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# THE REMOVAL OF $CO_2$ FROM FLUE GASES USING MAGNESIUM SILICATES, IN FINLAND

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**Abstract**

At this moment the options for reducing $CO_2$ emissions from power generation are a decrease of fuel consumption, increase in process efficiency or changing to renewable, $CO_2$-neutral fuel. Only a few technical applications for direct $CO_2$ reduction are in use. Earlier studies showed that it is possible to remove $CO_2$ from flue gases with the help of serpentine or other magnesium silicates. Laboratory experiments were done to get an insight to the kinetics of the chemical reaction. The availability of the minerals and the possibility of applying the method to large-scale combustion facilities were the main topics of this study.

## Introduction

Fossil fuel is still the most important energy source. On the other hand it is also the major source for greenhouse gases that are assumed to cause global warming. At the Kyoto conference in 1997 most countries of the world agreed on a reduction of $CO_2$ emissions. So far the only reliable methods for reducing the carbon dioxide emissions are a decrease of fuel consumption, increase in process efficiency or changing to renewable, $CO_2$-neutral fuel. Only a few technical applications for direct $CO_2$ reduction are in use.

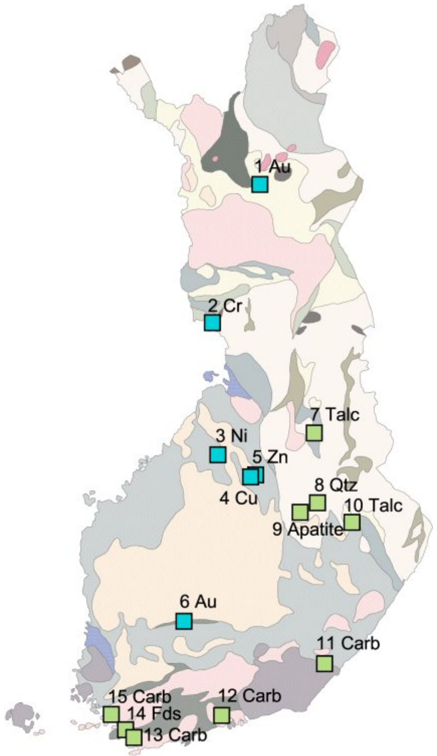
Until now many methods for $CO_2$ capture for example from flue gases have been developed. The capture of $CO_2$ seems to be technically possible, but the deposition of the captured $CO_2$ is a much bigger problem. Attempts have been made to store $CO_2$ in either liquid or gaseous form. These methods are economically feasible, but they include the risk of $CO_2$ release after a shorter period of time. Nature itself has stored $CO_2$ also as a solid in the form of a carbonate. Dolomite, for example, is a mixture of calcium carbonate and magnesium carbonate.

At a few laboratories researchers are looking for solutions to perform the carbonization of magnesium with carbon dioxide technically. The most promising results have been achieved at Los Alamos (NM, USA) where a process with a magnesium carbonation efficiency of 40 - 50% has been developed. High costs and a huge amount of required energy are still problems that seem to be most difficult to solve. At Helsinki University of Technology basic research on mineral carbonization using magnesium-based minerals available in Finland started in August 2000, results of which are given here.

## Minerals

For mineral carbonation the use of magnesium based silicates is favored because they are worldwide available in huge amounts. Magnesium silicates are divided into several subgroups. The largest quantities are olivine ($Mg_2SiO_4$) and serpentine ($Mg_3Si_2O_5(OH)_4$). Some other suitable minerals exist in smaller amounts. 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 [1]. In this work the mineral carbonization is based on serpentine mined near Kittilä north of Rovaniemi, Finland.

In Finland there are many mining activities, mainly mining for metals (nickel, copper). But also talc and limestone is mined. There are 15 major active mines in Finland of which 9 are found in areas with rich magnesium silicate deposits (see Figure 1). For example at the Hitura mine in northern Finland 720000 tons of ore are mined per year with a content of 3500 tons of nickel. 4 - 5% of the ore is pure serpentine and most of this serpentinite which is a mixture of mainly serpentine, talc and sand. [2]




Major active mines in Finland

Metallic
1. Pahtavaara: Au 1996-
2. Kemi: Cr 1969-
3. Hitura: Ni, Cu 1970-
4. Pyhäsalmi: Cu, Zn, S 1962-
5. Mullikkoräme: Zn, Cu 1996-
6. Orivesi: Au 1994-

Non-metallic

7. Lahnaslampi: Talc, ni 1969-
8. Kinahmi: Quartz 1910-
9. Siilinjärvi: Apatite, limestone, mica 1979-
10. Horsmanaho: Talc, Ni 1980-
11. Ihalainen: Limestone, wollastonite 1910-
12. Sipoo: limestone, dolomite 1939-
13. Förby: limestone 1917-
14. Kemiö: Feldspar, quartz 1966-
15. Parainen: Limestone 1898-

**Figure 1:** Major active mines in Finland. [3]

**Reactions of $CO_2$ and magnesium silicates**

Mineral carbonization is a process where the magnesium silicate is reacting with $CO_2$ to carbonate, quartz and water. The overall reactions are exothermic and at temperatures below 400°C the carbonation is thermodynamically favored. At Los Alamos the direct carbonization of serpentine has been analyzed. The result showed that the reaction requires more 2 hours to an efficiency of 25 per cent. Very high pressure (340 bar) and a temperature of 500°C were used and the reaction rate was strongly influenced by the particle size. A higher efficiency would require minerals as very fine powder. At Los Alamos the process was considered to be too slow for large scale applications. [4]

A higher efficiency and faster reactions were achieved by using magnesium hydroxide which was produced by extracting magnesium from ore by using hydrochloric acid. The process consists of several steps, including dissolving the mineral in acid, the hydrolysis of $MgCl_2$ to $Mg(OH)_2$ and the vaporization of water. The magnesium hydroxide can be extracted from the process very easily, since it is solid and hardly soluble in water. It can be directly carbonated to $MgCO_3$ at 550°C and 50 bar. In laboratory tests researchers succeeded to carry out the carbonation step to 90 % efficiency in less than 30 minutes, which would be short enough to use the process for example at power plants. [5,6,7]

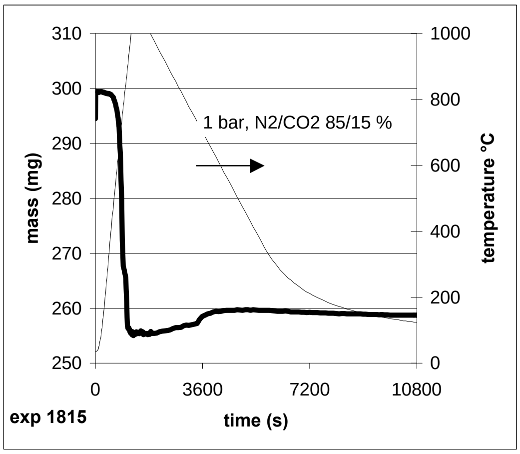
Although some of the reactions are exothermic the whole process requires a huge energy input. The process of capturing the $CO_2$ produced by an 1 GW power plant requires a heat input of 400 MW. On the other hand the process has also benefits. In the extraction step of the process all other elements in the ore can be recovered. This would allow to produce considerable amounts metals, for example iron or nickel. This would decrease the overall cost of the whole process. For US conditions the costs were estimated to 10US$ per ton of $CO_2$. [4]

## The experiments

Due to the fact that the process developed in Los Alamos is very energy intensive, at Helsinki University of Technology we try to get an insight to and optimize the reaction kinetics for the direct carbonation. Some experiments were done that should specifically relate to power plant processes.

First calculations showed that the process will depend on the kinetics of break up of serpentine into magnesium oxide, water and quartz. To get some basic knowledge about the process kinetics five experiments have been carried out at different temperatures and pressures in a pressurized thermobalance (at an external laboratory).

The experiments showed results that have been expected. With increasing temperature (beyond 400°C) the mass of the sample decreased which indicates the break up of serpentine into water and solids. After the temperature decreased back to below 500°C the mass increased slowly again as a sign of $CO_2$ uptake (see Figure 2).



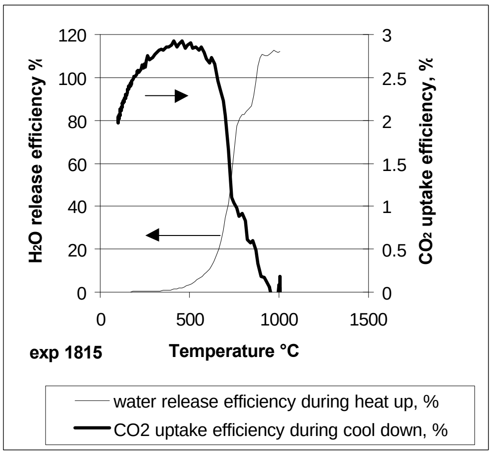




**Figure 2**: Change in mass with temperature; water release and $CO_2$ uptake efficiency between 100°C and 1000°C at 1 bar with dry gas.

## $CO_2$ sequestration in Finland

Finland is slowly shifting its fuel consumption to renewable fuels like wood and waste derived fuels. Nevertheless the growing economy in Finland is now asking for more energy which can be covered only by an additional nuclear power plant or by increasing the use of carbon based fuel (fossil and non-fossil). This will result in growth of $CO_2$ emissions in the near future, making it impossible to realize the $CO_2$ emission limits set in international contracts. The problem could be solved by $CO_2$ sequestration. The only option for Finland appears to be mineral carbonization, because Finland doesn't have deep oceans or exhausted oil or gas fields, and improved forestry, biofixation and the utilization of $CO_2$ do not have enough capacity.

For the purpose of this study four power plants in Helsinki were chosen to estimate the required amount of serpentine for the mineral carbonization. The data for these different power plants is given in Table 1.

**Table 1:** Power plants in Helsinki fuel consumption and $CO_2$ emissions in 1999 [8].

| | Power | | Fuel consumption and emission per year | | | | |
|---|---|---|---|---|---|---|---|
| **Power plant** | Electricity [MW] | District heat [MW] | hard coal [kt] | heavy fuel oil [kt] | light fuel oil [kt] | gas [$Nm^3$] | $CO_2$ emissions [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 | $169.5 \cdot 10^6$ | 342 |
| Vuosaari B | 480 | 420 | - | - | 0.024 | $595.6 \cdot 10^6$ | 1202 |

At a carbonization efficiency of 100% for each ton of $CO_2$ 2,18 tons of mineral serpentine would be required. To carbonize the $CO_2$ released by the Salmisaari power plant at least 2 Mt serpentine would be required per year. A 5 % reduction in $CO_2$ emissions for all Finland would require a quantity of 6,11 Mt serpentine per year. Every ton of carbon dioxide would result in 0,66 tons of quartz and 1,92 tons of magnesium carbonate. The reaction transforms 1 ton of serpentine into 1,2 tons of reaction products (that should be returned to the mine).

## Conclusions

In the experiments of this study only the direct carbonization of a pure mineral serpentine has been tested. The results proved that the reaction between the mineral and $CO_2$ is very slow. The direct carbonization seems to be possible, but will need a catalyst. The results from Los Alamos (NM, USA) show that the mineral carbonation is a possible method for $CO_2$ sequestration. The process requires a huge amount of energy, even if the reaction is actually exothermic. An improvement of the thermal efficiency and a system for using the low temperature heat output will be a big step forward to success.

From the Finnish point of view, mineral sequestration seems to be the only possibility to reduce the $CO_2$ emissions. The capture is also the only option, if Finland doesn't shift its energy generation towards nuclear power. A reduction of about 5% $CO_2$ emissions would be enough to decrease $CO_2$ close to the level agreed on in Kyoto in 1997. In Finland the required mineral is available in sufficient amounts for such a reduction. 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. As reported the process using hydrochloric acid releases a valuable amount of metals like iron, nickel or zinc.

The cost factor will be very important for this process in the future. At this point magnesium silicate is still a side product of metal mining. As soon as a valuable use for the mineral is discovered, its price will increase. The costs will be reflected directly into the price of energy. How much will people be ready to pay to avoid climate change?

## Literature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