Leaching of Steelmaking Slag using Acetic Acid Solution and Deionized Water for CO\textsubscript{2} Sequestration

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Abstract
CO\textsubscript{2} mineral sequestration is an important technology for reducing greenhouse gas emissions. The steelmaking slag was interested for CO\textsubscript{2} sequestration because of its containing high CaO. This research aimed to investigate the CaO leaching efficiency using two common solutions which are acetic acid solution and pure deionized water. Several operating variables including initial acetic acid concentration (0 and 2 M), liquid-to-slag ratio (10:1 g/g), reaction temperature (70 °C) and reaction time (0-60 min) were investigated. The alkalinity of leaching solution obtained from both solutions were also studied. The results show that leaching solution of steelmaking slag using deionized water gave higher pH and alkalinity than acetic acid. The efficiency of both leaching solutions on CO\textsubscript{2} sequestration was also investigated and reported in this work.

Keywords: Leaching, Precipitation, Steelmaking Slag

1. Introduction
The increasing CO\textsubscript{2} concentration mainly caused by fossil fuel combustion associated with the greenhouse effects represented a worldwide problem [1, 2]. A possible technology that can contribute to the reduction of carbon dioxide emissions is CO\textsubscript{2} sequestration by mineral carbonation. Sequestering carbon dioxide in synthesized carbonates is a long-term solution to global warming that will keep CO\textsubscript{2} out of the atmosphere on geologic timescales [3]. Mineral sequestration research pointed to accelerate the reaction for a potential industrial process. Research on the aqueous carbonation route has focused on alkaline and concentration of Ca\textsuperscript{2+} [4]. These residues are likely to be more reactive for carbonation than primary minerals due to their chemical instability and thus their use might enable to reduce energy consumption and costs of CO\textsubscript{2} mineral sequestration. The interesting in using the industrial residue materials as a source of calcium for mineral carbonation has increased since they are readily available and cheap. Furthermore, the carbonation of these wastes could reduce the amount of harmful substances, such as trace elements, released to the environment, as they are trapped in inert carbonates. The slag from steelmaking process is known as a material has the ability to capture and convert CO\textsubscript{2} to calcium carbonate (CaCO\textsubscript{3}), due to their high contents of calcium (Ca\textsuperscript{2+}) in the form of calcium oxide (CaO). So, the leaching of Ca\textsuperscript{2+} from slag is an important step for CO\textsubscript{2} sequestration via carbonation process [5]. This research focuses on method of CO\textsubscript{2} sequestration: permanent CO\textsubscript{2} fixation as environmentally benign carbonate minerals. In this case, the steelmaking slag was used as a precursor for Ca\textsuperscript{2+} and the main objective was to determine the optimum condition for Ca\textsuperscript{2+} leaching process.

2. Materials
The steelmaking slag is a byproduct of the electric arc furnace (EAF) obtained from Siam Steel Syndicate co., Ltd. (Samut Prakan, Thailand). Glacial acetic acid (99.7 wt %) analytical grade, was obtained from Baker, Inc. USA and used as received without further purification. The deionized water was produce onsite at our laboratory.

3. Experimental
3.1 Preparation of the steelmaking slag
The steelmaking slag was dried at 105 °C in an oven and roughly ground with jaw crushers. The steelmaking slag was then finely ground by gyratory crusher and sieved to get particle size of smaller than 45 \(\mu\)m. The fine ground material was then dried overnight at 105 °C. The compositions of prepared slag were analyzed using X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF) and Atomic absorption spectrometry (AAS).

3.2 Ca\textsuperscript{2+} leaching procedure
The leaching experiments were carried out in 2 L beaker glass. The prepared slag which particle size smaller than 45 \(\mu\)m is added into 1 L of acetic acid solution with different concentrations (0 and 2 M) which corresponded to the ratio of the liquid/solid mass ratio (L/S) of 10:1 g/g. The solutions were well mixed by using a mechanical stirrer at 300 rpm. The leaching temperature was 70 °C. For each experiment, the liquid samples of 10 ml were taken during the leaching period at 0, 1, 5, 10, 15, 30 and 60 minutes. The samples were filtered by syringe membrane filter (0.45 \(\mu\)m) before analyzed by XRD, XRF and AAS.

3.3 CO\textsubscript{2} removal efficiency
The CO\textsubscript{2} removal efficiency using steelmaking slag leaching solution obtained from section 3.2 was
performed using a lab scale absorption reactor as described in figure 1.

![Figure 1. A schematic of laboratory CO₂ absorption reactor](image)

From figure 1, the gas mixture containing 15.0 vol % CO₂ and 85.0 vol %N₂ was fed to 1 L of steelmaking slag leachate in absorption reactor at a flow rate of 0.73 l/min. The CO₂ concentrations at the inlet and outlet of reactor were measured. The CO₂ removal efficiency (CO₂ RE) was determined from the inlet (Cᵢ) and outlet (Cₒᵤₜ) CO₂ concentrations according to equation (1).

$$\text{CO}_2 \text{ RE} = \frac{C_i - C_{oupt}}{C_i} \times 100 \quad (1)$$

Where
- Cᵢ = inlet CO₂ concentration (ppm)
- Cₒᵤₜ = outlet CO₂ concentration (ppm)
- CO₂ RE = CO₂ removal efficiency (%)

### 3.4 Analysis

The structure of the steelmaking slag is analyzed by X-ray diffraction (XRD), using a Philips X’Pert MPD, and the elemental composition of the steelmaking slag is analyzed by X-ray fluorescence spectroscopy (XRF), using a Philips PW2400. The concentration of calcium (Ca²⁺) in the leaching solution is measured by using Atomic Absorption Spectrometry (AAS) (AAAnalyst 100 spectrometry manufactured by Perkin-Elmer, USA).

### 4. Results and Discussion

#### 4.1 Slag composition

The XRF was applied to evaluate the slag compositions. The compositions of the fresh slag, precipitated solid leached with acetic acid and deionized water were presented in Table 1. From Table 1, the fresh slag contains 51.61 % of CaO. After extraction with acetic acid, CaO content in a remaining precipitate was 6.56% where as the amount of CaO in the precipitate when using deionized water as leaching solution was almost the same as original found in fresh slag. The XRD patterns of fresh slag, and the solid slag leached with acetic and deionized water were compared in figure 2. It can be seen from figure 2 that the main compositions of slag in all cases are tricalcium magnesium orthosilicate (Ca₃Mg(SiO₄)₂), and gehlenite (Ca₂Al₂SiO₇). This composition characteristic make them suitable candidates for the industrial sequestration of CO₂ [6]. The extraction of Ca²⁺ from fresh steelmaking slag by acetic acid and deionized water gave a leachate and leached hydrated-matrix. The XRD patterns (see figure 2) revealed that the leached hydrated-matrixes obtained from steelmaking slag leaching with acetic acid (slag - acetic acid) contains Tricalcium magnesium orthosilicate (Ca₃Mg (SiO₄)₂) structure (calcium acetate hydrate) indicating that some elements in steelmaking slag have reacted with acetic acid resulting in structure change. While the leached hydrated-matrixes obtained from steelmaking slag leaching process using only deionized water (slag-water) has no structural changes.

![Figure 2. XRD patterns of the steelmaking slag used in the experiment; □ Tricalcium magnesium orthosilicate (Ca₃Mg (SiO₄)₂) • gehlenite, and ○ calcium acetate hydrate](image)

### Table 1 Composition of remained – solid from XRF analyses (units: wt.%)

<table>
<thead>
<tr>
<th>Components</th>
<th>Fresh slag</th>
<th>Solid slag leached with acetic acid</th>
<th>Solid slag leached with deionized water</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>51.61</td>
<td>6.56</td>
<td>51.1</td>
</tr>
<tr>
<td>MgO</td>
<td>4.51</td>
<td>1.33</td>
<td>3.75</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.32</td>
<td>10.71</td>
<td>7.67</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14.19</td>
<td>24.31</td>
<td>13.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>14.46</td>
<td>6.84</td>
<td>14.44</td>
</tr>
<tr>
<td>MnO</td>
<td>4.78</td>
<td>0.52</td>
<td>5.09</td>
</tr>
</tbody>
</table>

#### 4.2 Concentrations of calcium

The concentrations of calcium (Ca²⁺) in the leaching solution in time period of 60 min are shown in figure 3. It clearly shown that the acetic acid can extract CaO from fresh slag much better than deionized water. Since Ca²⁺ is a metal thus it was better dissolved in acid solution than water. The concentration of Ca²⁺ in leachate using acetic acid and deionized water leaching were up to 4755 mg/l and 502 mg/l, respectively.
4.3 CO₂ removal efficiency

The concentrations of Ca²⁺ in precipitate (solid) from CO₂ removal using leachate of steelmaking slag obtained by using acetic acid and deionized water as extracted solvent were compared in figure 4.

It can be seen from figure 4 that Ca²⁺ in acetic acid solution and deionized water hold with carbon dioxide, to from calcium carbonate as indicated by the reduction of Ca²⁺ concentration. The CO₂ removal efficiencies using these solution were shown in figure 5. Although Ca²⁺ eluted with acetic acid was even high, the maximum CO₂ removal efficiency was only 39 %. Where as that of Ca²⁺ in deionized water was up to 72 %. It is surprised that the leachate of steelmaking slag obtained by deionized water gave much higher CO₂ removal efficiency than that of acetic solution. The leachate properties using acetic acid and deionized water are compared in table 2. It was found that the Ca²⁺ concentration in leachate of acetic acid solution was about 9.5 times of deionized water. The leachate of steelmaking slag obtained by deionized water, however, posses much higher pH and alkalinity than that obtains by using acetic acid solution. This results implied that the alkalinity and pH are the most important parameters for CO₂ removal instead of Ca²⁺ concentration in solution.

5. Conclusions

The conclusion of this work can be drawn as follow. The leaching of Ca²⁺ from steelmaking slag using acetic acid and deionized water as extracted solution was investigated. The concentration of Ca²⁺ in acetic acid solution were much greater than that of deionized water. Although Ca²⁺ eluted with acetic acid was even high, the maximum efficiency of CO₂ removal was much lower than of deionized water extraction. In addition, the alkalinity in water leaching was very high. It can be concluded that the alkalinity and pH are the most important parameters for CO₂ removal instead of Ca²⁺ concentration. Thus deionized water leaching process is adequate for steelmaking slag extraction for CO₂ sequestration.

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7. Reference


