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# Production of magnesium hydroxide from magnesium silicate for the purpose of $CO_2$ mineralization – Part 2: Mg extraction modeling and application to different Mg silicate rocks

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ABSTRACT

Mineral carbonation of Mg silicates via a gas/solid carbonation of magnesium hydroxide, $Mg(OH)_2$ in a fluidized bed (FB) reactor process route is the most actively investigated route of carbon capture and storage by $CO_2$ mineralization (CCS) research in Finland. This paper reports Mg extraction behavior and production of magnesium hydroxide, $Mg(OH)_2$ from different Mg-silicate rocks from worldwide locations (Finland, Lithuania, Australia and Norway). Magnesium hydroxide, the reactive material for gas/solid mineralization of $CO_2$ can be produced from different Mg-silicate minerals via a staged solid/solid reaction with ammonium sulfate (AS) salt followed by precipitation in aqueous ammonia solution. A comparison is made for five different minerals. The kinetics of Mg extraction from Mg-silicate minerals and the possible effects of iron by-products on reactivity and kinetics were studied and modeled as well.

## 1. Introduction

Increasing energy demand and use of fossil fuels present difficulties in stabilizing atmospheric $CO_2$ levels. However, the development and application of carbon capture and storage (CCS) may allow for both current and future energy demands to be met in a "carbon neutral" manner (IPCC, 2005) without potential disruptions due to climate change (Huesemann, 2006). Among the various carbon sequestration options, mineral carbonation is unique in terms of capacity and 'permanence' (Alexander et al., 2007). Mineral carbonation is a $CO_2$ sequestration scheme that mimics and accelerates the natural weathering process of alkaline-earth-based silicates (especially the more abundant magnesium silicate minerals like dunites, peridotites and serpentinites) consequently forming stable carbonates. An analogue of mineral carbonation is a phenomenon for accelerated weathering reported of minerals from serpentine-rich mine tailings and mine waste at Clinton Creek, Yukon Territory, and Cassiar, British Columbia, Canada (Wilson et al., 2006, 2009). This phenomenon was attributed to the dramatic increase in surface area, which occurs during the milling of the mineral ore.

Mineral carbonation offers virtually unlimited capacity to permanently store $CO_2$ in an environmentally benign form which takes little or no effort to either verify or monitor (Krevor and Lackner, 2008; Alexander et al., 2007). It is attractive in many countries like Finland with large resources of silicate rocks suitable for carbonation, and where absence of underground formations excludes carbon dioxide capture and geological storage (CCGS) or the risk of leakage of underground stored $CO_2$ is considered unacceptable (Zevenhoven and Fagerlund, 2010). Mineral carbonation is in the research phase – both *in situ* and *ex situ*, the latter is addressed here – and faces setbacks associated with its development and large scale application for a large part as a result of limited attention when compared to CCGS. So far methods proposed for mineral carbonation suffer from low chemical conversion rates, high energy requirements and chemicals costs. Despite the fear for an energy penalty, interest in mineral carbonation stems from two features that make it unique among the different storage approaches, namely the abundance of metal oxide bearing materials, particularly of natural silicates, and the permanence of storage of $CO_2$ in a stable solid form (IPCC, 2005). Also, the overall chemistry of mineral carbonation is exothermic, allowing for a process with – in theory – a zero or negative overall energy input (Zevenhoven et al., 2008a,b). Most of the routes presented in the literature do, surprisingly, not take benefit of this energy output.

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In Part 1 of this paper (Nduagu et al., 2012), see also (Nduagu, 2008), a method of producing magnesium hydroxide, $Mg(OH)_2$ from Finnish serpentinite was described that addresses reaction conversion and rate, chemicals costs and recovery rates. This method involves a staged solid/solid reaction of Finnish serpentinite and ammonium sulfate (AS) followed by precipitation of $Mg(OH)_2$ in an aqueous ammonia solution. The present work studies and compares the magnesium hydroxide production potential of different Mg silicates (serpentinites and olivine minerals) for subsequent carbonation using a pressurized gas/solid fluidized bed reactor. The motivation was to investigate the applicability of the staged process of producing magnesium hydroxide from Finnish serpentinite to other Mg-silicate minerals from different geological locations worldwide. Of interest also is the modeling and optimization of the solid/solid reaction of Mg silicates and AS salt.

## 2. Carbonation of Mg silicate minerals via gas/solid route

Among the abundant rock types rich in alkaline earth metals (Mg and Ca) peridotites and serpentinites appear to have the most potential for sequestrating $CO_2$ as their mass ratios of rock to $CO_2$ are relatively low compared to other rock types (Newall et al., 2000). Magnesium silicates can be divided into several subgroups: the largest quantities are Mg-rich peridotites and serpentinites (Zevenhoven et al., 2006b). Peridotites contain >90% olivine ($(Mg,Fe)_2SiO_4$), pyroxene and hornblende, with olivine being predominant (Newall et al., 2000). Zevenhoven et al. (2006a) noted that the most interesting of the magnesium silicate rocks for CCS purposes are serpentinites, because they contain mainly serpentine, $Mg_3Si_2O_5(OH)_4$, which contains about 40% MgO.

$$\begin{aligned}&Mg_2SiO_4(s) + 2CO_2(g) \rightarrow 2MgCO_3(s) + SiO_2(s),\\ &\Delta H(298\ \mathrm{K}) = -86\ldots-109; -69\ldots-92\ \mathrm{kJ/mol}\ CO_2\end{aligned} \tag{1}$$

$$\begin{aligned}&Mg_3Si_2O_5(OH)_4 + 3CO_2(g) \rightarrow 3MgCO_3(s) + 2SiO_2(s) + 2H_2O(l),\\ &\Delta H(298\ \mathrm{K}) = -46; -64\ \mathrm{kJ/mol}\ CO_2\end{aligned} \tag{2}$$

Direct carbonation of Mg-silicate minerals (without pretreatment of olivine; Eq. (1)[2] and serpentinite; Eq. (2)[3] would have been the preferred route for mineralization of $CO_2$ due to simplicity in design and better energy efficiency. More so, the overall carbonation reactions of olivine and serpentinite are exothermic. However, these reactions suffer from very slow kinetics, low conversion and high energy requirements for activation (Zevenhoven et al., 2008a,b). Direct carbonation of Mg silicate minerals is not technically and economically feasible for large scale $CO_2$ sequestration. Therefore, there is a preference for an indirect and staged process that would speed-up the carbonation chemistry kinetic via extraction or activation of the reactive component (MgO) from the Mg silicate mineral. Aqueous phase “wet” and gas/solid “dry” carbonation routes have mostly been investigated for this purpose (Huijgen and Comans, 2005; Sipilä et al., 2008).

While most research concentrates on methods that use aqueous solutions, research in Finland still primarily addresses high temperature gas/solid (“dry”) methods besides aqueous solution (“wet”) routes. The main scope of mineral carbonation work in Finland is the production of magnesium in the form of $Mg(OH)_2$ from Mg silicate minerals followed by conversion into $MgCO_3$ using a pressurized fluidised bed (PFB) reactor (Fagerlund et al., 2009, 2010; Fagerlund and Zevenhoven, 2011). Although producing magnesium hydroxide from magnesium silicates involves a high temperature Mg extraction stage at 400–500 °C, the carbonation step should offset (most of) this energy penalty. Proper process integration should – in theory – allow for operating at zero or negative net energy input. We are motivated by the exothermic nature of the reaction between $Mg(OH)_2$ and gaseous $CO_2$ and its potential to produce significant amounts of steam or electricity, provided that high carbonation conversion levels (85–90%) are reached (Zevenhoven et al., 2008a,b). In order to realize high carbonation conversion levels, a fluidized bed reactor is chosen due to the following reasons; (1) a continuous motion of the bed enhances particle–particle collisions allowing for fresh unreacted core material to be exposed to $CO_2$. (2) the temperature distribution inside a fluidized bed is nearly uniform. (3) the material being chipped off is lighter than the initial particles allowing for it to be carried away by the passing $CO_2$ and separated in a cyclone while the unreacted material is recycled back to the fluidized bed (Fagerlund et al., 2009) and (4) only $Mg(OH)_2$ goes into the PFB, without inert materials that require reactor volume and contribute to pressure drop. Besides this, Fe rich compound produced in significant amounts from the magnesium hydroxide production process may be a useful raw material in the iron and steel industry which at the same time is Finland’s largest $CO_2$ producer. More reasons for preferring a gas/solid carbonation route by the mineral carbonation group at ÅAU can be found elsewhere (Fagerlund et al., 2009, 2010; Fagerlund and Zevenhoven, 2011; Nduagu et al., 2012; Zevenhoven et al., 2006a,b; Zevenhoven et al., 2008a,b).

## 3. Mg extraction from different Mg-silicate rocks

Magnesium hydroxide was produced from different serpentinites and olivines and the results were compared with results obtained from earlier tests with Finnish serpentinite as reported in Part 1 of this paper (Nduagu et al., 2012). Further, the reactivity (with respect to Mg extraction) of the Mg-silicate minerals with ammonium sulfate (AS) salt was studied. The Mg-silicate rocks tested include; Finnish serpentinite from Hitura nickel mine (Finn Nickel Oy); Australian serpentinite from the Great Serpentinite Belt of New South Wales (NSW); Serpentinite from the Varena region of Southeast Lithuania; Olivine from Åheim, Norway and Olivine diabase from Satakunta, Finland (see Fig. 1). The latter is of special interest due to its proximity to the Meri-Pori coal-fired power plant (565 MWe). The mineral compositions are presented in Table 1.

Different mass ratios of Mg-silicate minerals to AS salt (reagent grade, 99.5%, Merck) were reacted in an oven operated at different temperatures and reaction times. The same experimental procedures as described in Part 1 of this paper (Nduagu et al., 2012) for Mg extraction and precipitation of FeOOH and $Mg(OH)_2$ in aqueous ammonia solution were applied also here.

Extraction results obtained from tests with the three serpentinite rocks depict that the elemental composition, especially the proportion of Mg to Fe (Mg:Fe ratio) in the Mg-silicate rock, affects their reactivity in relation to the extent of extraction of Mg and Fe. It was expected that the higher the Mg content of the rock the higher would be the extent of Mg extraction. This may be true for Mg extraction from serpentinite but cannot be generalized to include olivine. At relatively similar reaction conditions, the Mg extraction results from the tests with the serpentinites seem to follow a trend as shown in Fig. 2.

The extent of Mg extraction becomes significant as reaction temperatures are increased above 400 °C, reaches an optimum

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[2] Several values are given for reaction enthalpies: a range is found when calculating values for different forms of $Mg_2SiO_4$. Moreover, thermodynamic data from Robie, Hemingway and Fisher, 1979 (first values) gives a result different from when using Knacke et al. (1991), Glushko (1994), Landolt-Börnstein (1999) as in HSC 5.11 (2002) (second values).

[3] Using data for crysotile (Saxena et al., 1993) as in HSC 5.11 (2002). Two values for $\Delta H$ as explained above.

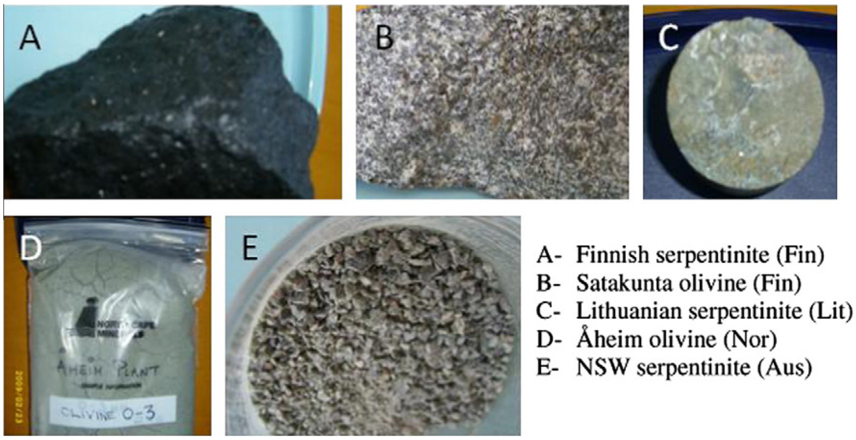

**Fig. 1.** Mg silicate mineral samples used in this study.

**Table 1**
Elemental compositions (wt.%) of Mg-silicate rocks studied. Mg:Fe refers to the ratio of Mg to Fe in mineral.

| Mg-silicate rock | Composition of atoms (wt.%) | | | | | | | | | | Mg:Fe (kg/kg) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mg | Fe | Si | Ca | Mn | Ti | Cu | Ni | S | Al | |
| Åheim olivine (Nor.) | **29.55** | **5.03** | 19.49 | 0.14 | 0.07 | – | – | 0.24 | – | 2.79 | **5.9** |
| NSW serp. (Aus.) | **23.04** | **4.80** | 19.54 | 0.04 | 0.07 | 0.01 | **–** | – | – | 0.47 | **4.8** |
| Finnish serp. (Fin.) | **21.80** | **10.10** | 11.6 | 0.34 | 0.08 | 0.02 | 0.01 | 0.02 | 0.48 | 0.02 | **2.2** |
| Lithuania serp. (Lit.) | **18.94** | **12.30** | 15.89 | 0.86 | 0.04 | – | 0.01 | 0.01 | – | 0.12 | **1.5** |
| Satakunta olivine (Fin.) | **3.30** | **10.67** | 21.92 | 6.25 | 0.13 | 1.53 | – | – | – | 8.53 | **0.3** |

The bold values represent the most important parameters considered in this study.

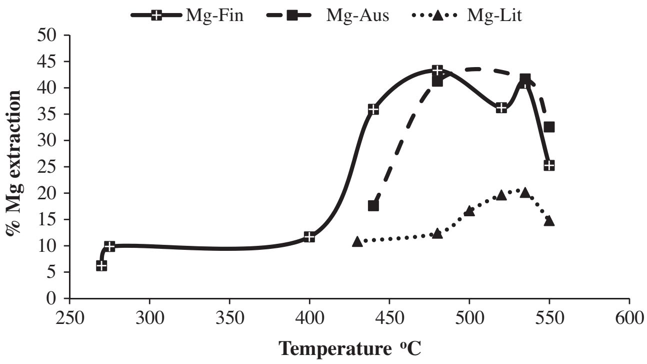

**Fig. 2.** Mg extraction values from different serpentinite rocks at increasing temperatures (reaction times: below 30 min and S/AS: 0.5–0.77 g/g).

and afterwards decreases at temperatures above 520 °C. The decrease in the amount of Mg extracted and subsequently precipitated may be a result of conversion of magnesium sulfate (solubility in water, ~255 g/L at 0 °C) to almost insoluble magnesium metasilicate ($MgSiO_3$).

Thermodynamic modelling with HSC software (v.5.11) for Gibbs energy minimization (HSC Chemistry, 2002) shows that $MgSO_4$ product would decompose at high temperatures (>600 °C) resulting in the formation of $SO_3$ gas followed by $MgSiO_3$ (see Fig. 3). Here, a slight deviation of experimental results from the thermodynamic equilibrium compositions is observed. Thermodynamically, the reaction of serpentine, $Mg_3Si_2O_5(OH)_2$ (the active compound in the serpentinite rock material) proceeds almost to completion at about 250 °C while the decomposition of the predominant solid product ($MgSO_4$) is observed to start at 600 °C. In contrast, experimental results show no significant extent of reaction below 400 °C while the decomposition of $MgSO_4$ product takes place first above 520 °C. This can be explained by temperature-dependent chemical kinetics.

An interesting observation is made when a comparison of results from tests with all the Mg silicate minerals is made (see Fig. 4). Only 6.4% Mg extraction was achieved from each of the two tests with Åheim olivine under the following conditions; S/AS = 1 kg/kg, *T* = 450 °C, *t* = 20 min; S/AS = 0.5 kg/kg, *T* = 480 °C and *t* = 10 min). Here “S” refers to the mineral (serpentinite or olivine) and “AS” to the ammonium sulfate salt. Low extraction results from experiments with Norwegian olivine were surprising as higher Mg extraction results were expected because the rock is the richest in Mg. The low reactivity of olivine may be attributed to the hardness of the minerals and the structure of Mg–Fe-silicate matrix. Olivine $(MgFe)SiO_4$ is considerably harder (6.5–7 on Moh’s hardness scale) than serpentinite (2.5–3.5 on Moh’s hardness scale). Also, a high chemical bonding energy as well as a low surface area and porosity are factors that can contribute to its low reactivity. Surface area and porosity of the rocks are addressed further in later sections.

The experimental results show that reaction temperature has a considerable effect on Mg extraction from the Mg silicate rocks. While the reaction of Finnish and Australian serpentinites with AS seems to proceed significantly at temperatures above 400 °C attaining an optimum extraction at ~500 °C, in contrast somewhat higher reaction temperatures seem to favor the reaction of Lithuanian serpentinite and AS. Notable increases in % Mg extraction was observed from 480 °C up to 535 °C, which appears to be the optimum reaction temperature of tests with Lithuanian serpentinite. It is not yet clear if this effect is attributable to composition of Fe in the mineral since Lithuanian serpentinite has the highest composition of Fe (12.3 wt.%) among the Mg silicates tested.

## 4. Fe extraction

In the process route used, apart from Mg also Fe was extracted and leached in water using $NH_4OH$. The extracted Fe is thereafter precipitated in its oxidized form as FeOOH, an important by-prod-

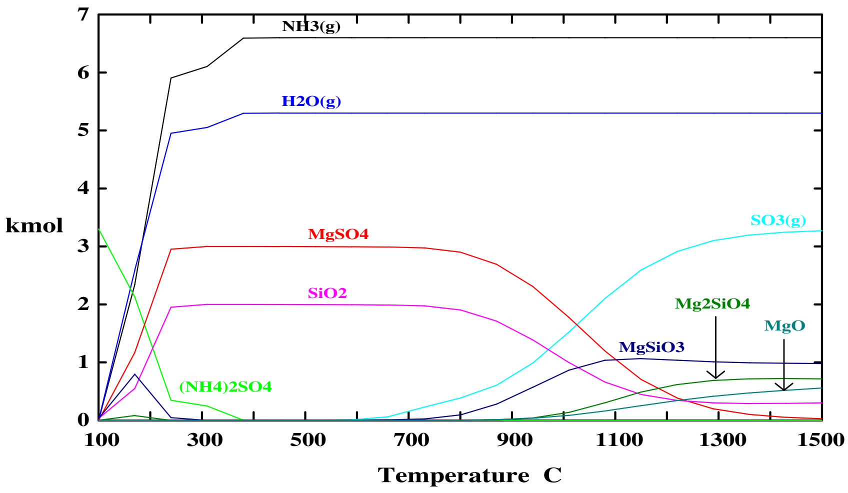

**Fig. 3.** Thermodynamic equilibrium compositions showing decomposition of $MgSO_4$ product (at higher temperatures) of the reaction of serpentinite (1 kmol $Mg_3Si_2O_5(OH)_4$) and AS salt (3.3 kmol $(NH4)_2SO_4$).

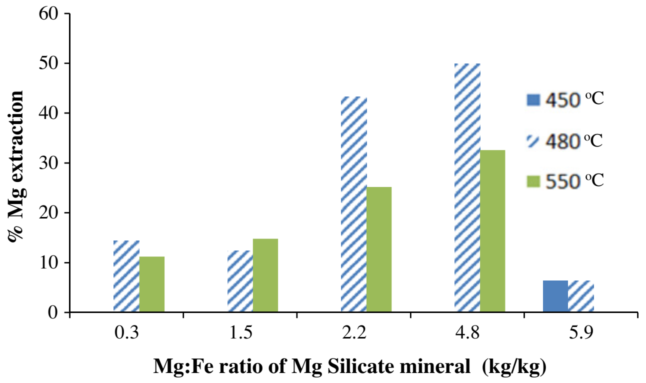

**Fig. 4.** Mg extraction from different magnesium silicate minerals compared at similar reaction conditions (except at $T = 450$ °C where only Åheim olivine with Mg:Fe ration of 5.9 was tested). Mg:Fe ratios: 0.3 – Satakunta olivine (Fin.); 1.5 – Lithuanian serpentinite; 2.2 – Finnish serpentinite; 4.8 – NSW serpentinite (Aus.); 5.9 – Åheim olivine (Nor.).

uct that may be a useful raw material in the iron- and steelmaking industry. Under similar reaction conditions the effect of temperature on the extent of Fe extraction from different serpentinite rock samples is shown in Fig. 5.

Unlike tests with Finnish and Lithuanian serpentinite rocks that show no clear pattern for Fe extraction, results from Australian serpentinite exhibit a parabolic Fe extraction trend with distinct optimum reaction temperature as also obtained from Mg extraction (Fig. 5A). Similar to results from Mg extraction the Mg:Fe ratios seem to have a remarkable influence on Fe extraction especially among the serpentinites (see Fig. 5B). Experimental results (Fig. 5A) show that the production of $FeSO_4$ and/or $Fe_3(SO_4)_2$, which is leached in water, comes to an optimum (at ~520 °C) and thereafter starts to decrease.

Thermodynamic stability modeling (HSC Chemistry, 2002) of Fe-containing reactant ($Fe_3O_4$ in serpentinite) and likely products shows a two-staged thermal decomposition $FeSO_4$ at 400 °C and 650 °C (see Fig. 6). The decrease in Fe extraction values obtained experimentally after reaching a supposed maximum extraction may be a result of the formation of more insoluble $Fe_2O_3$ when water-soluble $FeSO_4$ decomposes.

## 5. Effect of surface area and pore volume on reactivity of material

### 5.1. Specific surface area determination

Nitrogen adsorption measurements at 77 K were done to the particles with a TriStar 3000 gas sorption apparatus (Micromeritics, Norcross, USA). The specific surface area of the particles was determined from the obtained ad-sorption isotherm using the Brunauer, Emmett and Teller (BET) equation (Brunauer et al., 1938). The total pore volume was determined (or approximated) from the nitrogen adsorption isotherm using the adsorbed amount at relative pressure, $p/p_0 = 0.95$.

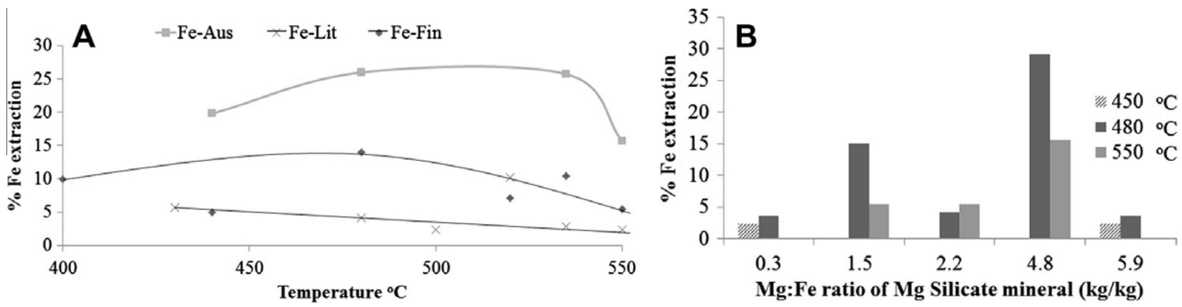

**Fig. 5.** (A) Fe extraction values from different serpentinite rocks at increasing temperatures (reaction times: below 30 min and S/AS: 0.5–0.77 g/g). (B) Fe extraction from magnesium silicate minerals (with different Mg:Fe ratios) are compared. Mg:Fe ratios: 0.3 – Satakunta olivine (Fin.); 1.5 – Lithuanian serpentinite; 2.2 – Finnish serpentinite; 4.8 – NSW serpentinite (Aus.); 5.9 – Åheim olivine (Nor.).

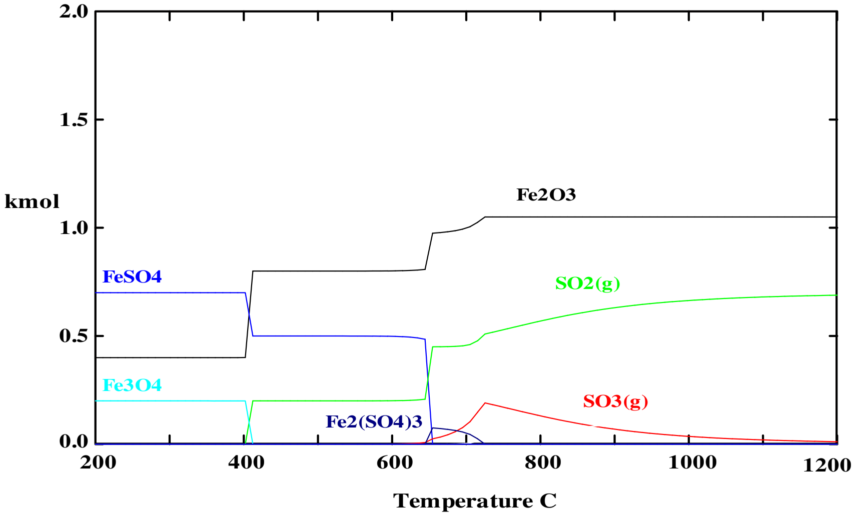

**Fig. 6.** Thermodynamic stability of Fe-containing reactant and products of the reaction of serpentinite and ammonium sulfate. Input values are 0.5 mol $Fe_3O_4$, 0.4 mol $FeSO_4$ and 0.1 mol $Fe_2(SO_4)_3$.

### *5.2. Effects on reactivity of material*

The reactivity of the Mg-silicate rocks may be influenced by a combination of chemical and physical properties, specifically the Mg:Fe ratio, specific surface area and porosity of the mineral. Finnish and Australian serpentinite samples show similar type IV physisorption isotherm shapes indicating mesoporosity (Sing et al. 1985). Finnish serpentinite has the highest measured for pore volume (~0.035 $cm^3/g$) while that of Australian serpentinite is lowest among the serpentinites. However, the higher Mg:Fe ratio in Australian serpentinite may be the most important contributing factor to its reactivity, thereby making surface area of less significance.

Åheim (Norway) and Satakunta (Finland) olivine samples were also identified as similar pairs of adsorption isotherms. The adsorbed amounts of gas and pore volumes in the case of Åheim and Satakunta olivines were miniscule (therefore small BET area). Lithuanian serpentinite falls in between these two groups of mesoporous serpentinites and the low specific surface area olivines. However, Lithuanian serpentinite sample has the largest pore volume after the Finnish serpentinite. Its low reactivity may be as a result of its low Mg:Fe ratio. It would be interesting to study the effect of the reaction on the surface properties of the mineral samples and consequent effects on reaction rate.

### *5.3. Reactivity of $Mg(OH)_2$ produced from serpentinite*

Fernández et al. (1999) showed that an increase in surface area of MgO resulted in increased carbonation of MgO slurries in water. In a similar study, but in this case gas-phase carbonation of $Mg(OH)_2$ was found to be influenced by chemical, physical, and morphologic factors (Bèarat et al. 2002). High surface area of the carbonation material is one of the factors essential for high gas-phase carbonation activity. An ongoing work that uses a gas–solid pressurized fluidized bed (PFB) reactor to carbonate a synthetic $Mg(OH)_2$ (particle size 125–212 μm) from Dead Sea Periclase (DSP) Ltd., has so far achieved a conversion degree of just under 50% at 500 °C and 20–30 bar within 10–15 min (Fagerlund and Zevenhoven, 2011). The BET surface areas of both synthetic and $Mg(OH)_2$ produced from serpentinite were determined in order to compare their carbonation activities. Results obtained gave values of BET surface areas of 5.38 $m^2/g$ for $Mg(OH)_2$ from DSP Ltd. and 46.85 $m^2/g$ for $Mg(OH)_2$ produced from Finnish serpentinite. Although surface area may not be the sole determinant of the gas–solid reactivity of $Mg(OH)_2$ with $CO_2$, under the same conditions a carbonation conversion (much) higher than for DSP-$Mg(OH)_2$ has been obtained for $Mg(OH)_2$ produced from serpentinite since it has a surface area of more than eight times larger than the DSP material. Also, $Mg(OH)_2$ produced from Finnish serpentinite has a pore volume 10 times larger than the DSP material (see Table 2).

SEM images (Fig. 7) show that magnesium hydroxide produced from Finnish serpentinite mineral has a rougher surface, and constitute of apparently more porous particles than the DSP magnesium hydroxide.

## 6. Data modeling of solid/solid reaction of serpentinites and AS salt

The kinetics of Mg extraction from the solid–solid reaction of serpentinite minerals and AS salt, like other solid state reactions can be described using its degree of conversion of reaction, $\alpha$. This is represented as; $\alpha = m/m_0$, where $m$ is the mass of Mg extracted during the reaction and $m_0$ the mass of Mg in serpentinite mineral. The kinetics of Mg extraction is presented in its integral form in the following equation:

$$g(\alpha) = \mathrm{kt} \qquad (3)$$

where $g(\alpha) = \int_0^\alpha (d(\alpha)/f(\alpha))$, $f(\alpha)$ is a function of $\alpha$ and $k$ is the Arrhenius rate constant, which is given as $k = A\exp(E_a/RT)$.

Using this, the data from tests with serpentinite minerals were analyzed. A regression analysis, including backward elimination and partial F-tests, confirms that the dependence of $\alpha$ on reaction temperature $T$ and reactants' mass ratios S/AS is statistically significant. It is apparent that $\alpha$ is proportional to S/AS to the power of a negative exponent $p$ (see Fig. 8). This of course indicates the rather obvious, i.e. that more AS in contact with serpentinite gives a higher degree of extraction. The kinetic behavior of this reaction has to be understood in order for (the S/AS) parameter to be chosen optimally.

Other varying mineral characteristics, such as surface area, pore volume and hardness, as discussed earlier, affect the extraction as well.

By running a Quasi-Newton optimization routine in MATLAB® (R2007b) different models were fitted to the data, by minimizing the residual sum of squares. The best fit was achieved using the

**Table 2**
Surface area of Mg-silicate mineral and magnesium hydroxide samples ($75 < d_p < 125$ μm).

| Rock sample | Mg:Fe ratio (kg/kg) | BET surface area ($m^2/g$) | Pore volume ($cm^3/g$) |
|---|---|---|---|
| Satakunta olivine (Fin.) | 0.3 | 0.25 | 0.0003 |
| Lithuania serp. (Lit.) | 1.5 | 10.93 | 0.0125 |
| Finnish serp. (Fin.) | 2.2 | 26.45 | 0.0347 |
| NSW serp. (Aus.) | 4.8 | 6.25 | 0.0086 |
| Åheim olivine (Nor.) | 5.9 | 0.18 | 0.0002 |
| $Mg(OH)_2$ from DSP Ltd. | NA | 5.38 | 0.0238 |
| $Mg(OH)_2$ from serpentinite (Fin.) | NA | 46.85 | 0.2396 |

NA-not applicable.

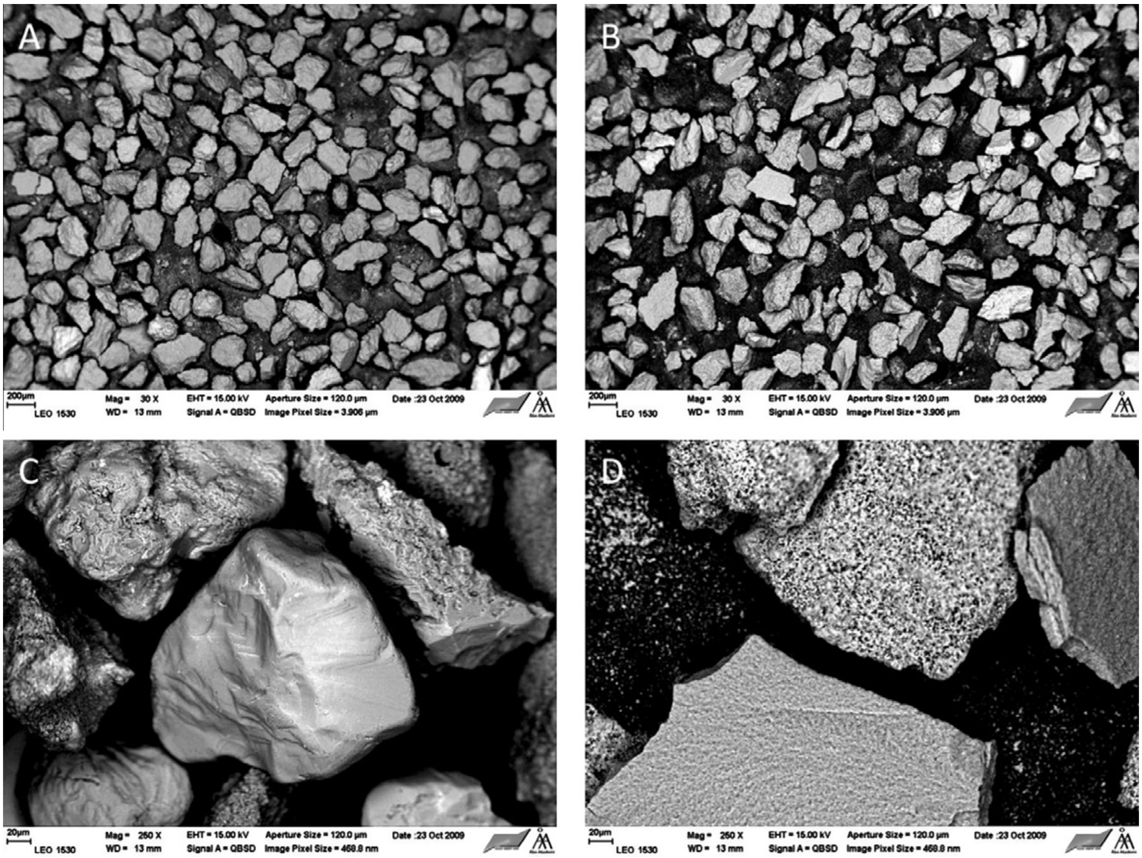

**Fig. 7.** SEM images: (A) $Mg(OH)_2$ from Dead Sea Periclase (30×); (B) $Mg(OH)_2$ produced from serpentinite (30×); (C) $Mg(OH)_2$ from Dead Sea Periclase (250×); (D) $Mg(OH)_2$ from Dead Sea Periclase (250×).

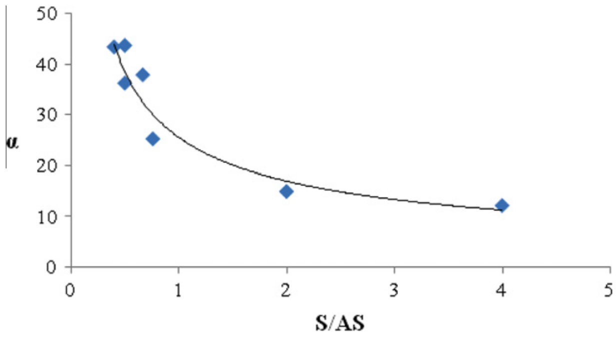

**Fig. 8.** The relationship between % Mg extraction, α and the S/AS ratio (Finnish serpentinite) $\alpha \sim \left(\frac{m_S}{m_{AS}}\right)^p$. The experiments where done under similar conditions, apart from the reactant ratio.

contracting area phase boundary controlled model given by Eqs. (4) and (5).

$$f(\alpha) = (1 - \alpha)^{1/2} \tag{4}$$

and
$$g(\alpha) = 2\{1 - (1 - \alpha)^{1/2}\} \tag{5}$$

Modification of Eq. (3) to $g(\alpha) = kt^m$, with time $t$, was used in other to make the model more versatile, and the introduction of the reactants' mass (S/AS) and mineral Mg:Fe (Mg/Fe) ratios gives an explicit form of equation for Mg extraction in the following equation:

$$\alpha = [A\exp(-E_a/(RT))t^m - (A\exp(-E_a/(RT))t^m)^2] \times (S/AS)^p(Mg/Fe)^q \tag{6}$$

The values for the parameters in Eq. (6) can be found in Table 3. Note that $t$ is given in seconds, $T$ in Kelvin and that $R = 8.314$ J/mol K is the universal gas constant. The residual sum of squares $R^2$ value for the model is 0.80, with a low significance (determined using F-tests) value (22%). Although $E_a$ is called activation energy, here, it is worth noticing that the actual $E_a$ is probably higher when compared with the total activation energy for tests with Finnish ser-

Table 3
Parameter values.

| Eq. (6). | | Eq. (7) | |
|---|---|---|---|
| Parameter | Value | Parameter | Value |
| $A$ | 0.220 $s^{-m}$ | $A$ | 2.035 $s^{-m}$ |
| $E_a$ | 17,903 J/mol | $E_a$ | 29,770 J/mol |
| $m$ | 0.344 | $m$ | 0.406 |
| $p$ | −0.754 | $p$ | −0.827 |
| $q$ | 0.362 | | |

pentinite and reaction enthalpy from thermodynamic modeling reported in Part 1 of this paper (Nduagu et al., 2012). A low value of apparent activation energy suggests that mass transfer phenomena (especially due to intra-particle diffusion) may play a significant role (Schneider and Mitschka, 1969).

When only considering the Finnish serpentinite and thus being able to disregard the distinct properties of different serpentinite rocks (i.e. Mg:Fe ratios) a simpler model can be created (Eq. (7)). Here, $R^2 = 0.99$ and a 97% significance was achieved.

$$\alpha = [A\exp(-E_a/(RT))t^m - (A\exp(-E_a/(RT))t^m)^2](\mathrm{S/AS})^p \tag{7}$$

This model establishes the dependence of Mg extraction on temperature, reactants' mass (S/AS, kg/kg) ratios and reaction time. The earlier model (Eq. (6)) incorporating all the serpentinite minerals (with the introduction of Mg:Fe ratios) did not describe the experimental data as well as the latter (Eq. (7)). The reason may be explained from the effects of surface area and pore volumes of the minerals on the minerals which were not accounted for in the development of the model.

## 7. Conclusions

This work demonstrated the applicability of a method used to produce $Mg(OH)_2$ from Finnish serpentinite rock to different Mg-silicate rocks (serpentinites and olivines) from several worldwide locations (Finland, Lithuania, Australia and Norway). The reactivity of these minerals with respect to Mg and Fe extraction were compared. Solid/solid reaction of the Mg-silicate minerals and ammonium sulfate (AS) carried out at high temperatures (400–520 °C) resulted in significant Mg extraction especially among the serpentinites. Results showed that among the Mg-silicate rocks tested Australian and Finnish serpentinites exhibited remarkable potential as raw materials for production of $Mg(OH)_2$ for purposes of gas/solid carbonation. Quite significant amounts of Fe were extracted from the serpentinites and precipitated in the form of FeOOH.

The high reactivity of Australian and Finnish serpentinite rocks is attributable to their desirable chemical compositions (high Mg:Fe ratios), surface and mesoporous properties. Although Åheim olivine has the highest Mg:Fe ratio among the minerals, it has the lowest BET surface area as well as lowest pore volume. The effects of surface area and porosity in the case of Åheim olivine seem to outweigh that of high Mg content of rock. Besides this, olivines and serpentines have a different silicate structure which can explain some of the differences in behavior. It can be assumed that also combination of Mg:Fe ratio, specific surface area and porosity are necessary factors in considering the suitability of a mineral as raw material for the production of $Mg(OH)_2$ for the purposes of carbon dioxide sequestration.

Data analysis shows that the experimental results from the serpentinite minerals, especially the Finnish serpentinite, conform to the contracting area phase boundary controlled model and temperature-dependent chemical kinetics. The model for tests with Finnish serpentinite also established the dependence of Mg extraction on reactants' mass (S/AS, kg/kg) ratios. The model that incorporated all the serpentinite minerals with the introduction of Mg:Fe ratios did not describe the experimental data as well as that obtained with data from only Finnish serpentinite. The reason can be explained from the effects of surface properties (specific surface area and pore volumes) of the minerals, which were not accounted for in the development of the model.

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