Process efficiency and optimisation of precipitated calcium carbonate (PCC) production from steel converter slag

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Abstract:
CO\textsubscript{2} emissions could be reduced with capture and storage (CCS) methods. CCS causes costs for the industry, creating an extra barrier for implementation of these techniques. A recently developed mineral carbonation process producing a valuable product covering process implementation costs is advanced towards commercial scale. In this two-step process, calcium-rich steel converter slag is treated with an aqueous ammonium salt solution to selectively extract the calcium. Then the dissolved calcium is removed from the process liquid as pure precipitated calcium carbonate (PCC) by introducing gaseous CO\textsubscript{2} to the system. This concept would utilise waste material from steel industry, and spare the natural resources used for conventional PCC production. Experimental results have shown that papermaking grade PCC can be produced with ammonium nitrate, chloride or acetate solvents. The used solvent has also been regenerated and recycled between the process stages, which reduces the need for fresh solvent and lowers the process costs. To maximise the PCC production in a continuous process, a thermodynamic process model in Aspen Plus is now constructed. The modelling results are validated with a series of semi-continuous experiments. It is found that by using staged carbonate precipitation the yield of pure product is increased. Ammonium nitrate is observed to enable the highest conversion of calcium from steel slag to calcium carbonate also in continuous operation. At ambient conditions the process steps generate heat but this low temperature heat cannot be utilised. The mixing and pumping energies for process operation are small in comparison to the heat duties in chemical reactors. Preliminary results on solid-liquid separation studies, on washing of the solid outlet streams, as well as on recovery and make-up needs of process chemicals are discussed. The work is a continuation of work presented by Said et al. at 22\textsuperscript{nd} ECOS in Brazil 2009.

Keywords:
Ammonium salt solution, Chemical thermodynamics, Mineral carbonation, pH swing process, Steel converter slag.

1. Introduction
It is a widely accepted fact that the climate on Earth is changing because of human activities. One major factor causing global warming is the high emission rate of so-called greenhouse gases. Of these, carbon dioxide is an especially problematic one, since modern economies are based on combustion of fossil, carbon-based fuels. Thus the amount of CO\textsubscript{2} emissions is also high compared to other greenhouse gas emissions like N\textsubscript{2}O that are possibly more harmful to the climate calculated per mass only [1].

Various methods have been proposed to diminish CO\textsubscript{2} emissions. Apart from improving the efficiencies of existing combustion processes, choosing CO\textsubscript{2} neutral fuels and decreasing the need
of power and electricity on global scale, carbon capture and storage (CCS) technologies are seen as one means of reducing carbon dioxide emissions. In CCS, carbon is removed from the gases at different stages in combustion or gasification processes depending on the chosen technology. The capture techniques are already on a relatively mature level, especially for oxygen-free gases, since they have during several decades been applied for industrial processes to produce pure CO\textsubscript{2} [2]. Thus, one major threshold in CCS applications is currently the lack of a permanent, leakage-free storage [1].

Mineral carbonation, where the carbon dioxide gas is reacted directly with some magnesium or calcium containing compounds, is one option for safe storage. Simultaneously it offers the possibility of removing the separate capture stage. However, the mineralization reactions with natural materials are very slow by their nature, and thus development is still needed before industrial applications [3].

Apart from this, there are industrial waste materials, in which calcium or magnesium is present in more reactive forms [3-7]. For example, steel slags from steelmaking plants have been found to react with suitable solvents in such a way that calcium is selectively extracted from the slag matrix. This selective reaction enables the utilization of the produced carbonates in other industrial processes. Thus, two waste streams, CO\textsubscript{2} in flue gases and calcium in steel slags can be used for generating a marketable calcium carbonate product [3, 6, 7].

In this paper, a two-step pH swing process (Fig. 1) operating at ambient temperature and pressure is discussed. In this concept, calcium from steel converter slag is first leached out with ammonium chloride, nitrate or acetate solution under slightly acidic conditions, and then, after separating the slag residue, the dissolved calcium is carbonated in a separate reaction vessel with a feed of gaseous CO\textsubscript{2}. This CO\textsubscript{2} gas could be absorbed to the process liquid directly from the flue gas stream from e.g. a lime kiln or a steel plant, and thus there would be no need for a separate capture unit. Naturally, the concentration of CO\textsubscript{2} in the flue gas would be a crucial factor for the process kinetics. In the carbonation step the ammonium salt solvent is regenerated and can be recycled back to the extraction reactor after the precipitated carbonate product has been separated.

![Fig. 1. A principal process scheme of the two-step pH swing process.](image-url)

In this text especially the efficiencies and losses of different process steps are evaluated based on both thermodynamic modelling and experimental work. The development and scale-up of the process from laboratory scale batch tests towards industrial applications is discussed too [8-9].

The general target of the current study is to produce calcium carbonate that would meet the demands of papermaking applications; if the product could be utilised as filler or a coating pigment, Precipitated Calcium Carbonate (PCC), the profits of selling this material would according to preliminary calculations cover the costs of the carbonation process. This in turn would remove or lower the financial threshold of the utilization of CCS technologies, which usually bring large costs to CO\textsubscript{2} generating industries or power plants. Also, the financial incentive would enable a larger scale demonstration of this mineral carbonation concept [3, 6, 9]. To ensure a high quality product, the CO\textsubscript{2} feed should be free of sulphur and particulate matter.
2. Process development

2.1. Background

During earlier studies [6, 10, 11], several batch experiments have been performed to verify the effects of different process changes such as temperature and CO₂ pressure on the process chemistry. It was found that the reaction steps, which both generate some heat (see Section 4), could be performed at room temperature (20–30 °C). An increase in temperature to 70 °C had hardly any effect on the extraction stage kinetics. In carbonation the shape of the precipitated particles changes with the temperature. This restricts the applicable carbonation temperatures below 30–40 °C. The effect of carbon dioxide pressure was limited to changes in process kinetics, the precipitation rate being slower at lower partial pressures of CO₂. Thus, 20–30 °C was chosen as a suitable process operation temperature interval. At these temperatures the kinetic reaction rates are acceptable [10] and solubility and volatility of gaseous components such as NH₃ and CO₂ are beneficial for the process.

Steel converter slag was reported to contain calcium as free lime (CaO), larnite (Ca₂SiO₄) and various calcium-iron compounds that seem not to react with ammonium salt solvents. The dissolution reactions of lime and larnite are presented as (R1) and (R2). Carbonate precipitation chemistry can be summarised as (R3) and (R4). X in the reaction equations represents Cl⁻, NO₃⁻ or CH₃COO⁻ (acetate), depending on the chosen salt.

\[ \text{CaO(s)} + 2\text{NH}_4^+X^- + \text{H}_2\text{O(l)} \rightarrow \text{CaX}_2(aq) + 2\text{NH}_3\text{OH(aq)} \]  \hspace{1cm} (R1)

\[ 2\text{CaO}^\text{aq} + \text{SiO}_2(s) + 2\text{NH}_4^+X^- + \text{H}_2\text{O(l)} \rightarrow \text{CaX}_2(aq) + 2\text{NH}_3\text{OH(aq)} \]  \hspace{1cm} (R2)

\[ 2\text{NH}_3\text{OH(aq)} + \text{CO}_2(g) \leftrightarrow \text{(NH}_3)_2\text{CO}_3(aq) + \text{H}_2\text{O(l)} \]  \hspace{1cm} (R3)

\[ \text{(NH}_3)_2\text{CO}_3(aq) + \text{CaX}_2(aq) \leftrightarrow \text{CaCO}_3(s) + 2\text{NH}_4^+X^- \]  \hspace{1cm} (R4)

In the batch experiments it was also observed that if solvents with molarities higher than 1.0 mol/L or solid-to-liquid ratios higher than 100 g/L were used, also some iron and manganese was extracted from the steel slag, decreasing the purity and whiteness of the process solution and the produced carbonates [10-12]. Thus, these specifications were used in the current work. Mainly ammonium chloride solutions were used, both in modelling work and in experiments, since the available data were most complete for this solvent, and also because it is cheaper than the other two ammonium salts. Some observations of experimental work with ammonium nitrate will be presented in later sections.

In larger scale, the process should preferably be operated on continuous basis to achieve presumably lower operational costs and better adaptability to changes in feedstock quality. Problems arising especially from the continuous operation as identified already by [9, 13] are the losses of solvent components (NH₃ and water vapour, ammonium and calcium salt precipitates) and dissolution of excess carbon dioxide as biconcave and carbonate ions in the carbonation step. The solvent losses cause an unnecessary increase in process costs, both as a need of a solvent make-up but also as a need for purification of precipitates and purged gases. On the other hand, if excess dissolved carbon species are recycled from carbonation to the extraction unit, solid calcium carbonate is precipitated on the slag particles, lowering the overall production rate of pure carbonate product (PCC). These problems exist to some extent also in a batch type process.

2.2. Process modelling

Thermodynamic modelling and simulation software Aspen Plus 7.2 were utilised to study the possibilities to decrease losses of both carbonate product and solvent components. The software
also provided information on sizes and compositions of different process streams. The model design is shown in Fig. 2. It consists of one extraction step “EXTRACTO”, and two carbonation steps, “CARBONAT” and “SETTLER”. All these reactors are so called RGIBBS units, which calculate the output by minimizing Gibbs’ free energy of the system. Carbonation is divided in two stages to enhance the precipitation rate of calcium (see Section 3.1.).

25 ton/h dry steel converter slag, containing 5%-wt CaO and 59%-wt Ca$_2$SiO$_4$, the remaining 36%-wt consisting of inert compounds, is fed to the extraction reactor together with an ammonium salt solution (~1 mol/L NH$_4$Cl). The solid-to-liquid ratio used in modelling is approximately 100 g slag in one litre of solvent [10-11].

In the first carbonate precipitation unit, “CARBONAT”, 85-100% of the calcium-rich solution from extraction unit is put in contact with 25 ton/h flue gas containing 20% CO$_2$ and 80% N$_2$, being approximately the composition of lime kiln flue gases. The 300 °C flue gas is fed to the process via a cooling unit to estimate the released heat, when the gas is brought down to room temperature (20°C). The flue gas feed amount is adjusted so that approximately 5% of the CO$_2$ gas leaves the system unreacted. After the first step the solution is flashed to 0.5 bar in “VAPORSEP”, thus removing the non-reacted gases. Re-pressureisation to 1.0 bar is done by a separate “PUMP” unit. The “SETTLER” unit is used to increase the pH of the once carbonated solution, so that the chemical equilibrium can be shifted to favour additional precipitation of calcium carbonate. This is done by introducing 0-15% of the calcium-rich solution coming from the extraction unit directly to “SETTLER” as a bypass stream of “CARBONAT”. At the same also some calcium is added to the “SETTLER” reactor, shifting the equilibrium even further towards carbonate. After this second precipitation unit the solution is again flashed to 0.5 bar in “VAPORSEP” and pressurised to 1.0 bar with “PUMP” to remove dissolved gases.

Fig. 2. A detailed process scheme of the pH swing process as simulated with Aspen Plus.

Solids are separated from the process solution with “RESIDSEP” for slag residue and “PRODSEP” and “PRODSEP2” for carbonate product. These units are based plainly on percentages of separation efficiency specified for each component. They can be thickeners, filters, hydrocyclones and combinations of these. Later in this paper some studies on gravitational separation of steel slag are presented. Both the slag residue (“RESIWASH”) and produced PCC (“PRODWASH”) are washed.
to dissolve the chloride salts precipitated on these particles. To demonstrate the recovery of vaporised ammonia from the carbonation steps, an additional RGIBBS unit, “NH3SCRUB” is introduced to the model. In this unit an HCl solution is reacted with NH₃ vapour to produce aqueous NH₄Cl. These aspects are discussed in more detail in Section 5.

The solvent liquid is recycled in the process. Also make-up streams for ammonia and water are included in the model to maintain the balance with vaporization losses. The “CO2SEPAP” unit is not active in this model, although it could be used to artificially decrease the concentrations of carbon species in the recycled stream.

2.3. Experimental work

A set of five experiments was performed to provide information that could not be obtained from the modelling work, but also to confirm that the modelling results can be applied for predicting the behaviour of the process in practice. Thus, the product yields and conversion rates from the Gibbs energy minimization performed in Aspen Plus software and experimental work could be compared with each other, but also the purity and crystal shape of PCC product, properties that are difficult to model, were studied in experiments. In future, the exact experimental result values may be used in modelling work to get better estimates for the large scale stream sizes and energy needs of the process.

The tests were done at ambient conditions (20°C, 1 bar), with a mechanical stirrer (170 rpm) in the extraction reactor, using 1 mol/L ammonium chloride or ammonium nitrate solution, and maintaining the slag-to-liquid ratio at approximately 100 g/L during extraction. After each experiment the process equipment was modified according to the obtained results before the next experiment (Tables 1 and 2).

Table 1. Experimental parameters

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction time, min</td>
<td>75</td>
<td>135</td>
<td>180</td>
<td>255</td>
<td>255</td>
</tr>
<tr>
<td>Ammonium salt</td>
<td>NH₄Cl</td>
<td>NH₄Cl</td>
<td>NH₄Cl</td>
<td>NH₄Cl</td>
<td>NH₄NO₃</td>
</tr>
<tr>
<td>Volume of ammonium salt, ml</td>
<td>750</td>
<td>1500</td>
<td>2500</td>
<td>3500</td>
<td>2500</td>
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<tr>
<td>System filled in the beginning</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Initial slag amount, g</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Total slag amount used, g</td>
<td>50</td>
<td>70</td>
<td>90</td>
<td>110</td>
<td>110</td>
</tr>
</tbody>
</table>

Table 2. Amount of equipment used in experimental set-ups

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filters</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Settlers</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Pumps</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>H₂O lock</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>pH adjustment unit</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CO₂ removal unit</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3. Volumes, volume flows and residence times in experiments 4 and 5

<table>
<thead>
<tr>
<th>Unit</th>
<th>Volume, ml</th>
<th>Volume flow, ml/min</th>
<th>Residence time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction</td>
<td>500</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Carbonation</td>
<td>300</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>pH adjustment</td>
<td>500</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>CO₂ removal</td>
<td>500</td>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>Filter equipment</td>
<td>600</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Figs. 3 and 4 represent the process equipment of experiments 4 and 5, for which the most successful and advanced setup was constructed. Volume flows and residence times for these tests are shown in Table 3. In experiment 4 the whole system was filled with ammonium chloride solution, of which 0.5 L with 50 g steel converter slag (size fraction 125-250 µm) was fed to the extraction reactor. 5 g slag was added to the extractor with 15 minutes interval during the whole experiment. To allow for the calcium concentration in the extractor to increase towards a constant level, the solution was allowed to react 5 minutes before the pumps were switched on. Fine particles were continuously removed from extraction reactor via an overflow of 20 ml/min. The overflow was filtered to prevent solid particles from entering the carbonation stages. 75% of the filtrate (15 ml/min) was pumped to the 1st carbonation reactor, where a small overpressure (0.02 bar) of carbon dioxide (99.9996%, Oy Aga Ab) was maintained with a water lock. CO₂ was introduced through a Waters 10 micron Hplc solvent inlet filter (WAT025531) to provide an even gas distribution. Pure CO₂ gas was used because of the impracticality of actual flue gas, but as mentioned above, this has been found to mainly affect the process kinetics, if the flue gas is sulphur-free and contains no solid particles.
The remaining 25% (5 ml/min) of the filtrate from extraction was fed to the 2nd precipitation stage to adjust the pH of this step to approximately 7. The neutralised solution was transferred by gravimetric flow into a vessel, where 99.9999% nitrogen (Oy Aga Ab, 0.5 L/min) was bubbled through the liquid to remove the unreacted CO2. Finally, the slurry was allowed to settle in another vessel, after which the overflow was filtered with 0.45µm/47mm membrane (Pall Life Sciences, Supor-450) and the particle-free solution (20 ml/min) was recycled back to the extraction reactor. Since the product was not continuously removed from the system, this process can be described as semi-continuous. For comparison, the experiment was repeated with ammonium nitrate solvent, other parameters unchanged. The settler, however, was not used in the nitrate experiment, since it was observed to have no effect in experiment 4.

Samples were taken of both the slag residue and the produced PCC. They were dried overnight at 105°C and analysed with SEM/EDX to get an approximate elemental composition. The concentrations of dissolved calcium ions were measured after each step with an ion selective electrode (NICO 2000).

3. Conversion efficiencies of calcium and CO2 to PCC
3.1. Modelling results

Theoretically, based on presented assumptions on extraction chemistry and slag composition, 44.7% of the calcium present in the feed can be extracted. However, if only one carbonation unit is used, almost 7% of this extracted calcium will precipitate as a mixture with slag residue in the extraction reactor. Table 4 represents the effect of different bypass fractions on the efficiencies of both calcium and carbon dioxide conversions. As can be seen, according to the model already a 5% bypass stream is enough to reduce the losses by 40%. With a 15% bypass practically all extracted calcium could be utilised as marketable product. On the other hand, the amount of sequestered CO2 remains constant, since the total amount of CaCO3 precipitate is not changing.

Table 4. Modelled conversion efficiency calculations of calcium and CO2 to PCC with various process configurations

<table>
<thead>
<tr>
<th>Bypass fraction</th>
<th>Reactive calcium feed kmol/h (ton/h)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCC product</td>
<td></td>
<td>101</td>
<td>104</td>
<td>107</td>
<td>108</td>
</tr>
<tr>
<td>PCC in residue</td>
<td></td>
<td>7</td>
<td>4</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

| Loss of marketable calcium % of reactive input | 6.5 | 3.7 | 0.9 | 0.0 |
| Conversion of total Ca to PCC % | 42 | 43 | 44 | 45 |

| CO2 feed kmol/h (ton/h) | 114 (5.0) |
| CO2 not sequestered kmol/h (ton/h) | 6 (0.3) |

<table>
<thead>
<tr>
<th>Bypass fraction</th>
<th>%</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH after extraction</td>
<td>10.61</td>
<td>10.70</td>
<td>10.83</td>
<td>11.13</td>
<td></td>
</tr>
<tr>
<td>pH after 1st carbonation</td>
<td>7.68</td>
<td>7.64</td>
<td>7.61</td>
<td>7.61</td>
<td></td>
</tr>
<tr>
<td>pH after 2nd carbonation</td>
<td>7.71</td>
<td>7.87</td>
<td>8.18</td>
<td>8.68</td>
<td></td>
</tr>
</tbody>
</table>
The chemical explanation for this behaviour can be summarised in Table 5 and Fig. 5. When the pH of solution is increased, the concentration of dissolved calcium at thermodynamic equilibrium is decreased. Consequently, the precipitation of CaCO$_3$ is favoured at higher pH values. In the Aspen model, the increase of pH after both carbonation steps at different bypass rates is almost one pH unit from 0 to 15% bypass, resulting in the above described shift in marketable carbonate production efficiency. Thus, pH measurement and adjustment can be used for process control purposes.

3.2. Experimental results

Experimentally obtained conversion rates (Table 6) are remarkably lower than modelling results (Table 4). This can be partially explained by experimental inaccuracies, the main reason being the lower extraction efficiency from the used steel converter slag. As discussed in [10], this might be due to a long storage time in laboratory conditions. However, in general it can be observed that by introducing the pH adjustment unit with a 25% bypass stream passing the first carbonation unit, the total conversion of calcium from slag to precipitated product can be enhanced. Compared to a case with only two reactors, one extractor and one carbonator (Experiment 1), the setup described in Figs. 3 and 4 (Experiment 4) was able to increase the conversion efficiency by 13 %-units. By changing the ammonium chloride solvent to ammonium nitrate an additional increase of 7 %-units was measured (Experiment 5). When carbon dioxide concentration was decreased before the pH adjustment unit (Experiment 3), the calcium conversion was 5 %-units lower than in experiment 4.

Nevertheless, results from experiment 2 show that only by introducing an additional settler unit, compared to experiment 1, a similar conversion efficiency as with the pH adjustment system can be obtained. From the measured calcium concentrations (Table 7) it can be seen that this is actually due to a more efficient extraction conversion, depending on the variation of the input slag composition and on the different operation of pumps during the experiments, which resulted in longer residence times during extraction.

Fig. 6 shows the recorded pH values from experiments 3-5, where the pH adjustment unit was used. It can be seen that the levels are stabilising quite well to constant values both in extraction and in carbonation, especially in experiments 4 and 5. Still, the extraction pH is slightly decreasing with time, indicating carbonate precipitation also in this reactor. The stable carbonation pH at approximately 6.3 with a calcium concentration of 0.004-0.007 mol/L is quite well corresponding to the theoretical values of Fig. 5 (pH 6.3 gives 0.002 mol/L), when the experimental inaccuracy is taken into account as well. Also, the pH values obtained from Aspen Plus are systematically 1.3-2 units too high compared to the experimental results.
Table 6. Experimental conversions of steel slag into PCC

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactive calcium feed g/h</td>
<td>5.8</td>
<td>4.5</td>
<td>4.3</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>PCC product (carbonator) g/h (% of total)</td>
<td>2.5(100)</td>
<td>4.2(75)</td>
<td>1.9(51)</td>
<td>1.4(31)</td>
<td>2.0(35)</td>
</tr>
<tr>
<td>PCC product (pH adjustment) g/h (% of total)</td>
<td>-</td>
<td>-</td>
<td>0.8(20)</td>
<td>2.3(51)</td>
<td>3.5(60)</td>
</tr>
<tr>
<td>CaCO₃ (other system) g/h (% of total)</td>
<td>-</td>
<td>1.4(25)</td>
<td>1.1(29)</td>
<td>0.8(18)</td>
<td>0.3(5)</td>
</tr>
<tr>
<td>CaCO₃ (total) g/h</td>
<td>2.5</td>
<td>5.6</td>
<td>3.8</td>
<td>4.5</td>
<td>5.8</td>
</tr>
<tr>
<td>Conversion of reactive Ca %</td>
<td>17</td>
<td>49</td>
<td>35</td>
<td>48</td>
<td>62</td>
</tr>
<tr>
<td>Conversion of total Ca %</td>
<td>8</td>
<td>22</td>
<td>16</td>
<td>21</td>
<td>28</td>
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</table>

Table 7. Experimental Ca²⁺ concentrations after and before extraction reactor

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺ after extraction reactor mol/L</td>
<td>0.026</td>
<td>0.041</td>
<td>0.012</td>
<td>0.015</td>
<td>0.018</td>
</tr>
<tr>
<td>Ca²⁺ before extraction reactor mol/L</td>
<td>0.007</td>
<td>0.019</td>
<td>0.004</td>
<td>0.007</td>
<td>0.004</td>
</tr>
</tbody>
</table>

A remark that can be made based on Fig. 6 is that the pH in the pH adjustment unit has been quite unstable during the experiments. Thus, applying a process control device to steer the bypass rate as proposed in the previous section would improve the performance of the experimental setup.

4. Energetic properties of the process

Based on the presented Aspen model, heat duties of different process steps can be estimated. In Table 8 values are shown for the case with a 15% bypass, which was in above discussion found to result in highest production rate of pure PCC. It can be observed that all process steps, except for the flashing units, are exothermic, i.e. release heat. However, as the process is operated at low...
temperature, this heat can in practice not be utilised. Only exception is the cooling unit for flue gas, where the gas is cooled from 300°C to 20°C. The maximum amount of reversible work from these process steps, when the ambient temperature is assumed to be 20°C, is shown as exergy in Table 8. Calculations were made using (1) for heat Q [15].

\[ \text{Exergy}(Q) = (1 - \frac{T_0}{T}) \times Q \]  

(1)

Table 8. Heat duties, inlet temperatures and pressures as well as exergies of heat in different process steps according to Aspen Plus model (Fig. 2) with 25 ton/h slag feed and a 15% bypass.

<table>
<thead>
<tr>
<th>Process unit</th>
<th>Q(kW)</th>
<th>( \Theta_{in}(^\circ C) )</th>
<th>p(bar)</th>
<th>( \text{Exergy}(Q) )@T(_0)=293.15K(kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXTRACTO</td>
<td>-1638</td>
<td>20</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>CARBONAT</td>
<td>-2614</td>
<td>20</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>COOLER</td>
<td>-2010</td>
<td>300</td>
<td>1</td>
<td>982</td>
</tr>
<tr>
<td>VAPORSEXP</td>
<td>258</td>
<td>20</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>SETTLER</td>
<td>-62</td>
<td>20</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>VAPORSE2</td>
<td>215</td>
<td>20</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>SUM</td>
<td>-5851</td>
<td></td>
<td></td>
<td>982</td>
</tr>
</tbody>
</table>

It must also be noted that the heat duties for process units where gas absorption into process solution, or vaporization of solvent liquid is occurring, include also these values, besides of the actual heats of chemical reactions. If the results are presented as specific values, the result becomes 66 W/kg slag for the extraction step. During carbonation, 390 W/kg PCC is generated. This value is a sum of all units listed in Table 8, excluding the extractor.

Two energy-related topics not yet discussed are the energy inputs needed for pumping the process liquids and mixing the contents of the reactor units, especially during extraction, where a large amount of solids is blended with a liquid stream. From the presented Aspen model the power consumption of the two pumps to pressurise the liquid streams after flashing is 2.8 kW for “PUMP” and 3.4 kW for “PUMP2”, calculated according to \( P = \Delta p \times V \) where \( \Delta p \) is the pressure change (0.5 bar) and \( V \) is the volume flow. Compared to heat duties in reactors, these are quite small numbers. In general, also other pumping equipment will be needed for the process, but since the pressure losses can be assumed to remain low with small distances and height differences, even for flows of 200-250 m\(^3\)/h.

For mixing, the energy dissipation \( \varepsilon \) from the stirrer can be calculated with (2) [16], where \( P_0 \) is Power number, \( n \) is the frequency of rotation for the mixer (1/s), \( d \) is the diameter of the mixer (m), and \( V \) is the total volume (m\(^3\)).

\[ \varepsilon = \frac{P_0 \times n^3 	imes d^5}{V} \]  

(2)

Power number can be estimated from Reynolds number of mixing according to (3) [16], where \( \rho \) is the density of the solution and \( \eta \) is the viscosity of slag-ammonium salt solution mixture, calculated from (4) [17] with \( \varepsilon_p \) as the volume fraction of slag (m\(^3\)/m\(^3\)) and \( \eta_p \) the viscosity of the dispersed material. Also is assumed that the viscosity of ammonium salt solution will not differ noticeably from viscosity of pure water.

\[ \text{Re}_e = \frac{\rho nd^2}{\eta_{\text{mixture}}} \]  

(3)
After the process had reached a steady-state, a sample was taken from the outflow to determine the concentration of particles. The samples were filtrated, dried in an oven at 105 °C and weighed. Calculated from (5), the separation efficiencies were 99.9% for both 30° and 45° experiments.
\[ \eta = \frac{c_{\text{in}} - c_{\text{out}}}{c_{\text{in}}} \times 100\% \]  

However, a SEM picture taken of an overflow sample revealed that the particle size in this fraction was approximately 1-2 µm, indicating thus that for the actual slag particles the separation efficiency had been 100%, in accordance with the glass particle experiments. Only a fraction of small particles released from the slag was leaving the separation unit through the overflow. Thus, according to these tests, a gravitational settler could be utilised for steel slag separation in a continuous process, but it should be accompanied with a filter to remove also the fraction of dissolved, micrometre scale particles. At the same, this filter could also be used to protect the pump needed to transport the process liquid from extraction to carbonation. In a larger scale process, the height of the settler tube would directly affect the needed pumping effect. Optimisation of the required tube dimensions and angle for particles of a known size and density with a known flow is on-going.

![Fig. 7. A 30° inclined settling tube 0 minutes (left) and 2 minutes (right) from the start of the test.](image)

### 5.2. Washing steps

As discussed above, losses of ammonia and water vapour as well as ammonium chloride precipitate, mixed with slag residue or the PCC product, should be minimised to increase the profitability of the process. During the described experiments it has been measured that residual slag exiting the process had moisture content of approximately 10%. Moreover, the chlorine level in dry residue was 5.5%-wt according to SEM/EDX measurements. For the modelled process, this would mean that 1670 kg/h ammonium chloride (~0.15 kg per kg PCC product) would be lost with the residue, assuming that all chlorine is bound with ammonia.

However, from the experimental results of applying one washing stage for the residue, with washing water amount of 0.50 m³/t residue, the reduction in calcium content was found to be 0.65 mol, while approximately 1.5 mol chlorine was dissolved. Thus, it would mean that only 14% of the chlorine would have been bound as NH₄Cl, the rest being CaCl₂. In other words, 230 kg/h ammonium chloride and 1485 kg/h calcium chloride would be lost with the slag residue.

According to experimental results the one-stage wash would lower the chlorine level in the residue to 0.7%-wt, corresponding to 28 kg/h NH₄Cl and 177 kg/h CaCl₂, if calculated with the same distribution as above. The used washing liquid of 10 m³/h would then contain 0.003 mol/L Cl⁻, 0.001 mol/L Ca²⁺ and 0.0004 mol/L NH₄⁺, that could be re-utilised in the process by evaporating the water in such extent that the need for make-up water for the process would be satisfied at the same. This, however, would bring an extra energy penalty to the process.

Regarding the produced PCC, washing tests will be done as a part of future work. It can be mentioned, that for unwashed PCC produced with 1 mol/L ammonium chloride, the experimental chlorine levels have been below 1 %-wt, being still too high for a marketable product. Using ammonium nitrate solvent instead of ammonium chloride would remove the problem of chlorine precipitates.
Calculating from the Aspen Plus model with 15% bypass of the 1\textsuperscript{st} carbonation unit, the vaporization losses of ammonia would be 18 kg/h (1.1 kmol/h) with PCC production of 10795 kg/h. This amount, 0.4% of the total ammonium species present, is of the same order of magnitude what has been obtained experimentally by FTIR measurements [13]. However, also this ammonia could be captured, e.g. by using an HCl-based scrubber for the flue gas stream leaving the system (Fig. 2).

The need for make-up water to replace the moisture lost with streams of solid matter and water vapour flashed from the separation units depends on many variables, and has not yet been quantitatively studied. However, assuming a 20% moisture content for the PCC product and 10% for slag residue, the need for make-up water for the above discussed process would be 5830 kg/h. This amount could easily be taken from washing units, but it requires further optimisation. In general, all the values presented in this section are based on preliminary studies, and thus need to be verified by additional experimental studies and analysis as a central part of future work. Only then can the usage of fresh make-up chemicals be optimised too.

6. Conclusions
The studied pH swing process possesses potential for commercial application. Based on both modelling and experimental work, precipitated calcium carbonate can be produced with a continuously operating system instead of batch reactors. By choosing the solvent with highest conversion efficiency (ammonium nitrate) and by dividing the precipitation step in two stages, the conversion of calcium in the input material to a valuable product can be enhanced. Energetically the process will require some mixing and pumping power, but the chemical reaction steps are exothermic. The recovery and separation units for process chemicals and for solids need to be studied in more detail in future work, but it seems to be possible to use a gravitational settler to separate slag residues from the process liquid. Also, washing the output streams will aid the recovery of chemicals, and thus decrease the need for make-up material. However, additional studies on particle quality, shape, purity and whiteness of the produced PCC must be performed to guarantee that a marketable product is manufactured.

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Nomenclature

\begin{align*}
  c & \text{ concentration, g/L} \\
  d & \text{ diameter of the mixer, m} \\
  \bar{d} & \text{ mean diameter, } \mu m \\
  n & \text{ frequency of rotation, 1/s} \\
  P & \text{ power, kW} \\
  p & \text{ pressure, bar} \\
  Po & \text{ power number, } – \\
  Q & \text{ heat duty, kW} \\
  Re_{v} & \text{ Reynolds number of mixing} \\
  T & \text{ temperature, K} \\
  T^0 & \text{ ambient temperature, K} \\
  V & \text{ volume, m}^3 \\
  \dot{V} & \text{ volume flow, m}^3/h
\end{align*}
Abbreviations
CCS  Carbon Capture and Storage
FTIR  Fourier Transform Infrared Spectroscopy
PCC  Precipitated Calcium Carbonate
SEM/EDX  Scanning Electron Microscopy – Energy Dispersive X-ray

Greek symbols
$\Delta$  difference
$\varepsilon$  energy dissipation, W/kg$_{\text{solution}}$
$\eta$  viscosity, Pa·s; efficiency, %
$\Theta$  temperature, °C
$\rho$  density, kg/m$^3$

Subscripts and superscripts
in at inlet
p particle

References


