-grade serpentinite; altered peridotite
Olivine	Forsterite	$Mg_2SiO_4$	Dunite; peridotite
Orthopyroxene	Enstatite	$MgSiO_3$	Peridotite
Clinopyroxene	Diopside	$CaMgSi_2O_6$	„
Amphibole	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	High-grade serpentinite
Amphibole	Anthophyllite	$Mg_2Mg_3Si_8O_{22}(OH)_2$	„
Spinel	Magnetite	$Fe_2FeO_4$	Serpentinite; peridotite; dunite
Spinel	Chromite	$Cr_2FeO_4$	Serpentinite; peridotite
Carbonate	Magnesite	$MgCO_3$	Altered serpentinite
Carbonate	Dolomite	$CaMg(CO_3)_2$	„
Silica	Quartz, chalcedony	$SiO_2$	„
Silica	Opal	$SiO_2 \cdot nH_2O$	„

### 3.2 Disposal and use of the end-products from mineral carbonation

As one of our objectives, it is necessary to assess the environmental impact of products from reaction (R1 + R2), and the possibilities for its use as raw material in some process. Reactions R1 and R2 indicate that roughly 2 kg serpentinite rock are necessary to bind 1 kg  $CO_2$ , generating magnesium carbonate and quartz at a typical mass ratio of 2½ : 1. The issue of waste or “product” from the carbonation process may present several challenges since materials are in particulate form.

For the carbonation reaction (R2), and its thermodynamic equilibrium constant  $K_p$ , which can be approximated by

$$\ln K_p = 11839/T - 20,219 = - \ln P_{CO_2, equilibrium} \quad (2)$$

we find  $K_p$  is greater than unity for air containing 400 ppm-vol  $CO_2$ , at 1 bar, at temperatures below roughly 150°C. It means that the product is environmentally stable (*i.e.* more stable than  $CO_2$ ) and it gives permanent storage space for  $CO_2$ , whilst the carbonates are environmentally inert and non-toxic [18].

There are huge world deposits of natural magnesite ( $\text{MgCO}_3$ ) in the order of 8600 million metric tonnes [19] which have not posed any threat to the environment. The Ministry of Environment in Finland also confirmed that the product magnesium carbonate is not listed as a hazardous waste (Ministry of the Social Affairs and Health Decree 624/2001) – see Appendix 3. Hence, this can be treated as an ordinary waste [20] and it can be used in other applications for which the product is suitable.

The use of (cleaned) magnesite has been documented in many sectors including, as filler materials for paint, paper and plastics, brick manufacturing, fertilizer production, ceramics, and also as a fire retardant [19]. Hence, it is necessary to find out how clean the product from our reaction ( $\text{R1} + \text{R2}$ ) will be, which will determine its further use as a raw material for some process. It is quite promising that serpentine waste and tailings can be used, for example, to produce anhydrous  $\text{MgCl}_2$  (releasing  $\text{CO}_2$  at the same time) which is then fed into the Alcan Multi Polar Cell to produce magnesium metal. This type of raw material is used by the Magnola Magnesium Plant located in Danville (Quebec) Canada, where over 50 000 metric tonnes of magnesium is produced annually [21]. Hence, the production viability of magnesium from serpentine waste products and its economy should also be evaluated in the Nordic countries. But still today, there is no environmental impact assessment study on the carbonation method for  $\text{CO}_2$  emission reduction, which is required to understand any environmental impact from the product of this carbon sequestration method before any waste handling plan is set up.

## 1. Part III : Mineral carbonation at a power plant; economic aspects

### 4.1 Mineral carbonation large-scale process and plant lay-out

To be able to apply mineral carbonation in large scale the problem of transporting of the mineral or the carbon dioxide must be solved. In Finland the most CO<sub>2</sub> sources are located far away from the mine where the mineral is coming from and the product returns to, preferably. To reduce costs and environmental effects the mineral should be transported as magnesium hydroxide. By extracting Mg(OH)<sub>2</sub> already at the mine the mass to be transported could be decreased by 37% for serpentine and 17% for olivine. Another benefit would be the integration of the extraction of magnesium hydroxide with other, already existing, mining activities. For example at Hitura nickel and copper are mined by Outokumpu Oy. Only a part of the mined ore is economically converted to metals. Huge amounts of ore with a too low metal concentration have to be stored as waste. The base mineral of the ore are various magnesium silicates, so-called serpentinite. A co-production of magnesium oxides and other mining products could make both processes profitable.

The extraction of magnesium oxides from the minerals is also energy intensive. As described the decomposition of the mineral to magnesium oxide, water and quartz requires temperatures above 900°C for serpentine. The wet process, using hydrochloric acid, with MgCl<sub>2</sub> as reaction intermediate, studied at different institutes in the USA during the early 1990's [3,7,9] is even more energy intensive. Although the carbonation process itself is exothermic the extraction of magnesium oxides (decomposition of the mineral) requires energy input. This energy input could be covered by waste heat from other industrial processes, such as metal production. At the same time the magnesium oxide could be used to capture the CO<sub>2</sub> emissions produced by those processes. This concentration of different processes near each other reduces the demand of transportation by almost 100%. At the same time the processes could be integrated into each other to maximize the efficiency of energy use.

Studies have not addressed processes at power plants yet. So far the attention has gone to combining mining activities for non-ferrous metals with possibilities to extract MgO from serpentine or serpentinite minerals.

### 4.2 Economic aspects

No economic evaluations were made at this point.

## 2. Conclusions and future work

### 2.1 Conclusions August – December 2001

From the Finnish point of view mineral sequestration seems to be the most suitable if not the only possibility to reduce the CO<sub>2</sub> emissions, especially if Finland doesn't shift its energy policy towards nuclear power. A reduction of about 5% CO<sub>2</sub> emissions would be enough to decrease CO<sub>2</sub> 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. The Hitura serpentinite deposit mentioned above could fixate all the CO<sub>2</sub> from a 500 MW<sub>elec</sub> coal-fired power plant for approximately 15 years (assuming complete conversion of MgO to MgCO<sub>3</sub>).

At a mineral carbonation efficiency of 100% for each ton of CO<sub>2</sub>, 2.18 tons of mineral serpentine would be required. To capture the CO<sub>2</sub> released by the Salmisaari power plant at least 2 Mt serpentine would be required per year. A 5 % reduction in CO<sub>2</sub> 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<sub>2</sub> 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 the direct carbonization of a rather pure mineral serpentine and a rather pure magnesium hydroxide have been tested. Earlier, isothermal tests with serpentine 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 level of carbonation after a relatively long time. Tests with a magnesium hydroxide sample showed a catalytic effect of H<sub>2</sub>O, whilst no significant effect of O<sub>2</sub> is found, when added to a CO<sub>2</sub>/N<sub>2</sub> mixture.

A kinetics analysis showed, for this sample at a total pressure of 1 bar, a maximum conversion rate at a temperature around 350°C, above which thermodynamics become unfavourable, and below which the carbonation rate

decreases. It is concluded that, at 1 bar, mineral carbonation should be carried out at this temperature optimum, which is slightly affected by the flue gas composition.

The effect of pressure (15 or 20 bar, with 15 vol-% CO<sub>2</sub> in the gas) could not yet be quantified since the release of H<sub>2</sub>O from the serpentine and Mg(OH)<sub>2</sub> samples during heat-up is accompanied by other effects that change the mass of the sample.

If direct carbonation is possible with Finnish magnesium silicate minerals it will certainly need a catalyst to reach reasonable conversions within a realistic timeframe. The first results with small amounts of NaCl, NaHCO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> added to Mg(OH)<sub>2</sub> did not show an improvement, however.

## 2.2 Future work January – May 2002

According to the time table, the second half of the kinetic tests will be carried out, the analysis of mineral resources and carbonated mineral disposal will be finalised. The major attention will go to a suggestion for a large-scale process at a power plant or steel works, and/or a process for carbonation at a mineral deposit to which CO<sub>2</sub> is transported by pipe-line. Fuel type, plant type and plant size -related as well as economic aspects will be included.

## 6. References Part 1

- [1] Helsingin Energia, Environmental report 1999 (*in Finnish*). Helsinki, Art print Oy. Feb. 2000. 35p.
- [2] Goff, F., and Lackner, K. S. "Carbon dioxide sequestering using ultramafic rocks" *Environmental Geosciences* 5(3) (1998) 89-101
- [3] Ziock, H. "Zero emissions coal to hydrogen" <http://www.lanl.gov/energy/ziock.html> (2000)
- [4] Lackner, K., Ziock, H. "From low to no emissions" *Modern Power Systems*, 20(3) (2000) 31-32
- [5] Barnes, V. E., O'Neil, J. R., Rapp, J. P., White, D. E. "Silicarbonate alteration of serpentine: Wall rock alteration in mercury deposits of the California Coast Ranges". *Econ. Geol.* 68 (1973) 388-398.
- [6] O'Hanley, D. S. "Serpentinites: Records of tectonic and petrological history". *Oxf. Monogr. Geol. Geophys.* 34 (1996) 277 pp.
- [7] Walters, R.P., Chen, Z-Y., Goldberg, P., Lackner, K., McKelvy, M., Ziock, H. "Mineral carbonation: a viable method for CO<sub>2</sub> sequestration" <http://www.fetc.doe.gov/products/gcc> (1999)
- [8] Goldberg, P., Chen, Z-Y., O'Connor, W., Walters, R., Ziock, H. "CO<sub>2</sub> mineral sequestration studies in US" *Proceedings of the First National Conference on Carbon Sequestration*, May 14-17, 2001, Washington, DC (2001) session 6C <http://www.fetc.doe.gov/events/01conferences/carbseq/carbseq01.html>
- [9] O'Connor, W.K. *et al.*, "Carbon dioxide sequestration by direct mineral carbonation: results from recent studies and current status", *ibid.* (2001)
- [10] Newall, P.S., *et al.* "CO<sub>2</sub> storage as carbonate minerals", report PH3/17 for IEA Greenhouse Gas R&D Programme, Cornwall (UK) 2000
- [11] Kohlmann, J. "The removal of CO<sub>2</sub> from flue gases using magnesium silicates, in Finland" Report TKK-ENY-3, Helsinki University of Technology, Finland (2001)
- [12] HSC 4 Chemistry for Windows, Outokumpu Research Oy, Pori (Finland) 1999
- [13] <http://webmineral.com/data/> (February 14, 2001)
- [14] <http://www.outokumpu.com/mining/> (March 28, 2001)
- [15] <http://www.gsf.fi/> (January 18, 2001)
- [16] Goff, F., Guthrie, G., Lipin, B., Fite, M., Chipera, S., Counce, D., Kluk, E., Ziock, H. "Evaluation of ultramafic deposits in the eastern United States and Puerto Rico as sources of magnesium for carbon dioxide sequestration". Los Alamos National Laboratory, New Mexico, LA-13694-MS, 2000, 1-36.
- [17] Isomäki, O.-P., Outokumpu Mining Oy, personal communication, October 9, 2001
- [18] Ziock, H.-J, Butt, D. P., Lackner, K. S., Wendt, C. H. "The need and options available for permanent CO<sub>2</sub> disposal". Presented at: 1998 Topical Conference on Pollution Prevention and Environmental Risk Reduction, Nov 15-20, 1998, Miami Beach (FL), 1999, 7 pp.
- [19] Mineral Council of Australia. [http://www.minerals.org.au/pages/page3\\_41.asp](http://www.minerals.org.au/pages/page3_41.asp)
- [20] Häkkinen, E., Ministry of the Environment of Finland, Helsinki, personal communication October 16, 2001
- [21] Noranda. "The production of magnesium by Noranda", Magnola Metallurgy Inc., Quebec, Canada, 2001. pp.1-23.

## Appendix 1 Experimental plan for thermogravimetric analyses

In the table below the input parameter of interest is printed **boldface**

Test #	1	2	3	4	5	6	7	8	9	10	11	12	13
<b>Experiment done</b>	*	*	*	*	*	*	*	*	*	*	*	*	*
VTT Energy test #	1853	1854	1855	1856	1863	1857	1878	1879	1877	1884	1882	1880	1881
<b>Sorbent, mg</b>													
Serpentine													<b>30</b>
Mg(OH) <sub>2</sub>	<b>300</b>	297	297	297	300	300	300	300	300	297	300	297	270
Al <sub>2</sub> O <sub>3</sub>			<b>3</b>										
NaCl		<b>3</b>											
NaHCO <sub>3</sub>				<b>3</b>									
CaCO <sub>3</sub>												<b>3</b>	
Final mass of sample							211	214	211	211	210	213	217
<b>Gas composition</b>													
CO <sub>2</sub> %-vol	15	15	15	15	15	15	15	15	15	15	15	15	15
N <sub>2</sub> %-vol	85	85	85	85	rest	85	85	85	80	75	80	85	85
H <sub>2</sub> O %-vol									<b>5</b>	<b>5</b>			
SO <sub>2</sub> ppm-vol					<b>488</b>								
O <sub>2</sub> %-vol										<b>5</b>	<b>5</b>		
HCl ppm-vol													
<b>Temperature</b>													
constant °C													
up/down: minimum °C	100	100	100	100	100	100	<b>200</b>	200	200	200	200	200	200
heating rate, K/min	50	50	50	50	50	50	50	50	50	50	50	50	50
up/down: maximum °C	1000	1000	1000	1000	1000	1000	1000	<b>600</b>	1000	1000	1000	1000	1000
time at max. T, min	10	10	10	10	10	10	10	10	10	10	10	10	10
cooling rate, K/min	10	10	10	10	10	10	10	10	10	10	10	10	10
<b>Pressure, bar</b>	1	1	1	1	1	<b>20</b>	1	1	1	1	1	1	1
<b>Test #</b>	1	2	3	4	5	6	7	8	9	10	11	12	13

The experimental plan for tests 14 - 25 has not been made yet, and will depend on further analysis of the results from tests 7 – 13 (received January 4, 2002).

## Appendix 2 Mineral map from Geological Survey of Finland, 3.10.01

### Ultramafic rocks of Finland

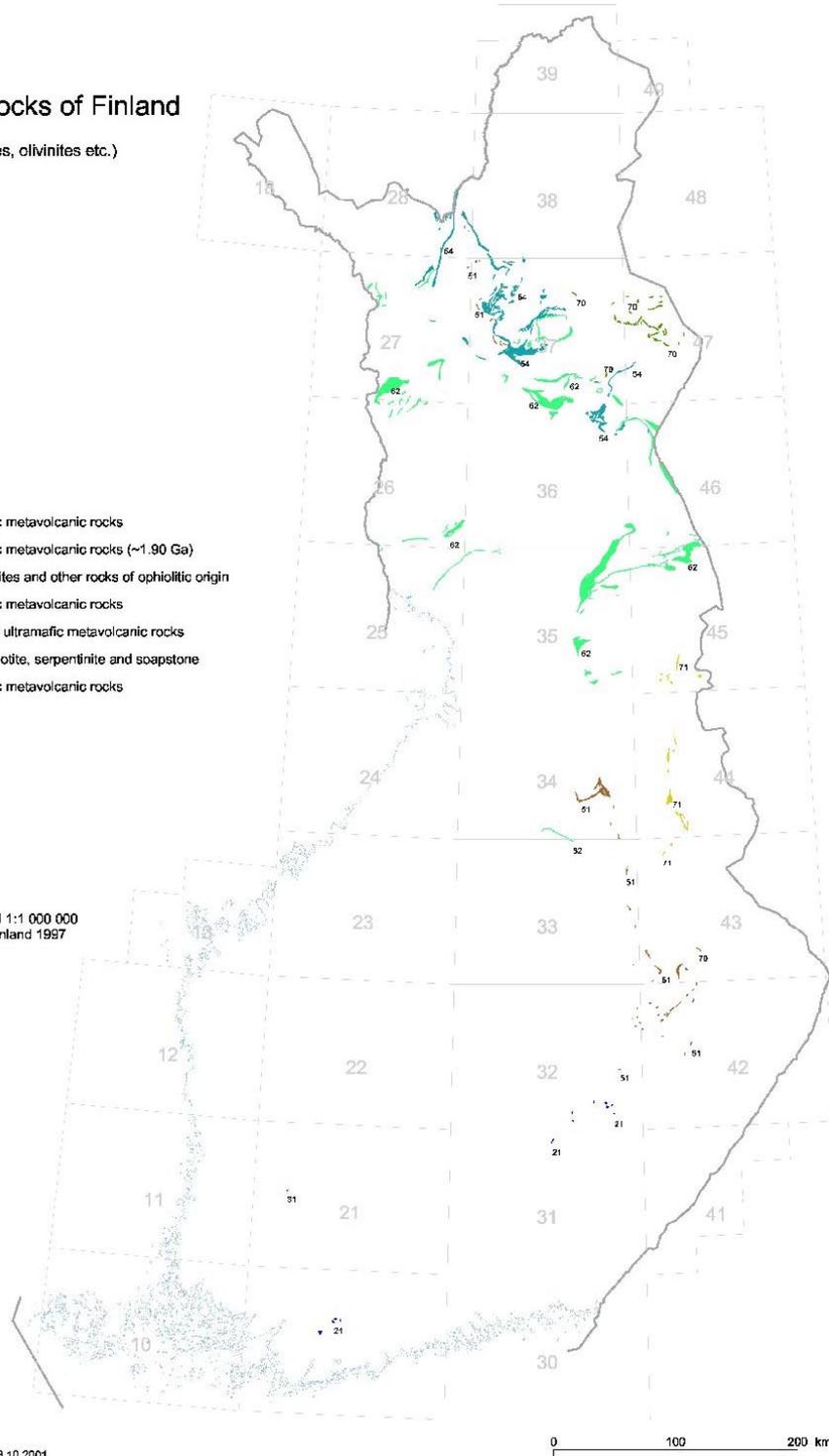
(serpentinites, olivinites etc.)

- 21 Ultramafic metavolcanic rocks
- 31 Ultramafic metavolcanic rocks (~1.90 Ga)
- 51 Serpentinites and other rocks of ophiolitic origin
- 54 Ultramafic metavolcanic rocks
- 62 Mafic and ultramafic metavolcanic rocks
- 70 Metaperidotite, serpentinite and soapstone
- 71 Ultramafic metavolcanic rocks

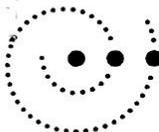
Source data :  
Bedrock map of Finland 1:1 000 000  
Geological Survey of Finland 1997



GTK A.Lindh 03.10.2001



## Appendix 3 Letter from Finnish Ministry of the Environment, 16.10.01



MINISTRY OF THE ENVIRONMENT

Date

Dr. No.

16 October 2001

Mr. Arun B. Mukherjee  
Department of Limnology and Environmental Protections  
P.O. Box 62  
FI-00014 University of Helsinki

**Ref: Your letter dated 1 October, 2001**

Dear Mr. Mukherjee,

Referring to your letter concerning the classification of  $MgCO_3$  and  $SiO_2$ , please find below some information on the waste classification and licencing of waste management operations in Finland as well as on imports and exports of waste.

### *Principles of the waste classification*

The definition of hazardous waste is given in Section 3 (3 §) of the Waste Act (1072/1993), and it has been further defined in Section 3a of the Waste Decree (1390/1993). According to this Section 3a, a waste is considered to be hazardous if it is referred as hazardous in the list of the most common wastes and hazardous wastes. The waste list currently in force is given in Ministry of the Environment Decision No. 867/1996. This waste classification is legally binding. The regional environmental centre may decide in an individual case that a waste classified in the list as hazardous is not hazardous if the holder of the waste can reliably demonstrate that the waste in question does not have any of the hazardous properties listed in Annex 4 of the Waste Decree, or that other waste is also hazardous if the waste has any of the hazardous properties listed in Annex 4.

The hazardous properties listed in Annex 4 of the Waste Decree (see annex) are based on the EC Council Decision on hazardous waste (91/689/EC). These hazardous properties are further defined by a reference to the Finnish chemicals legislation (the present decisions in force are Ministry of the Social Affairs and Health Decrees 807/2001 and 624/2001).

The basic classification principle is that if the waste contains (over a certain limit value) substances that are classified as hazardous under the chemicals legislation the waste is considered as a hazardous waste, taking also into account its classification in the aforementioned list of the most common wastes and hazardous wastes.

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Neither  $MgCO_3$  nor  $SiO_2$  is mentioned as such in the list of the most common wastes and hazardous wastes. According to the information received from you the process producing the waste is treatment of flue gas, and I assume the waste producing sector would be power stations and other combustion plants.

In the present list of wastes entry

10 01 06 "other solid wastes from gas treatment"

could to my opinion describe the waste most closely. That entry is not considered as hazardous waste. However, the list of wastes and hazardous wastes is going to be changed in the near future. The new classification is based on the recent changes in the EC list of wastes and hazardous wastes (Commission Decisions 2000/532/EC, 2001/118/EC, 2001/119/EC and Council Decision 2001/573/EC). EC Member States have to implement the new classification from 1 January 2002. In Finland the new classification will be implemented by a new Ministry of the Environment Decree on the list of the most common wastes and hazardous wastes which will repeal the present Decision No. 867/1996.

According to the new EC classification there are both hazardous and non-hazardous entries for wastes from treatment of flue gas from power stations and combustion plants. These entries are:

10 01 18\* "wastes from gas cleaning containing dangerous substances" (hazardous)  
 10 01 19 "wastes from gas cleaning other than those mentioned in [10 01 05, 10 01 07 and] 10 01 08" (non-hazardous)

When deciding to which one of these entries  $MgCO_3$  and  $SiO_2$  belong to one has to use the classification criteria given in the chemicals legislation. In the present list of dangerous substances (Ministry of the Social Affairs and Health Decree 624/2001) neither of the substances in question are mentioned. However, that does not necessarily mean they would be non-hazardous, they just might not yet have been classified by the relevant EC body. When I did a preliminary search on the internet about the properties of these substances I found some indication of both having health hazard qualities.  $MgCO_3$  n-hydrate is considered as an irritant (EC chemicals classification R36, R37, R38). According to the chemicals legislation, the limit value for such substances is 20 %.  $SiO_2$  causes pulmonary fibrosis (silicosis) and is possibly carcinogenic in powder form. In the chemicals legislation, limit value for a substance known to be carcinogenic of category 1 or 2 is 0,1 % and of category 3, 1 %.

Since these substances are not specifically classified in the list of dangerous substances it is not possible to make a definite classification without more detailed information of the waste and a search from various information sources for the health properties of the material. Further assistance on the possible classification according to the criteria in the chemicals legislation can be received from the Chemicals Information Service

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(kemikaalitietopalvelu) in the Finnish Environment Institute. The service is chargeable (tel. (09) 4030 0593 telefax (09) 4030 0591, e-mail: KemInfo@vyh.fi).

#### *Requirements for disposal of waste on landfills*

The requirements for the disposal of waste on a landfill are given in the Government Decision on landfills (No. 861/1997). The provisions are based on the EC Council Directive 1999/31/EC. The Government Decision sets general requirements for the location and structure of the site, as well as for the procedures on acceptance of wastes at landfills. One basic principle in the Decision is that hazardous waste may only be placed on a landfill which is designed and licenced to operate as a hazardous waste landfill. Detailed requirements on what kind of waste can be accepted at a certain landfill site are set in the facility's environment permit issued by the regional environment centre, in accordance with the Environment Protection Act (No. 86/2000) and Environment Protection Decree (169/2000).

#### *Use of waste as raw material*

Besides final disposal, also recycling, recovery and storage of waste on a professional basis need an environment permit. According to the Section 15 of Waste Act (1072/1993) the waste holder may deliver waste only to such receiver that has necessary licences in accordance with the legislation. Therefore, before waste can be sent to any facility for recycling, recovery or disposal the holder of the waste must ascertain that the receiving factory is licenced to treat such waste in its processes.

#### *Shipments of waste to other countries*

The transfrontier shipments of waste are regulated by the EC Council Regulation 259/93 (amended by 120/1997 and 1999/816/EC). The Regulation is directly applicable in all EC Member States and it gives detailed provisions on the necessary licences required for such shipments. The basic principle is that all transfrontier shipments of waste need a licence, with the exception of shipments of certain non-hazardous wastes for recovery; these wastes are explicitly listed in Annex II of the Regulation. Since  $MgCO_3$  and  $SiO_2$  are not mentioned in Annex II their export will need to be notified to the authorities and authorised by them.

The notification is made to the competent authorities of all concerned countries, that is the countries of export, import and transit. Each of these authorities will give their decision independently and the shipment is allowed only if all competent authorities consent to it. The shipments shall be based on a written contract fulfilling certain criteria set in the Regulation, and covered by financial guarantee that can be used by the authorities to return the waste into the country of origin if the waste is not treated as planned in the country of import.

The shipments of all hazardous waste to non-OECD countries are prohibited. Shipments of non-hazardous waste for recovery in non-OECD countries may be accepted if the

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recovery operation is environmentally sound. Shipments of hazardous waste for recovery in other OECD countries may be accepted if the facility is licenced to recover such waste and the shipment fulfils certain other criteria. Shipments of waste for final disposal are prohibited to all other countries except EU Member States, Norway, Switzerland, Lichtenstein and Iceland. Also, the competent authorities have much wider possibilities to object to the intended shipments for final disposal than for recovery. Shipments for disposal can be objected on the basis of proximity and self-sufficiency in waste management.

In Finland the rules for consenting or objecting to a transfrontier movement have been further stipulated in Government Decision on the part of the National Waste Plan concerning transfrontier waste movements (No. 495/1998). According to that plan, a certain waste may be shipped from Finland for final disposal to another country if Finland does not have the technical means or capacity to treat the waste, if the facility in another country uses more advanced technology, if the technology is at least as good as in Finland but essentially cheaper, if small amount of waste is shipped for testing a new treatment method, or (in case of non-hazardous waste) the waste shipment is part of municipal waste management co-operation between Finland and Sweden or Finland and Norway.

*Sources of further information*

The competent authority for transfrontier shipments of waste in Finland is the Finnish Environment Institute (contact persons: Mr Ulrich Jeltsch, tel. (09)4030 0543, Mr. Kenneth Holm (09)4030 0544 and Ms. Tuulia Innala tel. (09)4030 0542). They can also assist you to contact the competent authorities in other countries.

Contact information of all regional environment centres can be found from the internet address <http://www.vyh.fi/aluek.htm>.

Finnish national legislation can be obtained from the Ministry of Justice legislation database FINLEX on the internet address [www.finlex.fi](http://www.finlex.fi).

I hope this gives you a general idea of the relevant legislation. Should you have any further questions, please contact me again.

Sincerely,



Eevaleena Häkkinen  
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**Annex 4 of Waste Decree 1390/1993**

Liite 4

**OMINAISUUDET, JOIDEN PERUSTEELLA JÄTTEET LUOKITELLAAN  
ONGELMAJÄTTEIKSI \***

- H1 Räjähävä:** aineet ja valmisteet, jotka voivat räjähtää liekin vaikutuksesta tai jotka ovat dinitrobentseeniä herkempiä iskuille tai hankaukselle.
- H2 Hapettava:** aineet ja valmisteet, jotka voivat aiheuttaa voimakkaasti lämpöä vapauttavan reaktion muiden, erityisesti syttyvien aineiden kanssa.
- H3-A Helposti syttyvä:**
- nestemäiset aineet ja valmisteet, joiden leimahduspiste on alle 21oC mukaan lukien erittäin helposti syttyvät nesteet,
  - aineet ja valmisteet, jotka voivat kuumentua ja syttyä itsestään palamaan ilmassa ympäristön lämpötilassa ilman energian lisäystä,
  - kiinteät aineet ja valmisteet, jotka voivat välittömästi syttyä palamaan jouduttuaan lyhytaikaisesti kosketuksiin sytytyslähteen kanssa ja jotka jatkavat palamista tai kytemistä sytytyslähteen poistamisen jälkeen,
  - kaasumaiset aineet ja valmisteet, jotka voivat syttyä ilmassa normaalipaineessa tai
  - aineet ja valmisteet, jotka veden tai kostean ilman vaikutuksesta muodostavat vaarallisia määriä helposti syttyviä kaasuja.
- H3-B Syttyvä:** nestemäiset aineet ja valmisteet, joiden leimahduspiste on yhtä suuri tai suurempi kuin 21oC ja pienempi tai yhtä suuri kuin 55oC.
- H4 Ärsyttävä:** aineet ja valmisteet, jotka eivät ole syövyttäviä, mutta voivat aiheuttaa tulehduksen välittömässä, pitkäaikaisessa tai toistuvassa kosketuksessa ihon tai limakalvojen kanssa.
- H5 Haitallinen:** aineet ja valmisteet, jotka hengitettynä tai nieltynä tai ihon kautta imeytyneinä voivat aiheuttaa haittaa terveydelle.
- H6 Myrkyllinen:** aineet ja valmisteet mukaan lukien erittäin myrkylliset aineet ja valmisteet, jotka hengitettynä tai nieltynä tai ihon kautta imeytyneinä voivat aiheuttaa vakavan akuutin tai kroonisen terveydellisen haitan tai kuoleman.

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**H7 Syöpää aiheuttava:**

aineet tai valmisteet, jotka hengitettynä tai nieltynä tai ihon kautta imeytyneinä voivat aiheuttaa syövän tai lisätä sen esiintyvyyttä.

**H8 Syövyttävä:** aineet ja valmisteet, jotka voivat tuhota elävän kudoksen ollessaan kosketuksessa sen kanssa.**H9 Tartuntavaarallinen:**

aineet, jotka sisältävät elinvoimaisia mikro-organismeja tai niiden toksineja, joiden tiedetään tai perustellusti oletetaan aiheuttavan sairauksia ihmisille tai muille eläville organismeille.

**H 10 Lisääntymiselle vaarallinen:**

aineet ja valmisteet, jotka hengitettynä tai nieltynä tai ihon kautta imeytyneinä voivat aiheuttaa muita kuin periytyviä epämuodostumia tai lisätä niiden esiintyvyyttä.

**H 11 Perimää vaurioittava:**

aineet tai valmisteet, jotka hengitettynä tai nieltynä tai ihon kautta imeytyneinä voivat aiheuttaa periytyviä geneettisiä vaurioita tai lisätä niiden esiintyvyyttä.

**H 12** Aineet ja valmisteet, joista vapautuu myrkyllisiä tai erittäin myrkyllisiä kaasuja niiden joutuessa kosketuksiin veden, ilman tai hapon kanssa.**H 13** Aineet ja valmisteet, joista voi käsittelyn jälkeen syntyä toista ainetta, kuten suotonestettä, jolla on jokin yllä luetelluista ominaisuuksista.**H 14 Ympäristölle vaarallinen:**

aineet ja valmisteet, jotka aiheuttavat tai voivat aiheuttaa välitöntä tai viivästynyttä vaaraa ympäristölle.

\* Tämän liitteen kohdassa 1, 2, 3-A, 3-B, 4, 5, 6, 7, 8, 10, 11 ja 14 mainitut ominaisuudet määritellään tarkemmin kemikaalien luokitusperusteista ja merkintöjen tekemisestä 30 päivänä heinäkuuta 1993 annetun sosiaali- ja terveysministeriön päätöksen (739/93) perusteella.

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## **Part 2 :**

### **Progress report January – May 2002**

**(report date June 7, 2002)**

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# 1. Introduction

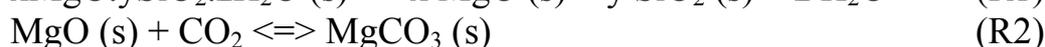
## 1.1 Objectives and scope

The energy statistics for Finland for year 2001 show that the total emissions of carbon dioxide from combustion of fossil fuels and peat were around 60 million tonnes [1]. This is 11% higher than the 54 million tonnes that were emitted in 1990. In order to comply with Finland's commitments to the 1997 Kyoto protocol, Finland aims at reducing the consumption of coal and oil in favour of that of natural gas, peat and wood. Other measures that reduce CO<sub>2</sub> emissions are increased use of renewable energy sources and improved efficiency of thermal processes. And recently a small majority of Finnish parliament voted for the construction of a fifth nuclear reactor in Finland.

Nevertheless, these changes may not prevent that active measures are needed to further reduce Finland's carbon dioxide emissions in the future. Partly this may be accomplished by CO<sub>2</sub> sequestration, *i.e.* the removal of CO<sub>2</sub> from flue gases followed by long-term storage. Apart from exporting carbon dioxide for storage elsewhere, for example below the seabed of the North Sea, the only option for Finland appears to be mineral carbonation, which implies storage of carbon dioxide in the form of magnesium carbonate (magnesite). Finland appears to have access to large mineral (for example serpentine) resources that may be carbonated. Finland doesn't have deep oceans or exhausted oil or gas fields and improved forestry, biofixation and the utilization of CO<sub>2</sub> will not give 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. 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,  $(\text{Mg,Fe})\text{SiO}_4$ , and serpentine,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . Some other suitable minerals exist in smaller amounts.

The chemistry for this CO<sub>2</sub> fixation can be summarised as



Magnesium carbonate is more stable, thermodynamically, than carbon dioxide, and the overall carbonation reaction (R1+R2) is exothermal: the heat effect is +64 kJ/mol and +90 kJ/mol MgCO<sub>3</sub>, for serpentine and olivine/forsterite, respectively.

Large-scale flue gas CO<sub>2</sub> 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<sub>2</sub> may require 2 kg of serpentine for disposal.

Only a few laboratories 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.* Los Alamos National Laboratory (NM), Columbia University, New York (NY), Albany Research Center at Albany (OR) and Arizona State University at Tempe (AZ) [2-6]. Whilst the research in the USA is concentrating increasingly on wet methods, using aqueous solutions, see reference [7], our research (started in August 2000) at the Helsinki University of Technology (still) aims at dry methods.

Two problems must be solved to make this approach more attractive, as also concluded in a recent feasibility study from the UK [8]:

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

The three major objectives of our studies at the Helsinki University of Technology, for which results are reported in the following chapters, are as follows:

- optimisation of the chemistry of direct, dry, magnesium silicate mineral carbonation, addressing process conditions, flue gas composition and the use of catalysts;
- more detailed mapping of Finland's magnesium silicate mineral resources and the quality of these minerals, and reviewing the aspects of carbonated mineral disposal; and
- progress integration and economic aspects of CO<sub>2</sub> sequestration by mineral carbonation, considering the type and size of fossil fuel-fired power plant and whether to transport mineral or CO<sub>2</sub>.

Considering the last point, there is consensus within the research team in the USA that transportation of mineral to and from a CO<sub>2</sub>-generating site will never be feasible. CO<sub>2</sub> is to be removed from off-gases and transported to a suitable mineral deposit where the carbonation will then take place [9].

## 1.2 Time table (August 2001)

	2001					2002						
	8	9	10	11	12	1	2	3	4	5	6	7
Kick-off meeting	x											
Reaction kinetic tests	x	x	x	x	x	x						
Catalytic influence tests				x	x	x	x	x	x			
Mineral resources			x	x	x	x						
End-product disposal		x	x	x	x	x	x					
Process plant lay-out						x	x	x				
Economic aspects						x	x	x				
Effect of power plant type						x	x	x				
27 <sup>th</sup> Clearwater Conference								x				
Helsinki U of T final report									x			
Climtech final report									x	x	x	

In 2002, a progress meeting was held at Nordkalk Oyj Abp, Helsinki, April 15 (present: RZ, JK, ABM, TK) and the Climtech annual seminar was held at Hanasaari, Espoo, May 15 (present: RZ, ABM, TK).

Results were presented at international conferences in Geneva, Switzerland, in February (RZ), at Clearwater Beach, FL in March (RZ) and in Estoril, Portugal, in April (JK).

Jens Kohlmann is currently with Jaakko Pöyry Oy at Vantaa, but intends to produce his lic. tech. thesis before the end of this year. That will certainly contain additional information that is not yet available while completing this report.

## 2. Part I : Optimisation of mineral carbonation chemistry

The settings for the experiments made in year 2002 are given in Appendix 1. Below, also some tests that were not yet discussed in the previous progress report will be discussed.

### 2.1 Experimental procedure

#### 2.1.1 Test facility

Carbonation reaction kinetics were analysed for fine powered samples of a serpentine and a magnesium hydroxide – see section 2.1.2. These were carbonated at various temperatures and pressures, under various gas mixtures, and with various solid additives to the sample, in a vertical pressurised thermogravimetric analyser (PTGA) at VTT Processes, Espoo. A schematic of this device is shown in Figure 1. Solid sample masses, contained by a sample holder as shown in the figure were of the order of 300 mg. Gas flows were 2 liter<sub>STP</sub>/min plus 3 liter<sub>STP</sub>/min helium purge for the tests at 1 bar. (For the pressurised tests (15 or 20 bar), these were 3 liter<sub>STP</sub>/min plus 6 liter<sub>STP</sub>/min.) Maximum controllable heating/cooling rates in this device were 50 °C/min.

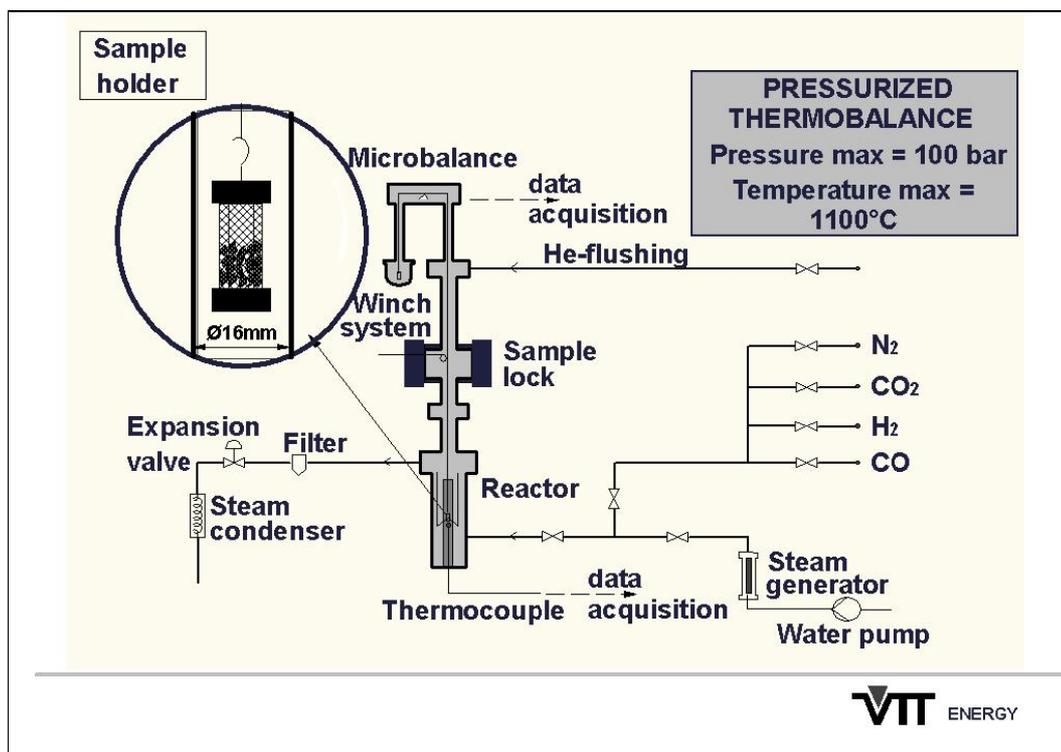


Figure 1 The pressurised thermogravimetric analyser at VTT Processes, Espoo (picture January 2001)

The upwards gas-flow contacting the sample results in an upwards buoyancy force (*in Finnish: "nostovoima"*) that changes the weight signal from the PTGA. The correct mass of the sample can be calculated using mass = PTGA mass signal + buoyancy correction, or  $m = m_{\text{PTGA}} + \Delta m$ . For heat-up and cool-down the buoyancy corrections were determined from a blank run (*i.e.* with empty sample holder) and can be expressed as

$$\Delta m = -7.2308 \times 10^{-6} \times (\phi T)^2 - 1.3385 \times 10^{-2} \times \phi T + 4.8755 \quad (\text{mg}) \quad (R^2=0.9993)$$

and

$$\Delta m = -9.0589 \times 10^{-6} \times (\phi T)^2 - 1.0957 \times 10^{-2} \times \phi T + 4.4600 \quad (\text{mg}) \quad (R^2=0.9986)$$

respectively, with temperature T in K, and pressure correction factor  $\phi$ . For 1 bar total pressure,  $\phi=1$ ; for elevated pressure a pressure correction factor  $\phi$  is given by  $\phi = (\{\text{gas flow in } l_{\text{STP}}/\text{min}\} / \{\text{gas flow in } l_{\text{STP}}/\text{min for 1 bar test}\})^2 / p$ , with p in bar. For test #6 this gives  $\phi = (3/2)^2 / 20 = 0.1125$ .

More detail on PTGA data processing is given in Appendix 3.

### 2.1.2 Magnesium oxide-based mineral samples

The two magnesium oxide – containing samples for which carbonation kinetics were determined were a Finnish serpentine from the Kittilä area in Finnish Lapland (average particle size approx. 50  $\mu\text{m}$ ) and a rather pure magnesium hydroxide sample provided by Nordkalk Oyj Abp (average particle size approx. 20  $\mu\text{m}$ ). Their chemical analyses obtained by wet chemical analysis and X-ray fluorescence (XRF) are given in Table 1.

Table 1 Chemical analysis of the serpentine and magnesium hydroxide samples tested

%-wt, dry	Mg(OH) <sub>2</sub>	Mg	Si	CO <sub>3</sub>	Ca	MgO	SiO <sub>2</sub>	Other
Serpentine #		26.3	18.1	4.41	0.69	43.6 *	38.7 *	12.6*, **
Serpentine ###					5.1 ####	37.1	40.5	17.3
Mg(OH) <sub>2</sub> #	99.7							0.3

\* Assuming all Mg as MgO, all Si as SiO<sub>2</sub> \*\* Pure serpentine contains ~ 13 % bound H<sub>2</sub>O

# Wet chemical analysis ### XRF analysis #### Ca as CaO

The XRF analysis, for which the total result is given in Appendix 2, was made as to get information of the “contaminants” in the serpentine. The XRF analysis shows that the sample contains oxides of magnesium, silicon and calcium, and less than 1 %-wt other oxides. For calcium the XRF exceeds the wet chemical analysis result by an order of magnitude. The LOI (loss on ignition) found with XRF is a mixture of water and carbon dioxide. In the previous report it was assumed (based on the carbonate content) that the serpentine may be a mixture of serpentine (93.8 %) and magnesium carbonate (6.2 %). The XRF suggests, however, that it may also be a mixture of serpentine (91.7 %) and calcium carbonate (8.3 %).

Recalculating the earlier result for serpentine given in the previous progress report, Figure 4, gives the same result: the mass changes of a 93.8% serpentine + 6.2% MgCO<sub>3</sub> sample mass are less than one percent different from those calculated with a 91.7% serpentine + 8.3% CaCO<sub>3</sub> sample. The presence of larger amounts of CaCO<sub>3</sub> in the sample than earlier thought does, however, explain the behaviour in the temperature range 600-800°C: this must be calcination/recarbonation of calcium carbonate/oxide.

## 2.2 Magnesium hydroxide and serpentine carbonation – new results

### 2.2.1 Experiments with magnesium hydroxide at increasing/decreasing temperature - effect of calcination temperature

While the heat-up/cool-down tests, aiming at calcination (giving free MgO) followed by carbonation were made with 1000°C as the maximum temperature, it may be that a lower temperature gives sufficient calcination and at the same time, less sintering of the solid. Thus two tests (#7 and #8) were made where this maximum temperature was 1000°C and 600°C, respectively – the results are given in Figure 2.

The result shows that the calcination is practically complete at 600°C, and that the carbonation performance is identical in the temperature range 600 → 200°C, (corresponding to 40 minutes) giving a carbonation level (increase) of 1.3 %. Both tests show an increasing rate below 300°C, which agrees to the thermodynamics of MgO carbonation and the kinetic rate analysis given in the previous progress report, section 2.2.2.

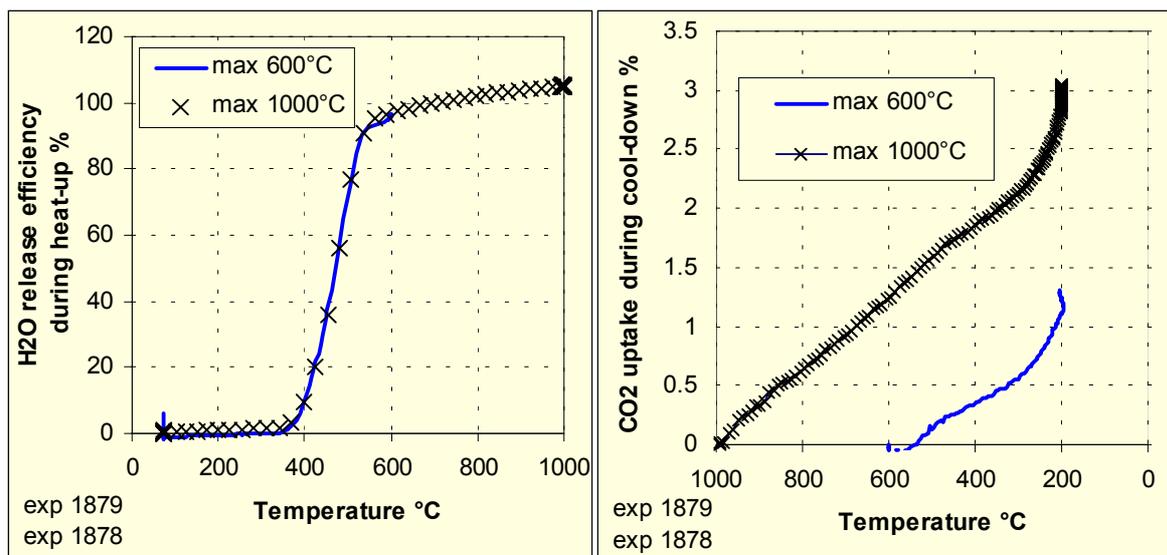


Figure 2 Calcination of  $\text{Mg}(\text{OH})_2$  (left) and carbonation of  $\text{MgO}$  (right) with maximum temperature  $1000^\circ\text{C}$  and  $600^\circ\text{C}$ , respectively. Gas phase  $\text{CO}_2/\text{N}_2$  15%/85%, pressure 1 bar

### 2.2.2 Experiments with magnesium hydroxide at increasing/decreasing temperature - effect of solid additives

The presence of some calcium carbonate,  $\text{CaCO}_3$ , mixed with the magnesium hydroxide will give calcination to calcium oxide,  $\text{CaO}$ , and recarbonation to calcium carbonate, at typically somewhat higher temperatures than  $\text{Mg}(\text{OH})_2$  calcination and  $\text{MgO}$  carbonation. The cross-effects of this were analysed during a test (test #12) with a 99%/1%  $\text{Mg}(\text{OH})_2 / \text{CaCO}_3$  sample, involving heatup (50 K/min) to  $1000^\circ\text{C}$  followed by cool down (10 K/min) to  $200^\circ\text{C}$  in 15%/85%  $\text{CO}_2/\text{N}_2$  at 1 bar. The result is given in Figure 3, which includes the test result obtained with pure  $\text{Mg}(\text{OH})_2$  (test #7).

The results in Figure 3 show no sign of a separate calcination/recarbonation of calcium carbonate/oxide. However, an increased reaction speed is seen during the final stage of the carbonation (right hand Figure) at below  $300^\circ\text{C}$ , with the small amount of calcium present. This may point to a catalytic effect. It should be verified whether this occurs also when the gas contains more gaseous species including  $\text{H}_2\text{O}$ . On the other hand this result is surprising when compared to the puzzling results obtained earlier with similarly small amounts of  $\text{NaCl}$ ,  $\text{Al}_2\text{O}_3$  or  $\text{NaHCO}_3$  mixed with the  $\text{Mg}(\text{OH})_2$  (tests # 2,3 and 4).

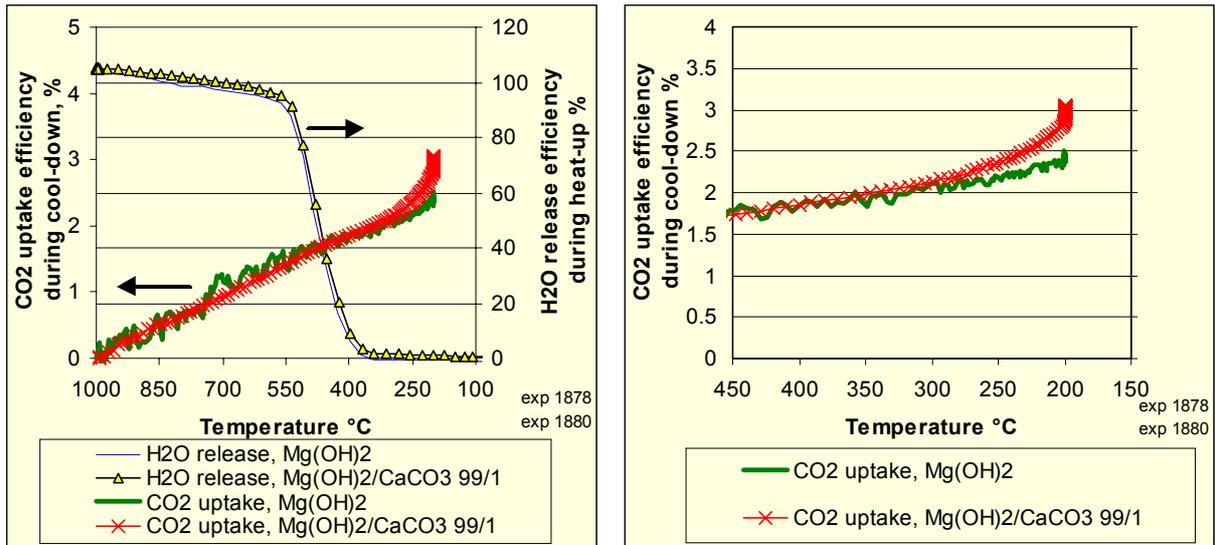


Figure 3 Calcination and carbonation of a  $\text{Mg}(\text{OH})_2 / \text{CaCO}_3$  99% / 1% mix and  $\text{Mg}(\text{OH})_2$ . Gas phase  $\text{CO}_2/\text{N}_2$  15%/85%, pressure 1 bar.

### 2.2.3 Experiments with magnesium hydroxide and serpentine at various temperature levels

Earlier results indicated a maximum carbonation speed at a temperature of around  $350^\circ\text{C}$  (for the magnesium hydroxide sample, at 1 bar) – see previous progress report, Figure 7. Therefore, tests were made with the magnesium hydroxide (test # 14) as well as the serpentine sample (test # 15), at a pressure of 1 bar, following a temperature trajectory as shown in Figure 4a: periods of 45

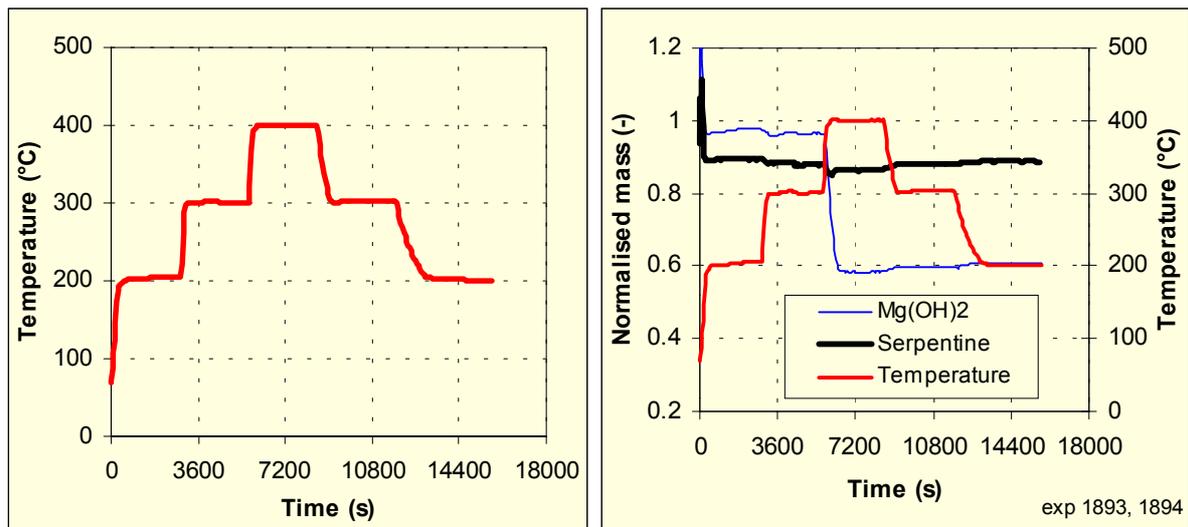


Figure 4 a (left) Temperature trajectory, and b (right) Dimensionless mass (*i.e.* mass/initial mass) and temperature during calcination and carbonation of a  $\text{Mg}(\text{OH})_2$  or serpentine. Gas phase  $\text{CO}_2/\text{N}_2 / \text{H}_2\text{O}/\text{O}_2$  15%/75%/5%/5%, pressure 1 bar.

minutes at three temperature levels with rapid heating/cooling (50 K/min) between them. Although the temperature stays below the level where the water is rapidly released from the sample, mineral carbonation can occur immediately after water release. The results are shown in Figure 4b.

The test with the serpentine shows a negligible change in sample mass (would be, for complete carbonation, 1.28 times the initial mass), with only a small mass loss, apparently due to water release, at 400°C. For the magnesium hydroxide (dimensionless mass for complete carbonation 1.45) the same result is found, be it that the mass loss due to water release is stronger and suggests full calcination of Mg(OH)<sub>2</sub> to MgO. At lower temperatures this is later followed by some carbonation, which is stronger at 200°C than at 300°C. More information may be obtained from analysing the product sample for carbonate content.

#### 2.2.4 Experiments with magnesium hydroxide and serpentine at 350°C, 1 bar.

The direct carbonation of serpentine and magnesium hydroxide at 350°C, 1 bar was analysed for a pure CO<sub>2</sub> gas stream and for CO<sub>2</sub> containing a small amount (1 %-vol) water (water appears to catalyse the MgO carbonation – see previous progress report section 2.2.2). This temperature lies between the higher temperature level where MgO is “set free” by calcination of a magnesium oxide-based material, and the lower temperature where MgO is carbonated. Reaction (R3)



or, more general, reaction



is not thermodynamically very favourable; for reaction (R3) the equilibrium constant, however, at 350°C equals  $K_p = 9.57 \text{ bar}$  [11]. At this temperature the equilibrium constant for reaction



equals  $K_p = 0.297 \text{ bar}^{-1}$ . The results of the three tests (#16, 17, 18) are shown in Figure 5.

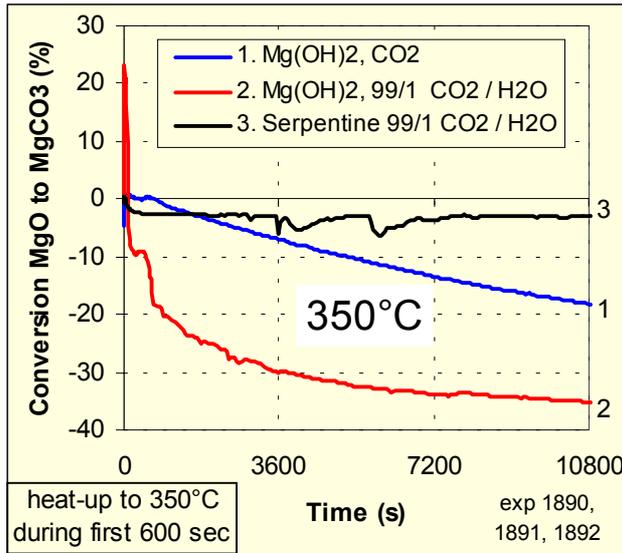
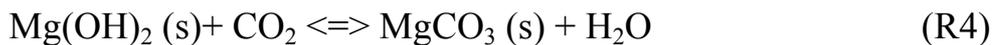


Figure 5 Direct calcination and carbonation of  $\text{Mg}(\text{OH})_2$  and serpentine in 100%  $\text{CO}_2$  and 99%/1%  $\text{CO}_2/\text{H}_2\text{O}$ , at 1 bar, 350°C

These results show negligible, if any, calcination or carbonation of for the serpentine sample. Apparently temperature is too low for activating any of the bound  $\text{MgO}$ , and no carbonation occurs.

For the magnesium hydroxide sample the negative values for both tests in Figure 5 indicate a steady mass loss of the sample. The temperature appears sufficient for calcination reaction (R3), which gives a mass loss, if slow than still at a much higher rate than the carbonation reaction (R2) that would give mass increase. Also shown is a significant effect of the small amount of water present: the mass loss due to calcination reaction (R3) is much faster with 1%  $\text{H}_2\text{O}$  present in the gas. For the test with  $\text{Mg}(\text{OH})_2$ ,  $\text{CO}_2/\text{H}_2\text{O}$  99%/1% it would have been interesting to see whether the mass would eventually increase after a longer time, although 3 hours must be considered too long for technical application.

It may be that a more detailed chemical kinetics model for the reactions (R3) and (R1) gives a value for the reaction rate constants. This is made more difficult by the role of water, which appears to affect not only calcination reaction (R3) but also the carbonation reaction (R2). Alternatively, the combined, direct reaction



should be considered (with, for 350°C, equilibrium constant  $K_p = 2.365$  [11]). Attempts for this will be made when preparing a journal paper on the kinetics of magnesium oxide based carbonation for  $\text{CO}_2$  sequestration.

### 3. Part II : Mineral resources and quality; end-product disposal

#### 3.1 Magnesium oxide-based mineral resources and their quality

Magnesium silicates are often a base component of ores that are mined to produce metals like nickel or gold. The silicates usually exist in mixtures of different silicates [12]. In Finland there are many mining activities, mainly mining for metals (nickel, copper), although also talc and limestone are mined. There are 15 major active mines in Finland of which 9 are found in areas with rich magnesium silicate deposits – see Figure 6 [13]. 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 [14]. The three serpentinite massives at Hitura add up to an estimated 95 million m<sup>3</sup> [15].

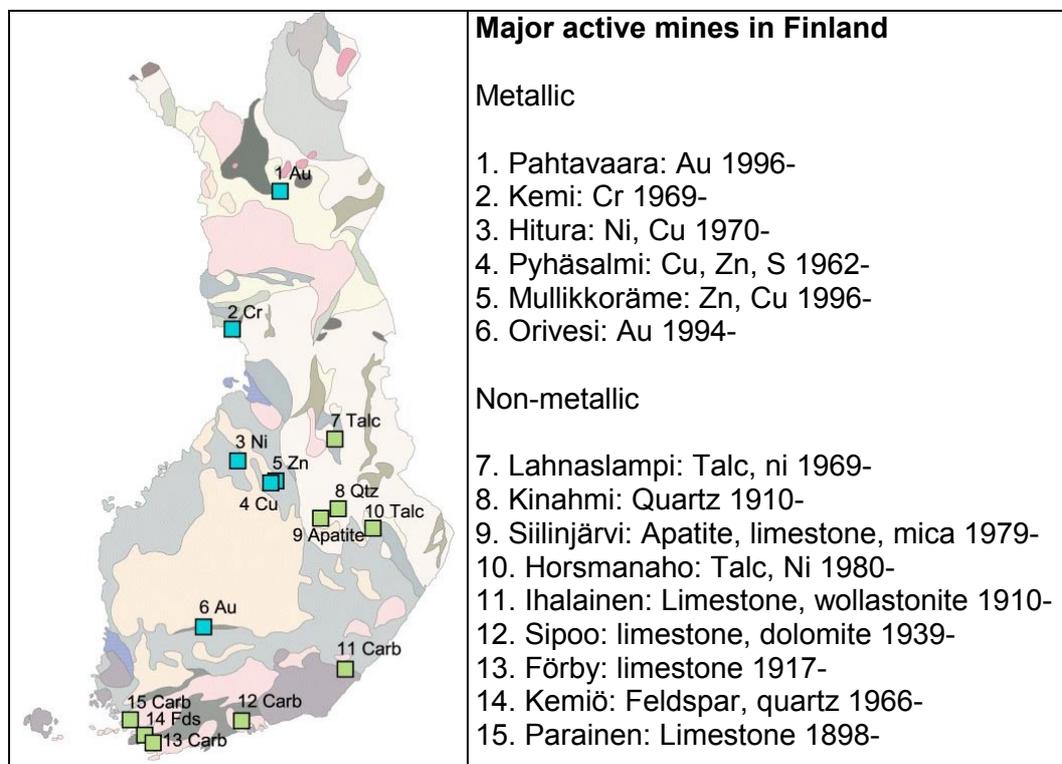


Figure 6 Major active mines in Finland [13]

A mapping of so-called ultramafic mineral, *i.e.* magnesium oxide rich deposits in Finland, made by the Geological Survey of Finland was given in the previous progress report – see also Figure 8. This indicates widespread deposition of ultramafic rocks in the eastern and northern part of Finland. Unfortunately, without knowledge on the depth of the ultramafic rock, the total volume cannot be estimated.

### 3.2 Disposal and use of the end-products from mineral carbonation

Magnesium carbonate produced by carbonation of magnesium oxide-based mineral is environmentally stable, in fact thermodynamically more stable than CO<sub>2</sub>. This may be an important factor when considering the public acceptance of this route for CO<sub>2</sub> emissions reduction. It gives permanent storage space for CO<sub>2</sub>, whilst the carbonates are environmentally inert and non-toxic [16]. Huge world deposits of natural magnesite (MgCO<sub>3</sub>) in the order of 8600 million metric tonnes [17] have not posed any threat to the environment. The Ministry of Environment in Finland also confirmed that the product magnesium carbonate is not listed as a hazardous waste (Ministry of the Social Affairs and Health Decree 624/2001) – see Appendix 3 of the previous progress report. Hence, this can be treated as an ordinary waste [18] and it may be used in other applications for which the product is suitable.

## 4. Part III : Mineral carbonation at a power plant; economic aspects

### 4.1 Mineral carbonation large-scale process and plant lay-out

Although mineral carbonation is an overall exothermic reaction, it does require energy input, not only the process itself, but also for the transportation of the materials or the gas (air, CO<sub>2</sub>). To estimate the environmental impact and the economics of mineral carbonation, three basic possibilities can be compared. In the base case CO<sub>2</sub> is captured (separated from flue gases) and transported via pipeline to the carbonation plant. For transportation the gas has to be pressurized to 60-100 bar (based on natural gas transport in pipelines). The CO<sub>2</sub> separation itself is relatively easy, because of the high CO<sub>2</sub> contents in flue gases (up to 25%).

The second option is the transport of the required mineral to the CO<sub>2</sub> source. In this case a pre-treatment of the mineral (Mg(OH)<sub>2</sub> production) is required to reduce the mineral mass. After carbonation the product (mainly MgCO<sub>3</sub>) has to be returned to where the mineral came from or to another suitable site (preferable old mines).

An alternative option for CO<sub>2</sub> transport is the CO<sub>2</sub> capture from air in the atmosphere. In this case the transport doesn't introduce costs or environmental influences. The problem is the low efficiency of CO<sub>2</sub> separation, because of a low content of carbon dioxide in the air (approximately 0.04 %). In all three options the costs of CO<sub>2</sub> separation and the carbonation process were not taken into account, because they are so far too difficult to estimate reasonably.

To get an idea of the ecological and economic consequences of the different options, two cases have been studied: The Meri-Pori power plant at the west coast of Finland and the Rautaruukki Raahe steel plant. For comparison also some data of plants of different industry branches has been collected (pulp and paper, metal).

#### 4.1.1 Case Meri-Pori

Meri-Pori (Figure 7) is a condensing power plant at the west coast of Finland (see also Figure 8). Electrical power output is about 590 MW. For cooling in the condensing cycle 14,5 m<sup>3</sup> of water per second are needed. The plant (when operated 8000 h/year) consumes about 1,2 million tons of Polish coal per year with a carbon content of about 74%. This results in 2,8 million tons of CO<sub>2</sub> per year (770 kg/MWh<sub>e</sub>).



Power generation	590 MW
Efficiency	43,1%
Fuel demand	1,195 Mt/a
CO <sub>2</sub> emissions	2,8 Mt/a
CO <sub>2</sub> emissions of material transport	12500 t/a

Figure 7 The Meri-Pori power plant and its technical data (for 8000 h/year operation) [19].

The fuel is transported by ship from Poland to Finland. The distance of the power plant to the closest available source of magnesium silicates (Hitura mine) is about 300 km. To be able to compare the different transportation options, the amount of required mineral has been calculated assuming an ideal carbonation efficiency of 100%. For the transportation of mineral, the required mass (mineral as well as pure magnesium hydroxide) was transferred into the required amount of lorry loads of mineral (see Table 2). The mass load of one lorry is approximately 35 tons [20].

Table 2: Required mineral mass and amount of carbonation products as well as resulting amount of lorry loads per year assuming 100% carbonation efficiency (Polish coal, 8000 h/ year operation).

Demand [t]	Per t <sub>CO2</sub>	Per t <sub>coal</sub>	Lorries per year
Serpentine	2,100	5,691	194310
Mg(OH) <sub>2</sub>	1,325	3,593	122676
<b>Product [t]</b>			
MgCO <sub>3</sub> + SiO <sub>2</sub>	2,823	7,663	261624
MgCO <sub>3</sub>	1,912	5,195	177372
<b>For comparison</b>			
Coal			34143
Other pollution abatement materials			997

The required amount of pure  $Mg(OH)_2$  is about 3,5 times the mass of consumed fuel (see Table 2). The calculation of the additional  $CO_2$  emissions caused by the transportation was based on the data for the coal transport. The return of the products to the mine is taken into account as well (Table 3). The  $CO_2$  emissions caused by the transport of serpentine and its carbonation product are about 10% of the  $CO_2$  emissions of the power plant itself.

Table 3:  $CO_2$  emissions for railroad transport of minerals and carbonation products.

<b>Demand [t]</b>	<b><math>CO_2</math> emissions from railroad transport per year (estimated)</b>
Coal	12500
Serpentine	165000
$Mg(OH)_2$	110000

The carbon dioxide transport via pipeline has the advantage of a one-way transport. The carbonation products won't have to be transported, but could be deposited near the carbonation facility. Still the transport is connected to additional costs and environmental effects. The main environmental problems are caused by the construction of large on-shore pipelines. The use of pipelines results in  $CO_2$  emissions by the use of energy for compression and pumping. A small part of the  $CO_2$  may leak into the environment. The transport of large amounts of compressed  $CO_2$  carries also the risk for large-scale accidents.

The costs for the use of  $CO_2$  pipelines was estimated by Norwegian companies for the return of separated  $CO_2$  to gas fields (Table 4) [21].

Table 4:  $CO_2$  transportation via pipeline, volume and costs

$CO_2$ emissions	2,8 Mt $CO_2/a$
$CO_2$ volume flow	1542,492 $Mm^3n CO_2/a$
Distance to serpentine mines	300 km
Approximate costs	0,2 c/kWh (73 M\$/a)

#### 4.1.2 Case Raahe steel plant

The Raahe steel factory is located at the west coast, about 100 km from the Hitura mine (Figure 8). In this plant fossil fuel (coal, oil, liquified gas) is used for the production of steel. The annual emissions of CO<sub>2</sub> are approximately 5 million tons (about 1,8 ton/ton of steel). The plant is designed for a recovery of about 1/3 of the used energy.

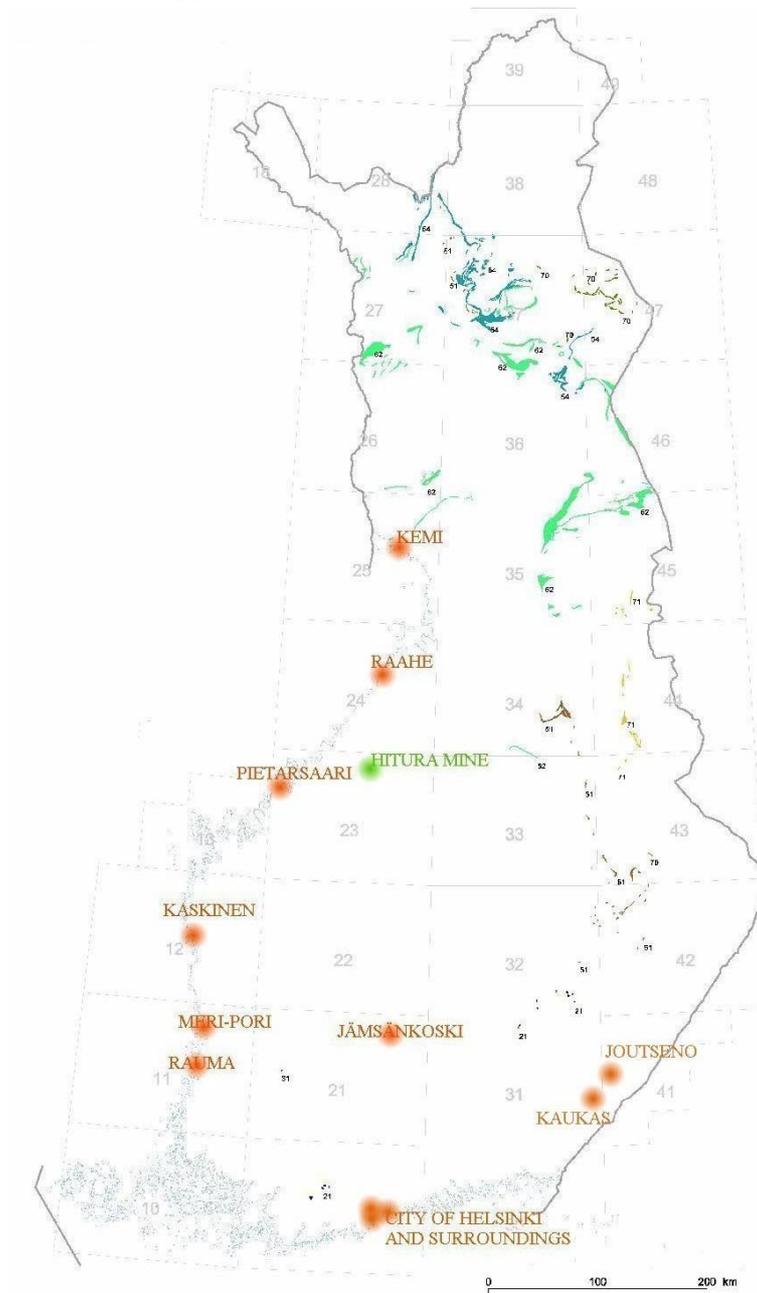


Figure 8 Location of important CO<sub>2</sub> sources in Finland, and Hitura mine

Table 5 shows the approximate costs and emissions calculated for mineral carbonation with an efficiency of 100% [22], [23].

Table 5: Emissions and required mineral for Raahe steel plant.

CO <sub>2</sub> emissions	5 Mt/a
Required Mg(OH) <sub>2</sub>	6,6 Mt/a
Carbonation product	5,2 Mt/a

#### 4.1.3 Case pulp and paper industry

The pulp and paper industry is an important energy consumer in Finland. A large share of the used energy is generated in in-house power plants using non-fossil fuel, like bark and black liquor, a rest product of the pulping process. Although the fuel is non-fossil, the capture of “green” (*i.e.* greenhouse effect neutral) CO<sub>2</sub> from pulp and paper factories is an option. Emission factors are higher for biomass fuel and black liquor, and the flue gases typically contain less pollutants: two factors a CO<sub>2</sub> capture process can take advantage of. The plants are distributed all over Finland, partly very near to magnesium silicate resources (for example factories in Pietarsaari, Kaskinen, Oulu, Kemi). In the future CO<sub>2</sub> might also be utilized in the pulp and paper plants themselves, for bleaching processes.

Table 6: Pulp and Paper factories and their CO<sub>2</sub> emissions.[24], [25]

Factory	CO <sub>2</sub> emissions, Fossil [1000 t/a]	CO <sub>2</sub> emissions, Non – fossil [1000 t/a]
Joutseno	85	937
Kaskinen	29	584
Kemi	79	1006
Rauma	52	922
Äänekoski	57	738
Jämsänkoski	194	not known
Kaukas	145	not known
Pietarsaari	101	not known
Kymi	163	not known
Tervasaari	264	not known

One example for a medium sized plant is the Kaskinen pulp factory. Its annual emissions in CO<sub>2</sub> are 613000 tons (29 from fossil fuel, 584 non-fossil fuel). The emissions equal about 50% of the Meri-Pori plant. Other examples are listed in Table 6.

#### 4.1.4 Integration of Processes

To reduce the CO<sub>2</sub> emissions and costs of transportation to a minimum, the carbon dioxide source should be located near to the mineral mine. The ideal case would be to capture the CO<sub>2</sub> emitted by a mine and the plant where the metal is produced from the ore. The waste energy flows from the metal production process could be used for mineral make-up (*i.e.* separation from ore and/or preparation for carbonation). The heat produced by the carbonation process could be returned to the mining and metal production processes. Some data exists for the iron and steel industry (section 7.3 of [26]), but no data on CO<sub>2</sub> emissions and energy streams inside the non-ferrous metal ore mining and metal make up process were available for this study. The scheme in Figure 9 is a simplistic flow diagram for an integrated carbonation process. Here the CO<sub>2</sub> source is separated from the carbonation process itself, but the source could as well be the process of the metal industry. If the source is to be assumed a condensing power plant near the mine; the condensed heat can be used for the make-up process of the mineral. This would save not the only required heat input, but also cooling water for the power plant.

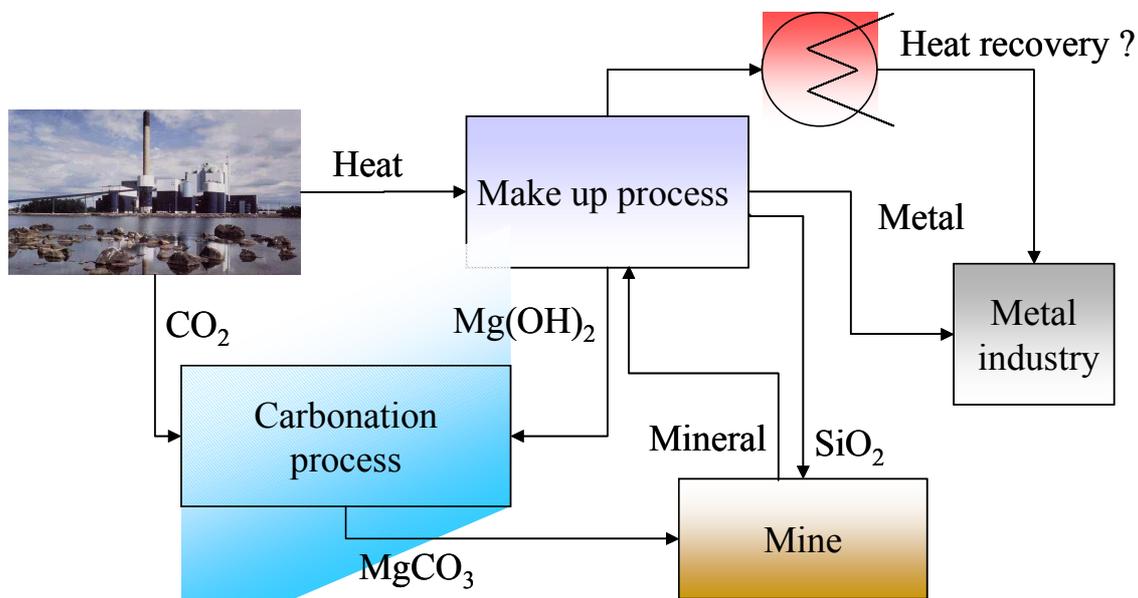


Figure 9: Flow diagram for an integrated carbonation process.

In the 1990s Lackner *et al.* worked on a wet mineral make-up process [27] that uses hydrochloric acid for the production of magnesium hydroxide. This make-up process requires heat input, which is needed for the recycling of the used chemicals (*i.e.* hydrochloric acid). For a 500MW<sub>e</sub> power plant (about the size of Meri-Pori) or a comparable metal production plant approximately 200 – 300 MW heat would be required. The condensed heat of the power plant or in this case the waste heat of a metal production plant could easily provide this heat. The carbonation process also produces heat that could be used for other processes inside the mine or factory. The heat that could be recovered is about two times the heat inserted into the process: for a 500 MW<sub>e</sub> power plant about 500 MW<sub>thermal</sub> (Figure 10). The extra output of heat would make the carbonation process interesting for also for other process industry like pulp and paper industry.

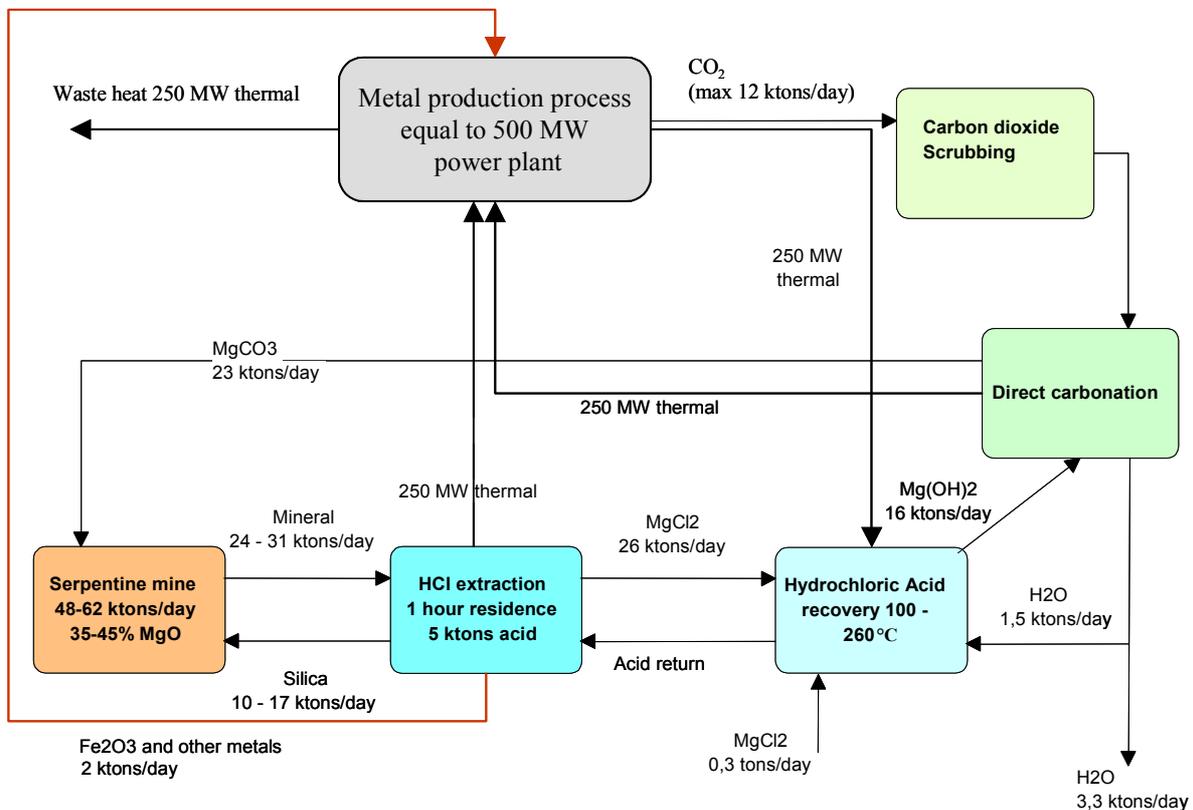


Figure 10: Wet mineral make up process for a metal production plant equal to 500 MWe power.

## 4.2 Economic aspects

It was planned to make an evaluation of the economic aspects of large-scale CO<sub>2</sub> sequestration by magnesium oxide-based mineral carbonation. Reasonably accurate data exists on the costs of CO<sub>2</sub> removal from gas streams, CO<sub>2</sub> transportation by pipeline, crushing and grinding of solid rock and the process efficiency penalty resulting from CO<sub>2</sub> emissions control expressed as costs. For several reasons, however, this plan in the end had to be abandoned:

- There is no good data on the cost or economic value of magnesium oxide-based minerals. Although Finnish serpentine-type minerals are considered to be worthless wastes or by-products from metal mining activities, they will receive a price tag as soon as their potential use is being recognised. The enormous amounts of material involved further complicate this.
- The most efficient use of mineral to be carbonated is probably obtained when magnesium oxide is extracted from the mineral, which is best accomplished by process integration with the ore processing at the mine. This results in a very complicated system from a cost evaluation point of view, introducing the world market value of metals such as nickel and chromium into the picture.
- There is not yet sufficient data as to the degree of carbonation of the magnesium oxide in the minerals that is most feasible from reaction kinetics and process engineering points of view. This directly affects the mineral consumption, which will probably be the largest cost factor.

Tax incentives related to CO<sub>2</sub> emissions, trading in emission quota and other financial approaches to fulfilling Finland's commitments under the 1997 Kyoto protocol add further unknowns to the picture.

## 5. Conclusions and future work

### 5.1 Conclusions January – May 2002

The carbonation process still presents many questions. Whether the carbonation process could be performed by direct carbonation using a mineral or a pure  $\text{Mg}(\text{OH})_2$  is not clear. Also the results presented show that although the temperature level of around  $350^\circ\text{C}$  may be the optimum for carbonation (of  $\text{MgO}$  at 1 bar), the role of small amounts of  $\text{H}_2\text{O}$ , pressure and the catalytic properties of, for example, calcium oxide/carbonate are still far from clear. However, against a background of a practically non-existing scientific literature on the kinetics of mineral carbonation chemistry a wealth of information has been obtained.

More, and probably a lot more, experimental work on the reaction kinetics should still be conducted – unfortunately the kinetics test series was suddenly halted for financial reasons. For future projects also the construction of a test facility (for example a small fluidised bed reactor) should be considered.

The sequestration of  $\text{CO}_2$  using magnesium oxide-based mineral carbonation seems to suit best for integration with other existing processes, mainly of the mining and metal industry, for example at companies like Outokumpu Oy. The transport of mineral to/from the carbon dioxide sources is not reasonable. For a typical, state-of-the-art coal fired condensing power plant the emissions caused by the transportation are 10% of the original emissions, which equals the emissions from a medium-sized pulp factory.

$\text{CO}_2$  could also be separated from air, but the efficiency of the separation process is too low. The transport of  $\text{CO}_2$  via pipelines is economically and environmentally possible and at the moment the only reasonable option. For future studies only the transport of gas ( $\text{CO}_2$  or air) should be considered as options. This correlates well with the conclusions from the study by Koljonen and Siikavirta that was conducted parallel to our study [26], that  $\text{CO}_2$  transmission will play an important role in Finland's future  $\text{CO}_2$  sequestration.

A highly important positive feature, which justifies further work on improvement of this technology is that  $\text{CO}_2$  stored as  $\text{MgCO}_3$  is more stable than  $\text{CO}_2$  stored or disposed of as such. As discussed more extensively in the previous report, no problematic by-products are produced either. In the end, this will certainly support acceptance by the public.

## 5.2 Future work

Although this work will not continue under a Finnish national research programme that would be titled “CLIMTECH 2” the area of mineral carbonation for CO<sub>2</sub> sequestration appears to have a lot of potential for Finland.

The further development of this option may, however, have to benefit mostly from cooperation within international research consortia such as the Nordic Energy Research Programme. Also, since the research team in the USA has demonstrated great interest in this work a future cooperation within the framework of cooperation between the Finnish Technology Agency TEKES and the US Department of Energy is being considered. A central part of the work will be the optimisation of mineral carbonation chemistry, after which large-scale processing, energy efficiency and costs can be considered.

A somewhat deeper analysis of the kinetic data will result in a journal article to be submitted later this year, not to mention the lic. tech. thesis by Jens Kohlmann and papers that may follow from that.

## 6. References Part 2

- [1] Energiaennakko 2001/Preliminary energy statistics, Statistics Finland, Helsinki, March 22, 2002
- [2] Ziock, H. "Zero emissions coal to hydrogen" <http://www.lanl.gov/energy/ziock.html> (2000)
- [3] Lackner, K., Ziock, H. "From low to no emissions" *Modern Power Systems*, 20(3) (2000) 31-32
- [4] Walters, R.P., Chen, Z-Y., Goldberg, P., Lackner, K., McKelvy, M., Ziock, H. "Mineral carbonation: a viable method for CO<sub>2</sub> sequestration" <http://www.fetc.doe.gov/products/gcc> (1999)
- [5] Goldberg, P., Chen, Z-Y., O'Connor, W., Walters, R., Ziock, H. "CO<sub>2</sub> mineral sequestration studies in US" Proc. of the First National Conference on Carbon Sequestration, May 14-17, 2001, Washington, DC (2001) session 6C  
<http://www.fetc.doe.gov/events/01conferences/carbseq/carbseq01.html>
- [6] O'Connor, W.K. *et al.*, "Carbon dioxide sequestration by direct mineral carbonation: results from recent studies and current status", *ibid.* (2001)
- [7] O'Connor, W.K., *et al.* "Continuing studies on direct aqueous mineral carbonation for CO<sub>2</sub> sequestration", Proc. of the 27th Int. Tech. Conf. on Coal Utilization and Fuel Systems, Clearwater (FL), March 4-7, 2002, pp. 819-830
- [8] Newall, P.S., *et al.* "CO<sub>2</sub> storage as carbonate minerals", report PH3/17 for IEA Greenhouse Gas R&D Programme, Cornwall (UK) 2000
- [9] Lackner, K., Plenary lecture at 27th Int. Tech. Conf. on Coal Utilization and Fuel Systems, Clearwater (FL), March 4-7, 2002
- [11] HSC 4 Chemistry for Windows, Outokumpu Research Oy, Pori (Finland) 1999
- [12] <http://webmineral.com/data/> (February 14, 2001)
- [13] Kohlmann, J. "The removal of CO<sub>2</sub> from flue gases using magnesium silicates, in Finland" Report TKK-ENY-3, Helsinki University of Technology, Finland (2001)
- [14] <http://www.outokumpu.com/mining/> (March 28, 2001)
- [15] Isomäki, O.-P., Outokumpu Mining Oy, personal communication, October 9, 2001
- [16] Ziock, H.-J, Butt, D. P., Lackner, K. S., and Wendt, C. H. "The need and options available for permanent CO<sub>2</sub> disposal". Presented at: 1998 Topical Conference on Pollution Prevention and Environmental Risk Reduction, Nov 15-20, 1998, Miami Beach (FL), 7 pp.
- [17] Mineral Council of Australia. [http://www.minerals.org.au/pages/page3\\_41.asp](http://www.minerals.org.au/pages/page3_41.asp)
- [18] Häkkinen, E., Ministry of the Environment of Finland, Helsinki, personal communication October 16, 2001
- [19] <http://www.fortum.com>
- [20] ExternE Info System, <http://externe.jrc.es>
- [21] "Pipeline transmission of CO<sub>2</sub> and energy – Transmission study report", Woodhill engineering consultants. (Third issue) IEA Greenhouse gas R&D programme (2002)
- [22] Rautaruukki Steel ja ympäristö. report 2000,
- [23] <http://www.rautaruukki.fi/environ/>
- [24] Oy Metsä-Botnia Ab. Ympäristöraportti 2001.
- [25] UPM-Kymmene. Environmental Report 2001

- [26] Koljonen, T., Siikavirta, H., Zevenhoven, R. "CO<sub>2</sub> capture, storage and utilisation in Finland", VTT Processes, project report PRO4/T7504/02, Espoo, June 2002
- [27] Lackner, K.S.; Butt, D.P.; Wendt, C.H., 1998. "Binding carbon dioxide in mineral form: a critical step towards a zero emission coal power plant" Los Alamos National Lab., (NM) internal report LA-UR—98-2237., 9p.

## Appendix 1 Experimental plan for thermogravimetric analyses: test 14-25

In the table below the input parameter of interest is printed **boldface**

Test #	14	15	16	17	18	19 → 25
<b>Experiment done</b>	*	*	*	*	*	\$
VTT Processes test #	1893	1894	1890	1891	1892	
<b>Sorbent, mg</b>						
Serpentine		304.2			302.7	
Mg(OH) <sub>2</sub>	299.9		298.5	308.2		
Al <sub>2</sub> O <sub>3</sub>						
NaCl						
NaHCO <sub>3</sub>						
CaCO <sub>3</sub>						
Final mass of sample	211.4	301.3	277.6	276.7	299.8	
<b>Gas composition</b>						
CO <sub>2</sub> %-vol	15	15	<b>100</b>	<b>99</b>	<b>99</b>	
N <sub>2</sub> %-vol	75	75				
H <sub>2</sub> O %-vol	5	5		<b>1</b>	<b>1</b>	
SO <sub>2</sub> ppm-vol						
O <sub>2</sub> %-vol	5	5				
HCl ppm-vol						
<b>Temperature</b>						
°C	<b>200</b> → 300 → 400 → 300 → 200	<b>200</b> → 300 → 400 → 300 → 200	<b>350</b>	<b>350</b>	<b>350</b>	
time at certain temperature	45 min	45 min	3h	3 h	3h	
heating /cooling rate, K/min	50	50				
<b>Pressure, bar</b>	1	1	1	1	1	
<b>Test #</b>	14	15	16	17	18	19 → 25

\$ Test series 19-25 could not be made for financial reasons: the budget estimated for test 1 through 25 was consumed after test 18.



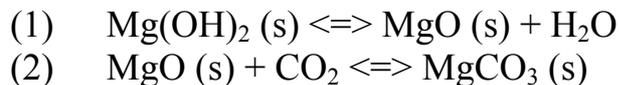
### Appendix 3 Processing of PTGA data

This appendix gives the procedure for converting PTGA mass signal / time / temperature data into degree of water release (in %) *versus* time or temperature, or degree of carbonation *versus* time or temperature. See, for example, Figures 2 and 3.

Below, the sample mass,  $m$ , is the mass signal from the PTGA **after** correction for buoyancy effects – see section 2.1.1.

Consider an  $\text{Mg}(\text{OH})_2$  sample with purity  $\alpha$ , *i.e.* containing mass fraction  $(1-\alpha)$  impurity, which is considered inert. (For the sample used in the tests,  $\alpha=0.997$ ).

The two chemical reactions considered are



The total mass of the sample,  $m$ , is composed of 1) reactant,  $m_R$ , 2) product,  $m_P$ , and 3) inert material,  $m_i$ , *i.e.*  $m = m_R + m_P + m_i$ . Expressing the initial mass as  $m^\circ$ , gives  $m^\circ = m_R^\circ + m_i$ ; it is noted that  $m_i$  is constant at  $m_i = (1-\alpha) m^\circ$ .

During the reactions the mass of the solids increase according to their molar masses,  $M$  (g/mol), giving a factor  $Z_1 = M_{\text{MgO}} / M_{\text{Mg}(\text{OH})_2} = 40.3/58.3 = 0.6913$  for reaction (1), and  $Z_2 = M_{\text{MgCO}_3} / M_{\text{MgO}} = 84.3/40.3 = 2.0918$  for reaction (2).

The degree of conversion,  $0 \leq X \leq 1$ , of the reactant  $\text{Mg}(\text{OH})_2$  to  $\text{MgO}$ , or  $\text{MgO}$  to  $\text{MgCO}_3$  at a certain time,  $t$ , and temperature,  $T$ , equals

$X(t,T) = 1 - m_R(t,T)/m_R^\circ$ . Using the equalities

$m_R = (1-X)m_R^\circ = (1-X)\alpha m^\circ$ ;  $m_P = XZm_R^\circ = XZ\alpha m^\circ$ ; and  $m_i = \alpha m^\circ$ , gives for reaction (1), with sample mass  $m$  as the only variable :

$$\begin{aligned} X_1(t,T) &= 1 - \left[ \frac{m(t,T) - m_p(t,T) - m_i}{\alpha m^\circ} \right] = \\ &= 1 - \left[ \frac{m(t,T) - Z_1 X_1 \alpha m^\circ - (1-\alpha)m^\circ}{\alpha m^\circ} \right] = \frac{\frac{m(t,T)}{\alpha m^\circ} - \frac{1-\alpha}{\alpha} - 1}{Z_1 - 1} \quad (\times 100\%) \end{aligned}$$

If the degree of conversion for reaction (1) equals  $X_1$  as the point where the carbonation reaction (R2) is started (*i.e.* the temperature starts to decrease), the degree of conversion  $0 \leq X_2 \leq 1$  of the product from reaction (1) follows from

$$\begin{aligned} m_{R2} &= m - m_{P2} - m_{R1} - m_i; & m_{R2}^{\circ} &= Z_1 X_1 m_{R1}^{\circ} = Z_1 X_1 \alpha m^{\circ}; \\ m_{P2} &= X_2 Z_2 m_{R2}^{\circ} = X_1 X_2 Z_1 Z_2 \alpha m^{\circ}; & m_{R1} &= (1-X_1) m_R^{\circ} = (1-X_1) \alpha m^{\circ}. \end{aligned}$$

This then gives for the degree of conversion for reaction (2) when it sets in at the point where reaction (1) has reached conversion  $X_1$ :

$$\begin{aligned} X_2(t, T) &= 1 - \left[ \frac{m(t, T) - X_1 X_2 Z_1 Z_2 \alpha m^{\circ} - (1 - X_1) \alpha m^{\circ} - (1 - \alpha) m^{\circ}}{Z_1 X_1 \alpha m^{\circ}} \right] \\ &= \frac{\left( \frac{m(t, T)}{\alpha m^{\circ}} - (1 - X_1) - \frac{(1 - \alpha)}{\alpha} \right) - 1}{Z_1 X_1} \quad (\times 100\%) \\ &= \frac{\quad}{Z_2 - 1} \quad (\times 100\%) \end{aligned}$$

which for an ideal case with  $X_1 = 1$  and  $\alpha = 1$  would simplify to

$$X_2(t, T) = \frac{\frac{m(t, T)}{m^{\circ}} - 1}{Z_2 - 1} \quad (\times 100\%)$$

It is assumed that reactant  $m_{R1}$  is not participating in reaction (2).

For other materials mixtures of reactants, *e.g.*  $Mg(OH)_2 + CaCO_3$  (test #12) the above also applies, unless the correct molar mass ratio factors  $Z$  are taken into account. For test #12, for the calcination step  $Z_1 = 0.99 \cdot 40.3/58.3 + 0.01 \cdot 56.1/100.1$ ; and for the carbonation step  $Z_2 = 0.99 \cdot 84.3/40.3 + 0.01 \cdot 100.1/56.1$ . For pure serpentine,  $Z_1 = 0.870$ ,  $Z_2 = 1.548$ .