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Production of magnesium hydroxide from magnesium silicate for the purpose of CO_2 mineralisation – Part 1: Application to Finnish serpentinite

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ABSTRACT

Carbonation of abundantly available magnesium silicates such as serpentinites could be an attractive route to capture and store CO_2. In this paper we describe a novel route to produce magnesium hydroxide, $Mg(OH)_2$, from Finnish serpentinite. The resulting $Mg(OH)_2$ is much more reactive towards CO_2 than the parent serpentinite. The process route of producing $Mg(OH)_2$ as reported here involves a staged process of Mg extraction using a moderately high temperature solid/solid reaction of serpentinite and ammonium sulphate (AS) salt followed by precipitation of $Mg(OH)_2$ using aqueous ammonia. Tests at 400–550 °C showed promising results. An optimum range of reaction conditions for the extraction stage (Mg extraction) and precipitation stages (production of valuable products) of the process was also identified. The valuable solid products refer to Fe-containing compound (dark brown solid, exhibiting the properties of FeOOH) and $Mg(OH)_2$ (white precipitate), both precipitated in an aqueous solution with 25% (v/v) ammonia at pH 8–9 and 11–12, respectively. In some cases all Mg extracted from serpentinite was converted to magnesium $Mg(OH)_2$ with very small volumes of ammonia solution added. Apart from the relatively cheap AS salt reagent, the prospect of recovery and use of by-products of the process: ammonia gas, FeOOH, and AS salt presents significant benefits.

1. Introduction

CO_2 mineralisation (also known as mineral carbonation or sequestration) research in Åbo Akademi University (ÅAU) Finland addresses the gas/solid "dry" carbonation route. This method involves producing $Mg(OH)_2$ from Mg-silicate rocks and reacting it with CO_2 in a fluidized bed (FB) reactor, with the prospect of maximising the inherent energy gain of the process route (Zevenhoven et al., 2008; Fagerlund et al., 2009a,b; Fagerlund and Zevenhoven, 2011). But producing $Mg(OH)_2$ from Mg-silicates is not straightforward. Extraction of Mg from Mg-silicate minerals, specifically serpentinite rock and its subsequent conversion to $Mg(OH)_2$ suffer from setbacks arising from slow kinetics, low conversion, high energy requirements and chemical costs (Lackner et al., 1995; Lin et al., 2008; Nduagu, 2008; Newall et al., 2000; Teir, 2008; Zevenhoven et al., 2008). In this paper a novel method of producing $Mg(OH)_2$ from serpentinite which addresses some of these drawbacks is presented. While this Part 1 paper describes the method and gives results obtained with Finnish serpentinite rock, Part 2 (Nduagu et al., 2011) will give a comparison of results obtained with different minerals and rock types.

2. Solid/solid route for producing $Mg(OH)_2$ from serpentinite rock

2.1. Thermodynamic study

It has been reported that ammonium sulphate salt (in solid or aqueous states) when reacted directly with serpentinite rock has the capacity for extracting Mg (Abd-Elzaher, 1999; Nduagu, 2008; Teir, 2008). The extent of extraction, however, may depend on the route and reaction conditions. The reaction of serpentine $Mg_3Si_2O_5(OH)_4$ (the reactive component constituting 83 wt.% of the Finnish serpentinite rock was used in this work) with $(NH_4)_2SO_4$ (AS) seems to be thermodynamically feasible at temperatures between 200 °C and 550 °C. The thermodynamic equilibrium compositions of the reaction of serpentine and Fe compound (assumed to be Fe_3O_4 based on XRD analysis) in Finnish serpentinite rock were evaluated using HSC Chemistry (2002).

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Thermodynamic equilibrium compositions and reaction enthalpies of the reaction of serpentinite and AS are presented in Figs. 1 and 2. It can be observed that $MgSO_4$, SiO_2 and $FeSO_4$ are the dominant solid products of the reaction of serpentinite and AS while the main gaseous products are water and ammonia. Since thermal decomposition of AS salt could produce both SO_2 and SO_3 gases, we modelled the effect of the introduction of these gases on the thermodynamics of the reaction of serpentinite and AS salt. Introduction of SO_2 (as a product or reactant) besides SO_3 gas into the thermodynamic model dramatically changes the equilibrium compositions of the products (see Fig. 1B). The equilibrium compositions of magnesium sulphate ($MgSO_4$) appear to be exchanged with and/or replaced by those of magnesium orthosilicate (Mg_2SiO_4) and magnesium metasilicate ($MgSiO_3$). Thus, Mg_2SiO_4 and $MgSiO_3$ become the dominant solid products in lieu of $MgSO_4$. Based on what was found (reported below), it can be assumed that SO_2 gas is apparently not produced due to presumably slow kinetics of the reaction between SO_2 and SO_3. Moreover, the presence of SO_2 gas either as reactants, products or by-products in the reaction system should be avoided in order to achieve the process goal of extracting as much Mg (in the form of $MgSO_4$) as possible.

With slightly less than the stoichiometric amounts of AS salt needed for the reaction, SO_3 gas production from the solid/solid reaction is inhibited as shown in Fig. 1A. On the other hand, if AS salt supplied is more than the stoichiometric amounts (Fig. 2), $SO_3(g)$ production becomes significant at temperatures higher than 430 °C. This consequently leads to a more stepwise rise in the reaction enthalpy as can be seen in Fig. 2B.

The effect of pressure on the thermodynamics of the reaction was also simulated and was found to be insignificant.

2.2. Mechanism for the reaction of serpentinite and AS salt

Enthalpies for reactions presented in this paper (see Table 1) were evaluated using the data from HSC program for Gibbs energy minimisation (HSC Chemistry, 2002).

The reaction of serpentine and ammonium sulphate is thermodynamically feasible (with a negative Gibbs free energy) at temperatures above (roughly) 193 °C (HSC Chemistry, 2002). On the other hand, if no reaction of serpentine and AS occurs below 193 °C, ammonium sulphate will expectedly start to release ammonia at temperatures above 100 °C, according to the Reaction (1) – see Table 1.

At 160 °C, ammonium tri-sulphate is formed from the decomposition of ammonium sulphate – Reaction (2). This double salt releases ammonia on heating at 180 °C (Kiyoura and Urano, 1970).

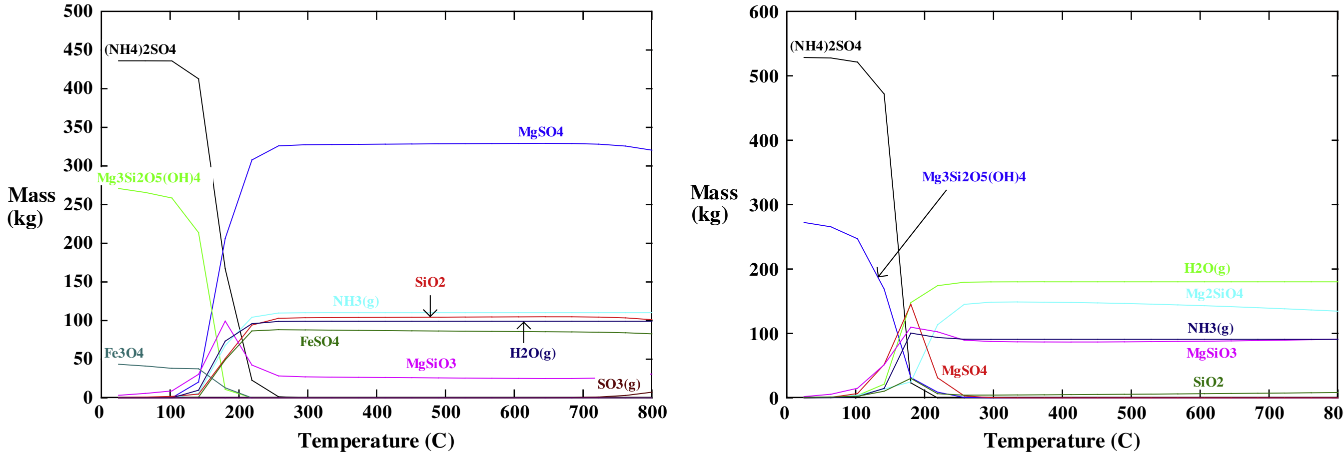
From the above thermodynamic and thermochemical behaviours of the possible reactions, the Mg extraction reaction through the solid/solid route may be presented as in Reaction (3).

Reaction equations (2) and (3) add up to (4) which is considered to be the global equation for the extraction of Mg from serpentinite using the solid/solid route (Nduagu, 2008).

Understanding the reaction behaviour of the iron compound(s) present in serpentinite during the solid/solid reaction is critical to modelling and optimisation of iron-based by-products of the process. There is conflicting information on the form that iron appears in the Finnish serpentinite rock used. Teir et al. (2007) reported an XRD analysis which shows that iron is present in serpentinite as magnetite (Fe_3O_4), constituting 14 wt.% of this serpentinite – see Table 2 .

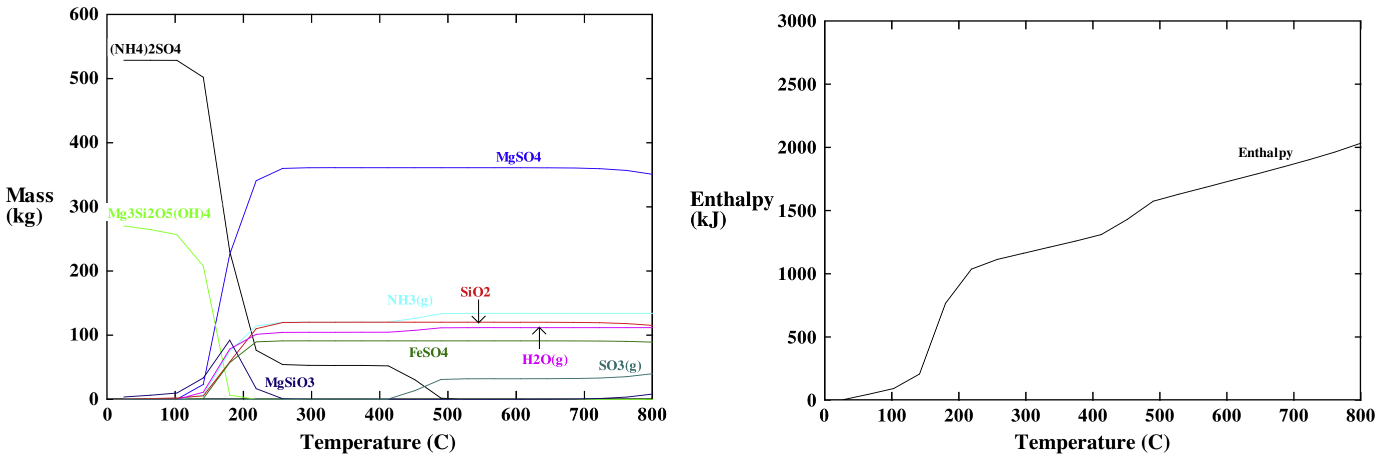
Recently, Rinne (2008) reported an XRD analysis showing that a combination of FeO and Fe_2O_3 compounds (which of course could be summed up to be Fe_3O_4) is present in the same mineral sample. Huang et al. (2006) points out that the valence of Fe in Fe_2O_3 is +3, but in Fe_3O_4 two-thirds of the Fe is +3, with the rest +2, with the "nominal" valence +8/3. Since FeO, Fe_2O_3 and Fe_3O_4 may all be present in Finnish serpentinite, modelling with the combined chemical formula of FeO and Fe_2O_3 (=Fe_3O_4) may be a good starting point. The possible thermodynamically feasible reactions of magnetite and AS salt are presented Reactions in 5 and 6.

The reactions are assumed to occur consecutively; as SO_2 produced from Reaction (5) is consumed in Reaction (6). The presence of sulphur dioxide (besides SO_3 gas which may be produced when ammonium sulphate is reacted in excess of stoichiometric amounts) in the reactor, as reported in Section 2.1, would dramatically change the equilibrium compositions of the products. Significant Mg extraction levels may only be achieved during the reactions if $SO_2(g)$ is not present in the reactor. It can therefore be assumed that if $SO_2(g)$ is produced in Reaction (5) it immediately takes part in the Reaction (6) without interfering with the conversion of Mg to $MgSO_4$. Since experimental results gave promising $MgSO_4$ extraction levels, that implies an absence of the inhibiting SO_2 gas – this could also mean that SO_2 (if produced)



(A) (B)

Fig. 1. Thermodynamic equilibrium compositions of reactants and products of the solid/solid reaction, in the presence and absence of SO_2. Main reactants are serpentinite rock (containing 1 kmol serpentine i.e. 3 kmol Mg and 0.2 kmol Fe_3O_4) and 3.3 kmol AS. The amount of AS supplied is slightly less than the stoichiometric amounts needed to react both Fe_3O_4 and $Mg_3Si_2O_5(OH)_4$. (A) SO_2 gas is not considered as reactants or products. (B) SO_2 gas is introduced as a reactant.



(A) (B)

Fig. 2. Solid/solid reaction of serpentinite rock (containing 1 kmol serpentine i.e. 3 kmol Mg and ~0.2 kmol Fe_3O_4) and 4 kmol AS. The amount of AS supplied (4 kmol) is slightly more than the stoichiometric amounts needed. (A) Thermodynamic equilibrium compositions. (B) Reaction enthalpy.

Table 1
Reaction equations and thermodynamics of major reactions considered in this study. Apart from the conventional reaction enthalpy calculation at 25 °C, it was also evaluated at the average optimum reaction temperature, 420 °C.

Reaction	Extraction reaction	ΔHr (298 K) kJ/mol	ΔHr (693 K) kJ/mol	Ref.element
(1)	$(NH_4)_2SO_4(s) \leftarrow\rightarrow NH_4HSO_4(s) + NH_3(g)$	111	114	S
(2)	$2(NH_4)_2SO_4(s) \leftarrow\rightarrow (NH_4)_3H(SO_4)_2(g) + NH_3(g)$	no data	no data	
(3)	$Mg_3Si_2O_5(OH)_4(s) + 1.5(NH_4)_3H(SO_4)_2(s) \rightarrow 3MgSO_4(s) + 4.5NH_3(g) + 2SiO_2 + 5H_2O(g)$	no data	no data	
(4)	$Mg_3Si_2O_5(OH)_4(s) + 3(NH_4)_2SO_4(s) \rightarrow 3MgSO_4(s) + 2SiO_2(s) + 5H_2O(g) + 6NH_3(g)$	244	220	Mg
(5)	$2Fe_3O_4(s) + 10(NH_4)_2SO_4(s) \rightarrow 3Fe_2(SO_4)_3(s) + 20NH_3(g) + 10H_2O(g) + SO_2(g)$	888	812	Fe
(6)	$Fe_3O_4(s) + 2(NH_4)_2SO_4(s) + SO_2(g) \rightarrow 3FeSO_4(s) + 4NH_3(g) + 2H_2O(g)$	323	282	Fe
(7)	$MgSO_4(aq) + 2NH_4OH(aq) \leftarrow\rightarrow (NH_4)_2SO_4(aq) + Mg(OH)_2\ (s)$	−70	does not apply	Mg
(8)	$MgSO_4(aq) + 2NaOH(aq) \leftarrow\rightarrow Na_2SO_4(aq) + Mg(OH)_2\ (s)$	1.5	does not apply	Mg

is immediately consumed probably via a reaction with Fe_3O_4 (see Eq. (6)).

2.3. Precipitation stages

The second step of this process (precipitation) was planned with minimisation of cost and prospects of recovery and recycling of chemicals as important considerations. Bases (such as sodium hydroxide and ammonia solutions, see Reactions (7) and (8) in Table 1) have been widely used to precipitate brucite from magnesium salt solutions (Giorgi et al., 2005; Henrist et al., 2003; Teir, 2008).

Table 2
Elemental analysis of serpentinite rock, particle sizes 74–125 µm. After Teir et al., 2007.

Element, i	m_i/m (mg/g)	Composition (%)	Method
Mg	218	21.8	ICP-AES
Si	116	11.6	ICP-AES
Fe	101	10.1	ICP-AES
S	4.8	0.48	XRF
Ca	3.4	0.34	ICP-AES
Cl	2.1	0.21	XRF
Al	0.208	0.02	ICP-AES
Ni	0.205	0.02	ICP-AES
Ti	0.18	0.02	ICP-AES
Mn	0.084	0.01	ICP-AES
Cr	0.074	0.01	ICP-AES
Cu	0.069	0.01	ICP-AES
Co	<0.015	0.00	ICP-AES
Ba	<0.015	0.00	ICP-AES

The Si content was 188 mg/g according to XRF analysis. Although the ICP-AES value was used for calculating Si extraction efficiencies, the actual content of Si is probably somewhere between the two values.

Teir (2008) concluded that a large amount of sodium hydroxide is needed for the precipitation of $Mg(OH)_2$ without an efficient recovery method. In an investigation of the influence of precipitant on the morphological characteristics of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution, Henrist et al. (2003) reported that the pH of the suspension when using NH_4OH as the alkaline precipitant was lower than that obtained by using NaOH. It can be interpreted that a smaller amount of base precipitant is needed in the precipitation reaction when ammonia solution is used as compared to using sodium hydroxide. More importantly, the use of NH_4OH as a precipitant is preferred because it results in the recovery of ammonium sulphate salt (an initial input chemical of the solid/solid process), thereby closing the process loop. Further advantages of using aqueous ammonia as a precipitant and its thermodynamic favourability have been discussed in detail elsewhere (Nduagu, 2008).

3. Materials and methods

3.1. Mg and Fe extraction

The reactivity (with respect to Mg extraction) of Finnish serpentinite from the Hitura nickel mine, of Finn Nickel was studied. One particle size fraction, 75–125 µm was used for the tests reported here. The Finnish mineral contains ca. 83 wt.% serpentine, molecular formula $Mg_3Si_2O_5(OH)_4$, with magnetite (Fe_3O_4) accounting for the largest proportion (~82 wt.%) of the impurities and 14 wt.% of the mineral. The elemental composition of the rock is presented in Table 2. 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 reaction container (see Fig. 3) was constructed by folding thin aluminium foil into a boat-like shape of dimensions; length ~10 cm, width 2.5 cm, height 2.5 cm and thickness 3 mm. This is about the dimension that can be inserted into the tube of the reaction oven (Fig. 4). The very good heat conduction properties of Al influenced its choice as a reaction container in lieu of a porcelain boat, which is a more inert material, and was first used in the trial experiments. Results from thermodynamics modelling and experimental tests show that neither the thermal decomposition of alumina nor its reaction with AS salt has a pronounced effect on the Mg and Fe extraction reactions of interest.

There was no special pretreatment performed considering that both reactants are solids of different physical properties. The two solids (serpentinite and AS salt) were measured into the reaction container and mixed together using a stainless steel spatula. It is difficult to mix solids (serpentinite and AS salt) having different physical properties, and even more difficult to measure the extent to which the solids are evenly mixed. However, the pretreatment method was the same with all the experiments. During the design of the experiments, the authors envisioned that using a rotary reactor during process scale-up should adequately address the issue of uneven solid mixing. Therefore, investigation of solid contact limitations of the reaction of serpentinite and AS salt is outside the scope of this paper; it is intended to be a subject of future scale-up study. In the scale-up reactor the reactants will be heated and agitated at the same time under a more process-like and controlled atmosphere. Besides, the application of any special pretreatment method was intentionally avoided in this preliminary study in order to reduce the energy requirements and costs of the process.

The reaction container (Fig. 3), after feeding in the mixed solid reactants was inserted into the oven/reactor (Fig. 4), which is regulated at different reaction temperatures. Two water bottles containing a measured volume of distilled water, connected in series, were used to scrub gases that exited the reaction vessel. The product of the reaction (with an appearance of sintered solid, see Fig. 3) was dissolved in a measured volume of water, and the mixture was afterwards filtered. Samples of the filtrate were taken for ICP-OES analysis. The residue from the filtration process was oven-dried for 2 h at 100 °C and weighed. This part of the tests aimed at determining, among other things: % extraction i.e. the mass fraction of elements (especially, Mg and Fe) extracted as sulphates from the mass of these elements present in serpentinite. The effects of reaction parameters (reactants' mass ratio, reaction temperature and time) on extraction and recovery of gaseous products (ammonia gas plus steam) from the reactor were also determined.

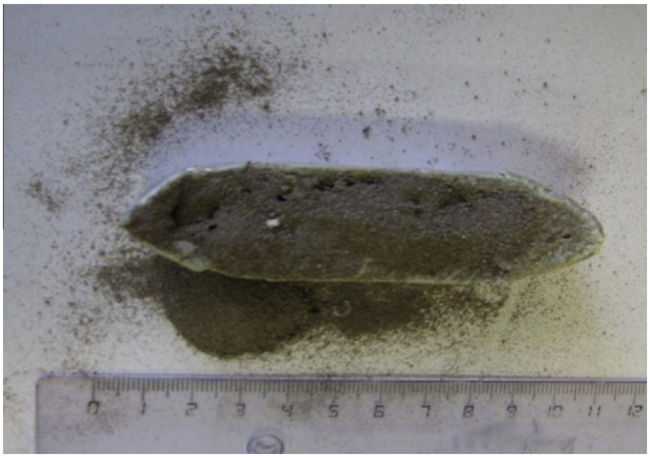


Fig. 3. Reaction container (made from Aluminium foil with dimensions length ~ 10 cm, width ~ 2.5 cm, height ~ 2.5 cm and thickness~3 mm) containing sintered solid product of reaction of Finnish serpentinite and AS.

Fig. 4. Reactor/oven used for the reaction of serpentinite and AS.

3.2. Precipitation stages

Aqueous ammonia solution (NH_4OH, 25% v/v, Sigma–Aldrich) was added to the aqueous filtrate obtained in Section 3.1 in order to raise its pH by stepwise precipitation of Fe and Mg compounds. At pH ranges of 8–9 and 11–12, compounds of Fe (presumably as FeOOH) and Mg as $Mg(OH)_2$ were expected to respectively precipitate out of the solution. Impurities in forms of oxides or hydroxides of metals found in serpentinite had been separated during the filtration and first stage of precipitation.

Removal of the impurities at the first precipitation stage is necessary in order to produce pure $Mg(OH)_2$ in the last precipitation step so that only this will have to be fed to the carbonation reactor. A process schematic and typical mass balance of the process are shown in Fig. 5.

From this stage of tests the amount of valuable products (Fe-rich by-product and magnesium hydroxide) produced per gram serpentinite reacted, purity of magnesium hydroxide produced, and effect of reaction parameters on conversion were determined. Also, a correlation between the Mg extraction and the magnesium hydroxide precipitation steps was identified and became useful in determining optimal reaction conditions as well as in predicting unavailable or unreliable data.

3.3. Purity of magnesium hydroxide product

In a separate test that served as a background experiment, used to simulate only the aqueous solution part of the process, 3 g of anhydrous $MgSO_4$ (reagent grade, 97%, Sigma–Aldrich) was dissolved in 50 ml water and reacted with 30 ml of aqueous ammonia solution (NH_4OH, 25%, Sigma–Aldrich) at room temperature. A white precipitate of $Mg(OH)_2$ was formed at the pH of 11.05. The mixture was allowed to settle, and was then filtered and oven-dried for 2 h at 100 °C. Quantitative and qualitative determinations of the products of the reaction were done using ICP-OES and/or XRD analysis.

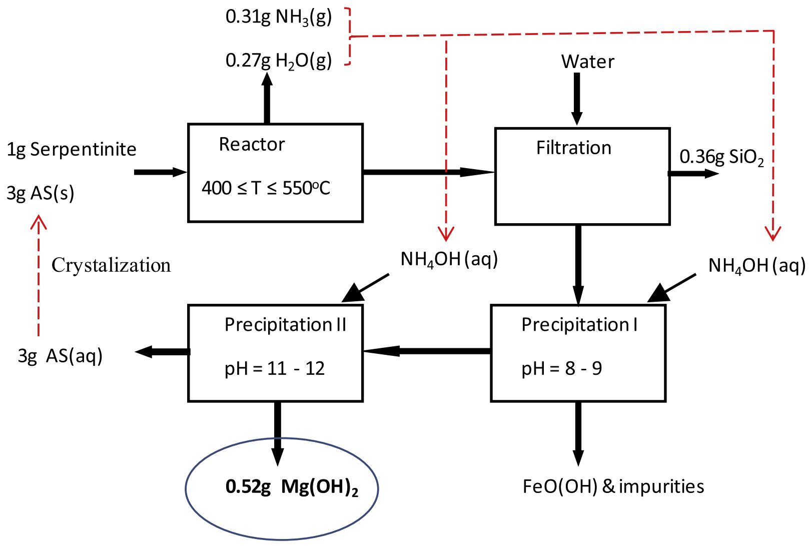


Fig. 5. Schematic of the staged route for $Mg(OH)_2$ production via solid/solid reaction of Finnish serpentinite and AS salt followed by precipitation. Dash lines represent the theoretical chemical recovery and re-use routes.

4. Results and discussion

The results of thirty-two laboratory tests that aimed at producing magnesium hydroxide from Finnish serpentinite (75–125 μm) are presented in this section. The extent of extraction of Mg and Fe was determined from sixteen tests where ICP-OES analysis of the $MgSO_4$-rich filtrate produced after separation of the dissolved from undissolved reaction products through filtration was available. This was useful for a full mass balance calculation. Extraction values represent the mass proportion of the extracted element to the mass of that element in the rock sample, expressed as percentage. A correlation of the magnesium extraction values and the amount of valuable products produced from the precipitation stages of the experiments was identified. The correlation is then used to estimate and/or validate Mg extraction results of the other sixteen tests where ICP-OES analysis were not done extensively or regarded as outliers (unreliable).

4.1. Extraction stage

4.1.1. Mg extraction

Fig. 6 shows the results obtained from experimental tests performed to evaluate the effects of reaction temperature, time and reactants' mass ratios (S/AS, g/g) on Mg extraction. Repeat experiments were performed at selected reaction conditions for the Mg & Fe extraction reactions, without significant deviations. In Fig. 6A the Mg extraction values, for almost all the time intervals tested, seems to decline after 440 °C. However, the effect of reaction time on Mg extraction is not well understood or cannot be interpreted based only on Fig. 6A. This may be because the effect of S/AS ratio and the interaction effects of one reaction parameter with the other were ignored. The reason for the surprisingly low Mg extraction values when the reaction times 60 min and 120 min may be attributed to non-optimal conditions of other operating parameters, especially S/AS ratio. This effect was not considered in Fig. 6A. For example, the Mg extraction values at 30 min and 60 min are higher than that obtained at 120 min probably because of the high reactants' mass ratio (1 g/g) of the latter, which is below the stoichiometric requirement. The Mg extraction trend becomes clearer if the effect of reactants' mass ratio (*S/AS*) is considered alongside the effects of temperature (Fig. 6B). Fig. 6B shows the plot of the mean of Mg extraction values against temperatures for two distinct ranges of *S/AS* ratios tested. The vertical lines in Fig. 6B (range plot) link the minimum and maximum Mg extraction values obtained at the same temperature for the case, $S/AS < 1$ g/g. A distinct maximum value of Mg extraction is identifiable for both

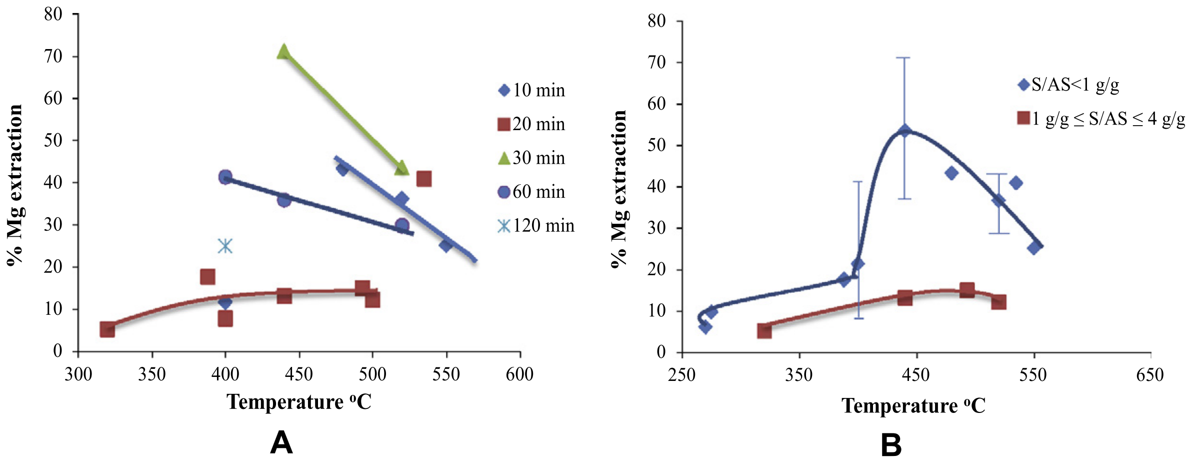


Fig. 6. (A) Effect of reaction temperature and reaction time on Mg extraction. (B) Effect of reaction temperature and reactant ratios (S/AS) on Mg extraction.

cases of S/AS < 1 g/g and 1 g/g ⩽ *S/AS* ⩽ 4 g/g at temperatures 440 °C and 480 °C respectively, after which the Mg extraction values decline. Important to note is the pronounced increase in Mg extraction values at temperatures higher than 400 °C and steep decline after 450 °C, especially for *S/AS* < 1 g/g. This case corresponds to slightly more AS than the stoichiometric amount required. The stoichiometric ratio of 3 mol of AS needed for 1 mol serpentine (with 83 wt.% serpentine in the serpentinite used) corresponds to a S/AS mass ratio equal to 0.84 g serpentine per g AS. Fig. 6A and B indicate that Mg extraction is most effective at temperatures 400–450 °C.

As expected from the endothermic reaction of serpentinite and AS salt, an increase in reaction temperature leads to an increase in the extent of Mg extraction. More heat added to the endothermic process is absorbed, which favours product formation. The reactants of an endothermic reaction have a lower chemical potential than the products. In order to form the products, an energy equivalent to the reaction enthalpy (ΔH_r see values presented in Table 1) plus the activation energy (E_a) must be added to raise the potential energy of the reactants to that of the products of the reaction. Increase in heat input into an endothermic process shifts reaction equilibrium from reactants to products thereby increasing the degree of conversion. (The reverse holds for an exothermic process.)

The decline in Mg extraction above 450 °C does not necessarily negate the basic concept that increase in heat input of endothermic reactions results in increase in product yield. Rather, the value of Mg extraction decreases at temperatures above 450 °C due to decomposition of AS salt. This was corroborated by a more recent study (Nduagu and Zevenhoven, 2010), which investigated the effects of reaction parameters on the extraction of Mg from serpentinite from different locations worldwide. This study showed that a significant decline in the Mg extraction value is evident above 440 °C; consequently due to the decomposition of AS salt. Decomposition of AS salt is an undesirable side reaction that can occur at high temperatures. It affects negatively the extent of Mg extraction from serpentinite.

4.1.2. Fe and Si extraction

Fe, Si and other elements present (though in minute amounts) in Finnish serpentinite were extracted simultaneously with Mg during the reaction of serpentinite and AS. ICP-OES results of the filtrate obtained when reaction products were dissolved in water show that the extraction reaction is most favourable to Mg extraction. Mg, Fe and Si together constitute about 90–98 wt.% of the extracted material (ICP-OES) while individual compositions of Mg, Fe and Si in the extract liquids are within the following ranges: 60–94 wt.%, 0–35 wt.% and 0–4 wt.% respectively. However, the amounts of Si extracted may be a low estimate. Teir et al. (2007) noted that the silicon concentrations in the filtrate may not be accurate because part of the silica can precipitate as gel on the filter thereby reducing the silicon concentration in the filtrate. ICP-OES analysis results of the filtrate show that the extent of Fe and Si extraction are of the ranges 0–35% and 0–2.5% respectively. Si was present in the $MgSO_4$-rich solution in unquantifiable low amounts (ICP-OES) in most of the tests. In case Si recovery becomes a point of interest, the residual solid mixture from the filtration process would need to be reprocessed in order to separate extracted Si. Fig. 7A shows the effect reaction temperature and time on Fe extraction if the effect of *S/AS* mass ratio is neglected while Fig. 7B maps the effect of temperature and *S/AS* mass ratio on Fe extraction when the effect of reaction time is ignored.

The effects of temperature and reactants' mass ratio on Fe extraction are more evident from Fig. 7A and B than that of reaction time. This is similar to the observations made in regards to Mg extraction. Optimal ranges of reaction parameters for Fe extraction are identifiable for temperature (400–480 °C) and S/AS ratio (⩽1 g/g). The optimal range of reaction time seems somewhat unclear, though it can be interpreted from Fig. 7A that the maximum extraction of Fe can be achieved within 30 min. Similarly, an increase in heat input (represented in Fig. 7 by increase in reaction temperature) into the process increases the reaction conversion as reaction equilibrium favours the formation of more products. But at temperatures higher than 440 °C the Fe extraction values begin to decrease. This is also due to the thermal decomposition of AS salt, which is undesirable. The outliers in the Fig. 7A probably result from the plausible effects of *S/AS* ratio (Fig. 7B), which are not considered. Equally important are the interaction effects of the reaction parameters which cannot be shown in the Fig. 7A and B, but were addressed in a recent study by Nduagu and Zevenhoven (2010). In this study they found that the interaction effect of reaction temperature and time is significant when analysing the combined $Mg(OH)_2$ and FeOOH products. Further analysis of the effects of the reaction parameters on the products of the $Mg(OH)_2$ process is provided in Section 4.3.

4.2. Precipitation stages

4.2.1. Precipitation of FeOOH

Addition of few drops of ammonia solution (25% v/v) to the $MgSO_4$-rich filtrate obtained from the extraction stage rapidly changes its pH from acidic (pH < 6) to slightly alkaline (8 ⩽ pH < 10), while also changing the colour of solution from colourless to dark green. The dark green precipitate after being filtered, upon exposure to air and drying at 100 °C (atmospheric pressure), quickly turns dark brown in colour. The dark-brown dry solid product exhibited no magnetic properties while XRD failed to recognise crystalline phases. This material was later (with support of our colleagues at the Laboratory for Inorganic Chemistry and of the Laboratory of Analytical Chemistry of ÅAU) identified as of iron oxide hydroxide (mineral goethite – FeOOH). This was concluded after attempting to dissolve the precipitate in various strong acids. The only successful attempt was achieved with HCl, which indicates FeOOH. Hägg (1988) also mentioned that dissolved iron (II) salts precipitate as $Fe(OH)_2$ upon addition of basic solutions, but immediately oxidise to FeOOH upon contact with air. Teir et al. (2007) who dissolved the same Finnish serpentinite mineral with mineral acids also mentioned goethite (FeOOH) and magnetite (Fe_3O_4) as the precipitated forms of iron using NaOH as a precipitant.

Samples of the FeOOH-rich product were analysed with ICP-OES analyses and were found to also contain large amounts of Mg and enrichments of Si, S and Al. While the elemental fractions of S and Si in the solid product remained fairly constant between 14–22 wt.% and 2–12 wt.% respectively, the fractions of Mg (12–52 wt.%), Fe (17–47 wt.%) and Al (2–30 wt.%) varied significantly. High Al levels in this by-product are presumably a result of contamination by the reaction container which is constructed from aluminium foil, and thus would be negligible especially when a more suitable/inert material is used as the reaction container. This conclusion has been validated by results from the extraction stage showing % Al extraction values from serpentinite at well above 100%.

The pH of precipitation of the FeOOH-rich product appears to play a prominent role in its elemental composition (normalised for the major elements extracted from serpentinite in Fig. 8). It is also expected that at lower pH the fraction of Fe in the precipitate would be the highest. However, the reverse would be the case for Mg. For example, at a pH of 8.48 Mg content was lowest when compared to other samples precipitated at higher pH values for this precipitation step (Fig. 8).

Mg composition exhibits a distinct and increasing trend with increasing pH. It is however desirable to regulate the pH of the first

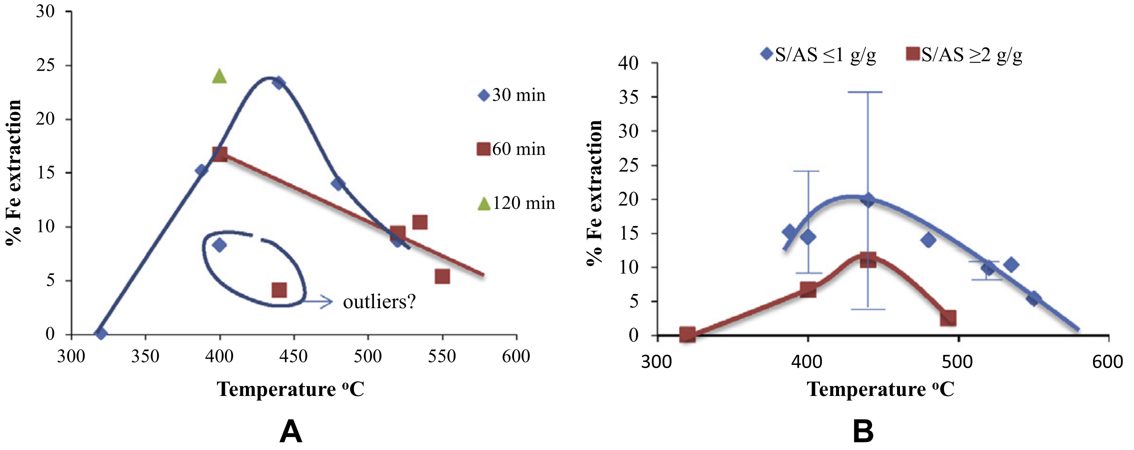


Fig. 7. (A) Effect of reaction time (*t*), reaction temperature (*T*) on Fe extraction. (B) Effect of reaction temperature and reactants' mass ratios on Fe extraction.

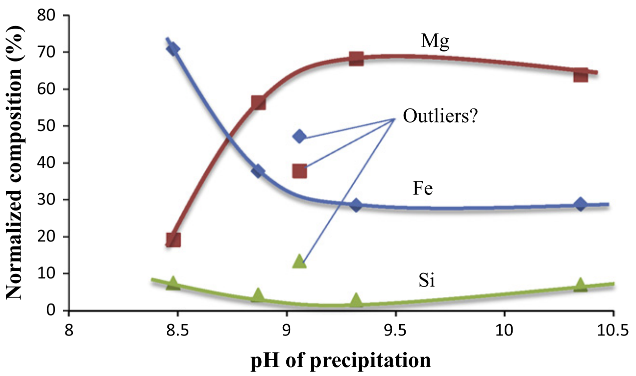


Fig. 8. Effect of pH of precipitation on the composition of FeOOH-rich by-product, normalised for extracts Fe, Mg and Si.

precipitation stage in order to ensure minimal Mg and maximum Fe compositions in the FeOOH-rich product. Thus, pH levels ⩽8.5 seem appropriate.

4.2.2. Precipitation of magnesium hydroxide

Adding more ammonia solution to the $MgSO_4$-rich solution obtained after filtering the precipitated FeOOH-rich by-product (in Section 4.2.1) leads to precipitation of $Mg(OH)_2$. At pH levels between 11 and 12 $Mg(OH)_2$ was produced as a white precipitate which was allowed to settle, was vacuum filtered on a filter paper and dried at 100 °C for at least 2 h. Complete conversion of $MgSO_4$ to $Mg(OH)_2$ is possible at this stage.

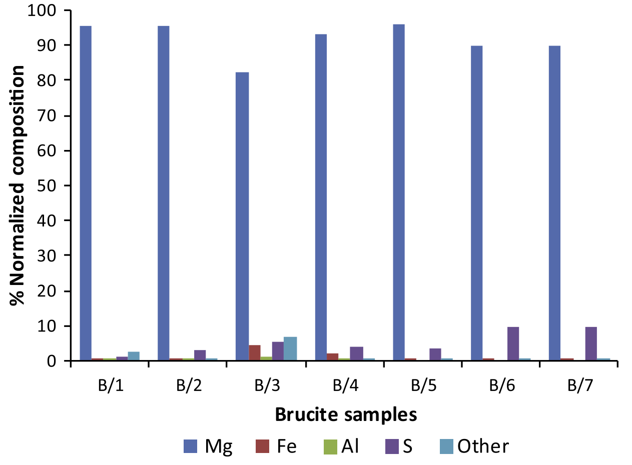


Fig. 9. Elemental composition from normalised ICP-OES analysis of seven brucite products. Note that the elements that were not considered in this calculation are oxygen, hydrogen and Nitrogen.

Seven samples of magnesium hydroxide were analysed using ICP-OES and XRD. The elemental compositions of normalised ICP-OES results are presented in Fig. 9. Mass balances show that magnesium hydroxide constitutes 82–96% of the compounds that make up the white solid product.

In Fig. 10A and B the $Mg(OH)_2$ samples produced from serpentinite show diffraction peaks corresponding to hexagonal structure magnesium hydroxide, according to JCPDS file No. 07-0239 (JCPDS, 1996). Similar XRD peaks were obtained with $Mg(OH)_2$ from a solution of $MgCl_2$ using NaOH solution (Hsu and Nacu, 2005). If the $Mg(OH)_2$ is produced in such a way that eliminates most of the enrichments, its XRD plot would look better. This implies using better material separation/filtration equipment than the filter paper we used. This can also be achieved by filtering and washing the $Mg(OH)_2$ sample as much as possible. However, producing an ultra-pure $Mg(OH)_2$ is not a priority in this process since the contaminants are not likely to hinder the carbonation of $Mg(OH)_2$.

4.3. Optimisation of magnesium hydroxide production from Finnish serpentinite

Relationships between the two main stages of the process; i.e. extraction and precipitation steps and possible effects of the reaction parameters on $Mg(OH)_2$ production were studied for the thirty-two tests. The precipitated solid products of two precipitation stages are regarded as the valuable products. There is an ongoing study (Zevenhoven et al., 2009) on utilisation of the Fe-rich by-product and integration of this process with the iron – and steelmaking industry. Iron is present in significant amounts in e.g. Finnish serpentinite (13 wt.%) and could provide a large and valuable by-product for this CCS route. The amount (in grams) of valuable solid products precipitated during the two stages of precipitation using an ammonia solution strongly correlate with the extent of Mg extraction. Experimental data and ICP-OES analysis of valuable solid samples obtained from the precipitation stages of the process show that Mg and Fe constitute respectively 50–74 wt.% and 10–25 wt.% of the extracted elements present in the precipitated products of the process.

A correlation between the % Mg extraction calculated from ICP-OES results of samples from sixteen experiments (Mg extraction,

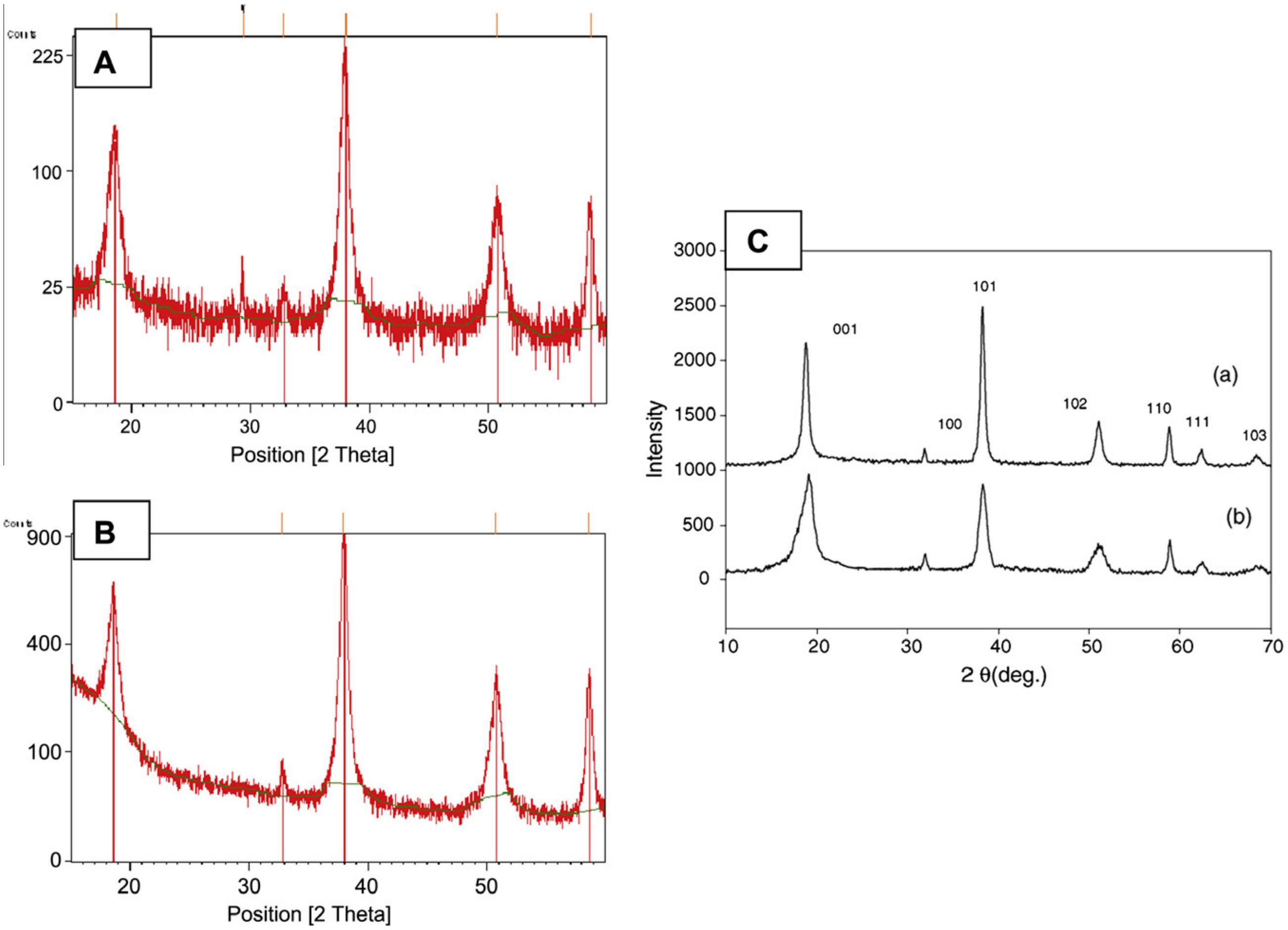


Fig. 10. (A) and (B) XRD pattern for $Mg(OH)_2$ produced from serpentinite. C: XRD powder diffraction pattern of $Mg(OH)_2$ produced from the reaction of $MgCl_2$ and NaOH by Hsu and Nacu (2005).

Section 4.1.1) and the mass of valuable products being FeOOH-rich by-product and $Mg(OH)_2$ product was identified using Eq. (9), and presented in Fig. 11.

$$\%\ \text{Mg extraction} = 206.5\left(\frac{\text{g products}}{\text{g } S}\right) - 3.1097 \quad (R^2 = 0.9256) \qquad (9)$$

where g products/g S is the combined mass in grams of FeOOH-rich by-product and $Mg(OH)_2$ produced per gram serpentinite reacted.

Using the developed relationships of Mg extraction and valuable products (Eq. (9)), an estimate of values of magnesium extraction is made for the experiments (especially for the second set of sixteen tests where the % Mg extraction were either not determined by ICP-OES analysis or were regarded as outliers).

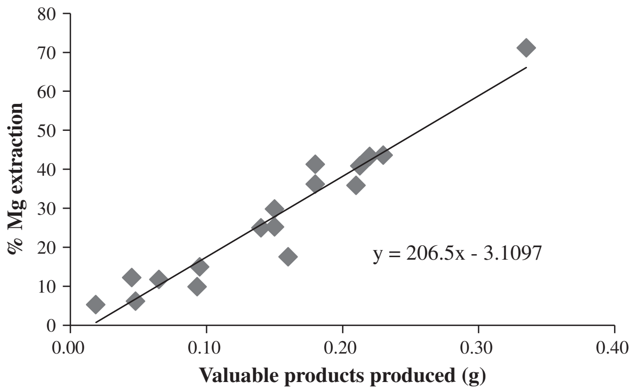


Fig. 11. Plot of model (Eq. (9)) against experimental values of % Mg extraction from 16 tests.

In general, S/AS, reaction temperature and time exhibit similar effects on both the extraction and precipitation stages. For example, the effect of reaction temperature on Mg extraction (Fig. 12B) is similar to that obtained for mass of valuable products (Fig. 12A). Fig. 12C and D shows the effects of S/AS and reaction time on mass of valuable products. Fig. 12A–D shows the plot of the mean of the results (y-values) against the reaction parameters (x-axis). The vertical lines (range plot) link the minimum and maximum of the y-values obtained at the same value of the reaction parameters presented in x-axis. A distinct maximum value of Mg extraction and valuable products is identifiable at the following conditions: S/AS = 0.4–0.5 g/g, temperatures, 480 °C and time, 30 min. Beyond this point the Mg extraction and valuable product yield decline.

An optimum value was determined by replacing the mean of the Mg extraction values with the original values. While plotting the mean values of Mg extraction against the reaction parameters is useful in examining the trend; however, it does not adequately represent the full picture. Therefore a combination of Figs. 6, 7 and 12 were used to determine the optimal value of Mg extraction and valuable products. The optimal Mg extraction value is 64–66%, which is obtained at the following reaction conditions; reactants' (S/AS) mass ratio, 0.5–0.7; reaction temperature, 400–440 °C and reaction time, 30–60 min. Under the same conditions, 0.33–0.34 g of valuable solid products (composing of >70% brucite and <30% FeOOH) were produced per gram of Finnish serpentinite reacted. The result of a recent study by Nduagu and Zevenhoven

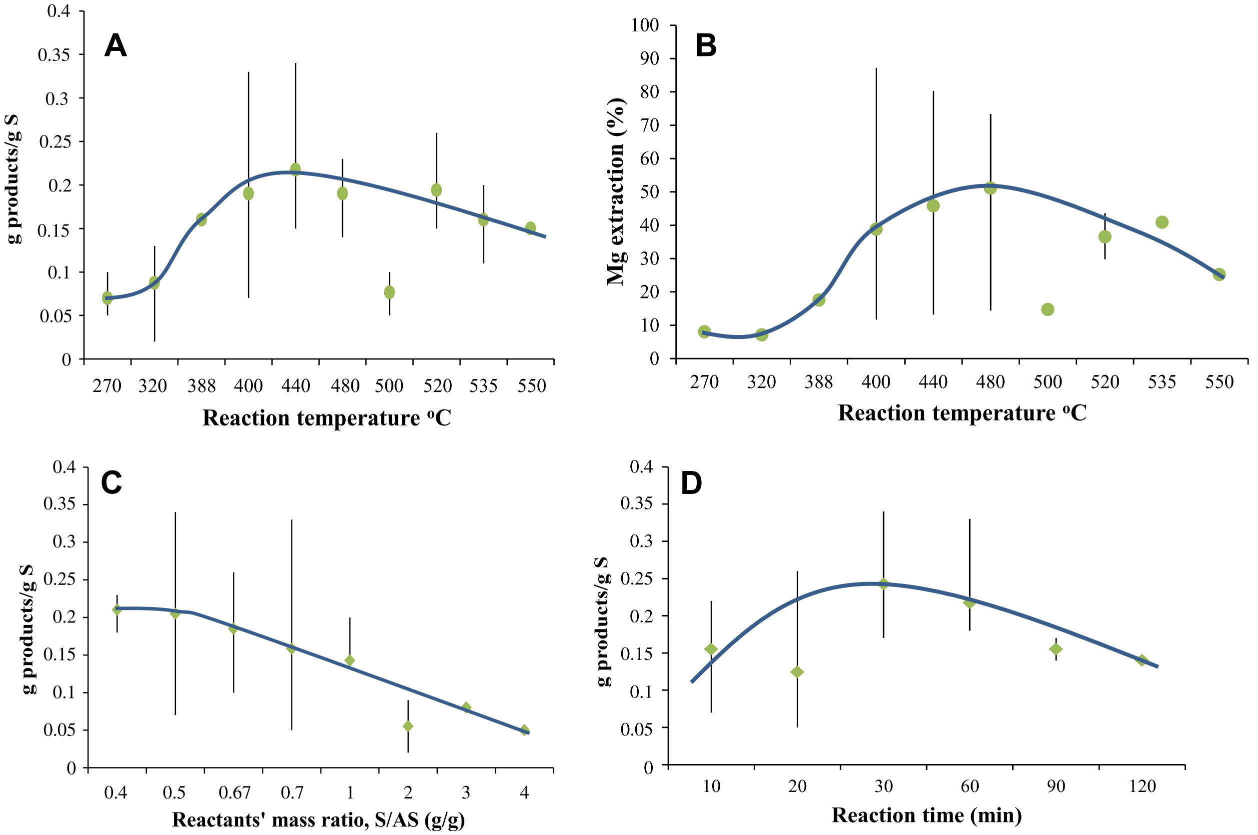


Fig. 12. (A) Effect of temperature on $Mg(OH)_2$ production. (B) Effect of temperature on Mg extraction. (C) Effect of reactants' mass ratio (S/AS) on magnesium hydroxide production. (D) Effect of reaction time on magnesium hydroxide production.

(2010) corroborates to some extent the findings presented here. That paper among other things reported that high levels of S/AS ratio (<0.67 g/g) do not favour Mg extraction at temperatures above 440 °C. However, contrary to what we found for most of the experiments reported here the paper by Nduagu and Zevenhoven (2010) reports that longer reaction times favour Mg and Fe extraction. This conflict may have resulted from the fact Nduagu and Zevenhoven (2010) investigated minerals of varying chemical compositions and from different worldwide locations. It also considered a broader range of values and interactions of reaction parameters while this paper focused mainly on presenting the method of producing $Mg(OH)_2$ from Finnish serpentinite. It can be inferred that the decreasing Mg extraction values obtained in this paper when reaction times increases above 60 min result from non-optimal conditions of other operating parameters (S/AS ratio and reaction temperature). The effect of pH on precipitation of Fe containing compound (from 1st precipitation stage with NH_4OH) and magnesium hydroxide (from 2nd precipitation stage with NH_4OH) was further studied.

Fig. 13 shows optimum pH levels for precipitation (production) of the valuable solid products, and this corresponds to pH values of around 8.5–9 for the first precipitation stage and around 11–12 for the second precipitation stage.

4.4. Other parameters

4.4.1. Effect of reaction parameters on solid (filtration) residue from the reaction of serpentinite and AS

Quantitative and qualitative analysis of the solid residue obtained after separation of the $MgSO_4$-rich solution (filtrate from extraction stage) are presented in this section. The solid residue was obtained through dissolution of the solid reaction product (in form of a hard crust, see Fig. 3) subsequently followed by filtration and drying of the solid samples at 100 °C. The amounts (in grams) of the solid filtration residue obtained in tests with Finnish serpentinite are tabulated in Table 3. The X-ray diffraction patterns of the solid filtration residue show peaks corresponding to those of lizardite [$Mg_3Si_2O_5(OH)_4$], a polymorphic form of serpentine. The ICP-OES analysis results of the $MgSO_4$-rich solution (filtrate) show that unreacted and undissolved AS may also be present in the solid residue.

It is desirable to minimise the amount of unreacted compounds. In order to investigate the effect of the reaction parameters on the amount of solid residues, experimental data for the tests with Finnish serpentinite are presented in Table 3. The amount of solid residue tends to a minimum at S/AS ratios of 0.5–1 g/g. It can also

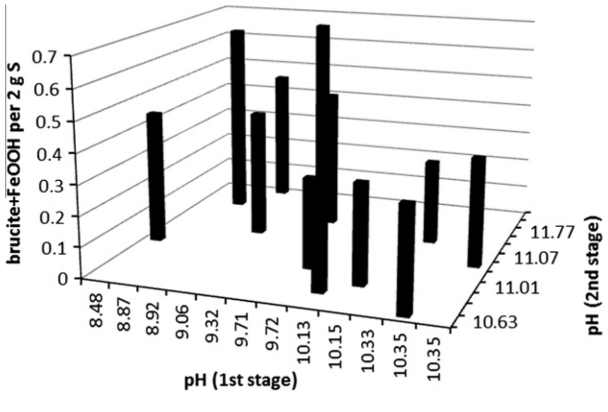


Fig. 13. Effect of pH of precipitation (1st and 2nd stages) on brucite production.

Table 3
Experimental data (from Finnish serpentinite) used to determine the amount of solid residue and recovered gaseous products.

Expt #	S (g)	AS (g)	S/AS (g/g)	Temperature (°C)	Time (min.)	Mass loss (g)	Solid residue (g)	pH [1]	pH [2]	pH [3]
1	2	5	0.4	400	30	NA	1.78	1.8	8.92	12.25
2	2	2.86	0.7	400	60	NA	1.48	3.56	8.87	11.77
3	2	2.22	0.9	400	120	1.2	1.35	6.9	10.33	11.16
4	2	4	0.5	440	30	1.51	1.69	2.62	9.32	12.06
5	2	2.86	0.7	440	60	1.61	1.62	3.9	9.06	11.07
6	2	1.67	1.19	440	90	1.18	1.72	4.44	10.15	10.91
7	2	5	0.4	480	10	NA	1.59	2.11	8.48	11.06
8	2	2.22	0.9	480	30	1.43	1.66	3.52	10.35	10.63
9	2	1.67	1.67	480	90	1.28	1.61	3.6	10.13	10.8
10	2	4	0.5	520	10	2.99	1.5	NA	10.35	11.06
11	2	4	0.5	520	30	3.25	1.45	3.69	9.71	11.5
12	2	2.22	0.9	520	60	1.73	1.54	3.67	9.72	11.01

pH[1]-pH of solid products dissolved in water.
pH[2]-pH of precipitation of Fe-rich compound (green to brown precipitate).
pH[3]-pH of precipitation of magnesium hydroxide (white precipitate).
NA – Not available.

be deducted that the mass of solid residue decreases as the reaction temperature increases. For example, at 400 °C, S/AS ratios had a significant effect on the amount of the residual solid. Increase in the mass of AS salt reactant below S/AS = 0.84 g/g resulted in sharp increases in mass of solid residue; suggesting that the increase may be as a result of excess and/or unreacted AS salt.

4.4.2. Recovery of reagents; ammonia gas and ammonium sulphate salt

For a set of experiments the gaseous product(s), mainly ammonia (according to stoichiometry) were collected in two class glass bottles, connected in series and each containing 150 ml water of a known pH of 8.85. The pH of the resulting solution was used to determine the concentration of gas(es) entrained. Since the collected gas is expected to be ammonia gas, an increase in the pH of the resulting solution was predicted. This was confirmed experimentally with an average of 1.43 points increase in pH of water recorded from twelve tests. However, thermodynamic studies (Section 2.1) showed the possible formation of “unwanted” SO_3 (or SO_2?) gas(es) at temperatures above 450 °C, a situation that may render “pH to concentration” calculation estimates unreliable.

ICIS® pricing information on chemical commodities[2], The Market, Fertilizer News and Analysis (17th September, 2009) and for HCl (18th September, 2009), for example, in US markets, show that AS (average cost, \$121/ton) is cheaper than HCl (average cost \$195/ton). The latter has been more frequently used for extracting Mg from Mg-silicate minerals (Newall et al., 2000). More so, the prospect of recovery of AS salt at the end of the process is another economically competitive aspect of this process. It has been emphasised that whatever agent is used for the extraction must be recoverable, and in case of inevitable losses must not be expensive. Experimental studies and results aimed at the recovery of AS salt are presented in this section. The experimental results show that AS by-product is recoverable, and the extent of recovery may be dependent on some factors identified here. Crystallization of AS salt was achieved by heating (to below 100 °C) and evaporating aqueous ammonium sulphate solution obtained after precipitation of magnesium hydroxide.

Maximum AS recovery of 72% was achieved for the tests reported here. This value may be much higher if the process is operated at large scale where some losses experienced in the experiments can be avoided. The temperature of the solid/solid reaction and the amount of alkaline precipitant used for precipitation seem to significantly affect the extent of recovery of AS. Increase in reaction temperature leads to a decrease in the extent of recovery. This may be as a result of possible decomposition and formation of SO_3 gas at temperatures $\geqslant$450 °C (see Section 2.1). The results also show an optimal amount of ammonia solution may be needed for optimum recovery of AS. Volumes of ammonia solution used in precipitation affect the amount of AS salt recovered. In volumetric terms, this is between 40 and 60 ml of 25% v/v ammonia per 2 g serpentinite.

5. Chemical and kinetic modelling

A mechanism for the reaction of serpentinite and AS salt has been proposed in Section 2.2. AS salt decomposes at temperatures >160 °C to ammonium trisulphate and ammonia gas (Reactions (2) or (10)). The ammonia trisulphate (A3S) starts to melt at temperatures exceeding 230 °C after which the solid serpentine particles (S) can react with the ammonium trisulphate melt (Reaction (11)). At temperatures (above 300 °C) $(NH_4)_2Mg_2(SO_4)_2$ may be formed, which later decomposes above 350 °C to water soluble magnesium sulphate (MS), silica, and gases (ammonia gas and water vapour).

$$2\mathrm{AS(s)} \longleftrightarrow 0.5\ \mathrm{A3S(s)} + 0.5\ \mathrm{NH_3(g)} \tag{10}$$

$$\mathrm{S(s)} + 1.5\ \mathrm{A3S(l)} \rightarrow 3\mathrm{MS} + 4.5\ \mathrm{NH_3(g)} + 2\mathrm{SiO_2(s)} + 5\mathrm{H_2O(g)} \tag{11}$$

The decomposition of AS salt to ammonium tri-sulphate and ammonia gas (Reaction (10)) is assumed to be irreversible since ammonia gas is removed from the reactor vessel during the reaction. A first order rate equation in respect to each component: AS, A3S and ammonia gas (A) was found to describe the reaction rather well:

$$\mathrm{r_1} = \mathrm{k_1 C_{AS}} \tag{12}$$

$$\mathrm{r_2} = \mathrm{k_2} * \mathrm{C_s} * \mathrm{C_{A3S}} \tag{13}$$

where k_1 and k_2 are the rate constants.

An analysis with other reaction orders than 1 was also performed but some initial parameter estimation results showed that the reaction order for the components A, S and A3S are very close to unity. The mass balances for all components in the system are as follows:

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[2] ICIS® is an independent analytical agency monitoring chemical commodities markets and proving independent pricing information on chemical commodities. More information on ICIS can be found at <www.icispricing.com>.

Table 4
Parameter estimation results.

Estimated parameters	Parameter values	Estimated standard error	Parameter standard error
A_1 (min^{-1} K^{-1}) A_2	0.204	0.351	0.6

(mol^{-1} min^{-1})0.0300.021.5E_{a1} (kJ/mol)75.8282.7E_{a2} (kJ/mol)43.31080.4Corr0.3960.015725

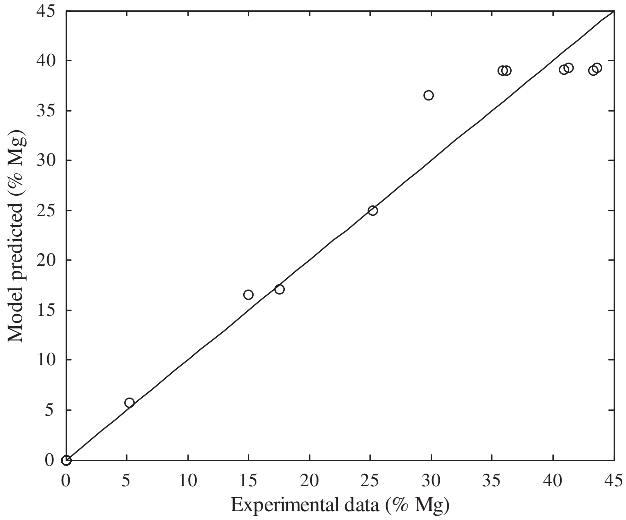

Fig. 14. Plot of the experimental data (% Mg extraction) against values generated by the model.

$$dC_S/dt = -r_2 \quad dC_{AS}/dt = -2r_2 \quad dC_{MS}/dt = 3r_2 \quad dC_{Si}/dt = 2r_2$$
$$dC_w/dt = 5r_2 \quad dC_A/dt = 0.5r_1 + 4.5r_2 \quad dC_{A3S}/dt = 0.5r_1 - 1.5r_2$$

These seven ordinary differential equations (ODEs) were solved with the backward difference method and the parameters were estimated with the Simplex and Levenberg–Marquardt method using the software Modest (Haario, 2006). The rate constants k_1 and k_2 are temperature dependent and follow the Arrhenius law. For Reaction (14) it was found that also the frequency factor was temperature dependent.

$$k_1 = A_1 * T * \exp(-E_{a1}z/R) \tag{14}$$

$$k_2 = A_2 * \exp(-E_{a2}z/R) \tag{15}$$

where $z = 1/T - 1/T_{mean}$, T_{mean} = 673 K, (reference temperature chosen at the average temperature of all the experiments) and T, the set point temperature of the experiments.

$$\alpha = C_{MS} * M_{MS} * 0.20/C_{S0}/0.263 * 100 * corr \tag{16}$$

The parameters in Eq. (14) and (15) were calculated and tabulated in Table 4. A degree of explanation or R^2 value of 93.50% is obtained (see Fig. 14).

Here, the objective function, α is the % Mg extraction expressed as mass of Mg extracted from the reaction of serpentinite and AS salt. The constant 0.20 in Eq. (16) represents the composition by weight (i.e. 20 wt.%) of Mg in the $MgSO_4$ produced from the reaction of serpentine and AS salt while 0.263 corresponds to the composition by weight (for this case, 26.3 wt.%) of Mg in Finnish serpentinite mineral).

C_{MS} and M_{MS} are the concentration (moles) and molar mass of $MgSO_4$ respectively, C_{S0} is the mass of serpentine in the Finnish serpentinite rock and *corr* is a correction factor. The correction factor accounts for size and shape factors, surface structure and porosity of the reactants and that of the reaction container, heat and mass transfer and uneven mixing effects. Future studies will

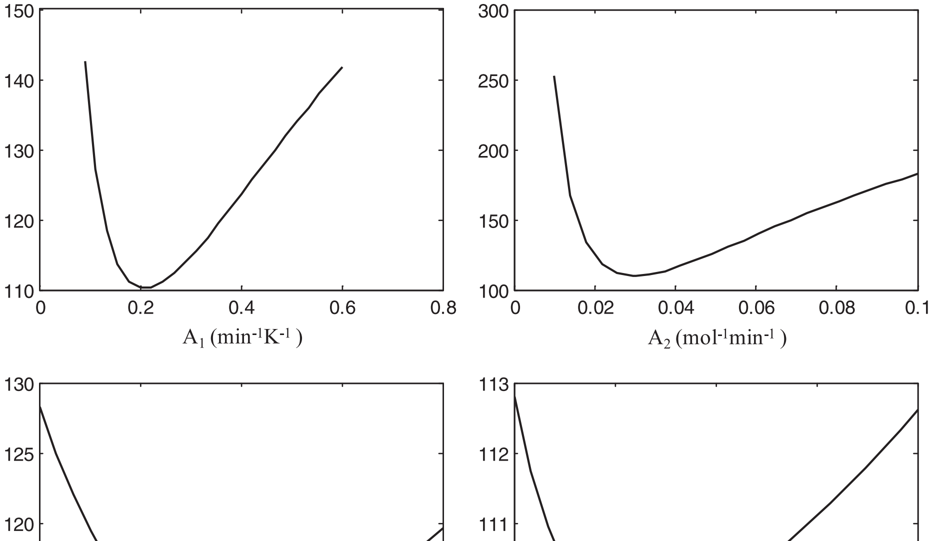

Fig. 15. Sensitivity analysis of the objective function, α (% Mg extraction) as a function of the kinetic parameters: frequency factors, A_1 (min^{-1} K^{-1}) and A_2 (mol^{-1} min^{-1}) and activation energies, E_{a1} (kJ/mol) and E_{a2} (kJ/mol). The *y*-axis represents the objective function while the *x*-axis the kinetic parameters. The plots show how well the parameters were identified with distinct minima.

quantify these effects and compare it with the value obtained for *corr.*

To check the identifiability of the parameters (A_1 and E_{a1} in Eq. (14) and A_2 and E_{a2} found in Eq. (15)) a sensitivity analysis was performed. The sensitivity of the objective function α with respect to the kinetic parameters (A_1, A_2, E_{a1} and E_{a2}) was carried out by calculating the objective function as a function of one of the parameters while keeping the other parameters at the values of the objective function minimum. The objective function as a function of parameters A_1 and E_{a1} (in Eq. (14)) and A_2 and E_{a2} (in Eq. (15)) are plotted in Fig. 15. Even if some of the parameters show significant variation (100%) the optimal parameter values are well identified with clear minima in the sensitivity analysis plots (Fig. 15).

6. Conclusions

This study shows that magnesium hydroxide ($Mg(OH)_2$) can be produced from serpentinite for subsequent carbonation via a staged process of Mg extraction (solid/solid) followed by precipitation from an aqueous solution. Experimental results aimed at finding optimum conditions for the process gave an optimum range of 64–66% Mg extraction at the following reaction conditions; reactants' mass ratio (S/AS), 0.5–0.7; reaction temperature, 400–440 °C and reaction time, 30–60 min. Under the same conditions, 0.33 – 0.34 g of valuable solid products (composed of >70% magnesium hydroxide and <30% FeOOH) were produced per gram of Finnish serpentinite reacted. The valuable solid products refer to the Fe containing (dark brown solid) compound and magnesium hydroxide (white solid), both precipitated with ammonia solution at pH 8–9 and 11–12, respectively.

In spite of the energy requirement of the process (to be addressed in more detail in a future paper), it is important to note its significance. Mg extraction shows promising results, and a high purity $Mg(OH)_2$ was produced. The Fe-rich compound produced in significant amounts from the process may be a useful raw material in the iron and steel industry. Ammonia gas is a by-product of the reaction, which was collected in water and can be used to act as or supplement the ammonia solution used for precipitation purposes. Interestingly, smaller volumetric amounts of ammonia solution are needed in the precipitation process compared to the amounts of NaOH used previously in other studies. AS salt used as reagent for extracting Mg from the minerals is relatively cheap, and is a product and by-product of several chemical processes. AS reagent is recovered at the end of the process; thereby, closing the process loop.

Scale-up of this route will be part of future work. The use of a lab-scale rotary kiln we have purchased will allow for tests with better mixing as well as address possible solid contact limitations.

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