Inclined Settlers for Separation of Magnesium Hydroxide and Iron Oxides for Mineral Carbonation

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Abstract:
One of the options under development for carbon capture, utilization and storage (CCUS) is referred to as the Åbo Akademi (ÅA) route, which is a two-stage route using serpentinite rock and ammonium sulphate to produce magnesium hydroxide that is subsequently carbonated in a gas-solid reactor. An issue for the process is to find a suitable way to precipitate and separate magnesium hydroxide and iron oxides from the obtained aqueous solution. Research presented in this paper will give some results from the separation of precipitated magnesium and iron oxides and hydroxides, as well as magnesium (hydro)carbonates (which are produced in the case where CO$_2$ is fed to the solution at the same time). Experiments were done with analytical grade magnesium and iron sulphates as well as with serpentinite rock-derived magnesium and iron sulphate solutions. Inclined settlers were used and solutions were pumped into the settlers at different flow rates. Precipitation of the species was done either in a mixer before the solution was pumped to the settler or in the inclined settler itself. Most experiments were run at ambient temperature. Recirculation was used in some experiments in order to try to increase the precipitation and sedimentation efficiency. It was shown possible to achieve continuous separation of the solids from the suspensions. Increased temperature did not seem to affect settling of the magnesium hydroxide particles. Separation in inclined settlers would dictate very low pumping rates to avoid a too turbulent environment in the settling zone. Sedimentation was enhanced by applying wet (aqueous) carbonation thus achieving a magnesium (hydro)carbonate product with larger particle size than the suggested magnesium hydroxide separated according to the conventional ÅA route. Effort needs still to be put to optimizing the separation step in order to create a continuous flow combined with preceding process steps.

Keywords:
Inclined Settler, Sedimentation, Mineral Carbonation, Magnesium Hydroxide, Magnesium (Hydro)carbonate.

1. Introduction and Background
One of the options being developed in Finland for carbon capture, utilization and storage (CCUS) is referred to as the Åbo Akademi (ÅA) route, which is a two-stage route using serpentinite (which is a magnesium silicate rock) and ammonium sulphate ((NH$_4$)$_2$SO$_4$) to produce magnesium hydroxide (Mg(OH)$_2$) that is subsequently carbonated in a gas-solid reactor. Serpentinite will initially be heated in a solid-solid reaction together with ammonium sulphate and intermediate, water-soluble products of magnesium and iron sulphates will form. Magnesium hydroxide will be precipitated when ammonia (NH$_3$(g), which is generated as vapour during the solid-solid reaction) is added and this is used in the final carbonation step where magnesium carbonates will be formed. The overall (exothermic) reaction for the ÅA route is according to [1]
\[
\text{MgSi}_2\text{O}_5\text{(OH)}_4\text{(s) + 3CO}_2\text{(g) } \rightarrow 3\text{MgCO}_3\text{(s) } + 2\text{SiO}_2\text{(s) } + 2\text{H}_2\text{O(l)}\Delta\text{H} = -64\text{kJ/mol (R1)}
\]
The conventional ÅA route suggests formation of magnesium hydroxide, which will continue to a fluidised bed reactor where it is reacted with flue gas forming magnesium carbonate (MgCO₃). Another option is to perform wet (aqueous) carbonation, meaning that carbon dioxide (CO₂) is pumped directly into the aqueous solution containing magnesium sulphate (MgSO₄). Ammonia is needed in order to produce an ammonium bicarbonate (NH₄HCO₃) intermediate when reacted with carbon dioxide. Ammonium bicarbonate will then react with magnesium sulphate to produce nesquehonite (MgCO₃·3H₂O) and finally hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O), if temperature is exceeding 50 °C according to [2].

\[
NH_3(g) + CO_2(g) + H_2O(l) \rightarrow NH_4HCO_3(aq), \Delta H = -99 \text{kJ/mol} \quad (R2)
\]

\[
MgSO_4(aq) + 2NH_4HCO_3(aq) + 2H_2O(l) \rightarrow MgCO_3 \cdot 3H_2O(s) + (NH_4)_2SO_4(aq) + CO_2(g), \Delta H = 52 \text{kJ/mol} \quad (R3)
\]

\[
5MgCO_3 \cdot 3H_2O(s) \rightarrow 4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O(s) + CO_2(g) + 10H_2O(l), \Delta H = 120 \text{kJ/mol} \quad (R4)
\]

Characteristics of magnesium hydroxide and magnesium carbonate particles produced in the conventional ÅA route were earlier studied by [3, 4]. The precipitation of hydromagnesite by the wet carbonation route was studied by [5, 6]. Serpentinite typically contains considerable amounts of iron which can be separated in a subsequent step before magnesium is precipitated. Iron will form sulphates during the solid-solid reaction that is the first step of the ÅA route. Precipitation will in the conventional ÅA route be done by the stepwise addition of ammonia to an aqueous solution (after filtration of unreacted products from the solid-solid reaction) where pH first is increased to 8-9 [1]. Iron will at this pH be precipitated according to

\[
Fe_2(SO_4)_3(s) + 6NH_3(g) + 4H_2O(l) \rightarrow 2FeOOH(s) + (NH_4)_2SO_4(aq), \Delta H = -720 \text{kJ/mol} \quad (R5)
\]

Magnesium can later be precipitated by increasing pH further (10-12), after removal of the precipitated iron. By applying longer precipitation times and by increasing precipitation temperature, it could be possible to precipitate magnetite (Fe₃O₄) instead of goethite (FeOOH) according to a change in crystal structure. The formation of magnetite at different conditions has earlier been discussed by [7-9]. One possible reaction which could form magnetite from iron hydroxide (Fe(OH)₂, will most likely form as an intermediate during precipitation of goethite) and goethite could according to [10] be

\[
Fe(OH)_2(s) + 2FeOOH \rightarrow Fe(OH)_2 \cdot 2FeOOH \rightarrow Fe_3O_4 + H_2O \quad (R6)
\]

One drawback applying wet carbonation is the fact that every four carbon dioxide molecule would need five magnesium molecules to form hydromagnesite, while the conventional ÅA route needs one magnesium for every carbon dioxide molecule captured to form magnesite. On the other hand precipitation and carbonation will take place in a single unit when applying wet carbonation, without intermediate separation of magnesium hydroxide as in the conventional ÅA route [11]. See schematic figures of the two different routes in Figure 1. Note that in both routes a pre-separation (capture) of CO₂ may be omitted.
An issue for the process is to find a more “streamlined” way to precipitate and separate magnesium hydroxide and iron oxides from the obtained aqueous solution, as a continuous process step between magnesium extraction from rock and the eventual carbonation. So-called inclined settlers [12] are used here for the separation of particulate sediment from the aqueous streams, in several cases combined with an upstream mixing vessel. Several different cases will be addressed:

- The use of pure sulphate chemicals or serpentinite-derived sulphates of Mg and Fe
- Precipitation of (hydr)oxides of Mg and Fe separately or combined
- Precipitation of Mg (or Fe) hydroxides, with or without presence of CO₂, the latter producing magnesium hydrocarbonates

Many mineral-separation processes involve handling of substantial quantities of water. The final concentrate might thus have to be separated from a suspension having a high water-solids ratio. Dewatering, which is a solid-liquid procedure, will in most cases produce a sufficiently dry concentrate for shipment. This paper will focus on the first stage of dewatering which is sedimentation. Filtration and thermal drying often follow the sedimentation step [13]. Theoretically, up to 80% of the water could possibly be removed in this stage. Filtration and thermal drying is needed in order to reach a higher solids content in the final product. The settling rate of particles in a fluid are governed either by Stokes’ law or Newton’s law. Particle size determines which law to follow. Very fine particles, below 50 µm typically, obey Stokes’ law, but settle extremely slowly by gravity alone. An alternative could therefore be to agglomerate or flocculate the solids to larger aggregates or lumps, so called flocs, which will settle more rapidly [13].

The most widely applied dewatering technique in mineral processing is gravity sedimentation. It is a relatively cheap and high-capacity process dealing with low shear forces. This also provides good conditions for flocculation of fine particles. Thickeners are often used to increase concentration of the specific suspension and to obtain a clear liquid. As concentration increases free settling often turns to hindered settling [13].
Specific gravity, shape of the particles and size are parameters which will affect the velocity of particles in a fluid medium. Another parameter is the concentration of the solids in the suspension. Either free or hindered settling will take place depending on concentration. Free settling takes place in solutions with large fluid volume. This enables particles to move in the suspension with minimal occurrence of collisions and crowding with other particles. Hindered settling takes place as the concentration of solids in the pulp increases. The falling rate of the particles becomes hindered by this. Hindered settling could roughly be explained as the density of the solution more and more reaches the density of the pulp rather than the carrier liquid. Hindered-settling conditions are used in order to increase the effect of density on the separation, as far as classifiers are concerned. Free-settling conditions uses more dilute suspensions which increase the effect of particle size. This could be taken into the process for sedimentation as well [13].

Thickeners have often diameters of 2-200 m and a depth of 1-7 m. This put requirements on footprint area [13]. Inclined settlers and lamella thickeners are also based on the concept of gravity sedimentation and could be used in order to decrease space required.

This paper will present results using inclined tube settlers for separation and sedimentation of iron and magnesium containing compounds from aqueous streams, see Figure 2. Research presented in this paper will report some results on the separation of precipitated magnesium hydroxide, magnesium (hydro)carbonate and iron oxides and hydroxides.

![Figure 2. Schematic figure of the principle for inclined settlers. Settling zones may vary depending on number and types of species involved.](image)

**2. Experimental work**

Experiments in this study were done with analytical grade magnesium and iron sulphates as well as with Finnish serpentinite rock-derived magnesium and iron sulphate solutions. Inclined settlers were used and solutions were pumped into the settlers at different flow rates, either with or without recirculation. Crystallization and precipitation of iron oxides, iron hydroxides, magnesium hydroxides or magnesium (hydro)carbonates which all require a certain pH range, was done either in a mixer before the solution was pumped to the settler or in the inclined settler itself. Most experiments were run at ambient temperature, after it was found that increased temperatures seem to have little effect on the settling of the particles. Ambient pressure was applied in all experiments.
Recirculation was used in some experiments in order to try to increase the precipitation and sedimentation rate and efficiency.

Two (identical) inclined tube settlers of acrylic plastic were used for the experiments. The design can be seen in Figure 3. Total inner length of the settlers is 47 cm and the inner diameter is 4.6 cm. The inlet was placed at the bottom of the settler above an outlet for the underflow stream which could be manually adjusted. An outlet for the overflow stream, a 12 mm opening with possibility to measure pH and a 3 mm opening to make it possible to add chemicals through a lance from different positions in the settler, respectively, were located at the top of the settlers. Silicone and Marprene hoses suitable for pumping solutions were used to connect different units. Pump model Watson Marlow 323 was used to pump the solution into the settler at 3, 6 or 30 L/h.

![Figure 3. Inclined settler used in all experiments. Two identical settlers were designed in order to handle iron and magnesium in separate settlers.](image)

All filtrated material in all experiments from overflow and underflow was dried overnight at 110°C. Whatman Glass Microfiber Filters GF/F were used for filtration.

Analyses of liquid samples were done with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Scanning Electron Microscopy/ Energy-Dispersive X-Ray Spectroscopy (SEM/EDX) of model LEO 1530 Gemini with a Scientific Ultra Dry Silicon Drift Detector.

An initial experiment was done in order to get some knowledge about the pH gradient and mixing directly in the settler. Deionized water and a few drops of hydrochloric acid were mixed and the solution obtained gave pH 2. The indicator mixture used consisted of a mixture of two parts of bromothymol blue (1 ml, per liter initial solution), four parts of phenolphthalein (2 ml) and three parts of thymolphthalein (1.5 ml). 10% ammonia was thereafter fed to the settler through a lance mounted on top of the settler at the same time as the acified solution was pumped into the settler from the bottom inlet. Inclination of the settler was 45° and pump speed 100 rpm corresponded to 30 L/h. Mixing and pH increase took place rapidly. A figure showing the pH interval for the chosen mixture together with a figure showing the inclined settler at the time when the solution started to flow out via the overflow can be found in Appendix A.

Figure 4 gives a view of the experimental setup with the spherical vessel acting as a mixer unit from which solution or slurry was pumped into the settler. pH could be measured in the mixer unit and overflow was either recycled back to the mixer or separated to an individual overflow stream.
3. Batch-wise sedimentation

3.1. Magnesium hydroxide and magnesium (hydro)carbonate sedimentation

Initially, tests were done batch-wise in order to be able to study the settling behaviour of the particles. It was found that carbonation of magnesium could give a faster sedimentation than sedimentation of magnesium hydroxide by comparing Figure 5 and Figure 6. Figure 5 shows a solution which was prepared by dissolving 10 g of anhydrous magnesium sulphate (≥ 97%, Sigma-Aldrich) in 250 ml deionized water. The solution was heated to 80°C and 150 ml plus 125 ml of 0.25 M and 1 M NaOH solution, respectively, were added droplet-wise to the solution to increase pH to 10.5. A pH of 10-12 is appropriate for magnesium hydroxide precipitation according to the conventional AA route for CO₂ mineralization. Higher temperature and slow addition of alkali could possibly favour larger particle size of the particles. Visible particles of magnesium hydroxide were formed at pH 10.5 and the solution was then pumped into the settler. Sedimentation was very slow from the beginning and somewhat faster when the solution was allowed to settle for a while. No further sedimentation could be noticed after 100 minutes.
Figure 6 shows a solution which was prepared by again dissolving 10 g of anhydrous magnesium sulphate (97%, Sigma-Aldrich) in 250 ml deionized water. 100 ml of 10% NH₄OH was used to increase pH to 10.5. According to earlier research a pH 8-11 is needed to precipitate hydromagnesite, which is one possible product from the carbonation route, [14]. Magnesium hydroxide started clearly to precipitate at pH 10. A similar approach was earlier used by [6], using a magnesium hydroxide slurry for carbonation, where CO₂ gas was bubbled through the solution. An initial increase in temperature from 22.6 to 36.7 °C was noticed the first 20 minutes and carbonates of magnesium started to form after 15 minutes. CO₂ was bubbled through the solution for 30 minutes in a separate mixer. Sedimentation was after this studied in the inclined settler, which started immediately when the solution was pumped into the settler. Already after 15 minutes sedimentation seemed to slow down/be more or less completed.

![Figure 6. Precipitation with 10% NH₄OH followed by wet carbonation in a separate mixer before the solution was pumped to the settler for sedimentation and separation.](image)

Since sedimentation seemed to be more successful in the case where magnesium was carbonated (instead of producing a hydroxide for subsequent carbonation), less attention was paid to the sedimentation of magnesium hydroxide after these experiments. Particle size analysis and estimation of the elemental composition of the settled solids of assumed magnesium hydroxide shown in Figure 5 were analysed with SEM/EDX, see images and table in Appendix B. The main point with this experiment was to study the behaviour of sedimentation of solid particles of magnesium hydroxide in the settler. Sodium hydroxide was used here since it was more convenient to handle, although ammonia is used to precipitate magnesium hydroxide in the conventional ÅA route. Magnesium content in the underflow dried solids was found to be higher than for the solid material crystallizing from the overflow suspension. Still, a very high content of sodium was reported in both underflow and overflow. Figure 7 shows a SEM image taken of the underflow dried material at 10 kX magnification. Studying the particle size it could be seen that
primarily flake-shaped crystals have formed. Besides these, more spherical particles can be seen to the left in the figure. Particle size of the more crystalline material was 20-50 nm in thickness and 0.2-0.5 µm in diameter. A similar structure of magnesium hydroxide was found in studies by [15, 16].

Figure 7. SEM image of underflow solids from sedimentation of a suspension with magnesium hydroxide.

3.2. Iron (oxy)hydroxide sedimentation

Iron hydroxide seemed to sediment even slower than magnesium hydroxide. 10 g of analytical grade iron sulphate heptahydrate (assay 101.2% VWR Chemicals) was dissolved in 250 ml of deionized water. 3 ml of 25% ammonia was added to increase pH to 8.5, which is assumed to be enough to precipitate iron hydroxide. The iron solution was pumped into the settler and was allowed to settle overnight since sedimentation was found to progress very slowly. See Appendix C for a picture series of the sedimentation.

4. Continuous sedimentation using analytical grade reagents

4.1. Precipitation and sedimentation of iron sulphate solution aiming for magnetite as end-product

Earlier studies by [7] and [8] showed the possibilities to precipitate iron as magnetite by preparing solutions containing ferrous and ferric iron with a (molar) ratio Fe²⁺/Fe³⁺ close to 0.5. Temperature seems also to have an influence on the formation of magnetite according to [9]. An experiment was done with analytical grade iron(II) and iron(III) sulphate. Sedimentation could possibly be improved by adjusting the ratio of ferrous and ferric iron since the density of magnetite is higher (5.15 kg/dm³) than that of goethite (3.8 kg/dm³) [17,18]. Goethite was shown to form in the conventional ÅA route [1]. It was also shown in later studies that it could be possible to precipitate magnetite instead by making some adjustments to the conventional ÅA route [19].

13.9 g of FeSO₄·7H₂O (101.2%, AnalAr NORMAPUR, VWR Chemicals) and 20.9 g of Fe₂(SO₄)₃·H₂O (min 21%, GPR RECTAPUR, VWR) were dissolved in 1500 ml deionized water. The solution was immersed into a water bath kept at 40°C and 100 ml 10% NH₄OH was added to the solution. pH was by this increased from 1.61 to 9.03, a pH high enough to precipitate both ferrous and ferric iron. The solution was kept in the water bath for 45 minutes and then sent into the inclined settler for sedimentation. The solution was continuously stirred and pumped into the settler. The settler underflow was manually adjusted to 3 L/h (10 rpm) so that a clear phase overflow was always obtained at the top of the settler. Samples from underflow and overflow were taken in two experiments. A constant pump speed of 3 L/h and an inclination of 45° were applied in both
experiments. Liquid samples and particles from underflow and overflow, respectively, were collected during a sampling time of 5 and 11 minutes, respectively. The solutions were filtrated and particle size was analysed with SEM from the solids obtained during the sampling time of 11 minutes. No differences in particle size could be detected from the images taken using SEM. Both overflow and underflow gave very small particle sizes of 40-50 nm. For more details, see all analyses made on the solids obtained from iron oxide with SEM/EDX in Appendix D together with volumetric flow rates and masses measured in the experiment. The total amount of iron (hydr)oxide product, assumed to mainly consist of magnetite, was 10.63 g. Based on ingoing iron this would correspond to a recovery of 91.2%.

4.2. Simultaneous recirculation and carbonation of a magnesium sulphate slurry

Magnesium could be precipitated either as magnesium hydroxide (Mg(OH)₂) or a magnesium (hydro)carbonate compound depending on how the process is chosen to be designed. Magnesium will precipitate as Mg(OH)₂ at pH 10-12. To maintain a selected value of pH while magnesium hydroxide is precipitated is not as important or sensitive as for iron (hydr)oxide. This makes the option of adjusting pH directly in the settler easier, thus making it possible to eliminate one process step or unit (See further section 7 below). One the other hand, it was found that the particles settled more rapidly by applying wet carbonation in aqueous solution combined with the MgSO₄ conversion step of the ÅA route instead of applying carbonation in a separate final gas/solid step as the conventional route suggests.

A solution was prepared by dissolving 20 g of MgSO₄ (>97%, Sigma-Aldrich) in 800 ml deionized water. pH indicators fenolftalein, bromothymol blue and thymolphthalein were added in small amounts to indicate pH fluctuations in the settler during carbonation and sedimentation. 10% NH₄OH was first added through a lance from the top reaching the middle of the settler. Solution was pumped from the bottom of the settler and recirculated back to the vessel holding the initial solution. Addition of NH₄OH was stopped when pH reached 10.5 (measured in the vessel) and magnesium hydroxide started to precipitate. The addition of NH₄OH was then replaced by a flow of CO₂ gas of 0.75 l/min into the settler. Visible magnesium (hydro)carbonate started to form after 33 minutes. According to [6] it seems that soluble magnesium bicarbonate is formed as an intermediate during in the beginning of the carbonation and that white precipitation of some form of
magnesium (hydro)carbonate will appear as the solution becomes saturated with magnesium bicarbonate. The solution was after these 33 minutes treated for another 7 minutes with CO$_2$ gas. No temperature increase indicating carbonation was observed after this time. Finally, the settler was emptied and the precipitates from the settler and the mixing vessel, respectively, were dried at 110°C overnight.

Effects on solid product structure and composition by the pH indicators used were neglected in calculations and analyses since they were added in very small amounts. The samples were analyzed with SEM in order to obtain information about particle size and indication of composition of the solid material precipitated, see Figure 8 and Table 1.

Elemental analyses are given for both underflow and overflow samples in Table 1. Numbers correspond quite well when comparing the elemental analysis with the theoretical composition of hydromagnesite. A slightly lower content of magnesium could be found in the overflow particles. It should be mentioned, however, that it would be necessary to make elemental analysis on an even surface in order to get accurate values. Values given in Table 1 should be considered indicative. Nitrogen was found in one point in the overflow particulates and sulfur was found in small amounts in the material in all analysed points.

Table 1. Elemental analyses with SEM/EDX in points and areas marked in Figure 8. Theoretical compositions of hydromagnesite and nesquehonite are also given based on calculations without hydrogen. (UF= underflow, OF=overflow)

<table>
<thead>
<tr>
<th>Atom%</th>
<th>C-K</th>
<th>N-K</th>
<th>O-K</th>
<th>Mg-K</th>
<th>S-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydromagnesite UF <code>_pt1</code></td>
<td>15.67</td>
<td>62.55</td>
<td>21.36</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite UF <code>_pt2</code></td>
<td>11.30</td>
<td>65.41</td>
<td>23.11</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite UF <code>_pt3</code></td>
<td>12.93</td>
<td>66.55</td>
<td>20.24</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite UF <code>_pt4</code></td>
<td>15.36</td>
<td>63.91</td>
<td>19.26</td>
<td>1.47</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite OF <code>_pt1</code></td>
<td>16.38</td>
<td>70.17</td>
<td>13.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite OF <code>_pt2</code></td>
<td>29.04</td>
<td>55.63</td>
<td>15.08</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite OF <code>_pt3</code></td>
<td>17.28</td>
<td>64.84</td>
<td>17.61</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite OF <code>_pt4</code></td>
<td>14.66</td>
<td>63.10</td>
<td>13.22</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesite OF <code>_pt5</code></td>
<td>17.19</td>
<td>65.37</td>
<td>17.30</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>HYDROMAGNESITE THEORETICAL</td>
<td>14.81</td>
<td>66.67</td>
<td>18.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NESQUEHONITE THEORETICAL</td>
<td>12.50</td>
<td>75.00</td>
<td>12.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The total amount of precipitate was 14.42 g, which gives a conversion based on the amount of magnesium added to the solution of 92.8% if all magnesium is assumed to contribute to hydromagnesite formation. The conversion becomes 62.8% if only nesquehonite is assumed to form. Earlier studies present precipitates consisting mainly of hydromagnesite. Lansfordite (MgCO$_3$·5H$_2$O) and nesquehonite should, at least theoretically, be able to precipitate at low temperatures below 50°C. Drying the samples at high temperature (110°C in these experiments) could have led to the eventual formation of hydromagnesite [6, 11].

Visible differences in particle size could be found from images taken by SEM, see Figure 9. Settler underflow gives particle sizes of approximately 50-100 µm (width-length) for the clusters and approximately 2-20 µm (width-length) for the needle shaped particles. Overflow products seem to contain only the elongated type of particles with particle sizes 2-20 µm (width-length) and not as much distinct clusters as in the underflow can be found in the overflow.

Studying the structure seen in Figure 9F, this could to some extent agree to the elongated structure of nesquehonite. Parts of the cluster shown in Figure 9F also possess the shape of very thin plates which is characteristic for hydromagnesite [20].
Analyses with X-Ray Diffraction (XRD) were not made since earlier studies showed that any magnesium (hydro)carbonate precipitated at ambient temperature had clearly less crystallinity than samples produced at higher temperatures [21].

5. Continuous sedimentation using a rock derived solution

A batch of iron and magnesium sulphate solution derived from serpentine rock (Finnish Hitura nickel mine overburden) reacting with ammonium sulphate was used in the experiments. Iron content in the rock was initially 10.1 wt% and magnesium content 21.8 wt%. 200 ml of the initial solution of 324 ml was taken for precipitation and sedimentation of iron (hydr)oxide and magnesium hydroxide or magnesium (hydro)carbonate. The solution was further diluted with deionized water to 900 ml of total solution, see elemental composition as analysed by ICP-AES in Table 2.

Table 2. Elemental composition analysed by ICP-AES of the initial ingoing diluted solution presented in section 5 analysed by ICP-AES.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Cr (mg/L)</th>
<th>Cu (mg/L)</th>
<th>Fe (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Mn (mg/L)</th>
<th>Ni (mg/L)</th>
<th>S (mg/L)</th>
<th>Si (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial solution going into 1st settler</td>
<td>30</td>
<td>56</td>
<td>6</td>
<td>14</td>
<td>731</td>
<td>2581</td>
<td>9</td>
<td>22</td>
<td>9247</td>
<td>37</td>
</tr>
</tbody>
</table>

Figure 9. Overflow material from carbonation of magnesium shown in the left column (A-C) and corresponding underflow material in the right column (D-F). Images are taken with magnification 50X (A and D), 250X (B and E) and 1 kX (C and F).
5.1. Effect of angle or pump speed for iron (hydr)oxide precipitation

A pH between 8 and 9 is appropriate to precipitate iron but leave magnesium in solution. 30 ml of 10% NH₄OH was added to increase pH to 9.

Since a proper adjustment to pH 8-9 is needed to precipitate iron separately from magnesium, an accurate adjustment was done in a mixer before the solution containing precipitated particles was pumped into the settler section. More effort needs still to be put into developing accurate pH adjustment directly into the settler since the precipitation of iron will take place in a narrow pH range. Losses of magnesium to the iron fraction will occur if a too high pH is reached (>10) in the settler/mixer used for iron precipitation.

The solution with precipitation of iron was continuously stirred and pumped into the settler at low speed to avoid a too turbulent flow and enable sedimentation. Three different angles of inclination (39°, 45°, 53°) and two different inlet flow rates (3 L/h, 6 L/h) were used. Results from the elemental analyses of the overflow for the three different cases using ICP-AES are given in Appendix E. The settler was emptied and washed after each experiment and the same solution was used in all experiments minus the amount of sample (10 ml) taken from the overflow in each experiment. Values are given as concentrations to be able to compare between each other.

Figure 10 below shows samples taken from the overflow for every experiment. Increasing the speed to 6 L/h (20 rpm) resulted in a much more contaminated overflow with respect to iron. No improved sedimentation with respect to adjusted inclination of the settler could be detected by visually studying the overflows.

5.2. Continuous sedimentation after carbonating a magnesium hydroxide slurry

The solution presented in section 5.1. derived from serpentinitite rock was further used for precipitation of magnesium hydroxide. Iron (hydr)oxides were precipitated, filtrated and dried and the remaining solution continued to precipitation of magnesium hydroxide. 525 ml of 10% NH₄OH was added to further raise pH. In order to increase pH sufficiently, another 120 ml of 25% NH₄OH was added. Final pH was 10.9. The solution was kept in a continuously stirred mixer while pumped into the settler at 3 L/h and an incline of 45°. No clear sedimentation was achieved and a significant part of the agglomerates of magnesium hydroxide followed the overflow.

The settler was emptied and another experiment was done using the same solution, but this time with CO₂ bubbling through the mixed vessel with a flow of 0.75 L/min for 60 minutes. Particles of magnesium (hydro)carbonate were visibly formed during the reaction with CO₂ and temperature increased from 22.2 °C to a maximum of 45.1 °C. The solution was continuously stirred and after mentioned 60 minutes it was pumped into the settler at 6 L/h (20 rpm). No recirculation was applied in this experiment. Samples of overflow and underflow were collected during 2 minutes. These are shown in Table 3.
Table 3. Measured volumes and masses to underflow and overflow, respectively, during sedimentation and separation of magnesium (hydro)carbonate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total volume including particulates (ml)</th>
<th>Flow rate (L/h)</th>
<th>Total solids in batch (g)</th>
<th>Mass separation (g/h)</th>
<th>Ratio overflow/underflow (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Underflow 2 min</td>
<td>95</td>
<td>2.85</td>
<td>4.58</td>
<td>137.4</td>
<td>2.05</td>
</tr>
<tr>
<td>Overflow 2 min</td>
<td>195</td>
<td>5.85</td>
<td>1.07</td>
<td>31.2</td>
<td></td>
</tr>
</tbody>
</table>

At the pumping speed of 6 L/h, disorders occurred easily either as air bubbles or uneven pumping into the settlers. The value of 6 L/h for the set 20 rpm is an average value, but as can be seen in Table 3 the value has been fluctuating. For example, a total flow rate of 8.7 L/h was measured during the two minutes sampling was made. This short sampling time might also have affected the total average flow rate. Longer time would have been needed to get a more proper average flow rate. Numbers in Table 3, however still show the conditions right at the sampling time.

The filtrates (10 ml) were sent for ICP-AES analyses while the precipitates were analyzed with SEM/EDX. Results from ICP-AES analyses are found in Table 4. No differences in composition could be seen for the filtrated solutions. Copper and nickel are originating from the serpentinite rock described in the beginning of section 5.

Table 4. ICP-AES elemental analyses of overflow and underflow after filtration, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca (mg/L)</th>
<th>Cu (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Ni (mg/L)</th>
<th>S (mg/L)</th>
<th>Si (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Underflow</td>
<td>13</td>
<td>5</td>
<td>13</td>
<td>4</td>
<td>4252</td>
<td>2</td>
</tr>
<tr>
<td>Overflow</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td>4</td>
<td>4614</td>
<td>3</td>
</tr>
</tbody>
</table>

No visible differences with respect to particle size between underflow and overflow could be seen from images taken by SEM, see Figure 11. The elongated shape studied in section 5.2. could be seen also in the SEM images taken from this experiment. Clusters of the elongated particles could be found in both the underflow and overflow material. Particle sizes in both underflow and overflow were 20-30 µm in length and 1-10 µm in width.

Figure 11. SEM images of underflow (left image) and overflow (right image) showing particles from magnesium carbonation.

Analyzing both underflow and overflow gave very similar results for the elemental composition of the solids. Figure 12 and Table 5 present the SEM/EDX analysis done on some agglomerates of the
underflow solids. The composition corresponds approximately to that of hydromagnesite. The elongated shape which is characteristic for nesquehonite, however, could still be found. It should be pointed out again that the analyzed surfaces are uneven. Analyzing the areas by SEM in this manner might thus give some difference from the actual elemental compositions.

![SEM image of magnesium (hydro)carbonate from underflow.](image)

**Figure 12. SEM image of magnesium (hydro)carbonate from underflow.**

<table>
<thead>
<tr>
<th>Atom %</th>
<th>C-K</th>
<th>O-K</th>
<th>Mg-K</th>
<th>S-K</th>
<th>Cl-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydromagnesit UF _pt1</td>
<td>13.01</td>
<td>65.72</td>
<td>21.02</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesit UF _pt2</td>
<td>13.32</td>
<td>64.67</td>
<td>21.81</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Hydromagnesit UF _pt3</td>
<td>13.74</td>
<td>64.87</td>
<td>20.97</td>
<td>0.23 0.19</td>
<td></td>
</tr>
</tbody>
</table>

Assuming that all magnesium in this case was converted to hydromagnesite would give a conversion of 64.7%. The ingoing magnesium is based on an average value of magnesium taken from ICP-AES analyses of the samples given in Table E1 in appendix E.

### 7. Flow scheme taking time into consideration

Very low pumping velocities ($\leq 6L/h$) were applied for the settler inlet during sedimentation of magnesium and iron rich precipitates, respectively. The entire process could be modified so that both the mixing and the settling process steps get a retention time of 30 minutes to 1 hour. This requires of the pumping speed into the settler to be low. Longer sedimentation times would favour separation efficiency. Figure 13 below gives more detail.
Figure 13. Upper scheme shows the process scheme with optional precipitation of iron as magnetite and wet carbonation. Lower image gives estimated retention times for some of the process steps, showing that several steps possibly could have the same duration. Times are indicated for the experimental setup used for the experiments presented in this paper. Magnetite will need approximately as much time to precipitate as magnesium(hydro)carbonate. Precipitation of goethite, on the other hand, will take place immediately and does not necessarily need any specific retention time. The Carbonation unit could also be excluded. Ammonia would in that case be pumped into the settler together with overflow from the iron precipitation unit.

8. Conclusions
The possibilities of producing and separating magnesium hydroxide and iron (oxyhydr)oxides from aqueous solutions, as the conventional AA route for CO₂ mineralization suggests, were investigated in this study. The behaviour for the sedimentation of magnesium (hydro)carbonates, while being produced from magnesium hydroxide slurries reacting with carbon dioxide in a solution with ammonia present was also studied. Carbonating the magnesium hydroxide upstream in a mixing vessel significantly improved the subsequent sedimentation in the inclined settler. However, the
carbonation step then would need up to one hour in the settler or in a separate reactor for carbonation to achieve an as high conversion as possible, giving one or several hydro carbonates of magnesium (depending on temperature). This puts demands on proper retention times in every unit while developing a continuous process. It was found that the particle size of all products were very small even if they varied to some extent with respect to both size and shape. This feature, giving a very milky slurry to work with, together with the fact that the underflow had to be manually adjusted made it hard to obtain any reliable separation efficiencies with respect to solid/liquid ratios.

As an alternative to sedimentation, centrifugal sedimentation could in future work be tested in order to enhance sedimentation rates. If the particles are in a size range smaller than 10 µm, there will be a risk of having particles appear in the overflow [13]. In the cases where particle size was measured, it was found that the magnesium (hydro)carbonates had an elongated shape with length 20-100 µm and width 1-50 µm. Magnesium hydroxide, on the other hand, was significantly smaller with flake like shape and a thickness of 20-50 nm and a diameter of 0.2-0.5 µm. Iron particles were found to be in the same size range as magnesium hydroxide and found to be in the shape of more spherical particles in the size range of 40-50 nm. Centrifugal sedimentation could thus primarily be an option for separation of magnesium (hydro)carbonates. Sedimentation behaviour of calcium carbonates in an inclined settler was studied by [22] where it was shown that particle sizes of 10-30 µm could be successfully separated. The use of hydrocyclones was mentioned also in this study as a way to possibly increase separation efficiency.

Iron could be agglomerated or flocculated in order to sediment more rapidly. This is something which should be tested further. Carbonating magnesium hydroxide gave somewhat faster sedimentation. This could be seen when comparing the batch wise experiments done with solutions containing magnesium hydroxide and magnesium (hydro)carbonates, respectively.

Quite low inlet flow rate was applied for most of the experiments as a result of the very fine particles of iron(hydr)oxide, magnesium hydroxide and magnesium (hydro)carbonates that had to be separated. It could still be possible to implement sedimentation to the conventional ÅA route (or wet carbonation route) by taking the time for the initial solid/solid reaction into consideration. This first process step where rock is heated together with ammonium sulphate needs 30 min -1 h to be completed, which puts demands on residence time for the subsequent process steps as well. Long sedimentation times could therefore feasible as long as they meet the retention times in upstream process steps.

Particle size and crystallization rate are two parameters which should be further investigated and optimized since both of them will affect the possibility to precipitate magnesium and iron (hydr)oxides, or magnesium hydrocarbonate. XRD analysis of the products can give further valuable information on the materials produced. Also, the design of the inclined settlers should be optimized in such a way that the inlet stream affects the sedimenting particulates as little as possible.

Acknowledgments

This work was funded by KH Renlund Foundation 2013. We acknowledge Sten Lindholm from the Laboratory of Analytical Chemistry at ÅAU for the ICP-OES analyses and Linus Silvander from the Inorganic Laboratory at ÅAU for help with the SEM/EDX analyses. Jacob Åbacka is also acknowledged for assisting with the experimental setup.
Appendices

Appendix A

Images from pH gradient test in inclined settler

Figure A1. Resulting spectra over the pH interval 0-14 for the indicator mixture as it was used in the experiments [23].

Figure A2. Tube settler at 45° inclination. The solution was pumped into the settler at 30 L/min. pH was found to reach 8-9 in the lower part of the settler and >10 in the upper part. Mixing of ammonia and acified water took place rapidly and the pH gradient did not become more distinct than what is shown in the figure.

Appendix B

SEM/EDX analyses of a suspension with magnesium hydroxide used in a batchwise experiment

Figure B1. SEM images of precipitates from a magnesium hydroxide solution dried at 110°C overnight. Underflow particles are shown in the left figure and overflow particles in the right figure.
Table B1. Table giving SEM/EDX analyses of areas marked in both images above.

<table>
<thead>
<tr>
<th>Atom%</th>
<th>O-K</th>
<th>Na-K</th>
<th>Mg-K</th>
<th>Al-K</th>
<th>Si-K</th>
<th>S-K</th>
<th>Cl-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)₂ OFₚt1</td>
<td>53.72</td>
<td>30.64</td>
<td>0.06</td>
<td>15.59</td>
<td>15.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(OH)₂ OFₚt2</td>
<td>57.96</td>
<td>27.70</td>
<td>1.41</td>
<td>0.06</td>
<td>12.87</td>
<td>12.87</td>
<td></td>
</tr>
<tr>
<td>Mg(OH)₂ OFₚt3</td>
<td>54.76</td>
<td>28.11</td>
<td>0.56</td>
<td>0.33</td>
<td>16.87</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Mg(OH)₂ UFₚt1</td>
<td>69.72</td>
<td>21.35</td>
<td>8.82</td>
<td>0.15</td>
<td>5.96</td>
<td>9.96</td>
<td></td>
</tr>
<tr>
<td>Mg(OH)₂ UFₚt2</td>
<td>63.18</td>
<td>8.96</td>
<td>22.23</td>
<td>0.15</td>
<td>5.63</td>
<td>5.63</td>
<td></td>
</tr>
<tr>
<td>Mg(OH)₂ UFₚt3</td>
<td>58.51</td>
<td>23.64</td>
<td>5.03</td>
<td>0.17</td>
<td>12.65</td>
<td>12.65</td>
<td></td>
</tr>
<tr>
<td>THEORETICAL SODIUM SULPHATE</td>
<td>57.14</td>
<td>28.57</td>
<td>14.29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Appendix C

Iron (oxy)hydroxide sedimentation

Figure C1. Sedimentation of iron hydroxide in an inclined settler at 45°.
Appendix D

SEM/EDX analyses of an iron product supposed to some extent to consist of magnetite

Figure D1. Iron (hydr)oxide particles of underflow (left) and overflow (right) for samples taken under 11 minutes sampling time from the inclined settler.

Analyzing the dried and filtrated iron (hydr)oxide precipitate by SEM/EDX of some areas from both overflow and underflow gave elemental compositions shown in the SEM images and table with elemental compositions below.

Figure D2. Overflow from experiment run for 11 minutes (left), underflow from experiment run for 11 minutes (right).
Table D1. Composition of the four areas analyzed in the right figure above and of the area analyzed in the left figure above.

<table>
<thead>
<tr>
<th>Atom%</th>
<th>N-K</th>
<th>O-K</th>
<th>Al-K</th>
<th>Si-K</th>
<th>S-K</th>
<th>K-K</th>
<th>Ca-K</th>
<th>Fe-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron OF 1kx (1)_pt1</td>
<td>12.67</td>
<td>62.70</td>
<td>0.19</td>
<td>4.26</td>
<td>0.12</td>
<td>20.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron OF 1kx (1)_pt2</td>
<td>12.28</td>
<td>64.49</td>
<td>0.10</td>
<td>0.39</td>
<td>3.20</td>
<td>19.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron OF 1kx (1)_pt3</td>
<td>11.32</td>
<td>58.85</td>
<td>0.08</td>
<td>0.23</td>
<td>3.98</td>
<td>25.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron OF 1kx (1)_pt4</td>
<td>12.77</td>
<td>63.62</td>
<td>0.18</td>
<td>3.90</td>
<td>0.08</td>
<td>0.10</td>
<td>19.34</td>
<td></td>
</tr>
<tr>
<td>Iron UF 11 X 50x (1)_pt1</td>
<td>55.50</td>
<td>0.17</td>
<td>1.32</td>
<td>43.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAGNETITE THEORETICAL</td>
<td>57.14</td>
<td>42.86</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Analyses, given in atom%, showed that the overflow contains sulfur and oxygen as well as nitrogen besides iron. Silica is supposed to originate from the glass fiber filter paper used for filtration. Contribution of nitrogen is originating from the added ammonia and could be present as (NH₄)₂SO₄ in the overflow samples. No nitrogen could be found in the underflow dried product. Elemental analysis of the underflow did not give any nitrogen and less sulfur. Magnetite, which was expected to form during precipitation, could quite clearly be found in the area analyzed from the underflow material (Fig. D2, left image). The theoretical composition of magnetite is 57.1 atom% oxygen and 42.9 atom% iron (Fe₃O₄). Looking at the composition of area analyses of the overflow material, it apparently is mainly goethite which has the composition of 66.7 atom% and 33.3 atom% iron (FeOOH, H not included in the analyses done by SEM). Sulphur is supposed to form sulphate ions, which then means that the amount of oxygen bound to iron is lower than the total amount of oxygen given in the table above. Density of magnetite is higher (5150 kg/m³) than for goethite (3800 kg/m³), which might explain the differences between overflow and underflow.

Table D2. Table of volumetric and mass flow rates and obtained amounts of solids from samples taken during 5 and 11 minutes, respectively. Underflow was adjusted manually during sampling in order to maintain a clear overflow phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total volume including particulates (ml)</th>
<th>Flow rate (L/h)</th>
<th>Total solids during measured time (g)</th>
<th>Mass separation (g/h)</th>
<th>Ratio overflow/underflow (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Underflow 5 min</td>
<td>30</td>
<td>0.36</td>
<td>0.61</td>
<td>7.33</td>
<td>7.7</td>
</tr>
<tr>
<td>Overflow 5 min</td>
<td>230</td>
<td>2.76</td>
<td>0.02</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Underflow 11 min</td>
<td>100</td>
<td>0.55</td>
<td>3.40</td>
<td>18.55</td>
<td>4.5</td>
</tr>
<tr>
<td>Overflow 11 min</td>
<td>450</td>
<td>2.45</td>
<td>0.02</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

Appendix E

ICP-AES for samples taken from sedimentation at different angles and flow rates

Table E1. Elemental composition of initial solution as well as overflow at three different angles and two different pumping speeds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al mg/L</th>
<th>Ca mg/L</th>
<th>Cr mg/L</th>
<th>Cu mg/L</th>
<th>Fe mg/L</th>
<th>Mg mg/L</th>
<th>Mn mg/L</th>
<th>Ni mg/L</th>
<th>S mg/L</th>
<th>Si mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial solution going into 1st settler</td>
<td>30</td>
<td>56</td>
<td>14</td>
<td>731</td>
<td>2581</td>
<td>9</td>
<td>22</td>
<td>9247</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>Fe overflow 45°, 6 L/h</td>
<td>7</td>
<td>59</td>
<td>12</td>
<td>164</td>
<td>2512</td>
<td>3</td>
<td>14</td>
<td>9132</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Fe overflow 53°, 3 L/h</td>
<td>59</td>
<td>8</td>
<td>6</td>
<td>2570</td>
<td></td>
<td></td>
<td></td>
<td>9336</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Fe overflow 39°, 3 L/h</td>
<td>59</td>
<td>11</td>
<td>5</td>
<td>2486</td>
<td></td>
<td></td>
<td></td>
<td>9072</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

309-20
Nomenclature

Abbreviations
CCUS  Carbon Capture, Utilization and Storage
ICP-OES  Inductively Coupled Plasma-Optical Emission Spectrometry
SEM/EDX  Scanning Electron Microscope/Energy-Dispersive X-Ray Spectroscopy
TGA/DTA  Thermal Gravimetric Analysis/Differential Thermal Analysis
XRD  X-Ray Diffraction
ÅA  Åbo Akademi University

Chemical Components
CO₂  Carbon dioxide
Fe₃O₄, FeO·Fe₂O₃  Magnetite
Fe(OH)₂  Iron(II)hydroxide, Ferrous hydroxide
FeO(OH)  Goethite, Iron oxyhydroxide
FeSO₄  Iron(II) sulphate, Ferrous sulphate
Fe₂(SO₄)₃  Iron(III) sulphate, Ferric sulphate
MgCO₃  Magnesium carbonate, Magnesite
Mg₅(CO₃)₄(OH)₂·4H₂O  Hydromagnesite
Mg₃Si₂O₅(OH)₄  Serpentine (Polymorphs: lizardite, antigorite and chrysotile)
MgSO₄  Magnesium sulphate
(NH₄)₂SO₄  Ammonium sulphate
NH₃  Ammonia
NH₂HCO₃  Ammonium bicarbonate
NaOH  Sodium hydroxide
Na₂SO₄  Sodium sulphate

References


[22] Filppula, S., Continuous separation of steelmaking slag and PCC particles from aqueous streams using an inclined settler. Thermal and Flow Engineering Laboratory, Åbo Akademi University, Turku, Finland; 2012.