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CARBONATION OF MINERALS AND INDUSTRIAL BY-PRODUCTS FOR CO₂ SEQUESTRATION

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ABSTRACT

Capture and storage of CO₂ is internationally considered as one of the main options for reducing atmospheric emissions of CO₂, but in Finland no suitable geological formations are known to exist for storing captured CO₂. However, fixing CO₂ as carbonates using silicate-based materials is an interesting alternative option for storage of CO₂. The magnesium silicate deposits in Eastern Finland alone could be sufficient for storing 10 Mt CO₂ each year during a period of 200 – 300 years. While calcium silicates seem to be too rare and expensive to be used for carbonation, many industrial waste materials and by-products have a high content of calcium oxides. For instance, carbonating all Finnish steelmaking slags produced annually, 0.5 Mt of CO₂ could be sequestered, while simultaneously producing roughly 0.8 Mt of calcium carbonate. A process that produces pure calcium carbonates from industrial wastes and by-products could reduce CO₂ emissions significantly and simultaneously produce usable filler and coating materials. Our research has focused on process development, since no economically feasible carbonation processes are currently available.

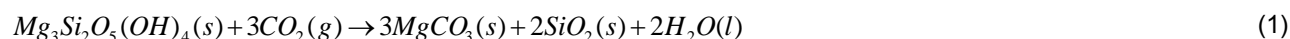
Experiments with aqueous extraction and precipitation processes have shown that magnesium and calcium can be easily extracted from steelmaking slags and natural silicate minerals using acids. Natural minerals seem to demand stronger acids for extraction than slags. Relatively pure calcium carbonate (80 – 90 % calcite) was produced at room temperature and 1 bar CO₂ pressure by adding sodium hydroxide to solutions prepared from slag. Serpentinite (magnesium silicate ore) was converted to 93 – 100 % pure hydromagnesite (a magnesium carbonate) using nitric acid or hydrochloric acid. The conversion of raw material to carbonate ranged from 60 – 90 %. Although pure carbonates can be produced, the process scheme suggested requires recycling of large amounts of sodium hydroxide and acid. Since the current methods for recycling the spent chemicals are expensive and cause CO₂ emissions due to power consumption, more research is needed for improving the process design.

Keywords: serpentine, serpentinite, slag, mineral carbonation, CO₂ capture and storage, extraction, precipitation.

INTRODUCTION

Carbon dioxide capture and storage (CCS) is considered as one of the main options for reducing CO₂ emissions from human activities (IPCC, 2005). This concept includes separation and compression of CO₂ from industry and power plants, and transportation of CO₂ to a suitable storage site. Carbonation of natural silicate minerals is an interesting alternative to using underground geological formations for storage of CO₂.

Alkaline-earth oxides, such as magnesium oxide (MgO) and calcium oxide (CaO), are present in large amounts and high concentrations in naturally occurring silicate minerals, such as serpentine and olivine (Goff and Lackner, 1998). Carbonation of these minerals traps CO₂ as environmentally stable solid carbonates that would provide storage capacity on a geological time scale. For instance, carbonation of serpentine (Equation 1) and wollastonite (Equation 2) minerals can be described with the following overall chemical reactions:



Carbonation of silicate minerals has the highest capacity and longest storage time of CO₂ of the storage options currently known (Lackner, 2003). Another advantage of mineralisation of CO₂ over geological storage methods is that monitoring after CO₂ fixation is not necessary. Although the net reactions described in Equations 1 and 2 are exothermic, the natural carbonation of silicate minerals is very slow, which means that the carbonation reaction must be accelerated considerably to be a technologically and economically viable large-scale storage method for CO₂.

Currently, no commercial technology is available for carbonation of silicate minerals. The most comprehensively studied process for carbonation is an aqueous carbonation process. Although 40 – 92 % conversion ratios has been achieved on laboratory scale, the process demands high CO₂ pressures (40 – 150 bar) and energy for pre-treatment of the mineral, which sets the estimated cost to 50 – 100 US\$/tCO₂ stored (O'Connor et al., 2005). Carbonation takes

place in a single step by CO₂ gas reacting with a slurry suspension of magnesium- or calcium silicate at high pressures, making simultaneous extraction of valuable metals or minerals difficult. Since serpentinites are an important source of a variety of metals and mineral products, integration of a carbonation process with mineral/metal production could be a more feasible approach. Also industrial by-products and residues may contain large concentrations of valuable metals, which could be extracted before carbonation. However, this would require a multi-step carbonation process, which would allow for separation of metals and minerals from serpentinite prior to carbonation. Multi-step processes suggested for carbonation involve extraction of calcium- or magnesium ions from silicates in a liquid media and precipitation of the extracted magnesium or calcium as carbonates (or hydroxides for subsequent carbonation). Mineral acids (Lackner et al., 1995, Park et al., 2003, Maroto-Valer et al., 2005), organic acids and ligands (Kakizawa et al., 2001, Park et al., 2003) as well as caustic soda (Blencoe et al., 2004) and ammonium salts (Yogo et al., 2004) have been suggested for dissolving silicates for subsequent carbonation. However, the available experimental data on these processes is scarce and occasionally contradicting.

In order to comply with the Kyoto agreement, the annual CO₂ emissions in Finland must be reduced with about 11 Mt (Ministry of Trade and Industry, 2005). In Finland, no geological formations suitable for CO₂ storage seem to exist, but ultramafic rocks, potentially suitable for carbonation, are abundant (Koljonen et al., 2004). Also industrial residues and by-products, such as steelmaking slags, exists that could be suitable for carbonation (Teir et al., 2005b).

In this paper, our recent research on using aqueous processes for carbonation of silicate minerals and steelmaking slags for storage of CO₂ is summarised. Extraction of calcium and magnesium from minerals and steelmaking slags, as well as subsequent fixation of CO₂ by precipitation of magnesium- and calcium carbonates, was studied by experiments. A process scheme, based on the experimental data, is suggested and the economical feasibility of the process is preliminarily studied.

SUITABLE RAW MATERIALS

The Finnish bedrock consists locally of rock types that contain large amounts of magnesium- and calcium silicates, such as serpentine, pyroxenes and amphiboles (Teir et al., 2006a). However, calcium silicates with a significant content of calcium, such as wollastonite, seem to be rare and expensive (Teir et al., 2005a). The most common Finnish magnesium-rich rocks are ultramafic intrusive or extrusive rocks, i.e. peridotites, dunites, hornblendites, pyroxenites and komatiites, and their metamorphic varieties, i.e. serpentinites, talc and asbestos rocks. Of these ultramafic rocks, the most interesting for CCS purposes are the serpentinites, because they consist mainly of serpentine, which may contain about 40 % MgO. Millions of tons of poorly documented in situ or hoisted serpentinite or tailed serpentine deposits situate mainly in central Finland.

To achieve the reduction required by the Kyoto target set for Finland (about 10 Mt/a) by carbonation of serpentinite, about 25 Mt/a of minerals would be required. It has been estimated, that the serpentinites in the Eastern Finland alone could be sufficient for 200 – 300 years of CCS processing (Teir et al., 2006a; Aatos et al., 2006).

In Finland, minerals or rocks that could be suitable for binding CO₂ in economical amounts are situated especially in those ultramafic rock formations that have already been mined for industrial minerals and metals, such as talc, soap stone, chromium and nickel. These rocks are being constantly piled or dammed as tailings for waiting later use in the extractive industry (Fig. 1). The currently available resources of hoisted serpentinite and serpentinite (33 – 39 % MgO) at Finnish Ni, Cr and talc mines are about 29 Mt (Aatos et al., 2006).

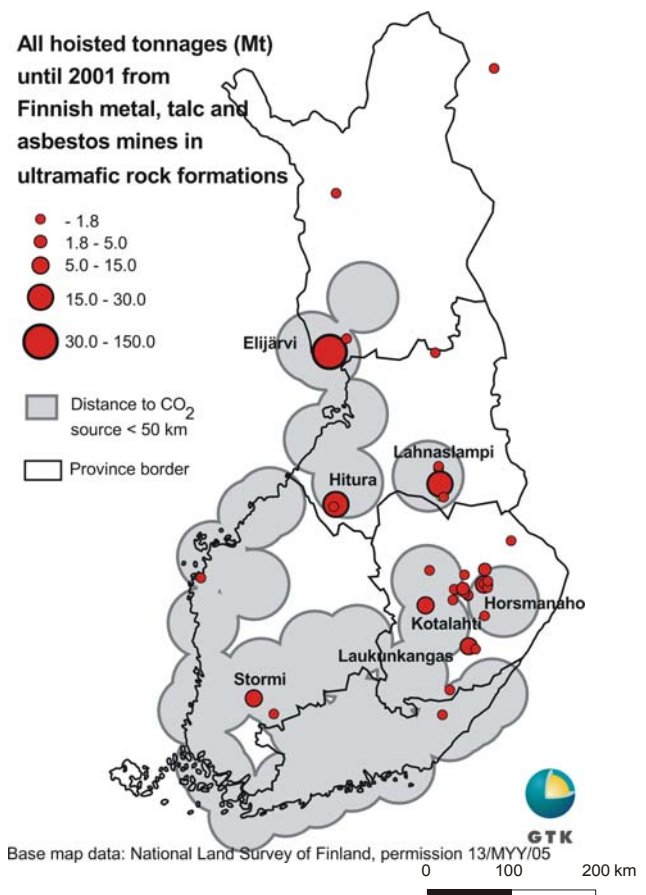


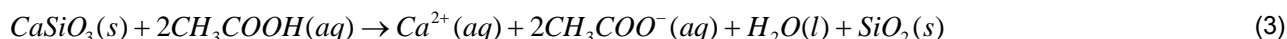
Fig. 1. Possible resources of serpentinite in Finland (Aatos et al., 2006).

Alkaline industrial wastes and by-products could also be used for providing the feedstock of magnesium or calcium for a carbonation process. Several industrial wastes and by-products have been successfully carbonated, such as iron and steel slag (steelmaking slag), municipal solid waste (MSW) incinerator ash, concrete wastes and several types of process ashes and dusts (Fernández Bertos et al., 2004, Huijgen et al., 2005). Considering that the by far largest single emitter of CO₂ in Finland is the Raahe steel mill, carbonation of steelmaking slag makes an interesting possibility for reduction of CO₂ emissions. The total annual production of steelmaking slag from the four steel mills in Finland is 1.4 Mt, which could theoretically store 0.5 Mt of CO₂ annually while simultaneously producing roughly 0.8 Mt of calcium carbonate (Teir, 2006). Although this is only 5 % of the reduction required by the Kyoto agreement, it could reduce the factory specific CO₂ emissions from the steel mills with 8 – 21 %. The market for the end product, calcium carbonate, is also significantly larger than for magnesium carbonates (Zevenhoven et al., 2006). For instance, precipitated calcium carbonate is a paper filler material with a growing market share. If pure, precipitated calcium carbonate could be produced from calcium silicate materials, the value of the product (>100 €/t CaCO₃) could allow for a more expensive process than the current cost for CO₂ emission allowances does (1 – 4 €/t CO₂) (Teir et al., 2005a; www.pointcarbon.com).

Since serpentinite resources in Finland have a large potential to sequester CO₂ emissions, the possibility to produce carbonates from these was investigated. However, calcium silicates, and especially industrial residues and by-products, are known to be more reactive towards carbonation than magnesium silicates. Therefore, the possibility to produce carbonates from steelmaking slags is discussed first.

PRODUCTION OF CALCIUM CARBONATE FROM STEELMAKING SLAG

Since Finnish steelmaking slag has an average CaO content of 41 % (Teir, 2006), the possibility to carbonate these slags using a multi-step process was studied. The carbonation process selected and studied uses an aqueous solution of acetic acid to dissolve calcium from calcium silicates, after which the produced calcium acetate solution is carbonated (Kakizawa et al., 2001). In the first process step, calcium is extracted from calcium silicate using acetic:



After separating silica out of the solution, CO₂ is introduced and calcium carbonate formed, which precipitates:



Acetic acid used in the extraction is recycled back to the first process step after carbonation. Since very little experimental data was found on the process (Kakizawa et al., 2001; Fujii et al., 2001), each process step was studied in more detail.

Extraction of calcium from steelmaking slag and wollastonite

The steelmaking slag types studied in our experiments were provided by Raahe steel works (Ruukki) and Tornio steel works (Outokumpu). Wollastonite from Lappeenranta (Nordkalk) was also used for comparison. Materials with a wide size distribution were sieved to 125 – 500 µm and only the sieved fractions were studied, while materials in powder form were used as such. The sieved fractions were characterised using XRF, XRD, and total digestion with ICP-AES. The results (Tables 1 – 2) showed that although the slags and wollastonite have very different compositions, they all have a high content of calcium bound as various calcium minerals. Wollastonite mineral had the most pronounced crystal structure, while blast furnace slag consisted mostly of amorphous phases.

Table 1. Minerals in calcium silicate-based materials identified by XRD-analyses (Teir et al., 2007a).

Material analyzed	Highest peak (counts) ¹	Phases identified
Wollastonite	2500	wollastonite CaSiO ₃ , quartz SiO ₂
AOD process slag	1000	fluorite CaF ₂ , periclase MgO, calcium silicate Ca ₂ (SiO ₄)
Electric arc furnace slag	350	gehlenite Ca ₂ Al(AlSiO ₇), merwinite Ca ₃ Mg(SiO ₄) ₂ , magnesiochromite (Mg, Fe)(Cr,Al) ₂ O ₄
Steel converter slag	300	srebrodolskite Ca ₂ Fe ₂ O ₅ , lime CaO, iron Fe, calcium silicate Ca ₂ SiO ₄ , calcium iron oxide Ca ₂ Fe _{15.6} O ₂₅
Blast furnace slag		Mostly amorphous phases

¹The peak count is an indication of the crystal structure of the material analyzed: a higher peak count means a more pronounced crystal structure.

Table 2. Composition of calcium silicate-based materials used in the experiments as determined by XRF-analysis, as well as dissolution/ICP-AES-analysis. Units: wt-%¹ (Teir et al., 2007a).

Element	Blast furnace slag (350-500 µm)	Steel converter slag (350-500 µm)	Electric arc furnace slag (125-350 µm)	AOD ² process slag (< 125 µm)	Wollastonite (< 250 µm)	Analysis method
CaO	39.0	41.4	38.9	69.4	38.8	ICP-AES
SiO ₂	25.7	11.0	21.2	22.0	32.2	ICP-AES
Fe ₂ O ₃	0.404	26.0	3.82	0.252	0.201	ICP-AES
MgO	11.9	1.42	6.05	6.51	0.506	ICP-AES
Al ₂ O ₃	8.64	1.88	6.34	1.22	1.17	ICP-AES
F	0.07	0	0.11	5.5	0.02	XRF
Cr	0.003	0.232	5.07	0.228	0.001	XRF
Ti	1.03	0.512	2.64	0.356	0.012	XRF
Mn	0.376	2.39	2.29	0.076	0.005	XRF
S	1.73	0.086	0.092	0.273	0.008	XRF

¹Only elements present at > 1 wt-% in at least one of the materials are shown.

²AOD = Argon-Oxygen Decarburisation

To compare the potential for extracting calcium from various steelmaking slags to that of wollastonite, the studied materials were dissolved in 33 wt-% aqueous solutions of acetic acid at a solution temperature of 50 °C. Filtered samples of the solution were taken during the experiments and analysed using ICP-AES. The results (Fig. 2.) show that while only 51 % of the calcium fixed in wollastonite was extracted during 2 h, almost all the calcium from steelmaking slags dissolved into the solution in 15 minutes. However, other elements of the slag, such as silicon, magnesium, iron, and aluminium, dissolve as well. By increasing the solution temperature to 70 °C, the dissolved silica was extracted as a gel. By varying the concentration of acetic acid in the solution, it was found that 6 – 7 ml acetic acid was required per gram of blast furnace slag for total dissolution, which is roughly 12 moles CH₃COOH per mole Ca. The results have been reported in detail elsewhere (Teir et al., 2007a).

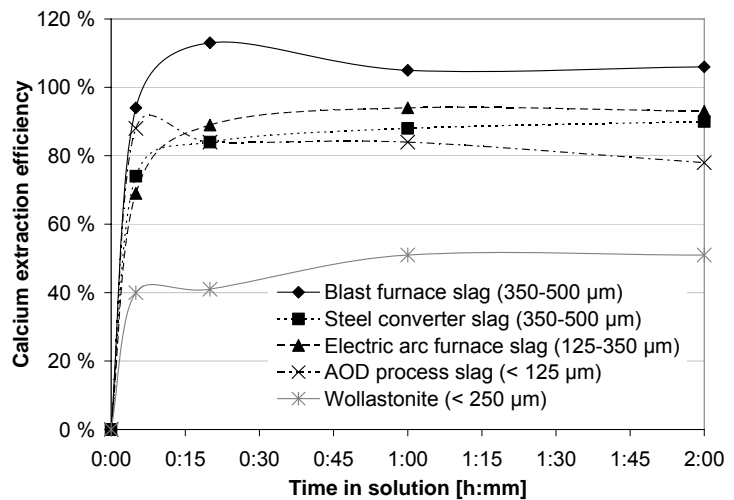


Fig. 2. Extraction of calcium from various materials in 33 wt-% aqueous solutions of acetic acid at 50 °C (Teir et al., 2007a). Due to the inhomogeneous composition of blast furnace slag, the calculated extraction efficiency exceeded 100 %.

Precipitation of calcium carbonates from solutions prepared from blast furnace slag

No carbonate precipitated when CO₂ gas was bubbled through filtered, aqueous solutions of acetic acid, containing dissolved blast furnace slag for several hours. The surplus of acid required to dissolve blast furnace slag caused the solution to have a pH of 3 – 4, which prevented any formation of carbonates. In order to precipitate carbonates, NaOH was added to raise the alkalinity of the solution. However, this caused neutralisation of the surplus of acid. To recycle the surplus of acid, the solvent was evaporated from the filtered, aqueous solutions of acetic acid, containing dissolved blast furnace slag. When the solvent had evaporated, a solid salt remained, which consisted mostly of calcium and magnesium acetates. The acetate, prepared from blast furnace slag, was dissolved in water, after which CO₂ gas was injected (1 l/min, 1 atm). The solution temperature was kept at 30, 50 or 70 °C. Although the initial solution pH was 7 – 8, the acidic CO₂ gas lowered the pH to 5, causing no carbonate to precipitate (Fig. 3). Raising the total gas pressure to 30 bar using pressurized CO₂ did not produce any carbonate either. However, raising the pH by adding NaOH (aqueous solution of 50 wt-%) precipitates were formed, which consisted to 60 – 90 wt-% of CaCO₃ as calcite. It was found that 1.2 – 1.3 kg of NaOH and 3.1 – 3.3 kg acetate (derived from 3.7 – 4.0 kg blast furnace slag), was required for production of 1 kg of CaCO₃. These experiments are reported in detail elsewhere (Eloneva et al., 2007; Teir et al. 2006b).

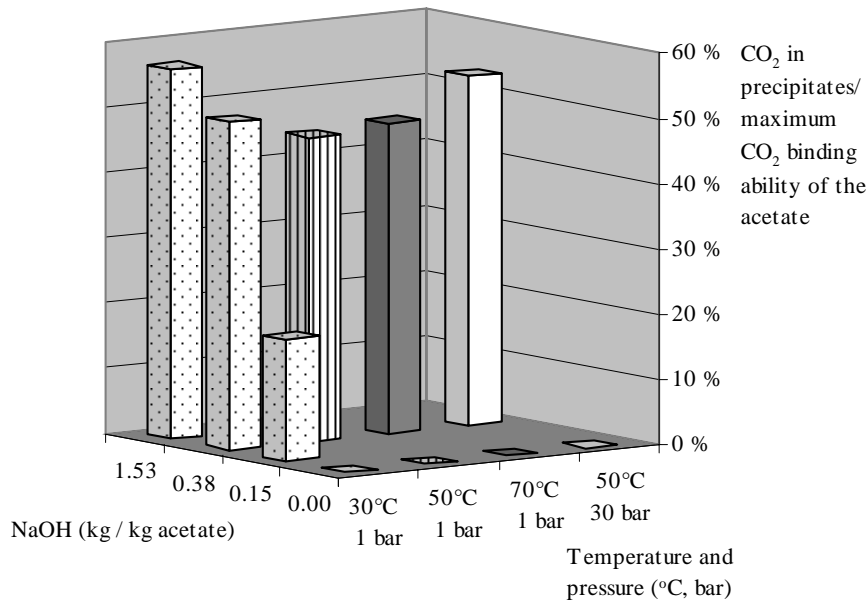


Fig. 3. CO₂ bound in precipitates as CaCO₃ as compared to the maximum carbon dioxide binding ability of the acetate (Eloneva et al., 2007).

PRODUCTION OF MAGNESIUM CARBONATE FROM SERPENTINITE

As mentioned above, the large resources of serpentinite rocks in Finland make them a high potential raw material for CO₂ storage by mineral carbonation. In order to study the possibility to bind CO₂ by producing magnesium carbonate from serpentinite, the process concept developed for carbonating steelmaking slags adapted for carbonating serpentinite. Since serpentinites are more difficult to dissolve and carbonate, the research started with studying the dissolution of serpentinite using various solvents. After suitable solvents had been selected, the precipitation of carbonates was studied in similar fashion as with steelmaking slag.

A batch of 7 kg of serpentinite rock was selected for experimental study from the stockpile of Hitura nickel mine, central Finland, and ground to a median diameter of 100 μm (<0.5 mm). The serpentinite was analysed using XRD, XRF, and ICP-AES. The serpentinite was found to consist of 83 wt-% serpentine, (Mg₃Si₂O₅(OH)₄; chrysotile, lizardite and antigorite) and 14 wt-% magnetite (Fe₃O₄).

Extraction of magnesium from serpentinite

In order to find a suitable solvent for leaching magnesium from serpentinite for subsequent production of magnesium carbonates, the most common acids used in mineral processing (HCl, H₂SO₄, HNO₃) were tested alongside two common weak acids (HCOOH and CH₃COOH). Although acids are known to extract magnesium from magnesium silicates, bases can dissolve silicates and were also found to favour the formation of carbonates (see above). Therefore, dissolution of serpentinite was also tested in aqueous solutions of NaOH, KOH, and NH₃. 1 g of serpentinite (74 – 125 μm) was dissolved in separate 50 ml aqueous solutions of 1 M, 2 M and 4 M concentrations of an acid or base under stirring at 1000 rpm at room temperature. After 1 h, the solutions were filtered and analysed with ICP-AES. All acids tested managed to extract 3 – 26 % of Mg from serpentinite in 1 h. H₂SO₄ extracted most magnesium (24 – 26 %), followed by HCl (17 – 24 %), HNO₃ (12 – 18 %), HCOOH (5 – 8 %) and CH₃COOH (3 – 4 %). Higher acid concentrations resulted in slightly more magnesium and iron ions dissolved, except for the solutions of CH₃COOH, which behaved more irregularly. None of the acids tested extracts Mg selectively from serpentinite: also Fe (2 – 16 %) and some Si (0 – 3 %) was extracted. No measurable amounts of magnesium or iron (< 0.05 % extracted) and very little Si (< 0.4 %) had dissolved in the alkaline solutions tested (NaOH, KOH, and NH₃).

To study the effect of temperature upon leaching, 10 g of serpentinite (74 – 125 μm) was dissolved in 500 ml of 2 M HCl, H₂SO₄, and HNO₃, respectively. The temperature was kept at 30, 50 and 70 °C and the solutions were stirred at 600 – 700 rpm. Filtered samples of the solution were taken during the experiments and analysed using ICP-AES. The results showed that all magnesium was extracted from serpentinite in 1 – 2 h at 70 °C with all three acids used (Fig. 4). However, 38 – 67 % of the iron as well as 3 % of the silicon in serpentinite was simultaneously dissolved. These results are reported in detail elsewhere (Teir et al., 2007c).

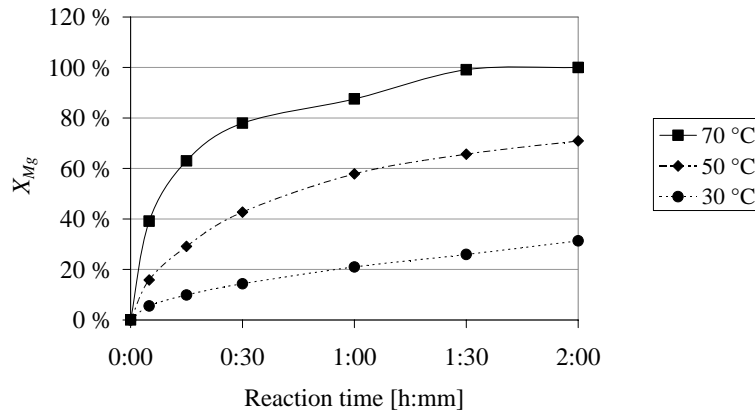


Fig. 4. Effect of temperature upon extraction of Mg from serpentinite using 2 M HNO₃.

Precipitation of magnesium carbonates from solutions prepared from serpentinite

Since mineral acids were found to be the most efficient for extracting magnesium from serpentinite, HCl and HNO₃ were selected (due to their relatively low boiling point) for experiments with precipitating carbonates. Two batches were prepared by dissolving 100 g serpentinite in 1 l of 4 M HNO₃ and 4 M HCl, respectively, at 70 °C for 2 h, using a mechanical stirrer at 650 rpm. This resulted in extraction of 88 – 93 % of the magnesium in serpentinite as dissolved magnesium. The residue consisted mainly of highly porous amorphous silica. The filtrates were evaporated at 104 – 105 °C, leaving concentrated slurries, which were dried in an oven for 1 – 2 days at 130 – 180 °C. After drying, the remaining magnesium salts were dissolved in 2 l H₂O, respectively. The resulting solutions contained no measurable concentrations of Si. During dissolution of the magnesium salt (prepared from HNO₃) in water, all of the dissolved iron precipitated spontaneously as hematite, Fe₂O₃. This produced a magnesium-rich solution (21 g Mg/l) of pH 7 that contained no measurable concentration of dissolved Fe. The magnesium salt prepared from HCl had formed a crust during drying, apparently preventing a small part of the acid from evaporating. When dissolving this magnesium salt in water, the acidity (pH 1) seemed to prevent iron from spontaneous precipitation. A large part of the dissolved iron was precipitated as magnetite, Fe₃O₄, by raising the pH to 7 with NaOH. However, the resulting solution contained still 9 g Fe/l, in addition to 22 g Mg/l. Enrichments of nickel and copper were found in the iron oxides precipitated from both the solution prepared using HCl and the solution prepared using HNO₃.

The magnesium-rich solutions, containing mainly dissolved magnesium nitrates or -chlorides prepared from serpentinite, were used for investigating the possibility to precipitate magnesium carbonates. For each pH level, 150 or 300 ml of each solution was exposed to 1 litre CO₂/min for 30 min in a glass reactor at 30 °C. The pH was regulated to a pH between 7 – 12 by drop-wise addition of an aqueous solution of 50 wt-% NaOH. The prepared solids were washed, filtered, and dried. The composition of the precipitates formed was analysed using XRF, XRD and the total carbon and carbonate content was measured. SEM was used for observing the morphologies of the samples.

Similarly to experiments with calcium acetate, the pH of the prepared solution dropped from 7 to 5 when CO₂ was introduced, preventing formation of a precipitate. Regulating pH by addition of NaOH produced precipitates from both solutions. For both solutions an optimum of pH 9 was found for precipitating carbonates. At pH 9, magnesium precipitated as 93 – 99 wt-% pure hydromagnesite powder, Mg₅(CO₃)₄(OH)₂·4H₂O (Fig. 5). Carbonation of magnesium was favoured at pH 7 – 11 for the solution prepared from HCl, and at pH 8 – 12 for the solution prepared from HNO₃. The solids, precipitated at pH 9, were measured to have the highest carbonate content (48 – 50 wt-% CO₃²⁻) of the precipitates formed. At pH 9, the conversion of magnesium ions in solution to hydromagnesite was also the highest (79 – 94 %), while the NaOH requirements were the lowest (0.9 – 1.1 g NaOH / g precipitate). Since the solution prepared from HCl had a high level of iron impurity the precipitates from that solution were also contaminated by iron compounds. These results are reported in detail elsewhere (Teir et al., 2007b).

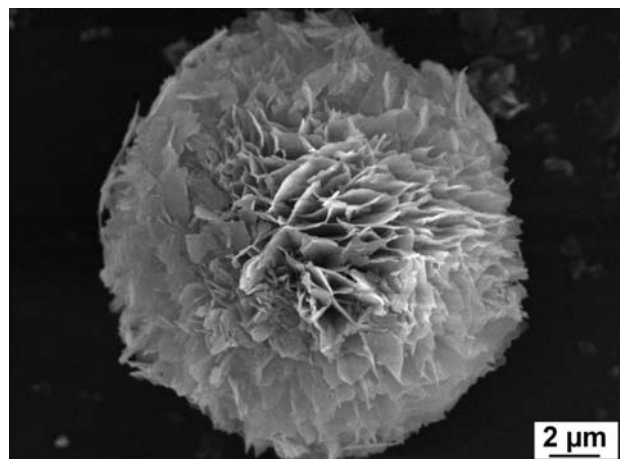
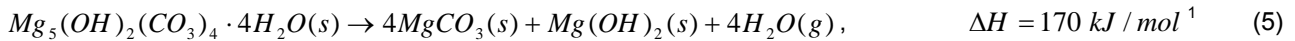


Fig. 5. SEM image of a hydromagnesite crystal precipitated at pH 9 from the solution prepared using HNO₃.

The thermal stability of the precipitate, produced at pH 9 with the solution prepared from HNO₃ (Fig. 5), was analyzed using thermogravimetric analysis (TGA). Thermodynamic equilibrium calculations (performed using Outokumpu HSC 5.11 software) predicted that magnesium hydroxide decomposes to magnesium oxide at temperatures over 265 °C, and the decomposition of magnesium carbonate to CO₂ and MgO should take place at temperatures over 406 °C. Three runs from 25 to 900 °C was performed in N₂ atmosphere, using a heating rate of 2 °C/min, 5 °C/min, and 10 °C/min, respectively. After an initial mass loss of 2 – 6 %-units during heat-up from 25 to 170 °C the material decomposed mainly in two clearly endothermic steps: first, at 170 – 300 °C a mass loss of an additional 12 – 17 %-units occurred, after which 35 – 38 %-units was lost during heat-up from 300 to 550 °C. The total mass loss that occurred during heat up from 25 to 300 °C (18 – 21 wt-%) is similar to the total molar weight of water that can be released by dehydration and dehydroxylation of hydromagnesite (19 wt-%):



The net loss of mass during heat-up from 300 to 550 °C (44 – 51 wt-%) corresponds to the expected loss of mass due to the release of CO₂ (47 wt-%):



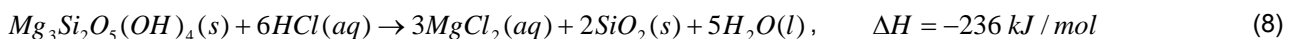
The TGA analysis and thermodynamic calculations shows that hydromagnesite should be a safe CO₂ storage media up to 300 °C.

PROCESS EVALUATION

By considering the new experimental data reported above, the following issues can be concluded:

- Acidic solutions extract calcium or magnesium from minerals and steelmaking slag efficiently, but the acidity of the solutions prevents precipitation of carbonate.
- Strong acidic solutions are required for dissolving serpentinite, while steelmaking slags dissolve in weak acids.
 - For maximum extraction² or gel facilitation³ the solution temperature should be 70 °C or possibly higher.
 - Evaporation of the solution recycles only part of the solvent, since part of the solvent is converted into a salt (e.g. magnesium- and calcium acetate, -nitrate or -chloride).
- While iron oxides and amorphous silica can be separated easily from the process, steelmaking slags contain many other compounds as well, which require additional separation measures.
- As CO₂ dissolves in the neutral, aqueous salt solution, the solution turns acidic and prevents precipitation of carbonate. Therefore, a base is required to raise the pH of the solution and precipitate dissolved magnesium, calcium and CO₂ as carbonates.
 - The solution temperature affects the morphology of the precipitated carbonates, but not the yield (Teir et al., 2007b; Eloneva et al., 2007).

From the experimental procedures and results, a generic process scheme can be constructed, which shows the current development stage of the process studied (Fig. 6). The carbonation of serpentinite using HCl is described next as an example for visualising the process (Fig. 7). First, magnesium and iron is extracted from serpentinite using HCl at 70 °C. This produces aqueous magnesium chloride and iron chlorides. All of the silicon dioxide in serpentinite can be recovered at this stage as highly porous, amorphous silica. Since serpentinite consists mostly of serpentine, the main reaction occurring is:



However, an excess of acid seems to be needed for maximising the extraction conversion. Therefore, the resulting solution is very acidic. In order to recover the excess acid and attain solid magnesium chlorides, the solution is evaporated. Evaporating all of the water released from serpentinite would require 200 kJ/mol serpentine dissolved plus 75 kJ for each mole of additional HCl required for dissolution (calculated for evaporation at 120 °C). However,

¹ All reaction enthalpies have been calculated for 25 °C, except where explicitly mentioned. Reaction enthalpies were calculated using Outokumpu HSC 5.1 software with additional data for MgCO₃, MgO and Mg(OH)₂ from Robie et al. (1978).

²Applies only to experiments with serpentinite

³Applies only to experiments with steelmaking slag

part of the water released from serpentinite is bound with the produced magnesium chloride as hydrates. Since the amount of water bound as magnesium chloride hydrate is not known, the mass balance of water in the process has not been accounted for. When the solvent is evaporated magnesium chloride, including iron compounds, precipitates. Upon dissolving the magnesium chloride in water (and possibly adding NaOH or another base for neutralising any remnants of the acid) iron oxides precipitate and can be removed prior to carbonation. By injecting CO₂ gas and regulating the pH of the solution to a pH of 9 using NaOH magnesium carbonate precipitates as hydromagnesite:

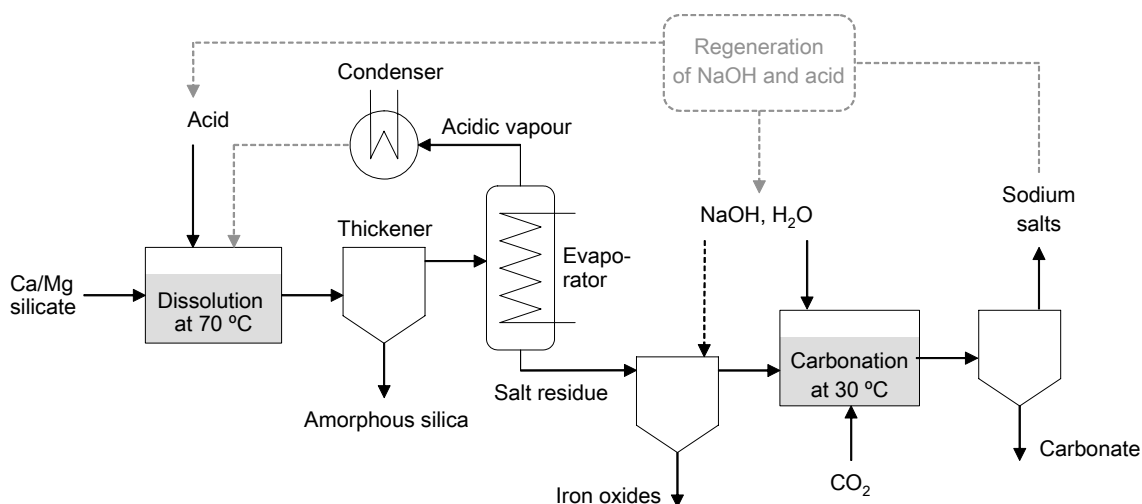
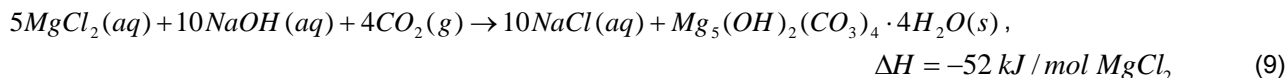
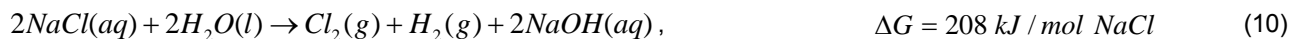


Fig. 6. A process scheme for production of carbonates from magnesium- and calcium silicates. The solid, black lines and boxes show process streams and -stages that have been experimentally verified, while dotted, grey lines and boxes show additional streams and stages not yet tested. The dotted, black lines indicate streams needed only for certain solvents.

Assuming that serpentinite consists of 85 wt-% serpentine and 15 wt-% magnetite, 3.1 t of serpentinite is required for storing 1 tonne of CO₂. This would produce 0.5 t of magnetite, 1.1 t of amorphous silica, and 2.7 t of hydromagnesite. Experiments indicate that it might be possible to absorb CO₂ from flue gas streams directly using this process step (Equation 9), which would eliminate the need for a separate CO₂ separation process. However, precipitation of carbonates from magnesium- or calcium salts demands large amounts of NaOH or another alkaline compound (over 2 t NaOH per tonne CO₂ stored in the example in Fig. 7). The process would also demand large amounts of acid (over 2 t HCl per tonne CO₂ stored in the example in Fig. 7). For the example presented here (Fig. 7), electrolysis could be one option for recycling the resulting aqueous sodium chloride solution. In the chlor-alkali industry, aqueous sodium chloride solutions are electrolyzed producing chlorine gas, sodium hydroxide, and hydrogen gas:



The pure chlorine gas can be re-combined with the hydrogen gas, forming chemically pure hydrogen chloride gas.



As the reaction is exothermic, it is carried out in an installation called an HCl oven. The resulting pure hydrogen chloride gas is absorbed in water, resulting in pure hydrochloric acid. The exothermic HCl production could cover for the heat needed for evaporation of the water released when dissolving serpentinite and a surplus of up to 11 mole acid per mole serpentine dissolved. However, the electrolysis of sodium chloride would require 11.8 MJ of electrical power per kg of CO₂ stored. Since the CO₂ emissions from a coal fired power plant is roughly 800 kg/MWh (IEA, 1993), the power consumed by electrolysis would release 2.6 times the amount of CO₂ that is bound in the carbonation process. Even if this power could be provided for using renewable energy sources, it would cost over 160 € per ton CO₂ stored⁴. Assuming that the carbonation process could be integrated with other chemical industries,

⁴ Calculated using the Finnish industrial consumer electricity price of 5 cent per kWh (Statistics Finland, 2006).

supplying HCl and NaOH, the heat requirements for evaporation of the water released would require at least 530 kWh/t CO₂ stored. Although this heat could be provided using low-grade waste heat (~130 °C or higher), the amounts of acid and base chemicals needed are large. In order to eliminate the need for regeneration of NaOH and HCl, serpentinite could be dissolved using a melt of MgCl₂ and HCl, producing MgOHCl as an intermediate product for carbonation, or carbonated directly in a melt of MgCl₂ (Wendt et al., 1998). However, these processes, which have not yet been experimentally verified, would require higher process temperatures and/or high CO₂ pressures.

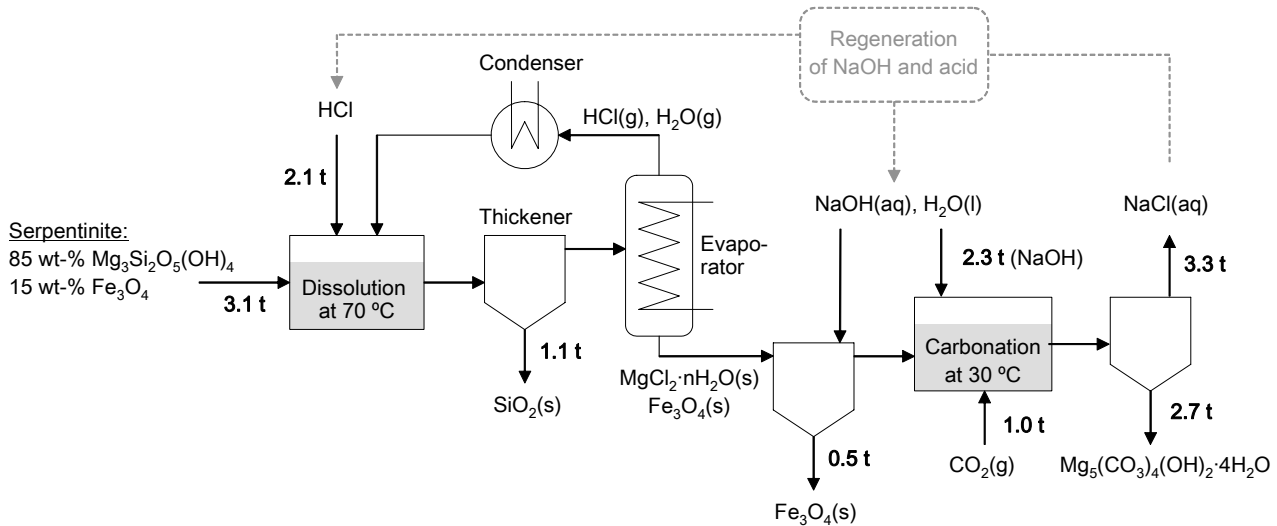


Fig. 7. Process scheme for production of hydromagnesite from serpentinite (100 % conversion of streams assumed). The solid, black lines and boxes show process streams and -stages that have been experimentally verified, while dotted, grey lines and boxes show additional streams and stages not yet tested.

CONCLUSIONS

Carbonation of magnesium- and calcium silicates is an interesting alternative to geological storage methods, providing for permanent storage of carbon dioxide in the form of solid carbonates. Finland has large resources of potentially suitable magnesium silicates that could be used during several hundreds of years for mitigation of CO₂ emissions from industrial sources. Industrial residues and by-products, especially steelmaking slags, are also suitable for carbonation. While the available resources of slags are significantly lower than natural minerals, these materials are annually produced and could help introduce carbonation technology, since slags are more reactive than natural minerals.

Experimental research has shown that CO₂ can be bond into pure and stable carbonate products using silicate-based materials. While relatively pure carbonate products and by-products, such as amorphous silica and iron oxides, can be produced using the processes proposed the current obstacle for the process scheme suggested seems to be the regeneration of additional chemicals spent in the process. The products and the by-products of the processes may have some commercial value, but the regeneration of NaOH and acid probably requires electrical power, which makes the process unfeasible for storing CO₂ in its current development stage. However, the potential to simultaneously produce pure minerals is a significant benefit, which warrants more research on development of these types of mineral CO₂ sequestration processes.

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