

Article

Elution of Divalent Cations from Iron Ore Mining Waste in an Indirect Aqueous Mineral Carbonation for Carbon Capture and Storage

Muhammad Hameer Soomro¹, Faradiella Mohd Kusin^{1,2,*}, Ferdaus Mohamat-Yusuff¹
and Nik Norsyahariati Nik Daud³

¹ Department of Environment, Faculty of Forestry and Environment, Universiti Putra Malaysia (UPM), Serdang 43400, Malaysia; engr.hameer@gmail.com (M.H.S.); ferdius@upm.edu.my (F.M.-Y.)

² Institute of Tropical Forestry and Forest Product, Universiti Putra Malaysia (UPM), Serdang 43400, Malaysia

³ Department of Civil Engineering, Faculty of Engineering, Universiti Putra Malaysia (UPM), Serdang 43400, Malaysia; nknor@upm.edu.my

* Correspondence: faradiella@upm.edu.my; Tel.: +60-103666160

Abstract: Mining waste is generated in vast quantities globally, which can have negative environmental consequences. This study highlights the utilization of iron ore mining waste as feedstock material in the preparatory step of an indirect aqueous mineral carbonation for carbon sequestration. The role of reactive cations (Ca^{2+} , Mg^{2+} , and Fe^{2+}) was investigated in view of their elution behavior to improve carbonation efficiency. An elution experiment was carried out for the divalent cations using different acids (oxalic, HCl, acetic, and formic acid) at different concentration solutions (up to 1.5 M) and times (up to 100 min) at ambient temperature. The initial analysis confirmed the presence of divalent cations in the sample. The elution approach at ambient temperature resulted in the elution efficiency of Fe^{2+} (30.4%), Mg^{2+} (54%) using oxalic acid, and Ca^{2+} (98%) using HCl at a relatively short time between 50 and 100 min. It was found that for the iron ore mining waste, oxalic acid and HCl were best suited as elution agents for the Fe^{2+} and Mg^{2+} , and Ca^{2+} , respectively. The CO_2 sequestration potential was calculated to be 131.58 g CO_2 /kg residue. A further carbonation step using a complexing agent (1,10 phenanthroline) confirmed the formation of siderite and magnesite along with phenanthroline hydrates. Findings have shown that the indirect mineral carbonation of the iron mining waste with complexing agent might improve carbonation efficiency, thus indicating that this material is useful for long-term carbon capture and storage applications.

Keywords: cations elution; carbon capture and storage; iron residue; mining waste; mineral carbonation; waste reutilization



Citation: Soomro, M.H.; Mohd Kusin, F.; Mohamat-Yusuff, F.; Nik Daud, N.N. Elution of Divalent Cations from Iron Ore Mining Waste in an Indirect Aqueous Mineral Carbonation for Carbon Capture and Storage. *Sustainability* **2024**, *16*, 836. <https://doi.org/10.3390/su16020836>

Academic Editors: Marc A. Rosen, Sumi Siddiqua and Sarat Das Kumar

Received: 9 August 2023

Revised: 10 January 2024

Accepted: 12 January 2024

Published: 18 January 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Mining waste is a potential source of minerals for carbon dioxide (CO_2) sequestration among other types of industrial solid waste. Globally, mining waste is produced at an amount of 13,000 Mt/y [1], from which the carbon sequestration potential can be estimated to be about 2800 MtC/y. Moreover, mining is considered a carbon-intensive industry and is typically linked with pollution and waste dumping issues [1,2]. Nevertheless, such waste carries valuable minerals that might have potential to be used as feedstock for carbon sequestration, which also helps in solving the waste dumping problem and provides an opportunity for reutilization of the waste. For this reason, various applications/methods have been reported in the reutilization of waste materials, e.g., Meseldzija et al. [3] reported an economical removal method of pollutants from mining wastewater by using agro-industrial residue, Azam et al. [4] reported a cost-effective method to remove heavy metals using ajwa date pits adsorbent; while, in a study by Syed Hasan et al. [5], eco-friendly bricks and carbon storage was developed by utilizing waste from a gold mine.

Alqadami et al. [6] developed a method to remove pollutants by utilization of food waste, and Khan et al. [7] developed a safe and efficient disposal of steel production waste. All of these studies have supported the potential for various environmental treatments to utilize waste materials.

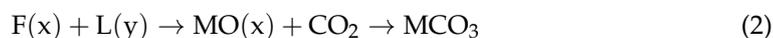
On the other hand, the current level of CO₂ in the atmosphere is around 400 parts per million (ppm), and the United Nations Intergovernmental Panel on Climate Change (IPCC) predicts that the CO₂ concentrations might increase up to 1150 ppm by 2100 if proper mitigation measures are not taken into account [8]. These emissions play a part in triggering global warming and ultimately leading to climate change, which is the most challenging issue globally [9]. Therefore, carbon capture and storage (CCS) is a much-necessary technology that can significantly capture and reduce CO₂ emissions before releasing into the atmosphere [10,11].

Carbonation-based CCS technologies refer to the removal of CO₂ from flue gases appearing from industrial applications or burning fuels by reacting with metal oxides (MO) and storage as stable carbonates [12,13]. In this technology, the basic minerals such as calcium (Ca), magnesium (Mg), or iron (Fe) oxides react with CO₂ to form harmless solid carbonates, also known as mineral carbonation. CCS via mineral carbonation is further divided into two methods: (i) direct carbonation and (ii) indirect carbonation [14]. In the direct carbonation method, the MO reacts with CO₂ under a controlled environment to form carbonates. It is a simple single-step method as shown in Equation (1).



However, this method requires pre-degree treatment such as fine grinding, heat treatment, or chemical activation to provide suitable reaction kinetics [15,16].

In the indirect carbonation method, also known as the two or more steps method, the reaction is as shown in Equation (2).



where F is the feedstock and L is the extraction agent. In this method, the mineral feedstock is treated with an extraction agent first to extract the reactive MO before reacting it with CO₂. The indirect carbonation method has been proven to be more effective with higher carbonation efficiency, shorter reaction time, kinetic favorability, as well as also permitting the disengagement and recovery of products (iron oxides, silica, and carbonates) with excellent levels of purity [17–20].

Processes such as mining and extraction for reactive MO from rock material require high energy and resources for CCS via mineral carbonation, and such limitations that make it a highly expensive process. Therefore, alkaline industrial residues or mining waste represent a substitute source as feedstock for mineral carbonation [21]. Previous studies have used different kinds of alkaline residue materials as feedstock for mineral carbonation such as limestone/gold/tin mine waste, cement waste or dust from cement production, steel slag from steel production industries, and concrete waste from construction sites [22–26]. Nearly all studies were aimed at Ca and Mg silicates as the source minerals for mineral carbonation. However, very few studies have assessed oxides of Fe as the source mineral since Fe oxides have been recognized as an important divalent cation that can also be used for carbonation reactions for CCS [27].

Ramli et al. [28] used a direct mineral carbonation approach in their studies using iron ore mining residues as feedstock at different pH, particle size, and temperature and reported up to 87.6 g CO₂/kg of waste that had been sequestered and 6.7% carbonation efficiency, respectively. However, such carbonation uptake results were considered relatively low, while a high percentage of MO was available in their feedstocks, which clearly showed an incomplete carbonation of the available reactive MO. Therefore, an indirect carbonation method is proposed to achieve a higher carbonation rate by leaching out the reactive MO first before reacting with CO₂.

In view of the indirect carbonation technique, the carbonation uptake is purely dependent on the metal extraction efficiency. The more metal extracted from the feedstock, potentially the more carbonation uptake. Even though Meyer et al. [29] already achieved almost 90% carbonation uptake, the extraction efficiency was rather low, i.e., lower than 1/3 of the total available minerals. Moreover, previous studies also reported that different parameters are affecting the extraction efficiency such as particle size, solid–liquid ratio, additive concentration, time, and temperature used in the experiment. For that, several studies have assessed different parameters/extraction agents to achieve optimum conditions for the extraction of MO. In terms of particle size, Owais et al. [30] investigated three distinct particle sizes ranging between 0.50 μm , 50–74 μm , and 74–125 μm and determined the optimum particle size of 0–50 μm with greater elution efficiency. Similarly, numerous investigations have found that smaller particle size leads to a higher elution efficiency [31,32]. Previous studies indicated that elution efficiency is directly proportional to extractant concentration and temperature. Vieira et al. [31] observed that the greatest extractant concentration (4 M) and temperature (70 °C) employed in their experiment yielded the best results for Fe^{2+} and Mg^{2+} elution efficiency. Similarly, Spinola et al. [33] observed the best Ca^{2+} elution efficiency when employing a 2 M (highest concentration) acetic acid solution. Furthermore, Arce et al. [34] investigated temperatures ranging from 25 °C to 100 °C and discovered that all solutions employed at 100 °C obtained the highest Fe^{2+} and Mg^{2+} elution efficiency. A similar trend was reported by Galina et al. [35], in that higher temperature (100 °C) leads to higher elution efficiency of Mg^{2+} using 2.5 M HCl solution. Moreover, Rahmani [26] used red gypsum (mainly consisting of calcium sulfate and hematite) as feedstock material and achieved up to 63% Ca^{2+} elution using 1.5 molar (M) sulfuric acid at 70 °C for 2 h. Kim and Jung [20] used cement kiln dust as feedstock and used citrate, malonate, and adipate salts to extract Ca^{2+} , and reported that citrate had promising results and could extract up to 42% of Ca^{2+} using 0.1 M concentration at 80 °C. Tier et al. [36] assessed different acids, bases, and ammonium salt solutions to extract Fe^{2+} and Mg^{2+} using serpentine samples as feedstock, where 2 M HCl showed promising results that can extract up to 67% of Fe^{2+} in 2 h at 70 °C. On the other hand, Razote et al. [37] used iron-rich siltation pond waste as feedstock and reported extraction efficiency of Fe^{2+} up to 94% using 2.5 M HCl at 75 °C in 2.5 h. Based on the previous studies, results with higher temperatures, concentrations, and higher reaction times for leaching or elution efficiency remain unpractical, e.g., due to energy consumption and its associated costs. Therefore, there is a need to assess the leaching behavior of the feedstock material with new solvents, shorter reaction time, and no heating required (at ambient temperature) to minimize overall cost, time, and energy consumption.

In this study, we assessed the iron ore mining waste collected from an iron ore mine located in the southern part of Malaysia, determined the elution or leaching efficiency of the iron mining waste using different extraction agents at different reaction times and concentrations, and assessed the indirect aqueous mineral carbonation. Malaysia's production of iron ore was estimated to be 5.4 million tons in 2020, with a market value of RM709.23 million, and is the largest metallic mineral commodity in the country. While the industry produces millions of tons of waste yearly, there is an opportunity to reuse or repurpose the production of such waste materials. Mining waste carries valuable minerals and in particular iron ore mining waste can be reutilized as feedstock for carbon capture and storage via mineral carbonation. This study may assist in solving the various problems linked with waste dumping and CO_2 emissions at most mining sites and may lead to the long-term benefits of reducing carbon emissions and waste production by reutilizing the mining waste.

2. Materials and Methods

2.1. Raw Sample Preparation

The iron ore mining waste material was collected from an active iron ore mining site located at Chaah town in Johor, Malaysia, with a total area of about 19.4 hectares. The

iron ore from the mine contains low levels of impurities, which enables the production of high-grade iron ore concentrate. Between 2008 and 2021, the mine produced around 6.3 million tons of iron ore products and 0.3 million tons of tailings. The composite samples were collected between 16 and 20 cm depth from the tailings pile in the vicinity of the mine. The collected samples were air-dried for 48 h in the lab at room temperature (<30 °C) and were then crushed into fine powder using agate mortar and pestle. The powder was then sieved using fine series particle sieves (<0.5 mm) to homogenize the samples for physicochemical and mineralogical analysis [38,39].

2.2. Physicochemical and Mineralogical Analysis

The microstructure, particle size, and chemical composition (determined as the percentage of weight) of the iron ore mining waste were analyzed using scanning electron microscopy attached with energy dispersive X-ray spectroscopy (SEM-EDX, Philips XL30, Netherlands-Inca Software 5.04). Furthermore, 5 spots were randomly scanned on each sample at 2 different places and all values were normalized. Under optimum conditions, its maximum resolution is 3.5 nm. The mineral phases of the samples were analyzed by X-ray diffraction (XRD, Bruker-AXS D8 Advanced diffractometer). The integrated intensity of peak areas was analyzed using software (Diffrac AT EVA v.9.0) to identify the mineral phases of the samples. The pH of the solution was measured by using a portable pH meter (Thermo SCIENTIFIC Orion Star A121).

2.3. Elution Experiment

An elution experiment was carried out in the lab as a pre-carbonation step to increase carbonation efficiency by extracting reactive MO from the iron ore mining waste, targeting Fe^{2+} , Ca^{2+} , and Mg^{2+} ions as these are the most favorable divalent cations for mineral carbonation [14]. An altered version of an elution experiment for mineral carbonation, i.e., an indirect method conducted earlier by Kim and Jung [20] was adopted in this study. Four different acids (analytical reagent grade) were used as extracting agents to assess their extraction efficiency and improve the leaching behavior of the iron ore mining waste.

2.3.1. Extracting Agent Concentration and Elution Time

The elution efficiency was evaluated using different acids at different concentrations. Four different acids (oxalic (Merck, Germany), formic (Merck, Germany), acetic (Merck, Germany), and hydrochloric acid (R&M Malaysia)) were used at varying concentrations of 0.25, 0.5, 0.75, 1.0, and 1.5 M, respectively. Waste powder and each acid solution were mixed at a ratio of 1:10 (15 g: 150 mL) in flasks and were put on an orbital shaker for 100 min and shaken at 220 rounds per minute at atmospheric pressure and room (ambient) temperature. To assess the elution efficiency based on time, each of the four solvents and waste powder were mixed and samples were taken at the interval time of 12, 25, 50, and 100 min in sequence to check for Fe^{2+} , Ca^{2+} , and Mg^{2+} concentrations.

2.3.2. Analytical and Post Elution Methods

Samples during the elution experiment were taken using 10 mL of disposable plastic syringe (Terumo, Somerset, NJ, USA) with the connected head of 0.45 μm membrane filter (Sterlitech, Auburn, WA, USA). The samples were kept in 15 mL centrifuge tubes (BIOFIL, Guangzhou, China) and were then analyzed for the concentrations of Fe^{2+} , Ca^{2+} , and Mg^{2+} in extracted solution using an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 7300 DV). The instrument was calibrated using a series of the ICP standard solutions to generate the standard calibrating curves with an analytical precision of between 86 and 110%. The concentration results (mg/L) were then calculated using the method used by Kim and Kim [40] to determine the elution efficiency of each element. For quality assurance/quality check (QA/QC), blank samples (deionized water was used to make up solutions) were also run in the same manner to make sure there were no impurities during the experiment. Moreover, to assess the significant difference in

elution experiment results, the Analysis of Variance (ANOVA) statistical test (single-factor or also known as one-way ANOVA) was applied to the cation extraction efficiency and the variables were (i) different solution concentrations (0.25, 0.5, 0.75, 1, and 1.5 M) of up to 100 min and (ii) different reaction times (12, 25, 50, and 100 min) of up to 1.5 M solution (See data in Supplementary Material Figure S5).

2.4. CO₂ Sequestration Potential

The CO₂ sequestration potential using the indirect mineral carbonation method of iron ore mining residue was calculated in two ways: (i) theoretical amount and (ii) experimental amount through the Fe²⁺, Mg²⁺, and Ca²⁺ elution from the waste sample. Based on the balanced stoichiometric ratio (1:1) between Fe²⁺, Ca²⁺, Mg²⁺, and the CO₃²⁻ (carbonate ion), the theoretical CO₂ sequestration potential of Fe²⁺, Ca²⁺, and Mg²⁺ were calculated using Equations (3), (4) and (5), respectively [37].

$$PCO_2 = \frac{\left(Ce * V_{sol} * \frac{1 \text{ mmolFe}}{55.85 \text{ mgFe}} * \frac{1 \text{ mmolCO}_2}{1 \text{ mmolFe}} * \frac{44.01 \text{ mgCO}_2}{1 \text{ mmolCO}_2} \right)}{Mi} \frac{\text{mgCO}_2}{g_{\text{sample}}} \quad (3)$$

$$PCO_2 = \frac{\left(Ce * V_{sol} * \frac{1 \text{ mmolCa}}{40.08 \text{ mgCa}} * \frac{1 \text{ mmolCO}_2}{1 \text{ mmolCa}} * \frac{44.01 \text{ mgCO}_2}{1 \text{ mmolCO}_2} \right)}{Mi} \frac{\text{mgCO}_2}{g_{\text{sample}}} \quad (4)$$

$$PCO_2 = \frac{\left(Ce * V_{sol} * \frac{1 \text{ mmolMg}}{24.3 \text{ mgMg}} * \frac{1 \text{ mmolCO}_2}{1 \text{ mmolMg}} * \frac{44.01 \text{ mgCO}_2}{1 \text{ mmolCO}_2} \right)}{Mi} \frac{\text{mgCO}_2}{g_{\text{sample}}} \quad (5)$$

where PCO₂ denotes the sequestration potential of CO₂ in unit mg CO₂/g residue sample, Ce denotes the concentration of the element in the solution (mg/L), V_{sol} denotes the volume of the solution (L), and Mi denotes the initial sample (g). On the other hand, the experimental amount was calculated in two ways: (i) based on the carbonation efficiency using the targeted cations (Fe²⁺, Mg²⁺, and Ca²⁺) from the previous experimental studies by Reynes et al. [41] and Kim and Kim [42] and (ii) from experimental results obtained in this study. Moreover, the projection of CO₂ sequestration was calculated based on the current amount of iron ore mining waste production in Malaysia (Equation (6)).

$$PsCO_2 = (X) \text{Kg CO}_2 / \text{t waste} * (Y) W t \frac{\text{KgCO}_2}{t_{\text{sample}}} \quad (6)$$

where PsCO₂ denotes the projection of CO₂ sequestration in unit KgCO₂/ton residue sample, X denotes the value of CO₂ sequestration potential, and Y denotes the waste produced in unit ton.

2.5. Post Elution CO₂ Sequestration

After the elution experiment, the solution was filtered to separate the remaining residue (solid) using grade 5 filter paper (Whatman), and elute (liquid) was prepared for subsequent step of indirect mineral carbonation using the iron ore mining waste samples. Two experimental settings were carried out: (i) direct carbonation of elute by adjusting the pH using ammonium hydroxide (Sigma-Aldrich, Saint Louis, MO, USA) 1.0 M solution, (ii) the elute was reacted with the chelating agent first to form a complex and adjusting the pH to prevent the Fe oxidization from ferrous (Fe²⁺) to ferric (Fe³⁺) at higher pH. In this study, we used 1,10 phenanthroline (Sigma-Aldrich, Saint Louis, MO, USA) as a chelating agent. In detail, 1,10 phenanthroline (Phen) is a heterocyclic organic ligand with a high sympathy for divalent metal ions (e.g., Fe, Cu, Zn) [43]. The stoichiometric amount of phen (prepared with 12% Ethanol and 88% D.I water) solution was mixed with the elute and then the pH was adjusted using sodium hydroxide (Sigma-Aldrich, Saint Louis, MO, USA) 1.0 M solution. The CO₂ gas (SMART Biogas Enterprise, Selangor, Malaysia) with 99.8% purity was used for the carbonation experiment.

The carbonation experiment was carried out in a closed stainless steel reactor system (Donowell Equipment, ACL03-250) consisting of heating mantle, pressure relief valve (outlet), gas inlet valve, pressure indicator, stirrer, and detachable Teflon cup [44]. The settings of each parameter (pressure: 1 bar, pH: 11, stirrer speed: 250 rpm, time duration: 1 h, temperature: ambient) were kept constant during both experimental settings in this study. The carbonated product was further analyzed by XRD.

3. Results and Discussion

3.1. Physicochemical and Mineralogical Properties

The morphological structure and particle size of iron ore mining waste were examined using SEM. Figure 1 depicts the microstructure of the sample, which revealed the granular form of waste particles. The SEM results (at 5.00k \times magnification) revealed the average particle size by measuring two random spots in each of two separate parts of the sample. The average particle size was determined to be <10 μm . Hence, it was proven that grinding of the sample may reach sufficient particle size for both the leaching experiment and the mineral carbonation reaction as our earlier experiment suggested that the suitable particle size of mining waste for effective carbonation to be <38 μm [44].

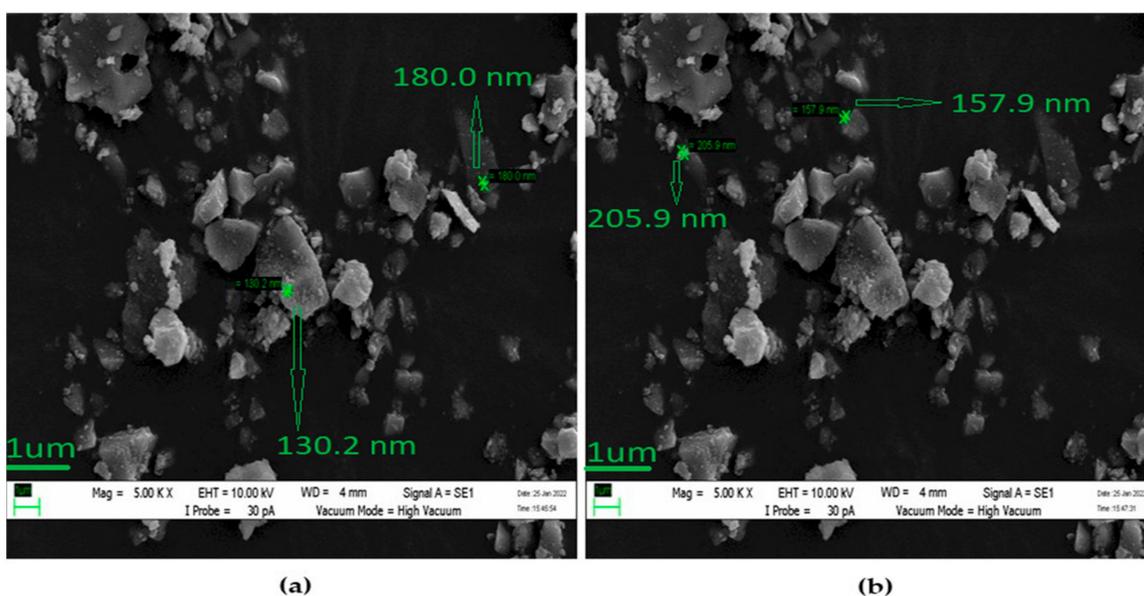


Figure 1. (a,b) SEM images of iron ore mining waste samples with their shape and particle size.

The chemical composition of iron ore mining sample was determined by EDX. Table 1 shows the mass percentage of elements discovered in the sample. The predominant mineral of the iron ore mining sample was Fe, with the highest content of Fe (45.95 wt.%), followed by O (34.56 wt.%) and Si (11.51 wt.%). The composition of Fe was mainly attributed to hematite minerals as suggested by the XRD analysis (Figure 2). The other reactive metal oxides for mineral carbonation such as Ca and Mg were also detected at 1.45% and 0.63%, respectively. Therefore, it was confirmed from the EDX results that iron ore mining sample can be used as feedstock to capture CO₂ via mineral carbonation due to the presence of the potential divalent cations (Fe, Ca, and Mg). The capture mechanism of these cations upon reaction with CO₂ to form carbonate minerals can be simplified as follows:



Figure 2 depicts the mineralogy of the sample and phase distribution using XRD. The XRD results show that hematite (Fe₂O₃), quartz (SiO₂), and calcium (Ca) were present in the sample. The phase distribution of the minerals shows that hematite (79 wt.%) was the

predominant mineral present in the sample, followed by quartz (16.9 wt.%). Specifically, hematite reaction with CO₂ to form iron carbonate is as shown in the following reaction [45]:

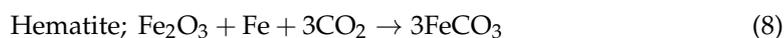


Table 1. Chemical composition of iron ore mining sample.

| Chemical Composition | Concentration (wt.%) |
|--|----------------------|
| Fe | 45.95 |
| Si | 11.51 |
| Al | 3.69 |
| K | 1.47 |
| Ca | 1.45 |
| Mg | 0.63 |
| O | 34.56 |
| * Other trace metals (Ti, Ba, Mn, S, Cl, Cr, As) | 0.74 |

* = All values were <0.18 wt.%.

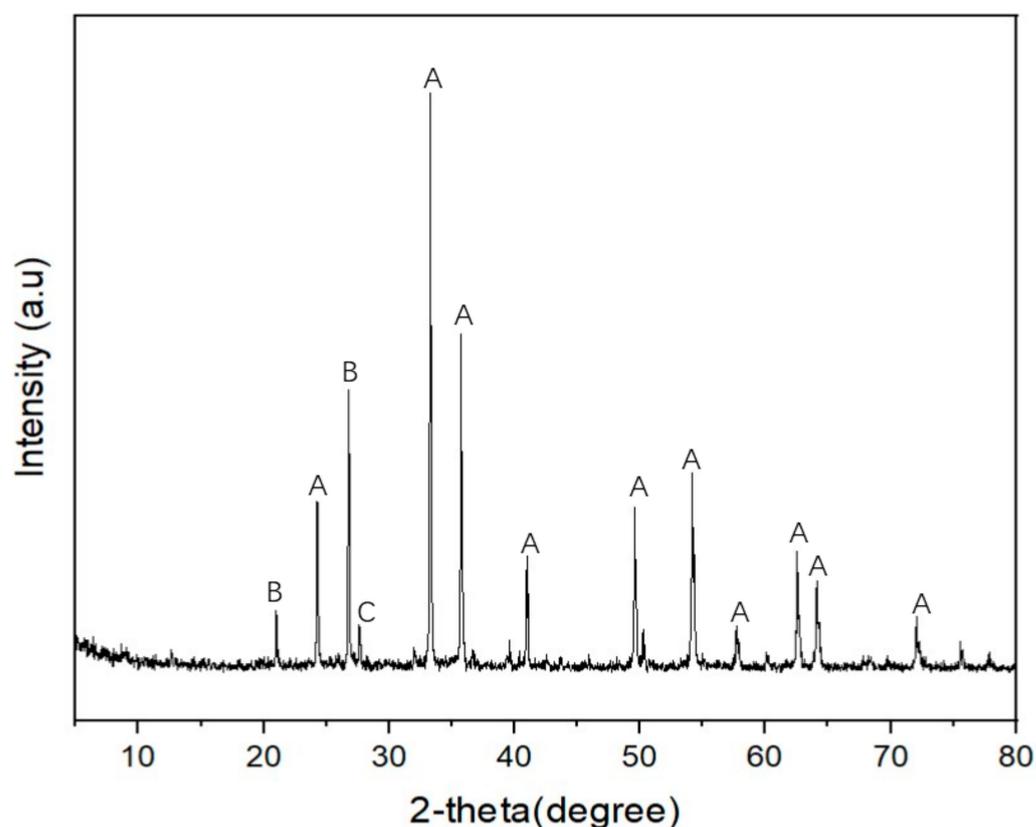


Figure 2. XRD diffractograms of iron ore mining sample (A = Hematite; Fe₂O₃, B = Quartz; SiO₂, C = Calcium; Ca).

On the other hand, Fe carbonate can also be formed by the reduction of hematite to magnetite, and then magnetite reacting with CO₂ in the presence of water [46]. Additionally, a small amount of Ca mineral was also discovered. This demonstrates the parent chemical composition of the iron ore sample as well as the presence of valuable minerals in mine waste. Hence, the overall XRD results also supported the EDX summary.

3.2. Elution of Fe, Mg and Ca

3.2.1. Oxalic Acid

The elution of elements using oxalic acid is also known as the oxalate method process. Figure 3 depicts the elution results of reactive elements (Fe²⁺, Mg²⁺, Ca²⁺) employing oxalic

acid as an extraction agent at the two most efficient results, while the remaining concentration data are included in the Supplementary Information (Supplementary Material Figure S1). The Fe^{2+} elution results indicated that the 1.0 M solution produced promising and consistent results, whereby using 1.0 M oxalic acid at 100 min achieved 30.4% efficiency followed by 24% using 0.75 M at 100 min. However, 1.5 M solution (maximum applied) tends to decline with 17% maximum efficiency (Supplementary Material Figure S1). The Mg^{2+} elution results indicated a nearly same trend across 0.25 M and 0.75 M solutions with the highest efficiency of 54% using 0.25 M and 0.75 M at 100 min. However, the maximum concentration solution declines with poor efficiency as with Fe^{2+} . In comparison to other reactive elements, the efficiency of Ca^{2+} elution using oxalic acid solution remains the lowest, whereas the 1.0 M solution showed consistently higher efficiency throughout the experiment with 20% at 25 min followed by 16% using 0.25 M at 100 min.

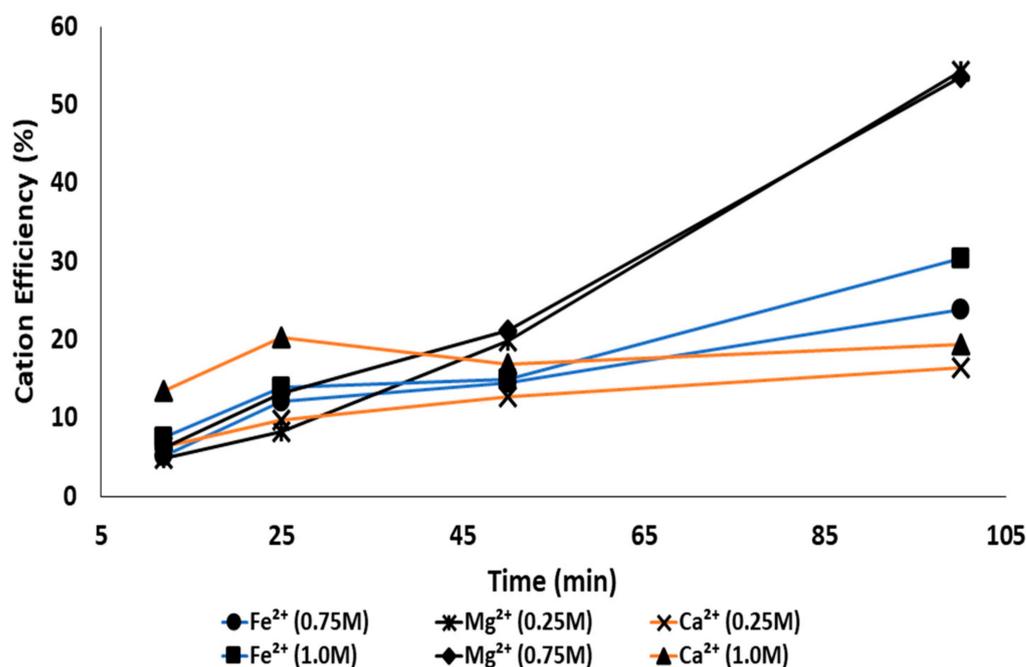


Figure 3. Elution efficiency of cation as a function of reaction time using different concentrations of oxalic acid.

The elution of Fe^{2+} is believed to occur via a photoelectrochemical reduction activity through a complex charge transfer mechanism between the two major types of oxalates, that is, ferrous oxalate and ferric oxalate [47]. At 1.0 M extractant, the Fe^{2+} elution efficiency was around 30.4%. For comparison, a previous study conducted by Lee et al. [48] using hematite mineral as feedstock reported around 50% Fe^{2+} elution efficiency using 0.38 M oxalic acid at 100 °C and less than 10% Fe^{2+} elution efficiency at ambient temperature using 0.19 M of oxalic acid. This indicates that a higher concentration of oxalic solution is preferable for more effective Fe^{2+} elution. Moreover, a study by Reynes et al. [41] used ammonium bisulfate as an extraction agent to extract Fe^{2+} from iron silicate mining waste (mainly Fe-rich olivine) and reported around 30–38% of Fe^{2+} extraction efficiency using 1.5 M ammonium bisulfate solution at 61 °C in 2 h. Therefore, it can be seen that the use of oxalic acid has demonstrated a comparable result in this study within a short time. The overall results using oxalic acid suggested that the Mg^{2+} elution efficiency (54%) was better than Fe^{2+} (30.4%) because of weaker covalent bonds of Mg, and results suggested that lower or medium concentrations are more favorable for Mg^{2+} elution. Moreover, the higher elution efficiency of Fe^{2+} and Mg^{2+} and a lower efficiency of Ca^{2+} using oxalic acid as an extraction agent in this study exhibited similar trends as Sun et al. reported [49].

3.2.2. Hydrochloric Acid

Figure 4 depicts the elution results using HCl as an extraction agent at the two most efficient results, and the remaining concentration data are included in Supplementary Material (Figure S2). The maximum Fe^{2+} elution efficiency with HCl was about 2.7% using 1.5 M solution at 50 min, followed by 1.6% using 1.0 M, which is considered quite low. This indicates that the HCl solution significantly restrained the leaching of Fe^{2+} and another possible cause was that the Fe^{2+} ions precipitated with other ions during leaching [50]. The Mg^{2+} elution results also showed a similar trend as for Fe^{2+} elution efficiency, where maximum Mg^{2+} elution efficiency was about 9% using 1.5 M solution at 50 min, followed by 6.8% using 1.0 M at 100 min. In comparison, a study by Matus et al. [51] observed nearly the same trend of elution efficiency for the Mg elution using HCl, where they employed a 50 °C temperature with 1.0 M HCl solution. In contrast, the Ca^{2+} elution demonstrated promising results as it can extract up to 98% at 50 min using 1.5 M HCl solution. Using HCl for the elution of Ca^{2+} shows that a higher concentration leads to a higher extraction efficiency in less than 1 h, such results are parallel to the study by Kim et al. [52], where they reported nearly 100% Ca^{2+} elution efficiency using higher concentrations of HCl solutions.

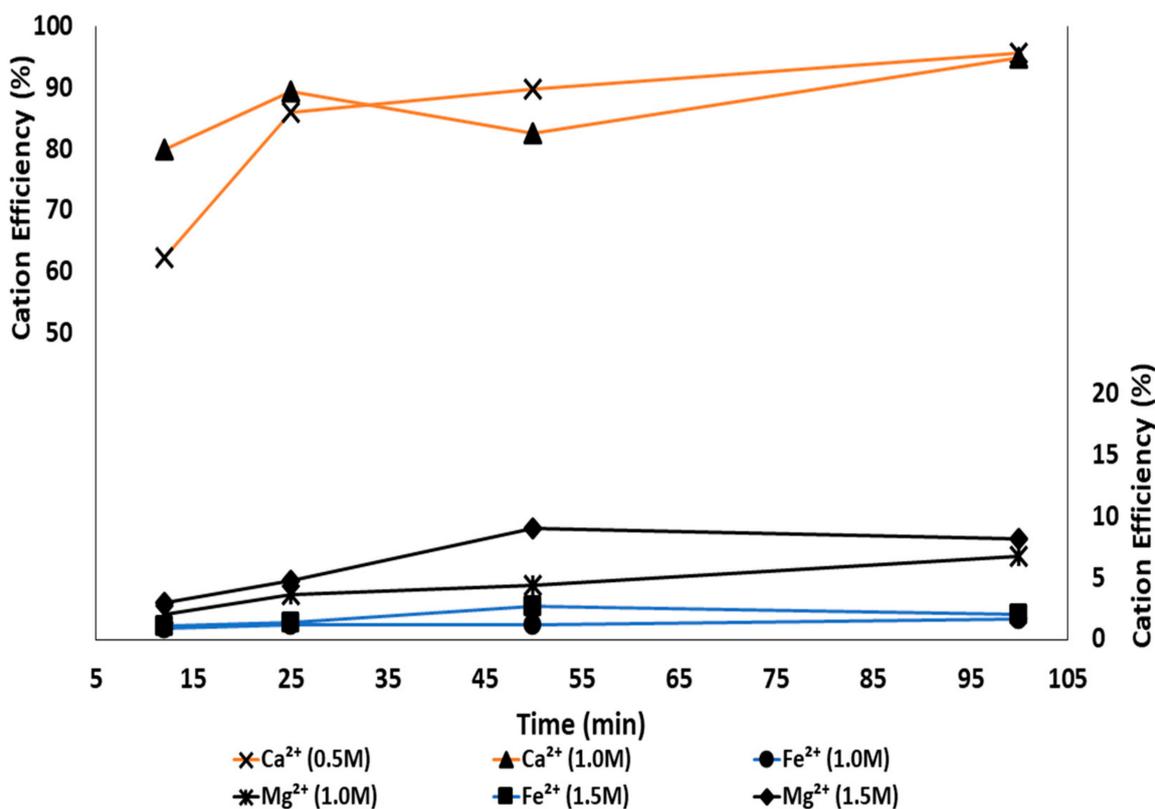


Figure 4. Elution efficiency of cation as a function of reaction time using different concentrations of HCl.

The common mechanism of reaction for iron oxide (i.e., hematite) reveals that dissolution occurs via several routes, one of which is proton adsorption to the iron oxide surface, which promotes Fe detachment [53]. This process is believed to have contributed to the increase in Fe^{2+} extraction as acid concentration was raised (Supplementary Material Figure S2). The overall results using HCl solution suggested that the higher concentration (i.e., 1.5 M) leads to higher elution efficiency for Fe^{2+} , Mg^{2+} , and Ca^{2+} ions. Moreover, hematite mineral is expected to have higher reactivity with HCl at higher concentration of acids, time, and elevated temperatures [54], as it is suggested that the maximum dissolution of hematite and other FeO requires high temperature (>70 °C) with lower pH values

(<1) [53]. This supported the other possible causes of low elution behavior of HCl solution with Fe^{2+} and Mg^{2+} due to insufficient contact time or incomplete reaction as the factors such as temperature, reaction time, and stoichiometry of experiment can influence the level of the elution efficiency.

3.2.3. Formic Acid

Results of the elution employing formic acid as the extraction agent at the two most efficient results are shown in Figure 5; the remaining concentration data are included in Supplementary Material (Figure S3). The maximum Fe^{2+} elution efficiency was 0.2% using 1.5 M solution at 25 min, followed by 0.13% using 1.0 M solution. Mg^{2+} showed similar trend to Fe^{2+} with the highest Mg^{2+} elution efficiency of 1.4% using 1.5 M solution at 25 min, followed by 1.2% using 1.0 M solution, which is considered relatively low. It reveals that the formic acid exhibits very poor dissolution reactivity with Fe^{2+} and Mg^{2+} at ambient temperature and short reaction time. Halli et al. [55] conducted an elution study using electric arc furnace dust and found up to 14% of Fe^{2+} elution using 0.27 M formic acid in 168 h, which was a longer reaction time. Lower elution reactivity of Fe^{2+} was also observed in other studies using formic acid as an extraction agent [56,57]. The Ca^{2+} elution showed better results with maximum elution of 30% using 1.5 M solution at 12 min and 25 min steadily, followed by 23.6% using 1.0 M solution within 12 min, demonstrating a rapid initial rate of elution. The Ca^{2+} trend indicated that formic acid can elute its maximum capacity in the first 12 to 25 min, then the efficiency slightly declined but remained steady until 100 min of reaction (Supplementary Material Figure S3). This pattern was observed in nearly all concentrations and cations of formic acid. The Ca^{2+} leaching is a little complicated as Ca^{2+} recrystallization may take place when pH exceeds 3.5, and the initial pH of solution was 1.65 without adding mining waste sample. In this case, pH might be the limiting factor for the declining trend of Ca^{2+} leaching after 25 min [58].

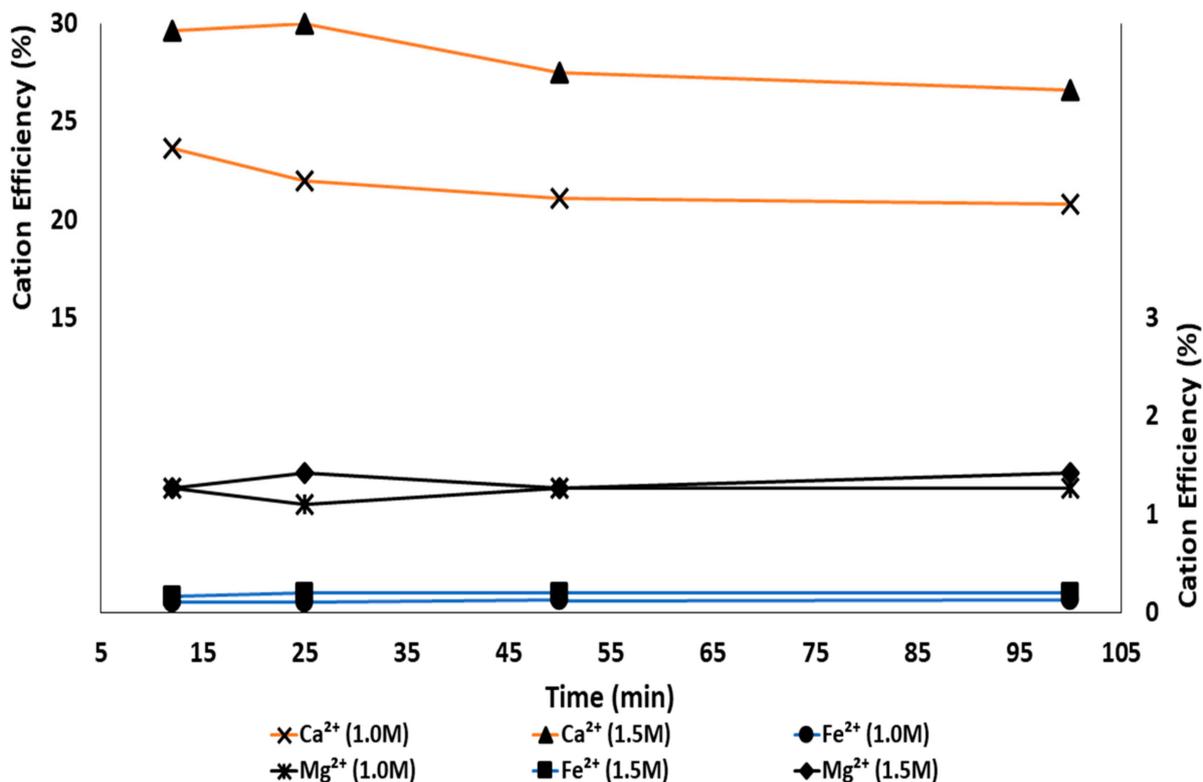


Figure 5. Elution efficiency of cation as a function of reaction time using different concentration of formic acid.

3.2.4. Acetic Acid

The acetic acid elution results at the two most efficient results are shown in Figure 6; the remaining concentration data are included in Supplementary Material (Figure S4). The maximum Fe^{2+} and Mg^{2+} elution efficiency using 1.5 M solution was 0.62% and 5.3%, respectively. The results for Fe^{2+} and Mg^{2+} using acetic acid exhibited similar trend to the formic acid, indicating poor elution efficiency at ambient temperature. For comparison, Bao et al. [59] employed steel slag as feedstock using acetic acid at different temperatures, and reported almost the same trend for Fe^{2+} leaching efficiency as this study, However, due to the higher temperature (94 °C), they obtained a greater Mg^{2+} elution efficiency (35%). The Ca^{2+} elution efficiency showed better results with the highest efficiency observed up to 24.6% using 1.5 M solution at 25 min followed by 23% using 1.0 M solution at 25 min. The overall findings of Ca^{2+} elution with acetic acid revealed that all solution concentrations exhibited optimal efficiency at 25 min. Moreover, due to low solubility of Fe^{2+} as compared to Ca^{2+} , this might suggest that the elution of Fe^{2+} is a highly pH-dependent process. The pH of the solution and iron precipitated as hydroxide might be the reason for poor Fe^{2+} elution with acetic acid, while similar results were reported by other researchers [60,61]. The low solubility of Mg^{2+} compared to Ca^{2+} using HCl (Figure 4) and acetic acid suggested that the Mg^{2+} mineral phase might affect the Mg^{2+} elution behavior. This was due to the presence of chromium (Cr) in the sample which was found to be magnesiochromite mineral, that has extremely low solubility compared to other Ca/Mg bearing minerals, as similarly suggested by Zhao et al. [62].

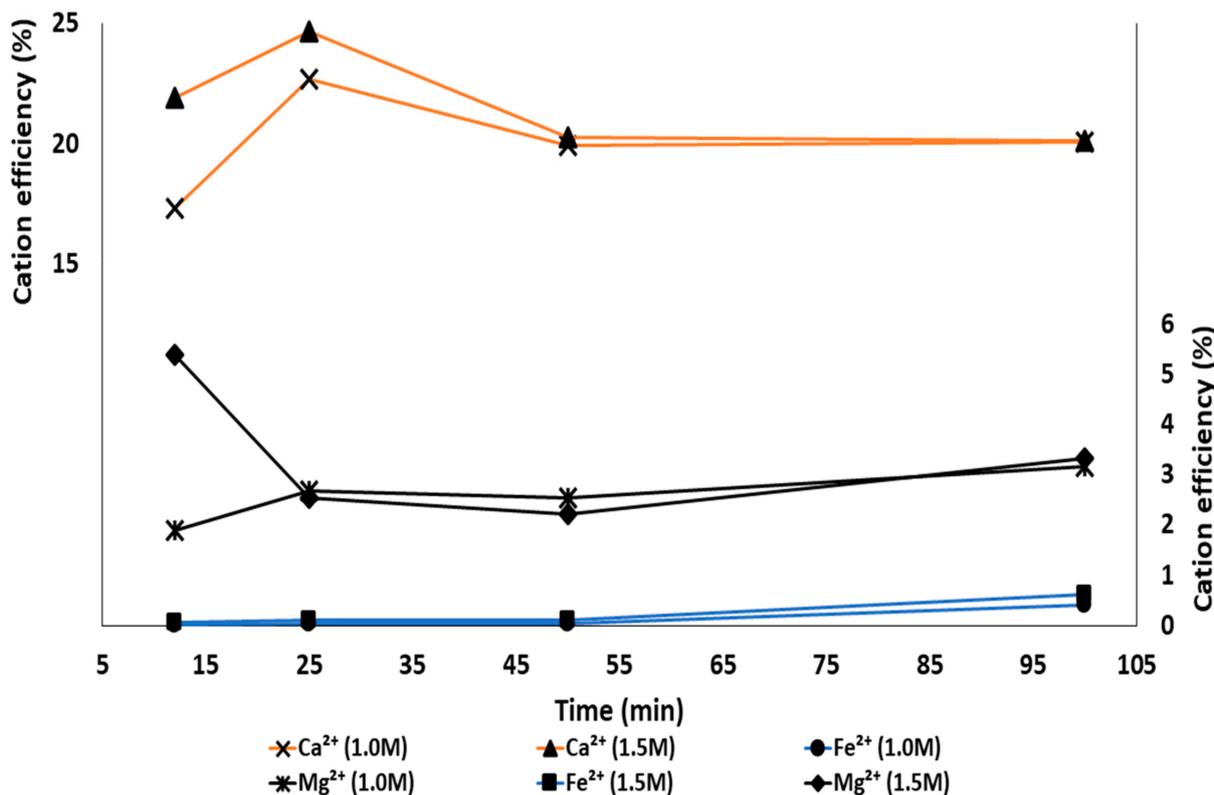


Figure 6. Elution efficiency of cation as a function of reaction time using different concentrations of acetic acid.

3.3. pH Variation

The pH variation was reported for oxalic acid since it had the highest elution efficiency for Fe^{2+} and Mg^{2+} . pH of the oxalic acid solution significantly affects the Fe^{2+} elution process [63]. In this study, it was observed that there was a slight fluctuation of pH with changes in time (up to 100 min) and at various concentrations (up to 1.5 M), while only

the 0.25 M concentration solution had a pH of >1, whereas other solutions had a pH of <1 throughout the study.

It appears that the variations in the concentration of the acid have little effect on the solutions pH due to the stability of the neutral species of $\text{H}_2\text{C}_2\text{O}_4$ at a pH of <1.5 [64]. This is further supported by the fact that oxalic acid predominates in its undissociated form ($\text{H}_2\text{C}_2\text{O}_4$) at lower pH values. It is also a stronger acid than the dissociated form (HC_2O_4^-), i.e., the undissociated form of oxalic acid can react with Fe oxide more effectively to form Fe^{2+} oxalate than the dissociated form. Therefore, Fe^{2+} elution is more effective at lower pH levels, as reported by Lee [65]. Moreover, the observed continuous decline in pH with time indicates that the consumption of protons prevailed in the experiment (Figure 7).

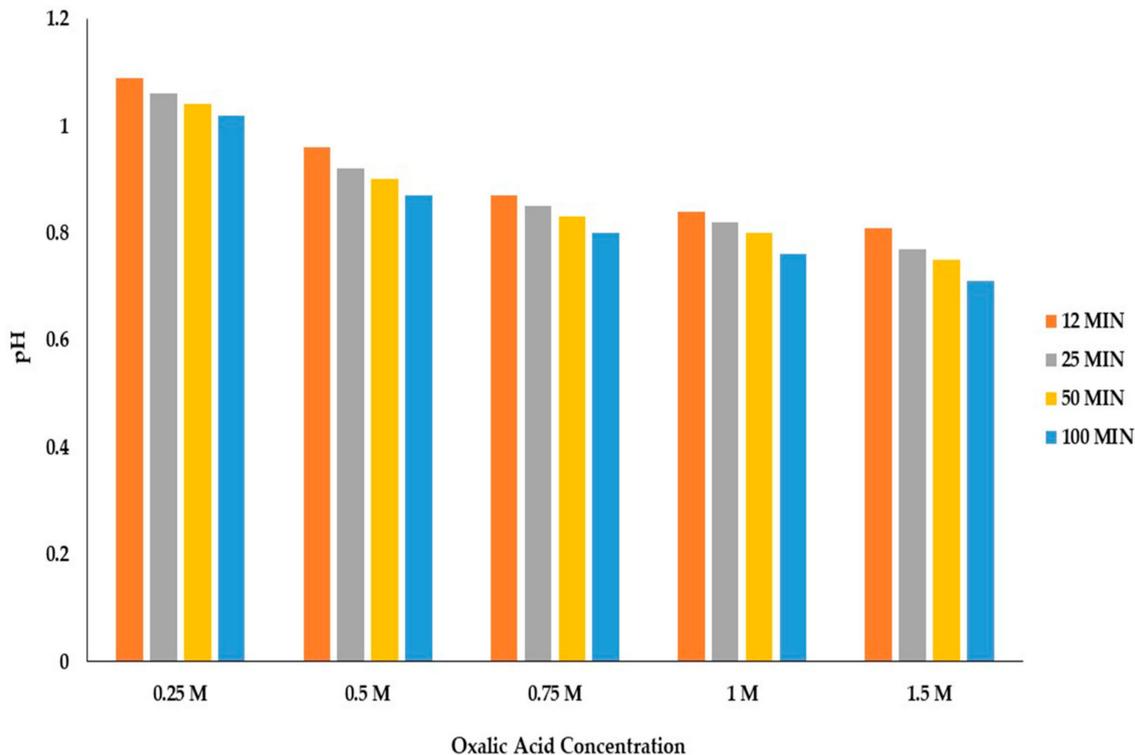


Figure 7. pH variation of oxalic acid solutions with the function of time.

3.4. Summary of Elution Results

Table 2 summarizes the elution results with the highest elution efficiency of Fe^{2+} , Ca^{2+} , and Mg^{2+} using four different acids at different solution concentrations and contact times. Oxalic acid exhibited the maximum elution efficiency for Fe^{2+} and Mg^{2+} with 30.4% and 54%, respectively, while HCl provided the highest Ca^{2+} elution efficiency (98%). A greater elution efficiency of Ca^{2+} ion compared to Fe^{2+} and Mg^{2+} ions was likely due to the high binding ability of Ca^{2+} with anion, when using a chloride-containing extractant, i.e., the observed higher Ca^{2+} leaching efficiency. This suggests that HCl is the most favorable extracting agent for Ca^{2+} and generated calcium chloride [66]. Comparing between acid solutions, the oxalic acid showed a better efficiency (due to its reducing power and high complexing capability) for the Fe^{2+} and Mg^{2+} elution which was achieved at 100 min reaction time even though slow elution reactivity of hematite have been reported in other studies [48,67]. Whereas the Ca^{2+} elution with HCl was achieved at a reaction time of 50 min. Therefore, it can be concluded that under ambient conditions the oxalic acid is best suited to Fe^{2+} and Mg^{2+} elution while HCl is best for Ca^{2+} to be used in the preparatory step for carbonation of iron ore mining waste.

Table 2. Summary of elution results with highest elution efficiency using 4 acids for Fe²⁺, Mg²⁺, and Ca²⁺ ions.

| Parameter/Acid | Oxalic | HCl | Formic | Acetic |
|-------------------------|---------|--------|--------|---------|
| Fe²⁺: | | | | |
| Elution efficiency | 30.4% | 2.7% | 0.2% | 0.62% |
| Reaction time | 100 min | 50 min | 25 min | 100 min |
| Concentration | 1.0 M | 1.5 M | 1.5 M | 1.5 M |
| Mg²⁺: | | | | |
| Elution efficiency | 54% | 9% | 1.4% | 5.3% |
| Reaction time | 100 min | 50 min | 25 min | 12 min |
| Concentration | 0.75 M | 1.5 M | 1.5 M | 1.5 M |
| Ca²⁺: | | | | |
| Elution efficiency | 20% | 98% | 30% | 24.6% |
| Reaction time | 25 min | 50 min | 25 min | 25 min |
| Concentration | 1.0 M | 1.5 M | 1.5 M | 1.5 M |

In addition, the ANOVA analysis supported the Fe²⁺, Mg²⁺, and Ca²⁺ elution efficiency at different concentrations and times at a confidence level of 95% (Table 3). The statistical analysis showed a non-significant difference in the Fe²⁺ and Mg²⁺ elution using oxalic acid of all solution concentrations and a significant difference in Fe²⁺ and Mg²⁺ leaching for all reaction times. Similarly, the Ca²⁺ elution using HCl also showed non-significant differences at different concentrations and significant differences between reaction times. This suggests that the reaction time significantly influenced the Fe²⁺, Mg²⁺, and Ca²⁺ elution, whereas the different concentrations (varied between 0.25 M and 1.5 M) of oxalic acid and HCl does not significantly influence the Fe²⁺, Mg²⁺, and Ca²⁺ elution. Thus, it is suggested that the elution efficiency of Fe²⁺ and Mg²⁺ might be increased with increasing time of experiment.

Table 3. ANOVA results for elution of Fe²⁺, Mg²⁺ (oxalic acid), and Ca²⁺ (HCl) as influenced by solution concentration and reaction time.

| Oxalic Acid | <i>p</i> -Value | Status |
|--|-----------------|-----------------|
| Fe leaching of all solution concentrations | 0.51 | Non-Significant |
| Fe leaching of all reaction time | 0.002 | Significant |
| Mg leaching of all solution concentrations | 0.85 | Non-Significant |
| Mg leaching of all reaction time | 0.001 | Significant |
| HCl | <i>p</i> -Value | Status |
| Ca leaching of all solution concentrations | 0.64 | Non-Significant |
| Ca leaching of all reaction time | 0.001 | Significant |

3.5. Potential CO₂ Sequestration

The CO₂ sequestration potential of the iron ore mining waste was calculated through the Fe²⁺, Mg²⁺, and Ca²⁺ elution from the waste sample (Table 4), where the Fe²⁺, Mg²⁺ and Ca²⁺ content in a waste sample reacts with CO₂ and converts to FeCO₃ (siderite), MgCO₃ (magnesite), and CaCO₃ (calcite), respectively, as shown in Equation (7). The experimental CO₂ sequestration potential of Fe²⁺ and Mg²⁺ was calculated based on Reynes et al. [41] studies, where they used iron silicate mining waste as feedstock for the mineral carbonation and reported up to 57% of carbonation efficiency (0.7 Fe/0.3 MgCO₃). Their leaching efficiency was 38% and 51% for Fe²⁺ and Mg²⁺, respectively, which was nearly similar in this study that recorded 30.4% and 54% of Fe²⁺ and Mg²⁺ elution efficiency, respectively. The experimental CO₂ sequestration potential of Ca²⁺ was calculated based on Kim and Kim [42] studies, where they reported up to 56.5% carbonation efficiency using HCl as an extraction agent. Therefore, in this study, the resulting theoretical and experimental CO₂ sequestration potential amount of Fe²⁺ and Mg²⁺ using 1.0 M oxalic acid solution at

100 min were estimated to be 110 mg CO₂/g (theoretical) compared to 44.1 mg CO₂/g (experimental), and 6.12 mg CO₂/g (theoretical) compared to 1.05 mg CO₂/g (experimental) iron ore mining waste, respectively. On the other hand, for the CO₂ sequestration of Ca²⁺ at 50 min with 1.5 M HCl elution solution, the theoretical and experimental potential amount were 15.46 mg CO₂/g and 8.73 mg CO₂/g iron ore mining residue, respectively. Thus, it can be concluded based on the elution results in this study, that all the three elements from iron ore mining waste can sequester up to 131.58 g CO₂/kg residue sample (Table 4). Moreover, while comparing the sequestration potential with other studies, e.g., Molahid et al. [44] that reported up to 83.80 g CO₂/kg waste using a direct mineral carbonation technique, it can be observed that by using the indirect mineral carbonation, a higher carbonation potential resulted in this study. Thus, it has been proved that using an indirect mineral carbonation where the divalent cations were first eluted and then reacted with CO₂, can increase the carbonation efficiency.

Table 4. Estimation of CO₂ sequestration potential of iron ore mining waste.

| | Fe * | | Mg * | | Ca * | |
|-------------------------------|---------------------------|----------------------------|----------------------------|----------------------------|-----------------------------|----------------------------|
| | Theoretical | Experimental | Theoretical | Experimental | Theoretical | Experimental |
| CO ₂ sequestration | 110 mg CO ₂ /g | 44.1 mg CO ₂ /g | 6.12 mg CO ₂ /g | 1.05 mg CO ₂ /g | 15.46 mg CO ₂ /g | 8.73 mg CO ₂ /g |

* Elution efficiency in this study: Fe²⁺ (30.4%); Mg²⁺ (54%); Ca²⁺ (98%).

3.6. Experimental CO₂ Sequestration

After the elution step, the subsequent step of CO₂ sequestration was using the iron ore mining waste in a pH-dependent process since the carbonation occurs at a higher pH. The results of the direct experimental settings (direct carbonation of elute by adjusting pH) showed no siderite formation in the solid residue after carbonation (Figure 8A). The XRD phase analysis suggested the crystals precipitate major portion as oxammite (NH₄)₂(C₂O₄)·H₂O (accounted for 75%), which was the product of a reaction between oxalates and ammonium hydroxides [68]. During this step, it was found that there appears to be oxidation of Fe²⁺ into Fe³⁺ at a higher pH which was not an appropriate condition to undergo carbonation. Thus, the results obtained from the direct carbonation settings indicated that the use of a chelating agent might prevent the oxidation of Fe²⁺ and maintains its stability.

Therefore, 1,10 phenanthroline (Phen) was used as a chelating agent to prevent the Fe²⁺ oxidation. Phen is a complexing agent with bivalent Fe (FePhen₃²⁺) that usually appears as a dark reddish or orangish color and blue color with trivalent Fe (FePhen₃³⁺) or in the oxidized state [69,70]. The bivalent Fe complex (FePhen₃²⁺) was confirmed before carbonation as it appeared in reddish color after mixing with the complexing agent (Figure 9A). The results of the carbonation with complexing agent showed a production of siderite (FeCO₃), magnesite (MgCO₃), amarantite (Fe³⁺₂(SO₄)O·7H₂O) along with phenanthroline hydrates (C₁₂H₈N₂·H₂O) with a total dry weight of 1.9 g (Figures 8B and 9B). The XRD phase distribution analysis suggested the mixture of crystals was formed with phenanthroline hydrates (accounted for 71.5%), siderite, magnesite (accounted for 21.7%, 0.77FeCO₃/0.23MgCO₃), amarantite (accounted for 5.2%), followed by magnesite (accounted for 1.6%). This suggests that once the phen started to precipitate, it opened the path to oxidize Fe ultimately leading to the occurrence of amarantite, as the phen complex with Fe remains most stable at a pH range of up to 9 [71]. Another possible scenario of the average performance of phen in this study was affected by its ability to complex with several metals such as zinc, nickel, copper, and chromium. These metals form quite stable complexes with phen, preventing Fe²⁺ complexation with the reagent [72]. Based on dry carbonation weight and % distribution phases of siderite and magnesite, it can be concluded that the iron ore mining waste can be used as feedstock for carbon capture and storage via indirect aqueous mineral carbonation. However, a low uptake efficiency of CO₂ using phen at pH 11 as compared to other studies

using other complexing agents was observed. Therefore, conducting a fully detailed study at different pH conditions is recommended.

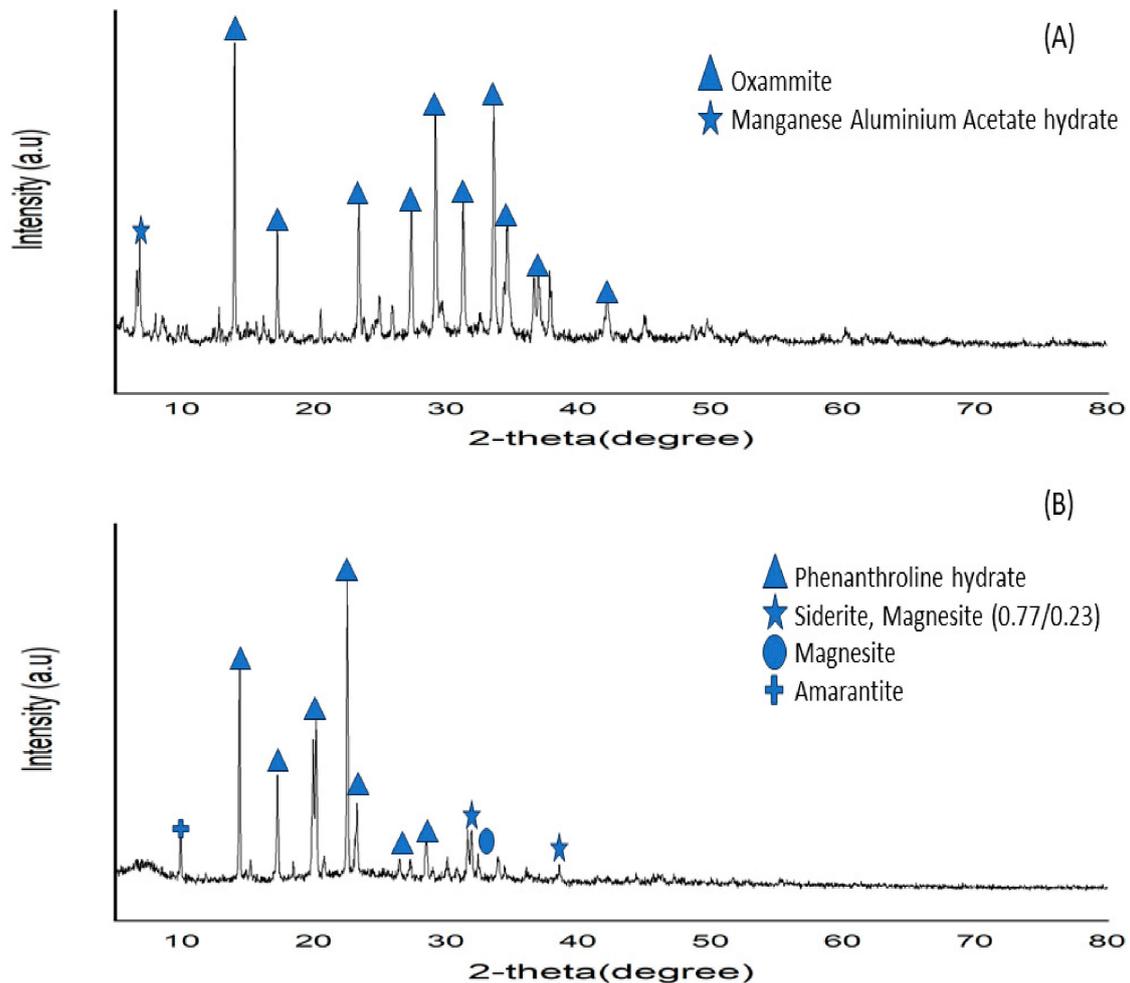


Figure 8. XRD of the carbonated products after carbonation at two different settings (A) without use of chelating agent, (B) with use of chelating agent.

Furthermore, the projection of CO₂ sequestration using iron ore mining waste had been carried out based on the current rate of iron ore mining waste production in Malaysia. According to a statistical survey, the annual production of iron ore mining waste reported up to 0.63 Mt of waste [73]. On the basis of the sequestration potential results obtained in this study, it can be concluded that it can sequester up to 82895.4 t CO₂/0.63 Mt (as per yearly waste residue) and 131580 t CO₂/Mt (as per 1 Mt waste residue), using iron ore mining waste as feedstock for CO₂ sequestration. Therefore, the results from this study suggest that iron ore mining waste is a potential feedstock for long-term carbon capture and sequestration via an indirect aqueous mineral carbonation as the waste material is largely produced in the country.

On the other hand, findings suggest the potential applications for utilizing the elution solution and remaining residues after elution. Since it shows a good amount of valuable minerals (Fe, Si, Al Ca, Mg, K) present in the iron ore waste samples, there is a potential to use it as a system that can be adopted for dual purposes. For instance, the cation-rich eluted solutions can be utilized for carbon capture and storage via mineral carbonation and due to their chemical composition the remaining residue can be utilized for the manufacturing of bricks, tiles, or clay products [74]. Vilela et al. [75] successfully developed a soil-cement brick with a 40% replacement of raw material with iron ore mining waste. According to Cao et al. [76] iron tailings can also be utilized as aggregates in asphalt mixture, and found

that asphalt mixed with coarse tailings performs better than asphalt mixed with tailings sand. Hence, this idea proposes a closed-loop economy with huge environmental and economic benefits.



Figure 9. (A) The reddish solution of complexing agent with Fe^{2+} ; (B) Carbonated product after carbonation using complexing agent.

4. Conclusions

The elution behavior of divalent cations of Fe^{2+} , Mg^{2+} , and Ca^{2+} from iron ore mining waste as the preliminary stage for an indirect mineral carbonation and carbon sequestration was studied in this paper. The elution approach using extraction agent (acid) at ambient temperature in a relatively shorter time was investigated. In this study, different concentrations of solutions were used with different acids (oxalic, HCl, acetic, and formic acid) at different reaction times with the intention to determine the effects on elution behavior of the divalent cations. The physiochemical analysis confirmed the suitable particle size ($<10\ \mu\text{m}$) for the elution and the presence of divalent cations in the samples with the proportion of 45.95%, 1.45%, and 0.63% of Fe, Ca and Mg, respectively. The maximum elution efficiency for Fe^{2+} (30.4%) and Mg^{2+} (54%) were obtained using oxalic acid at 100 min using 1.0 M and 0.75 M solution, respectively, whereas the highest elution efficiency for Ca^{2+} (98%) was obtained using HCl at 50 min using 1.5 M solution. It was discovered that oxalic acid solution is better suited if targeted elements are Fe^{2+} and Mg^{2+} , and HCl solution is better if analyte of interest is Ca^{2+} from iron ore mining waste. Findings also suggested that reaction time played an important role in affecting the elution efficiency whereby increasing the duration of experiment might increase the elution efficiency. In order to improve the elution efficiency, an extensive study should be carried out under controlled or swing pH as it is an important variable that can influence the elution behavior. In terms of CO_2 sequestration potential, the theoretical sequestration of the iron mining waste was calculated to be 131.58 g CO_2/kg residue. Furthermore, it was confirmed from the carbon sequestration with a complexing agent, i.e., 1,10 phenanthroline (Phen) that production of siderite and magnesite was resulted along with phenanthroline hydrates. Based on the amount of iron ore mining waste generated in Malaysia it can potentially sequester up to

82895.4 t CO₂/0.63 Mt (as per yearly waste residue). Therefore, it can be concluded that the iron ore mining waste has the potential to be used as feedstock for long-term carbon capture and storage via an indirect aqueous mineral carbonation due to its large yearly production and availability of the reactive minerals to sequester CO₂ permanently.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su16020836/s1>, Figure S1: Elution efficiency as a function of reaction time using different concentrations of oxalic acid (A) Fe; (B) Mg; (C) Ca elution efficiency; Figure S2: Elution efficiency as a function of reaction time using different concentrations of HCl (A) Fe; (B) Mg; (C) Ca elution efficiency; Figure S3: Elution efficiency as a function of reaction time using different concentration of formic acid (A) Fe; (B) Mg; (C) Ca elution efficiency; Figure S4: Elution efficiency as a function of reaction time using different concentrations of acetic acid (A) Fe; (B) Mg; (C) Ca elution efficiency; Figure S5: Statistical Analysis ANOVA data table.

Author Contributions: M.H.S. performed the experiments, data analysis and wrote the paper under the supervision of F.M.K.; F.M.K. verified the analysis and edited the manuscript. F.M.-Y. and N.N.N.D. co-supervised the work and reviewed the findings. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Higher Education Malaysia, grant number KPM FRGS/1/2023/TK08/UPM/02/9 Fundamental Research Grant Scheme (FRGS 5540604) and Universiti Putra Malaysia, grant number IPS 9709500.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available on request from the corresponding author.

Acknowledgments: The authors sincerely thank the laboratory staffs of the Centre for Research and Instrumentation (CRIM), Universiti Kebangsaan Malaysia, Bangi, Malaysia and Material Characterization Laboratory, Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, Serdang, Malaysia for providing technical assistance for laboratory analysis.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. El-Assaly, A.; Ellis, R. Evaluation of recycling waste materials and by-products in highway construction. *Int. J. Sustain. Dev. World Ecol.* **2001**, *8*, 299–308. [[CrossRef](#)]
2. Villa Gomez, D.; Sáez Salgado, E.; Mejías, O.; Pat-Espadas, A.M.; Pinedo Torres, L.A.; Jackson, L.; Parbhakar-Fox, A. Data Integration of Critical Elements from Mine Waste in Mexico, Chile and Australia. *Minerals* **2022**, *12*, 122. [[CrossRef](#)]
3. Meseldzija, S.; Petrovic, J.; Onjia, A.; Volkov-Husovic, T.; Nestic, A.; Vukelic, N. Utilization of agro-industrial waste for removal of copper ions from aqueous solutions and mining-wastewater. *J. Ind. Eng. Chem.* **2019**, *75*, 246–252. [[CrossRef](#)]
4. Azam, M.; Wabaidur, S.M.; Khan, M.R.; Al-Resayes, S.I.; Islam, M.S. Heavy metal ions removal from aqueous solutions by treated ajwa date pits: Kinetic, isotherm, and thermodynamic approach. *Polymers* **2022**, *14*, 914. [[PubMed](#)]
5. Syed Hasan, S.N.M.; Mohd Kusin, F.; Nik Daud, N.N.; Saadon, M.A.; Mohamat-Yusuff, F.; Ash'aari, Z.H. Characterization of gold mining waste for carbon sequestration and utilization as supplementary cementitious material. *Processes* **2021**, *9*, 1384. [[CrossRef](#)]
6. Alqadami, A.A.; Wabaidur, S.M.; Jeon, B.-H.; Khan, M.A. Co-hydrothermal valorization of food waste: Process optimization, characterization, and water decolorization application. *Biomass Convers. Biorefin.* **2023**, 1–12. [[CrossRef](#)]
7. Khan, M.A.; Wabaidur, S.M.; Siddiqui, M.R.; Alqadami, A.A.; Khan, A.H. Silico-manganese fumes waste encapsulated cryogenic alginate beads for aqueous environment de-colorization. *J. Clean. Prod.* **2020**, *244*, 118867.
8. Ma, J.; Wang, P. Effects of rising atmospheric CO₂ levels on physiological response of cyanobacteria and cyanobacterial bloom development: A review. *Sci. Total Environ.* **2021**, *754*, 141889. [[CrossRef](#)]
9. Moser, S.C. Communicating climate change: History, challenges, process and future directions. *Wiley Interdiscip. Rev. Clim. Chang.* **2010**, *1*, 31–53. [[CrossRef](#)]
10. Cebucean, D.; Cebucean, V.; Ionel, I. CO₂ capture and storage from fossil fuel power plants. *Energy Procedia* **2014**, *63*, 18–26. [[CrossRef](#)]
11. Lin, S.; Kiga, T.; Wang, Y.; Nakayama, K. Energy analysis of CaCO₃ calcination with CO₂ capture. *Energy Procedia* **2011**, *4*, 356–361.
12. Markusson, N.; Kern, F.; Watson, J.; Arapostathis, S.; Chalmers, H.; Ghaleigh, N.; Heptonstall, P.; Pearson, P.; Rossati, D.; Russell, S. A socio-technical framework for assessing the viability of carbon capture and storage technology. *Technol. Forecast. Soc. Chang.* **2012**, *79*, 903–918. [[CrossRef](#)]

13. Toroz, D.; Song, F.; Chass, G.A.; Di Tommaso, D. New insights into the role of solution additive anions in Mg^{2+} dehydration: Implications for mineral carbonation. *CrystEngComm* **2021**, *23*, 4896–4900. [[CrossRef](#)]
14. Bobicki, E.R.; Liu, Q.; Xu, Z.; Zeng, H. Carbon capture and storage using alkaline industrial wastes. *Prog. Energy Combust. Sci.* **2012**, *38*, 302–320.
15. Mouedhen, I.; Kemache, N.; Pasquier, L.-C.; Cecchi, E.; Blais, J.-F.; Mercier, G. Effect of pCO_2 on direct flue gas mineral carbonation at pilot scale. *J. Environ. Manag.* **2017**, *198*, 1–8.
16. Pasquier, L.-C.; Mercier, G.; Blais, J.-F.; Cecchi, E.; Kentish, S. Parameters optimization for direct flue gas CO_2 capture and sequestration by aqueous mineral carbonation using activated serpentinite based mining residue. *Appl. Geochem.* **2014**, *50*, 66–73. [[CrossRef](#)]
17. Arce, G.L.; Neto, T.G.; Ávila, I.; Luna, C.M.; dos Santos, J.C.; Carvalho, J.A., Jr. Influence of physicochemical properties of Brazilian serpentinites on the leaching process for indirect CO_2 mineral carbonation. *Hydrometallurgy* **2017**, *169*, 142–151. [[CrossRef](#)]
18. Dananjayan, R.R.T.; Kandasamy, P.; Andimuthu, R. Direct mineral carbonation of coal fly ash for CO_2 sequestration. *J. Clean. Prod.* **2016**, *112*, 4173–4182.
19. He, L.; Yu, D.; Lv, W.; Wu, J.; Xu, M. A novel method for CO_2 sequestration via indirect carbonation of coal fly ash. *Ind. Eng. Chem. Res.* **2013**, *52*, 15138–15145. [[CrossRef](#)]
20. Kim, M.-J.; Jung, S. Calcium elution from cement kiln dust using chelating agents, and CO_2 storage and $CaCO_3$ production through carbonation. *Environ. Sci. Pollut. Res.* **2020**, *27*, 20490–20499.
21. Sanna, A.; Dri, M.; Hall, M.R.; Maroto-Valer, M. Waste materials for carbon capture and storage by mineralisation (CCSM)—A UK perspective. *Appl. Energy.* **2012**, *99*, 545–554. [[CrossRef](#)]
22. Dri, M.; Sanna, A.; Maroto-Valer, M.M. Dissolution of steel slag and recycled concrete aggregate in ammonium bisulphate for CO_2 mineral carbonation. *Fuel Process. Technol.* **2013**, *113*, 114–122. [[CrossRef](#)]
23. Huntzinger, D.N.; Gierke, J.S.; Kawatra, S.K.; Eisele, T.C.; Sutter, L.L. Carbon dioxide sequestration in cement kiln dust through mineral carbonation. *Environ. Sci. Technol.* **2009**, *43*, 1986–1992. [[CrossRef](#)]
24. Jo, H.; Park, S.-H.; Jang, Y.-N.; Chae, S.-C.; Lee, P.-K.; Jo, H.Y. Metal extraction and indirect mineral carbonation of waste cement material using ammonium salt solutions. *Chem. Eng. J.* **2014**, *254*, 313–323.
25. Kusin, F.M.; Hasan, S.N.M.S.; Hassim, M.A.; Molahid, V.L.M. Mineral carbonation of sedimentary mine waste for carbon sequestration and potential reutilization as cementitious material. *Environ. Sci. Pollut. Res.* **2020**, *27*, 12767–12780. [[CrossRef](#)] [[PubMed](#)]
26. Rahmani, O. CO_2 sequestration by indirect mineral carbonation of industrial waste red gypsum. *J. CO2 Util.* **2018**, *27*, 374–380. [[CrossRef](#)]
27. Pullin, H.; Bray, A.W.; Burke, I.T.; Muir, D.D.; Sapsford, D.J.; Mayes, W.M.; Renforth, P. Atmospheric carbon capture performance of legacy iron and steel waste. *Environ. Sci. Technol.* **2019**, *53*, 9502–9511. [[CrossRef](#)]
28. Ramli, N.A.A.; Kusin, F.M.; Molahid, V.L.M. Influencing Factors of the Mineral Carbonation Process of Iron Ore Mining Waste in Sequestering Atmospheric Carbon Dioxide. *Sustainability* **2021**, *13*, 1866. [[CrossRef](#)]
29. Meyer, N.; Vögeli, J.; Becker, M.; Broadhurst, J.; Reid, D.; Franzidis, J.-P. Mineral carbonation of PGM mine tailings for CO_2 storage in South Africa: A case study. *Miner. Eng.* **2014**, *59*, 45–51. [[CrossRef](#)]
30. Owais, M.; Järvinen, M.; Taskinen, P.; Said, A. Experimental study on the extraction of calcium, magnesium, vanadium and silicon from steelmaking slags for improved mineral carbonation of CO_2 . *J. CO2 Util.* **2019**, *31*, 1–7. [[CrossRef](#)]
31. Vieira, K.R.; Arce, G.L.; Luna, C.M.; Facio, V.O.; Carvalho, J.A., Jr.; Neto, T.G.S.; Ávila, I. Understanding the acid dissolution of Serpentinites (Tailings and waste rock) for use in indirect mineral carbonation. *S. Afr. J. Chem. Eng.* **2022**, *40*, 154–164.
32. Tong, Z.; Ma, G.; Zhou, D.; Yang, G.; Peng, C. The indirect mineral carbonation of electric arc furnace slag under microwave irradiation. *Sci. Rep.* **2019**, *9*, 7676. [[CrossRef](#)] [[PubMed](#)]
33. Spínola, A.C.; Pinheiro, C.T.; Ferreira, A.G.; Gando-Ferreira, L.M. Mineral carbonation of a pulp and paper industry waste for CO_2 sequestration. *Process Saf. Environ. Prot.* **2021**, *148*, 968–979. [[CrossRef](#)]
34. Arce, G.L.; Neto, T.G.S.; Ávila, I.; Luna, C.M.; Carvalho, J.A., Jr. Leaching optimization of mining wastes with lizardite and brucite contents for use in indirect mineral carbonation through the pH swing method. *J. Clean. Prod.* **2017**, *141*, 1324–1336. [[CrossRef](#)]
35. Galina, N.R.; Arce, G.L.; Maroto-Valer, M.; Ávila, I. Experimental Study on Mineral Dissolution and Carbonation Efficiency Applied to pH-Swing Mineral Carbonation for Improved CO_2 Sequestration. *Energies* **2023**, *16*, 2449. [[CrossRef](#)]
36. Teir, S.; Revitzer, H.; Eloneva, S.; Fogelholm, C.-J.; Zevenhoven, R. Dissolution of natural serpentinite in mineral and organic acids. *Int. J. Miner. Process.* **2007**, *83*, 36–46. [[CrossRef](#)]
37. Razote, B.J.; Dela Cerna, K.M.; Patricio, M.J.; Eusebio, R.C.; Alorro, R.; Beltran, A.; Orbecido, A. Leaching characteristics of an iron-rich siltation pond waste and its viability in indirect carbon sequestration. *Int. J. Min. Reclam. Environ.* **2021**, *35*, 435–450. [[CrossRef](#)]
38. Filippov, L.O.; Filippova, I.V.; Barres, O.; Lyubimova, T.P.; Fattalov, O.O. Intensification of the flotation separation of potash ore using ultrasound treatment. *Miner. Eng.* **2021**, *171*, 107092.
39. Cengiz, S.; Karaca, A.C.; Çakır, İ.; Üner, H.B.; Sevindik, A. SEM-EDS analysis and discrimination of forensic soil. *Forensic Sci. Int.* **2004**, *141*, 33–37. [[CrossRef](#)]
40. Kim, D.; Kim, M.-J. Calcium extraction from paper sludge ash using various solvents to store carbon dioxide. *KSCE J. Civ. Eng.* **2018**, *22*, 4799–4805.

41. Reynes, J.F.; Mercier, G.; Blais, J.-F.; Pasquier, L.-C. Feasibility of a Mineral Carbonation Technique Using Iron-Silicate Mining Waste by Direct Flue Gas CO₂ Capture and Cation Complexation Using 2,2'-Bipyridine. *Minerals* **2021**, *11*, 343.
42. Kim, M.-J.; Kim, D. Maximization of CO₂ storage for various solvent types in indirect carbonation using paper sludge ash. *Environ. Sci. Pollut. Res.* **2018**, *25*, 30101–30109.
43. Sammes, P.G.; Yahioglu, G. 1,10-Phenanthroline: A versatile ligand. *Chem. Soc. Rev.* **1994**, *23*, 327–334. [[CrossRef](#)]
44. Molahid, V.L.M.; Mohd Kusin, F.; Syed Hasan, S.N.M.; Ramli, N.A.A.; Abdullah, A.M. CO₂ Sequestration through Mineral Carbonation: Effect of Different Parameters on Carbonation of Fe-Rich Mine Waste Materials. *Processes* **2022**, *10*, 432. [[CrossRef](#)]
45. Mendoza, E.Y.M.; Santos, A.S.; López, E.V.; Drozd, V.; Durygin, A.; Chen, J.; Saxena, S.K. Iron oxides as efficient sorbents for CO₂ capture. *J. Mater. Res. Technol.* **2019**, *8*, 2944–2956.
46. Chou, C.-Y.; Loiland, J.A.; Lobo, R.F. Reverse water-gas shift iron catalyst derived from magnetite. *Catalysts* **2019**, *9*, 773. [[CrossRef](#)]
47. Taxiarchou, M.; Paniais, D.; Douni, I.; Paspaliaris, I.; Kontopoulos, A. Removal of iron from silica sand by leaching with oxalic acid. *Hydrometallurgy* **1997**, *46*, 215–227. [[CrossRef](#)]
48. Lee, S.O.; Tran, T.; Park, Y.Y.; Kim, S.J.; Kim, M.J. Study on the kinetics of iron oxide leaching by oxalic acid. *Int. J. Miner. Process.* **2006**, *80*, 144–152. [[CrossRef](#)]
49. Sun, Y.; Guan, F.; Yang, W.; Wang, F. Removal of chromium from a contaminated soil using oxalic acid, citric acid, and hydrochloric acid: Dynamics, mechanisms, and concomitant removal of non-targeted metals. *Int. J. Environ. Res. Public Health* **2019**, *16*, 2771. [[CrossRef](#)]
50. Du, C.-M.; Yu, Y.-H.; Jiang, L.-D.; Yu, J.-K. Efficient extraction of phosphate from dephosphorization slag by hydrochloric acid leaching. *J. Clean. Prod.* **2022**, *332*, 130087.
51. Matus, C.; Stopic, S.; Etzold, S.; Kremer, D.; Wotruba, H.; Dertmann, C.; Telle, R.; Friedrich, B.; Knops, P. Mechanism of nickel, magnesium, and iron recovery from olivine bearing ore during leaching with hydrochloric acid including a carbonation pre-treatment. *Metals* **2020**, *10*, 811. [[CrossRef](#)]
52. Kim, M.-J.; Pak, S.Y.; Kim, D.; Jung, S. Optimum conditions for extracting Ca from CKD to store CO₂ through indirect mineral carbonation. *KSCE J. Civ. Eng.* **2017**, *21*, 629–635.
53. Cornell, R.M.; Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*; John Wiley & Sons: Hoboken, NJ, USA, 2006.
54. Pepper, R.A.; Couperthwaite, S.J.; Millar, G.J. Comprehensive examination of acid leaching behaviour of mineral phases from red mud: Recovery of Fe, Al, Ti, and Si. *Miner. Eng.* **2016**, *99*, 8–18. [[CrossRef](#)]
55. Halli, P.; Hamuyuni, J.; Revitzer, H.; Lundström, M. Selection of leaching media for metal dissolution from electric arc furnace dust. *J. Clean. Prod.* **2017**, *164*, 265–276. [[CrossRef](#)]
56. Ibiapina, V.F.; Florentino, U.d.S.; Afonso, J.C.; Gante, V.; Vianna, C.A.; Mantovano, J.L. Processing of spent Zinc-MnO₂ dry cells in various acidic media. *Quim. Nova* **2018**, *41*, 176–183. [[CrossRef](#)]
57. Gismonti, P.R.; Paulino, J.F.; Afonso, J. Recovery of metals from electroactive components of spent ni-mh batteries after leaching with formic acid. *Detritus* **2021**, *14*, 68.
58. Jang, K.; Choi, W.Y.; Lee, D.; Park, J.; Yoo, Y. Purification of landfill gas by extracted calcium ions from municipal solid waste incineration fly ash. *Sci. Total Environ.* **2022**, *807*, 150729. [[CrossRef](#)] [[PubMed](#)]
59. Bao, W.; Li, H.; Zhang, Y. Selective leaching of steelmaking slag for indirect CO₂ mineral sequestration. *Ind. Eng. Chem. Res.* **2010**, *49*, 2055–2063. [[CrossRef](#)]
60. Elomaa, H.; Seisko, S.; Lehtola, J.; Lundström, M. A study on selective leaching of heavy metals vs. iron from fly ash. *J. Mater. Cycles Waste Manag.* **2019**, *21*, 1004–1013. [[CrossRef](#)]
61. Borra, C.R.; Pontikes, Y.; Binnemans, K.; Van Gerven, T. Leaching of rare earths from bauxite residue (red mud). *Miner. Eng.* **2015**, *76*, 20–27.
62. Zhao, Q.; Li, J.; You, K.; Liu, C. Recovery of calcium and magnesium bearing phases from iron- and steelmaking slag for CO₂ sequestration. *Process Saf. Environ. Prot.* **2020**, *135*, 81–90. [[CrossRef](#)]
63. Chen, H.; Grassian, V.H. Iron dissolution of dust source materials during simulated acidic processing: The effect of sulfuric, acetic, and oxalic acids. *Environ. Sci. Technol.* **2013**, *47*, 10312–10321. [[CrossRef](#)] [[PubMed](#)]
64. Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; NACE: Bethlehem, PA, USA, 1966.
65. Lee, S.O. *Dissolution of Iron Oxides by Oxalic Acid*; UNSW Sydney: Sydney, Australia, 2005.
66. Lee, Y.H.; Eom, H.; Lee, S.M.; Kim, S.S. Effects of pH and metal composition on selective extraction of calcium from steel slag for Ca(OH)₂ production. *RSC Adv.* **2021**, *11*, 8306–8313. [[PubMed](#)]
67. Salmimies, R.; Mannila, M.; Kallas, J.; Häkkinen, A. Acidic dissolution of hematite: Kinetic and thermodynamic investigations with oxalic acid. *Int. J. Miner. Process.* **2012**, *110*, 121–125. [[CrossRef](#)]
68. Basiri, N. *A Curious Insight into Removal and Recovery of Ammonia from Struvite Thermal Decomposition Unit Outlet by Acidic Adsorption*; University of British Columbia: Vancouver, BC, Canada, 2016.
69. Abbaspour, A.; Mehrgardi, M.A.; Noori, A.; Kamyabi, M.A.; Khalafi-Nezhad, A.; Rad, M.N.S. Speciation of iron (II), iron (III) and full-range pH monitoring using paptode: A simple colorimetric method as an appropriate alternative for optodes. *Sens. Actuators B Chem.* **2006**, *113*, 857–865.
70. Marczenko, Z.; Balcerzak, M. *Separation, Preconcentration and Spectrophotometry in Inorganic Analysis*; Elsevier: Amsterdam, The Netherlands, 2000.

71. Yang, L.; Yao, G. A modified spectrophotometric method for the determination of ferrous ion during the Fenton process. *Int. J. Environ. Anal. Chem.* **2022**, *102*, 3194–3206. [[CrossRef](#)]
72. Vydra, F.; Marková, V. Sorption of ferriin on silica and its analytical use. *Talanta* **1963**, *10*, 339–346.
73. Shettima, A.U.; Hussin, M.W.; Ahmad, Y.; Mirza, J. Evaluation of iron ore tailings as replacement for fine aggregate in concrete. *Constr. Build. Mater* **2016**, *120*, 72–79. [[CrossRef](#)]
74. Das, M.R.; Satapathy, S.; Pothal, L. A study on waste management in iron mining. *Mater. Today Proc.* **2023**. [[CrossRef](#)]
75. Vilela, A.P.; Eugênio, T.M.C.; de Oliveira, F.F.; Mendes, J.F.; Ribeiro, A.G.C.; Brandão, L.E.V.d.S.; Mendes, R.F. Technological properties of soil-cement bricks produced with iron ore mining waste. *Constr. Build. Mater.* **2020**, *262*, 120883. [[CrossRef](#)]
76. Cao, L.; Zhou, J.; Zhou, T.; Dong, Z.; Tian, Z. Utilization of iron tailings as aggregates in paving asphalt mixture: A sustainable and eco-friendly solution for mining waste. *J. Clean. Prod.* **2022**, *375*, 134126. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.