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Mass and energy balance of NH₄-salts pH swing mineral carbonation process using steel slag

Marco Dri*, Aimaro Sanna*, M. Mercedes Maroto-Valera

Abstract

A basic evaluation of the entire NH₄-salts pH swing mineral carbonation process steel slag based system including CO₂ capture, ammonia absorption and regeneration of additives, has been investigated to evaluate its feasibility at industrial scale. Heat released from mineral dissolution, pH adjustment and precipitation of impurities, carbonation reaction and CO₂ capture was 2.3 MWh/tCO₂ and could be recovered using heat exchangers and reused within the mineralization process to heat-up the incoming streams of steel slag, ammonium sulphate and water. Heat required, mainly from water evaporation and regeneration of additives, is reported to be 20 MWh/tCO₂.

Keywords: CCS, Mineral carbonation, Metal waste materials, energy balance

1. Introduction

Mineral carbonation by pH swing is a promising technology for the sequestration of carbon dioxide (CO₂) [1]. One of the advantages of mineral carbonation compared to underground storage is that it may take place at the same site, where CO₂ is released. An industrial process emitting CO₂ which could be retrofitted on-site with a mineralization facility is a steel plant, where CO₂ is emitted and an appropriate waste material is produced [2]. It should be noted that steel making and cement production industries are large emitters of CO₂, where emissions from the industrial sector are 20% of the total and steel making accounts for about a quarter of the industrial emissions [3].

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The authors have previously studied dissolution and carbonation steps for NH₄-salts based mineral carbonation processes using steel slag from one of the main steel plants in UK [4-5]. In this work, the entire process is investigated, including CO₂ capture, ammonia absorption and regeneration of additives, and mass and energy balance calculations are performed.

2. Methodology

The steel plant considered emitted 7.4 Mt/year of CO₂ into atmosphere which means 965t/h (assuming 320 working days per year) and steel slag production was 43t/h [6]. The mass balance was conducted considering the chemical reactions, reactants and products and their stoichiometric values. Steel slag was the chosen material because of the impact of steel industry on the global CO₂ emissions. From the reaction [4] and data on the CO₂ emissions and steel slag production of a specific steel plant, a mass balance for the mineralization process was performed. These calculations allowed assessing the quantity of chemicals required and products obtained and, consequently, investigate their impact on the mineralization process in terms of energy consumption. Afterwards, the energy balance of the overall process was performed. Heat released and required from each single step was calculated using the thermodynamic calculations (from HSC Chemistry 5.1) and the quantity of different inputs and outputs of each step of the process, obtained from the mass balance. After the investigation of the energy balance, the CO₂ emissions due to the process were calculated.

![Diagram of the multi-step close loop mineral carbonation process.](image)

Figure 1 Multi-step close loop mineral carbonation process. [4].

3. Results and Discussion

Based on the chemical reactions reported in the previous works and the steel slag production of the plant considered (43t/h), a mineralization process with S/L ratio 15g/L able to sequester 13t/h of CO₂, employing all the steel slag produced, was developed.
The dissolution and carbonation steps of the mineralization process applied to the steel plant have a combined duration of 1.5 hour. The process takes place in a series of reactors of suitable size at S/L ratio of 15g/L and, because of the volumes of solution involved, most of the process equipment will consist of multiple plants operating in parallel.

Table 1 summarizes the energy balance, where negative values indicate heat released, while positive values represent heat required for each step. Results from the energy balance for each step of the process, obtained from the thermodynamic calculations and the mass balance indicate that the process investigated (mineralization system retrofitted into a steel plant) can sequester a theoretical maximum of 13t/h CO₂ (1.4% of the total emission) using 43t/h steel slag. The total heat released corresponds to 2.3MWh/tCO₂, while the total heat required is 20MWh/tCO₂. The highest heat demand is due to the water evaporation phase (18.6MWh/tCO₂). The regeneration step, instead, requires 1.8MWh/tCO₂, which is much lower than the value reported in a previous study for mineral carbonation with chemical regeneration using NaCl and HCl (3277 and 4361kWh/tCO₂, respectively) [7]. In comparison, direct mineral carbonation processes consume large amount of energy in the mineral activation stage (977kWh/tCO₂) and for recovering the employed chemicals (0.64M NaHCO₃ and 1M NaCl) [8]. Despite the large amount of water required (~2850t/h), it should be noted that the process can reuse it, and therefore, limiting the requirement of fresh water to 1t/h. Further work is required to decrease the energy consumption of the proposed process.

Table 1. Energy balance of the proposed mineralisation process applied to the steel plant, where 13 t/h CO₂ (43 t/h steel slag) are supposed to be captured.

<table>
<thead>
<tr>
<th>Heat released</th>
<th>kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ capture</td>
<td>-14628</td>
</tr>
<tr>
<td>mineral dissolution</td>
<td>-12201</td>
</tr>
<tr>
<td>precipitation of impurities</td>
<td>-3549</td>
</tr>
<tr>
<td>carbonation</td>
<td>-100</td>
</tr>
<tr>
<td><strong>Total Heat Released</strong></td>
<td>-30478</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat required</th>
<th>kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>water evaporation (MVR)</td>
<td>242000</td>
</tr>
<tr>
<td>regeneration</td>
<td>22945</td>
</tr>
<tr>
<td>ammonium adsorption</td>
<td>131</td>
</tr>
<tr>
<td><strong>Total Heat Required</strong></td>
<td>265076</td>
</tr>
</tbody>
</table>

4. Conclusions

This work presented the mass and energy balance for the overall mineralization process in the case of sequestering 13t/h of CO₂ from a steel plant producing 43t/h of steel slag and employing a S/L ratio of 15g/L. Because of the close loop used, the impact of the quantity of NH₄HSO₄ and H₂O needed to be fed continuously into the system is small (1t/h for H₂O, and 0.3t/h for NH₄HSO₄). However, the total heat required of 20MWh/tCO₂ was very large and future work will be required to decrease the overall energy consumption of the proposed process. The highest heat demand is due to the water evaporation phase (18.6MWh/tCO₂).

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References