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# Determination of the Carbon Dioxide Sequestration Potential of a Nickel Mine Mixed Dump through Leaching Tests

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**Abstract:** Carbon dioxide sequestration via mineralization is one of the methods that has the capability to efficiently store carbon dioxide in a stable form. A mixed dump sample collected from a nickel laterite mine in Southern Philippines was tested for its carbon dioxide sequestration potential through HCl leaching tests, employing the Face-Centered Cube (FCC) experimental design for Response Surface Methodology (RSM). Mineralogical analysis performed through X-ray diffraction (XRD) analysis suggests the presence of three minerals, namely goethite, khademite and lizardite; additional X-ray fluorescence (XRF) and inductively-coupled plasma optical emission spectroscopy (ICP-OES) results, however, established goethite as the main component due to the dominance of iron in the sample. Morphological analyses performed through a scanning electron microscope (SEM) and the Brunauer–Emmett–Teller (BET) method suggest high accessible surface area despite considerable variability in sample composition. Leaching tests further confirmed the high reactivity of the mixed dump as high extraction rates were obtained for iron, with the maximum iron extraction efficiency of 95.37% reported at 100 °C, 2.5 M, and 2.5 h. The carbon dioxide sequestration potential of the mixed dump was reported as the amount of CO<sub>2</sub> that can be sequestered per amount of sample, which was calculated to be 327.2 mg CO<sub>2/g</sub> sample using the maximum iron extraction obtained experimentally.

**Keywords:** indirect carbon sequestration; nickel mine waste; leaching test; iron extraction efficiency; face-centered cube design; iron carbonation; carbon dioxide sequestration potential

# 1. Introduction

The increasing threat of global warming has scientists rushing for immediate and sustainable solutions to carbon emissions. According to the United Nations (UN) Environment Emissions Gap Report, the total carbon emissions in 2017 had reached 53.5 GtCO<sub>2</sub>e, a record high and 0.6 GtCO<sub>2</sub>e more than the 2016 emissions [1]. Atmospheric CO<sub>2</sub> levels have also reached the highest levels since the Pliocene, recorded at 413.5 ppm as of April 2019 [2]. To achieve the target of limiting global warming to 1.5 °C in accordance to the Paris Agreement, emissions therefore must be cut by 55% by 2030 to achieve the least cost pathway [1,3]. However, with the policies and measures in place, it is estimated that the Paris Agreement target will not be met, and global warming is projected to be at 3.1–3.5 °C above



pre-industrial levels by 2100 [4]. Given these stark indicators, measures in order to reduce carbon emissions must be performed.

Carbon capture and sequestration (CCS) techniques have been perceived as one of the main solutions to the increasing threat of anthropogenic emissions. CCS techniques, methods, and technologies mainly involve the use of a carbon sink, wherein carbon dioxide can be diverted from the atmosphere whilst being stored in a secure and reliable manner [5]. These CCS methods can be classified into three main categories according to their sinks—namely oceanic, terrestrial, and geologic [6]. Oceanic carbon sequestration involves either injecting  $CO_2$  deep into the ocean or promoting photosynthetic  $CO_2$  fixation by aquatic organisms to sequester  $CO_2$  [7], whereas soil and vegetation (such as forests) are considered the sinks for terrestrial carbon sequestration [6]. On the other hand, geologic carbon sequestration utilizes rock formations and deep land traps, seams, and aquifers to securely store carbon [6].

Most of these methods are highly efficient as carbon capture and sequestration can reach up to 100% efficiency for most processes; however, some of these technologies are energy-intensive and cost-ineffective, and thus, cannot be used for industrial application [5].

One particular method stands out among others in terms of its capability to balance the efficiency and energy considerations. CCS via mineralization (CCS-M) is a process in which carbon is stored in geological formations, particularly minerals, which act as the carbon sink. These materials are more stable and reasonably inert, and are thus viable options [8]. CCS-M can be divided primarily into two types—direct or in situ mineralization, and indirect or ex situ mineralization. In situ mineralization involves directly injecting carbon dioxide (CO<sub>2</sub>) deep beneath earth's crust in order to form carbonates with the ions present, storing CO<sub>2</sub> underground [8]. This process requires a relatively low amount of energy; however, as utilization of the products is perceived in the long run, this method is not popular as the process yields products of low purity [9]. CO<sub>2</sub> conversion is very slow as well, as it relies solely on natural weathering, and is thus the main drawback of this method [8]. On the other hand, ex situ mineralization has become a more popular method recently due to its promising potential for industrial use. In this method, carbonation is performed above the ground, meaning minerals are excavated first and are subjected to a series of steps [8]. Among these, the pH swing method has showed great potential in recent years, due to its high reaction rates in comparison to other ex situ methods, as well as its ability to form products with very high purity even for low-grade raw materials [8].

In this study, the applicability of locally available and unutilized mine waste, i.e., mixed dump from a nickel laterite ore mine site, for carbon sequestration is to be determined by varying the process parameters mentioned in leaching tests using the pH swing method. Nickel mine waste contains a substantial amount of iron, particularly in the form of nickel oxides, such as goethite [10]. Nickel ions are hosted in goethite mainly through adsorption or substitution in the structure; thus, its abundance [10]. The report by the Philippine Statistical Authority and the Department of Environment and Natural Resources Mines and Geosciences Bureau also mentioned that the ratio amount of ore processed to actual nickel extracted is estimated to be at 77:1, which implies the huge amount of wastes generated in nickel mine sites [11]. With the growing need for waste utilization and conversion to valuable resources, tailings and residues from nickel mine sites must therefore be processed in order to reduce the risk that it poses to the environment, as well as to convert these materials into something usable and valuable.

Aside from determining the significance of process parameters, the study also aimed to establish the mineralogical, elemental, and morphological properties of the mixed dump. The study also aimed to optimize the parameters for possible industrial application, and lastly, to establish the carbon sequestration potential of the mixed dump through calculation of the theoretical amount of CO<sub>2</sub> sequestered per amount of sample.

#### 2. Theoretical Framework

The pH swing method is a type of indirect carbon sequestration that is comprised of two steps—extraction and carbonation, both of which performed in an aqueous setup. A simplified diagram of the pH swing method is shown in Figure 1. The material primarily is subjected to an extracting medium, to obtain as much ions as possible for use in the carbonation step. Whilst containing undesired ions, pH is usually adjusted prior to carbonation, to precipitate the undesired ions out of the solution. Once only the desired ions remain,  $CO_2$  is injected at high pH (pH 8 to 12) to achieve maximum  $CO_2$  absorption [12–15]. Through this manner, high quality of products is formed, making it feasible for actual industrial application [9].



Figure 1. Block flow diagram of the mineral carbonation process employing the pH swing method.

Extensive studies have been performed for various raw materials using the pH swing method. Industrial wastes, particularly, have been studied in-depth to address the growing concern on the volume of wastes generated globally and for their possible utilization in other industries and processes. Other materials of low market value, such as low-grade ores, have also been explored for possible conversion to valuable and profitable products. Utilization of high-grade material, on the other hand, was primarily abandoned due to the fact that these materials entail additional cost which would make carbon sequestration even more costly, as well as possible increased competition with industries that utilize these materials, making CCS more undesirable.

For industrial wastes, some of the raw materials used were waste cement powder and blast furnace slag, which are abundant sources of calcium (Ca) [12]. For these materials, Ca is present in the form of calcium silicate (CaSiO<sub>3</sub>), and reacts with an acid, e.g., acetic acid (CH<sub>3</sub>COOH), in a two-step scheme (Equations (1) and (2)) to form stable calcite [16]:

$$CaSiO_3 + 2CH_3COOH \rightarrow Ca^{2+} + 2CH_3COO^- + H_2O + SiO_2$$
(1)

$$Ca^{2+} + 2CH_3COO^- + CO_2 + H_2O \rightarrow CaCO_3 \downarrow + 2CH_3COOH$$
(2)

Other potential raw materials derived from waste that have been identified for calcium carbonation are electric arc furnace (EAF) slag [17,18], basic oxygen furnace (BOF) slag [17,18], cement kiln dust [19], pulverized-fuel ash [19,20], oil shale ash [21,22], air pollution control residue [23], and paper sludge incineration ash [19] which have shown experimental CO<sub>2</sub> uptakes ranging from 1.7–25 wt.% [24].

For magnesium carbonation, various studies have utilized serpentine-rich materials, particularly chrysotile- and antigorite-bearing ores. These materials have shown a lot of potential by posting high extraction rates at high temperatures of 70–100 °C [25,26]. Serpentines, with a general chemical formula of Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, react with the leaching agent to form magnesite in the sequence of reactions below (Equations (3) to (5)) [14]:

$$Mg_3Si_2O_5(OH)_4 + 3H_2SO_4 \rightarrow 3Mg^{2+} + 3SO_4^{2-} + 2SiO_2 + 5H_2O$$
 (3)

$$Mg^{2+}+SO_4^{2-}+2NaOH \rightarrow Mg(OH)_2+Na_2SO_4$$
 (4)

$$Mg(OH)_2 + CO_2 + H_2O \rightarrow MgCO_3 + H_2O$$
(5)

Olivines, another group of magnesium silicate minerals, have also manifested the same results, particularly for materials bearing forsterite [27]. Forsterite forms stable magnesite in the following series of steps (Equations (6) to (8)) [28]:

$$Mg_2SiO_4 + 4H^+ \rightarrow Si(OH)_4 + 2Mg^{2+}$$
(6)

$$Mg^{2+} + 2NaOH \rightarrow Mg(OH)_2 + 2Na^+$$
(7)

$$Mg(OH)_2 + CO_2 + H_2O \rightarrow MgCO_3 + H_2O$$
 (8)

Nonetheless, in the case of iron-rich minerals, limited studies have been performed for their viability in carbon sequestration via indirect mineral carbonation, particularly through the pH swing method. One study has utilized fayalite, a type of olivine with chemical formula  $Fe_2SiO_4$ , in carbon sequestration by subjecting the sample in a water-supercritical  $CO_2$  setup (Equations (9) to (11)) [29]:

$$Fe_2SiO_4 + 4H^+ \rightarrow Si(OH)_4 + 2Fe^{2+}$$
(9)

$$Fe^{2+} + 2NaOH \rightarrow Fe(OH)_2 + 2Na^+$$
 (10)

$$Fe(OH)_2 + CO_2 + H_2O \rightarrow FeCO_3 + H_2O$$
 (11)

Although siderite (FeCO<sub>3</sub>) formation was reported, low concentrations were observed even for an extended period of time (80 days), mainly due to the limited dissolution of the iron silicates in the aqueous medium [29]. Basalts, which are formed from the solidification of lava from volcanic eruptions, have also been sought as possible site for CO<sub>2</sub> injection as these deposits contain huge quantities of Ca, Mg, and Fe; however, the challenge of injecting supercritical CO<sub>2</sub> underground, and its accompanying reactions remain to be clearly defined [30]. Subsequently, studies have also been devoted to the utilization of iron for carbon sequestration in saline aquifers and sea beds due to its inherent abundance in the form of hematite and goethite [31–35]; nonetheless, these studies cited the slow rate of iron release to the solution as a possible hindrance to the carbonation process.

It is evident from the studies mentioned that the efficiency of carbon dioxide sequestration is highly dependent on the availability of ions capable of forming carbonates. A study on mine tailings obtained from a platinum group mineral (PGM) ore processing plant highlighted that, although carbonation rates of near completion (96–98%) for calcium and iron have been achieved, the transfer of ions in solution remained to be the determining step [13]. Process improvements have been performed in order to address this drawback; several leaching agents have been analyzed, both organic and inorganic acids, in order to increase the transfer of carbonation ions into the liquid matrix. Among these, hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) have been sought as possible leaching agents for Mg and Fe rich materials [25,36], whereas maximum extraction of Ca has been observed using acetic acid (CH<sub>3</sub>COOH) in the addition of 0.1 wt.% ethylenediamine tetra-acetic acid (EDTA) [12,18].

Aside from the choice of leaching agent, impurities in the minerals were also reported to play a main role in the carbon dioxide sequestration process. Silica formation, as observed in serpentines and olivines, hinders further release of ions in the aqueous solution due to the formation of a passivating layer that coats the surface of the material [28]. The presence of aluminum in the form of  $Al^{3+}$  also decreases the leachability of magnesium in the sample as the ion promotes layer-to-layer linkage by H-bonding, which hinders the release of the Mg<sup>+</sup> ions [37]. Similarly, the presence of Fe<sup>3+</sup> in magnesium rich samples has been observed to hinder the release of Mg<sup>+</sup> due to preferential leaching of iron in the solution [37].

Process parameters, such as reaction temperature, reaction time, and reagent concentration, have been reported to have significant effects in the effective transfer of carbonation ions, although

the magnitude of significance varies across a range of values. A three-fold increase in Mg extraction, from 28% to 75%, has been observed from a serpentinized lherzolite when the temperature was increased from 50 °C to 100 °C at a reaction time of 180 min, whereas the same study reported no increase in Mg extraction when the reaction temperature was further increased to 120 °C and 140 °C at the same timeframe [38]. A different study reported the effect of reaction time on the extraction of Mg and Fe in antigorites; for Mg, 55% of the initial content of the sample has been extracted at the first 30 min using  $1.4 \text{ M NH}_4\text{SO}_4$ , whereas a total of 70% extraction or only an additional 15% has been extracted after 3 h [39]. For Fe, the similar study has reported 40–45% Fe extraction after 30 min and further increase after an additional 2.5 h [39]. The study of Teir et al. (2007), on the other hand, has observed the extraction profile of natural serpentinite for HCl at different concentrations; an increase in the extraction efficiency of Mg from 16% to 24% has been observed when HCl concentration was increased from 1 M to 4 M at 20 °C and 1 h; for Fe, an increase from 9% to 16% has been observed [25]. The study of Sanna et al. focused on another reagent, NH<sub>4</sub>SO<sub>4</sub>, and observed a three-fold increase for Fe extraction, from 37.9% to 100.0% when the concentration was increased from 1 M to 3 M after 3 h [38]. The same study reported an increase in Mg extraction of about 15% from 66% to 82% at the same period [38]. Although the behavior of different combinations of process parameters has been reported in previous studies, the optimum set of parameters for different raw materials varies individually and therefore needs to be established.

## 3. Methodology

## 3.1. Sample Description and Preparation

The mixed dump sample used in this experiment was obtained from a nickel laterite ore mine in Agusan Del Norte, one of the provinces in Southern Philippines. Mixed dump is basically a type of mine waste referring to combined, accumulated, or collected mine wastes in solid form. As received, the sample had a brownish black color and had a composition of agglomerated fine particles (due to moisture) and small rock-like components ranging from 5–30 mm in diameter.

Prior to analysis and testing, the samples were dried in a Shellab 1600 Hafo Series convection oven at 105 °C for 24 h. The dried mixed dump samples were then grounded in an MRC Scientific RJM-102 ball mill for 4 h at 350 rpm and sieved in a W.S. Tyler RX-182 Ro-Tap Sieve Shaker for 30 min to obtain a particle size range of 75 to 150  $\mu$ m. Once the desired particle size range was obtained, the grounded and sieved samples were stored in an airtight container at room temperature to avoid contamination by moisture.

#### 3.2. Sample Characterization

The mineralogical characteristics of the sample were first established through X-Ray powder diffraction (XRD), using Multiflex Rigaku 150 (range [°2Th] =  $5^{\circ}-60^{\circ}$ , scan step time = 0.6000 s, step size [°2Th] = 0.02) available at Tokyo Institute of Technology. The oxide composition of the sample was determined via X-ray fluorescence microscopy through the Horiba Scientific XGT-7200 X-ray Analytical Microscope also available at Tokyo Institute of Technology, whereas the elemental composition was determined by fusing the sample with sodium peroxide, leaching it with HCl, and subjecting it to Agilent 5100 for Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES). This was performed by a third-party laboratory (Intertek Testing Services Philippines, Inc).

The morphological properties of the mixed dump were also analyzed in the Phenom XL Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX) at De La Salle University, with a magnification range of 2750×–10000×, a voltage of 15 kV, and gold sputtering. Brunauer–Emmett–Teller (BET) surface analysis was otherwise performed at the University of the Philippines–Los Baños using the Quantachrome Nova Station A to determine the pore volume, pore distribution and surface area of the sample.

#### 3.3. Reagent Solution Preparation

Hydrochloric acid (HCl) solutions with concentration of 1.0 M, 2.5 M, and 4.0 M were prepared using Duksan AR Grade Hydrochloric Acid (12.38 M). Fresh solutions were prepared every run to prevent degradation of the reagent.

## 3.4. Reactor Setup

The setup of the reactor was based on the study of Teir et al. (2007) [25] but with some modifications as shown in Figure 2. The leaching experiment was conducted in a Pyrex 500 mL angular three-neck spherical round bottom flask submerged in a 1000 cP silicone oil bath. The temperature of the bath was controlled by the Corning Laboratory Hot Plate, and the temperature inside the reactor setup was monitored regularly by an alcohol thermometer within  $\pm 1.0$  °C. The contents of the reactor were mixed using a magnetic bar stirrer, regulated also by the hot plate. To prevent excess evaporation, the reactor was coupled with a 300 mm Graham condenser, with cooling water coming from the nearby water supply.



Figure 2. Schematic diagram of the reactor setup; (1) water condenser, (2) iron ring, (3) rubber tubing, (4) thermometer, (5) glass basin, (6) reactor vessel, (7) oil bath, (8) iron stand, (9) water source, (10) pump, (11) hotplate with magnetic stirrer, and (12) mixture (solvent and sample).

## 3.5. Experimental Design

The study considered three parameters as possible significant factors in the leaching test—namely, solvent concentration, reaction temperature, and reaction time. The values for these factors were varied to three (3) levels, as shown in Table 1, and were established through precedent studies. The range of reagent concentrations used in the study was based on the studies that utilized HCl as the leaching agent [14,18], whereas for reaction time, the range of values was determined through a compilation of studies which examined the extraction efficiency as a function of time [14,18,38,39]. Lastly, the reaction temperature was established through a variety of studies that employed the pH swing method for carbon sequestration [12,13,38,39].

For this experiment, the Face-Centered Cube (FCC) Design of Response Surface Methodology (RSM) was employed as the experimental design, as optimization of the process parameters was desired. In this design, seventeen treatment combinations were considered, with the central point in triplicates to establish the deviation. The treatment combinations for the experiment are shown in Table 2.

Run	Level				
	Low	Center	High		
Reaction Temperature (°C)	50	75	100		
Reagent Concentration (M)	1.0	2.5	4.0		
Reaction Time (h)	1.0	2.5	4.0		

Table 1. Parameters for the leaching test and their corresponding levels.

		Parameter			Parameter			
Run	Temp. (°C)	Reagent Conc. (M)	Reaction Time (h)	Run	Temp. (°C)	Reagent Conc. (M)	Reaction Time (h)	
1	75	2.5	2.5	10	75	2.5	2.5	
2	75	4.0	2.5	11	100	4.0	4.0	
3	100	1.0	1.0	12	75	2.5	1.0	
4	50	4.0	4.0	13	100	4.0	1.0	
5	75	2.5	4.0	14	50	4.0	1.0	
6	50	2.5	2.5	15	75	2.5	2.5	
7	100	1.0	4.0	16	100	2.5	2.5	
8	50	1.0	1.0	17	50	1.0	4.0	
9	75	1.0	2.5					

Table 2. Experimental matrix of the variables for leaching test.

## 3.6. Leaching Test

Two hundred milliliters (200 mL) of HCl solution at the desired concentration was first poured into the reaction vessel and heated to the required temperature. Subsequently, 10 g of the mixed dump sample in powder form was added and mixed by a magnetic stirrer at a speed of 650 rpm. Temperature was monitored constantly throughout the reaction, and it was ensured that the deviation is within tolerance. The leaching test was allowed to proceed until the desired reaction time, and once completed, the angular three-neck spherical round bottom flask was detached from the setup and the reaction mixture was cooled down by dipping the flask in tap water for 20 min. The solution was then transferred to a beaker and filtered using an Advantec (Tokyo, Japan) 0.45  $\mu$ m syringe filter. The filtrates were stored in polypropylene falcon tubes and kept refrigerated to reduce the corrosive properties of the filtrate prior testing.

## 3.7. Leachate Characterization and Ion Extraction Efficiency Calculation

Similar to the raw sample, the ion concentrations in the filtrate were determined through Agilent 5100 ICP-OES. Four ions were analyzed—namely iron (Fe), magnesium (Mg), aluminum (Al), and silicon (Si).

To determine the efficiency of the extraction, individual ion extraction efficiencies were calculated using Equation (12), which was derived from the study of Daval et al. (2013) [40].

$$X_{i} = \frac{V_{sol} \times C_{i}}{M_{t} \times \% i_{M_{t}}} \times 100$$
(12)

where:

Xi	is the extraction efficiency for element <i>i</i> ;
Mt	is the initial mass of the sample used in the experiment (mg);
%i <sub>Mt</sub>	is the percent elemental composition of element $i$ in the raw sample;
V <sub>sol</sub>	is the leachate solution volume after the desired reaction time (L);
Ci	is the concentration of element $i$ in the leachate determined through ICP-OES (mg/L).

## 4. Results

# 4.1. Mineralogical and Elemental Composition

XRD results (Figure 3) indicate the following major minerals present in the sample, namely: (1) Goethite,  $\alpha$ -FeO(OH), an oxide ore commonly found in nickel mine sites; (2) lizardite-1M, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, a member of the serpentine group; and (3) khademite, AlSO<sub>4</sub>F·5H<sub>2</sub>O. XRF (Table 3) and ICP-OES (Table 4) results established the dominance of goethite in the sample as both analyses reported iron as the main component, with aluminum and magnesium present in significantly lower amounts. These findings also matched with the visual appearance of the mixed dump as its dark-brown appearance is highly indicative of the richness of iron in the sample.



Figure 3. Intensity peaks as reported by XRD.

Aside from Fe, Al, and Mg, the sample was found to contain silicon as well as nickel, which verifies the origin of the sample; that is, a nickel mine site. Chromium and calcium were also detected in the XRF, although in trace amounts. Table 3 summarizes the chemical composition of the mixed dump sample.

Table 3. Chemical composition of the raw mixed dump sample analyzed through XRF.

Sample	Composition (% wt./wt.)								
	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	$Al_2O_3$	NiO	$Cr_2O_3$	MgO	MnO	CaO	Trace & LOI
Mixed Dump	86.85	3.48	2.47	2.46	1.98	1.06	0.94	0.10	0.41

The results obtained from ICP-OES, as shown in Table 4, further verified the order of dominance of the ions present in the sample. Consistent with the chemical composition reported via XRF, the order of dominance (in increasing order) for the mixed dump sample is magnesium  $\rightarrow$  aluminum  $\rightarrow$  iron.

Sample	Composition (% wt./wt.)							
	Iron	Aluminum	Magnesium	Silicon	Calcium			
Mixed Dump	43.54	4.11	2.56	6.8	0.30			

Table 4. Elemental composition of the mixed dump sample as analyzed through ICP-OES.

# 4.2. Morphological Properties

Analyses by SEM-EDX (Figure 4) indicate that the raw mixed dump sample has high heterogeneity. Although Fe is consistently dominant in the sample, results suggest that its dominance varies considerably for each particle. As shown in Figure 4a, the sample with a rigid, plate-like structure contains higher levels of Fe and Al as compared to those composed mainly with flakes and spherical particles shown in Figure 4b. In addition, the presence of rod-shaped particles in Figure 4b suggests the presence of lizardite in the sample as verified by the spike of Mg in the EDX elemental analysis. The presence of silicon is also verified for both samples, particularly for the region bearing spherical particles and is consistent with existing data related to wastes and ores derived from mines [12,41–44].



**Figure 4.** SEM-EDX images (**a**) Al-rich component and (**b**) Mg-rich component of the mixed dump sample and their respective spectra (**c**,**d**).

Although variability is highly present in the sample, BET results (Table 5) suggest that the sample has conducive properties for leachability, due to its high surface area-to-volume ( $S_{BET}/V_p$ ) ratio, also denoted as *R*, in comparison to other materials. The ratio *R* is associated to the availability of

accessible surface for reaction [36,45,46], and as the reaction rates for heterogeneous reactions are highly dependent on the diffusion of the reactant to the active sites, porous materials with high *R* ratios have shown enhanced chemical activity than those with low ratios [45,47,48]. In addition, materials with high *R* values have been observed to have higher permeability to fluid, which also allows for the higher diffusion of the leaching agent into the void spaces [46].

Table 5. Morphological characteristics of the mixed dump as established through BET analysis.

Sample	Parameter					
I. I.	Pore Volume	Pore Radius	Surface Area	$R = S_{BET}/V_p$		
Mixed Dump	0.217 cc/g	19.006 Å	131.916 m <sup>2</sup> /g	608		

For the mixed dump sample, the ratio *R* is found to be 608. In comparison, a study on Brazilian serpentinites reported *R* values of 36 and 29 [41], which are both one magnitude lower than that of the mixed dump sample. The aforementioned Brazilian serpentinite samples also showed great *R* dependence in terms of ion extraction efficiency; for R = 36, the sample registered high extraction efficiencies for its two main components, Mg and Fe, at 95% and 93%, respectively [41]. In comparison, for R = 29, only 36% Mg and 71% Fe extraction efficiencies were reported [41], and thus, it is noteworthy to say that the extraction efficiency of the material is highly dependent on its accessible surface for reaction.

## 4.3. Ion Extraction Efficiencies

Table 6 presents the ion extraction efficiencies of Fe, Mg, Si, and Al for each run, calculated through the ion concentrations obtained through ICP-OES (Table A1) and Equation (12). As seen from the table, iron extraction was highly effective for a majority of the runs, reaching to as high as 95.37%. High extraction efficiencies for aluminum were also observed, with Run 16 posting an extraction rate of 80.31%. On the other hand, low extraction rates were recorded for magnesium, with the maximum %Mg extraction of approximately 68.92%, as well as for silicon, which had a reported maximum of 12.12%.

High Fe and Al values reported for this experiment are related with the morphological characteristics of the sample. As there is high accessible surface for reaction to take place, Fe and Al ions were able to leach out of the material and transfer to the aqueous solution at faster rates. High solubility of these minerals to hydrochloric acid can also be attributed to high extraction rates calculated [49]. On the other hand, the low extraction efficiencies of Mg reported can be attributed to the competing presence of Fe and Al in the sample. This phenomenon observed was similar to that reported by Lacinska et al. [42], in which they cited the presence of Al<sup>3+</sup> ions as the hindering factor in the release of Mg<sup>+</sup>, primarily due to the promotion of layer-to-layer linkage by H-bonding, which kept the Mg<sup>+</sup> ions bound to the solid. The preferential leaching of Fe<sup>3+</sup> in comparison to Mg<sup>+</sup> has also been observed in samples where both ions are present, such as in antigorites, thus contributing to low Mg extraction rates [37]. On the other hand, for Si, SiO<sub>2</sub> is generally unreactive with HCl, hence the minimal transfer to the aqueous phase [41].

Adapting the FCC design, the experimental runs utilized the central point as the basis for the consistency of the results, and thus were performed in triplicates. Runs 1, 10, and 15 were the experimental center points and showed relatively high values of standard deviation (Table 7). These deviations can be attributed to various reasons, mainly due to the heterogeneity of the sample. As the sample composition varies considerably every run, the number of ions initially present in actuality may not be similar to the bulk composition reported. Other possible sources of disagreement in the results are the fluctuations in the temperature, as well as the progression of the reaction even after cooling down the reactor.

n	Extraction Efficiency							
Kun	Iron	Aluminum	Magnesium	Silicon				
1	70.95	54.49	64.29	5.18				
2	72.12	54.61	61.89	4.17				
3	32.54	32.33	68.92	12.12				
4	79.61	62.06	58.73	3.29				
5	80.63	64.51	59.87	4.39				
6	1.94	4.77	28.74	2.58				
7	80.22	64.96	62.98	6.98				
8	1.95	4.19	26.91	5.05				
9	16.36	18.02	64.48	9.26				
10	47.66	36.46	60.59	7.66				
11	88.74	70.14	61.19	2.86				
12	54.48	39.94	61.51	6.90				
13	87.43	68.92	60.38	3.47				
14	5.21	6.52	34.65	3.87				
15	69.64	53.04	61.37	5.78				
16	95.37	80.31	59.76	6.99				
17	24.22	26.43	52.68	9.65				

Table 6. Iron, aluminum, magnesium, and silicon extraction efficiencies calculated for each run.

Table 7. Standard deviation reported for each set of ion extraction efficiencies.

Sampla	Standard Deviation					
Sample	Iron	Aluminum	Magnesium	Silicon		
Mixed Dump	13.08	10.02	1.95	1.29		

# 4.4. Significance of Parameters

With the consistent predominance of Fe in the sample, as well as the high variability and presence of the other ions, the most reliable way to verify the carbon sequestration potential of the mixed dump sample is by using Fe as the primary and sole basis. Therefore, the analysis of the significance of parameters will utilize iron extraction efficiencies to ensure reliability of the results.

Significance of parameters was determined using Design Expert v.11 (Stat-Ease, Inc., Minneapolis, MN, USA) to establish the extent of their effects in the leaching process. As shown in Table 8, all three variables—temperature, reaction time, and reagent concentration—were significant in the leaching tests performed at a p-value tolerance of 0.05.

Parameter	P-value	Findings
Model	<0.0001	Significant
A—Temperature	0.0004	Significant
B—Reaction Time	0.0013	Significant
C—Reagent Concentration	0.0017	Significant
ABC	0.0226	Significant
$AB^2$	0.0381	Significant

Table 8. Analysis of variance (ANOVA) for the experimental variables.

From the Analysis of Variance (ANOVA) performed (actual results available in the Appendix A, Table A2), interaction of parameters can be noted, as shown in the presence of cubic terms ABC and AB<sup>2</sup> with p-values within tolerance. Figure 5a–c shows the interaction of the different parameters mentioned. For low reagent concentrations (Figure 5a), the reaction temperature does not contribute significantly to the increase in the leachability of iron, whereas an increase in the reaction time significantly improves the extraction efficiency of iron. This is due to the fact that, at low reagent

concentration levels, extraction efficiency will not post high results when the temperature is high whilst keeping the reaction time short. The leaching process is controlled by the diffusion of the reactant to the surface of the solid primarily due to its low concentration. Furthermore, this problem is compounded by the time dependence of the reaction, as diffusion of the ions out of the solid is also one of the rate-determining steps.

Therefore, the results obtained from the experiment are in agreement with the theory that as the reaction time is increased the leaching agent has more time to infiltrate the solid, and at the same time, the molecules have more liberty to react with the acid and transfer to the liquid matrix [38].

On the other hand, at intermediate reagent concentration levels (Figure 5b), both an increase in the temperature and reaction time independently show significant effects in the leachability of the mixed dump. In this case, extraction rates increase with prolonged reaction time, as the active sites are infiltrated with the available leaching agents in solution. The increase in energy as the reaction temperature is increased also provides more energy for the reaction to take place, and thus is significant in the leaching process [25,38].

The trend at high reagent concentrations (Figure 5c) is reversed from that in low concentrations. This is because as the solution becomes more saturated with the leaching agent the number of possible sites for infiltration is constant, and thus further increase in concentration does not significantly affect the process. On the other hand, although a lot of leaching molecules are present in the sample, not all of them has enough energy to initiate the reaction, and thus the iron extraction efficiency is dependent highly on temperature at high concentrations [43,50,51].



**Figure 5.** Parametric interactions of temperature and reaction time at (**a**) low, (**b**) mid, and (**c**) high reagent concentration levels.

Figure 6a–c also depicts the contour plots for extraction efficiencies at low, mid, and high concentrations, respectively. As shown in Figure 6a, at low reagent concentrations, a temperature of at least 95 °C and a reaction time of at least 2.3 h must be utilized to achieve an extraction efficiency of 80%. On the other hand, in Figure 6b, at mid reagent concentrations (~2.5 M), an extraction efficiency near 100% can be achieved at a reaction temperature of near 100 °C and 2.5 h, with the extraction efficiency decreasing as the temperature and reaction time are decreased. Finally, for high reagent concentrations (~4 M), an extraction efficiency of at least 80% at temperatures around 60 °C and 4 h. The 3D and contour plots support the interactions and theoretical bases mentioned above.



**Figure 6.** Contour plots of reaction time vs. temperature at (**a**) low, (**b**) mid, and (**c**) high reagent concentration levels.

## 4.5. Carbon Dioxide Sequestration Potential

Using the results obtained from the XRD analysis, the following reactions took place to release the iron, magnesium, and aluminum ions into the solution (Equations (13) to (15)):

Goethite : 
$$FeO(OH) + 3 HCl \rightarrow Fe^{3+} + 3 Cl^- + 2 H_2O$$
 (13)

Khademite: 
$$AlSO_4F \cdot 5H_2O + 3 HCl \rightarrow Al^{3+} + H_2SO_4 + HF + 3 Cl^- + 5 H_2O$$
 (14)

Lizardite : 
$$(Mg, Fe)_3Si_2O_5(OH)_4 + 6 HCl \rightarrow 3 Mg^{2+} + 3 Fe^{2+} + 6 Cl^- + 2 SiO_2 + 5 H_2O$$
 (15)

From the ion concentrations determined through ICP-OES, it was established that iron is the predominant ion available for carbonation and thus is used as the sole basis for the carbon dioxide sequestration potential of the mixed dump. As Fe ions react with carbonates in a stoichiometric mole ratio of 1:1, the calculation of the amount of  $CO_2$  sequestered per mass of mixed dump can be calculated using Equation (16):

$$\frac{\text{mg CO}_2}{\text{g sample}} = \frac{\text{C}_{\text{Fe}}\left[\frac{\text{mg}}{\text{L}}\right] \times \text{V}_{\text{Sol}}[\text{L}] \times \frac{1 \text{ mole Fe}}{\text{MM Fe}} \times \frac{1 \text{ mole CO}_2}{1 \text{ mole Fe}} \times \frac{\text{MM CO}_2}{1 \text{ mole CO}_2}}{\text{mass sample} [g]}$$
(16)

The theoretical amount of CO<sub>2</sub> that can be stored or formed into iron (II) carbonate (siderite) is calculated to be 327.2 mg CO<sub>2</sub>/g sample, using the highest iron concentration of 20,761.39 mg/L obtained for Run 16 (100 °C, 2.5 M, and 2.5 h). This reported value is higher than that previously reported for calcium-rich waste cement (60 mg CO<sub>2</sub>/g sample) and blast furnace slag (40–90 mg CO<sub>2</sub>/g sample) [12,52], calcium-rich coal fly-ash (29.8 mg CO<sub>2</sub>/g sample) [46], as well as for grounded serpentine ores at different reaction temperatures (129.9–294.1 mg CO<sub>2</sub>/g sample) [14,39], which shows the potential of the mixed dump sample for carbon sequestration.

## 4.6. Challenges and Forecasts

Experimental results showed the potential of iron to be utilized in carbon dioxide sequestration, due to high extraction rates recorded. However, some drawbacks remain to be addressed, especially in an industrial-scale application.

The first challenge for iron utilization is that, unlike magnesium and calcium, it requires a certain state in order to form carbonates. In the case of goethite, once extracted and transferred to the aqueous phase, the iron is present as  $Fe^{3+}$ .  $Fe^{3+}$  has a very high polarizing power which deters it from forming carbonates, and thus must be reduced to  $Fe^{2+}$ . Therefore, in order to proceed with iron carbonation, particularly with a goethite-rich sample, a reducing agent must be added to transform  $Fe^{3+}$  to  $Fe^{2+}$ , of which one is sulfur dioxide, a gas commonly present in the stack together with  $CO_2$  [31,33–35]. The kinetics studies of dos Santos Alfonso and Stumm [53] and Poulton et al. [54] propose the following reaction mechanism for iron carbonation in order to address such drawback (Equations (17) to (23)):

 $FeO(OH) + 3HCl \rightarrow Fe^{3+} + 3Cl^{-} + 2H_2O$  (17)

$$Fe^{3+} + HS^{-} \rightarrow Fe^{3+}S^{-} + H^{+}$$

$$\tag{18}$$

$$Fe^{3+}S^{-} \rightarrow Fe^{2+}S^{\cdot}$$
 (19)

$$Fe^{2+}S^{\cdot} + H_2O \rightarrow FeOH_2^+ + S^{-}$$
 (20)

$$\text{FeOH}_2^+ \rightarrow \text{H}_2\text{O} + \text{Fe}^{2+}$$
 (21)

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3$$
 (22)

$$Fe^{3+} + HS^{-} + CO_3^{2-} \rightarrow H^+ + S^{-} + FeCO_3$$
 (23)

Although the mechanism of carbon dioxide sequestration via iron carbonation suggests an additional step in order to completely sequester carbon dioxide, the innate presence of  $SO_2$ in industrial flue gas inherently compensates for this extra requirement. Nonetheless, the ratio of  $CO_2$ to  $SO_2$  in the flue gas remains to be extensively studied and monitored when applied industrially, as excess  $SO_2$  is associated with the formation of undesired sulfides [33,34].

Another challenge observed for the application of the pH swing method is the need for pre-treatment of the sample. Feed particle size remains a major consideration in the process even though the kinetics of the leaching reactions relies on other factors such as temperature, stirring speed, and the presence of catalysts. It has been reported by a journal that reducing the particle size of the feed material to a certain extent brings about positive results. According to the study of Sanna et al. [38], the extraction of Mg using 1.4 M NH<sub>4</sub>SO<sub>4</sub> has improved by 250% when the particle size was further reduced to 75–150  $\mu$ m from 500–700  $\mu$ m after 30 min of leaching, and 80% improvement after 180 min of leaching. The same study reported however, that reduction of particle size from 150–300  $\mu$ m to 75–150  $\mu$ m showed only 25% improvement after 30 min of leaching and no significant improvement after 180 min of Mg extraction [38].

Extraction efficiency improvements, such as those mentioned, can be achieved through mechanical activation methods—such as crushing, grinding, and milling. Industrially speaking, particle size reduction is easy to implement, as crushers, ball mills, and other size reduction equipment are readily available and are widely used in conventional mineral processing. However, some challenges still remain when such procedure is applied in an industrial scale, particularly for the energy consumed by these processes. It is reported, for instance, that 50.6 wt.% of a lizardite sample can be reduced to <150  $\mu$ m using a grinding speed of 920 rpm for 5 min with an energy penalty of 16.2 kW-h/t [39]. The particle distribution can be further improved to 87.4 wt.% of particles less than 150  $\mu$ m by grinding it at 920 rpm for 10 min at an additional 17.0 kW-h/t [39]. Thus, the optimum conditions for sample preparation, i.e., optimum particle size range, grinding/milling speed, type of grinding media, among others, must also be established in order to reduce energy costs.

Lastly, material selection, such as the feed, leaching agents, and later on, base for carbonation, must be counterbalanced to make the pH swing method cost-appealing. The effect, for instance, of the variability of the sample must be monitored extensively to determine the associated process upsets. In addition, the reactor volumes required must be optimized to reduce construction and fabrication costs. Ideally, high solid-liquid (S/L) ratios are preferred due to the smaller reactor volume required; however, high S/L ratios tend to an extent, reduce the efficiency of the process. Cost of the reagents must be taken into consideration as well; hydrochloric acid (36 wt.%) is priced at around 165–235 USD/L, whereas the price of sodium hydroxide pellets (99 wt.%) varies at 350–600 USD/kg.

All of these factors must be collectively and intensively studied in order to make the pH swing feasible and appealing in an industrial scale setup, especially if the process is desired to be made profitable. Iron carbonates, which are the main product from the process, can be sold as raw materials for dyes, pigments, and even for dietary supplements, depending on the quality of the products produced. The residue from the leaching process, which is composed primarily of refractory materials such as silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>), can be washed with water and then sold as fillers and raw materials for building and road construction. Indeed, a thorough investigation of all of these aspects must be performed to ensure the viability of the pH swing method as a sustainable and cost-effective means of sequestering carbon dioxide.

## 5. Conclusions and Recommendations

X-ray diffraction analysis suggested three major minerals present in the mixed dump, namely: goethite,  $\alpha$ -FeO(OH), khademite, AlSO<sub>4</sub>F·5H<sub>2</sub>O, and lizardite-1M, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>. XRF and ICP-OES results further established goethite as the main mineral present for the sample, due to the dominance of iron recorded for both analyses.

The morphological characteristics of the sample were also analyzed, and SEM-EDX results reported high heterogeneity in the sample. Through region analysis, it was found that the composition differs from particle to particle; although Fe remained to be consistently dominant, Al and Mg appeared to be concentrated in specific regions in the sample. On the other hand, BET results suggested high accessible surface for the sample as the surface area-to-volume ratio is much higher to those previously reported.

Ion extraction efficiencies, particularly for iron, posted very high results, with the highest calculated extraction efficiency of 95.37% obtained at 100 °C, 2.5 h, and 2.5 M HCl. Promising results for ion extraction can highly be attributed to the accessible surface available for the sample, as well as the increased solubility of goethite in HCl at high temperature and high reagent concentration.

Significance of the parameters was determined using a face-centered cube design for response surface methodology. Outcomes of ANOVA revealed that all parameters were significant for iron extraction efficiency, with interactions highly pronounced at low and high reagent concentrations due to the dependence of the leaching process in reaction time and temperature.

Lastly, the carbon sequestration potential of the mixed dump was quantified through the theoretical amount of  $CO_2$  that can be sequestered per amount of sample. It is reported that the mixed dump can sequester a maximum of 327.2 mg  $CO_2$ /g sample at 100 °C, 2.5 h and 2.5 M HCl, which is higher than that of waste cement, blast furnace slag, fly ash, and grounded serpentinite. The challenge posted in this process however is, for iron carbonation to proceed, particularly in the case of goethite, an additional reduction step is required as  $Fe^{3+}$  cannot be readily utilized to form carbonates. Sulfur dioxide, which forms sulfide ions in aqueous solutions, is one of the reducing agents considered and is existent in combination with  $CO_2$  in industrial flue gas. Therefore, although iron carbonation requires an additional step to proceed into completion, the inherent presence of the reducing agent together with  $CO_2$  means that there is great potential for iron-rich materials in carbon dioxide sequestration via mineralization.

The authors suggest that material selection be evaluated concisely to make the pH swing process viable and cost-appealing. A thorough investigation of the energy penalties associated to the

sample preparation and its subsequent effect on the efficiency of the carbon sequestration process, is also recommended.

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# Appendix A

Table A1. Aluminum, iron, magnesium, and silicon concentrations from RSM-designed experiment.

Parameter					Concer	itration	
Temp. (°C)	Reaction Time (hr)	Reagent Conc. (M)	Run	Iron (mg/L)	Aluminum (mg/L)	Magnesium (mg/L)	Silicon (mg/L)
75	2.5	2.5	1	15,446.15	1119.74	822.92	175.95
75	4.0	2.5	2	15,701.15	1122.23	792.15	141.64
100	1.0	1.0	3	7084.35	664.43	882.12	412.20
50	4.0	4.0	4	17,330.89	1275.37	751.75	111.90
75	2.5	4.0	5	17,552.88	1325.74	766.39	149.15
50	2.5	2.5	6	422.70	98.12	367.82	87.64
100	1.0	4.0	7	17,463.46	1334.88	806.12	237.32
50	1.0	1.0	8	423.77	86.12	344.39	171.57
75	1.0	2.5	9	3560.95	370.29	825.34	314.93
75	2.5	2.5	10	10,375.45	749.21	775.51	260.44
100	4.0	4.0	11	19,318.50	1441.36	783.27	97.38
75	2.5	1.0	12	11,859.26	820.82	787.32	234.48
100	4.0	1.0	13	19,034.42	1416.21	772.89	118.07
50	4.0	1.0	14	1134.57	133.96	443.57	131.42
75	2.5	2.5	15	15,161.03	1089.89	785.55	196.43
100	2.5	2.5	16	20,761.39	1650.35	764.97	237.55
50	1.0	4.0	17	5273.72	543.16	674.30	328.11

Table A2. Actual Analysis of Variance (ANOVA) results obtained from Design Expert v.11.

Parameter	Sum of Squares	df	Mean Square	F-value	P-value	Findings
Model	15,649.06	5	3129.81	18.13	< 0.0001	Significant
A—Temperature	4364.58	1	4364.58	25.28	0.0004	Significant
B—Reaction Time	3162.00	1	3162.00	18.31	0.0013	Significant
C—Reagent Concentration	2951.87	1	2951.87	17.10	0.0017	Significant
ABC	1212.78	1	1212.78	7.02	0.0226	Significant
$AB^2$	958.25	1	958.25	5.55	0.0381	Significant
Residual	1899.41	11	172.67			0
Lack of Fit	1556.99	9	173.00	1.01	0.5912	Not Significant
Pure Error	342.42	2	171.21			-
Total	17,548.47	16				

 $R^2 = 0.8918$ , Adjusted  $R^2 = 0.8426$ , Predicted  $R^2 = 0.7772$ , Adequate precision = 11.9680.

# References

- 1. UN Emissions Gap Report 2018. Available online: https://www.ipcc.ch/site/assets/uploads/2018/12/UNEP-1. pdf (accessed on 31 May 2019).
- 2. The Paris Agreement. Available online: https://unfccc.int/process-and-meetings/the-paris-agreement/ d2hhdC1pcy (accessed on 11 June 2019).
- 3. NOAA Earth System Research Laboratory Global Monitoring Division. Available online: https://www.esrl. noaa.gov/gmd/ccgg/trends/ (accessed on 31 May 2019).
- 4. Climate Action Tracker. Available online: https://climateactiontracker.org/global/temperatures/ (accessed on 11 June 2019).
- 5. Leung, D.Y.C.; Caramanna, G.; Maroto-Valer, M.M. An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sustain. Energy Rev.* **2014**, *39*, 426–443. [CrossRef]
- USGS Carbon Sequestration to Mitigate Climate Change. Available online: https://pubs.usgs.gov/fs/2008/ 3097/pdf/CarbonFS.pdf (accessed on 10 June 2019).
- Chow, A. Ocean Carbon Sequestration by Direct Injection. In CO<sub>2</sub> Sequestration and Valorization, 1st ed.; Morgado, R.V.A., Esteves, V., Eds.; IntechOpen: London, UK, 2014. [CrossRef]
- 8. Olajire, A.A. A review of mineral carbonation technology in sequestration of CO<sub>2</sub>. J. Pet. Sci. Eng. **2013**, 109, 364–392. [CrossRef]
- Zevenhoven, R.; Björklöv, T.; Fagerlund, J.; Romão, I.; Jie, B. Assessment and improvement of a stepwise magnesium silicate carbonation route via MgSO<sub>4</sub> and Mg(OH)<sub>2</sub>. In Proceedings of the Third International Conference on Accelerated Carbonation for Environmental and Materials Engineering, Turku, Finland, 29 November–1 December 2010.
- 10. Butt, C.R.M.; Cluzel, D. Nickel laterite ore deposits: Weathered serpentinites. *Elements* **2013**, *9*, 123–128. [CrossRef]
- 11. Department of Environment and Natural Resources, Mines and Geosciences Bureau. Available online: http://mgb.gov.ph/attachments/article/162/Q1%202019%20Metallic%20Mineral%20Production.pdf (accessed on 6 June 2019).
- 12. Mun, M.; Cho, H. Mineral carbonation for carbon sequestration with industrial waste. *Energy Procedia* **2013**, 37, 6999–7005. [CrossRef]
- 13. Meyer, N.A.; Vögeli, J.U.; Becker, M.; Broadhurst, J.L.; Reid, D.L.; Franzidis, J.-P. Mineral carbonation of PGM mine tailings for CO<sub>2</sub> storage in South Africa: A case study. *Miner. Eng.* **2014**, *59*, 45–51. [CrossRef]
- 14. Teir, S.; Kuusik, R.; Fogelholm, C.-J.; Zevenhoven, R. Production of magnesium carbonates from serpentinite for long-term storage of CO<sub>2</sub>. *Int. J. Miner. Process.* **2007**, *85*, 1–15. [CrossRef]
- 15. Kunzler, C.; Alves, N.; Pereira, E.; Nienczewski, J.; Ligabue, R.; Einloft, S.; Dullius, J. CO<sub>2</sub> storage with indirect carbonation using industrial waste. *Energy Procedia* **2011**, *4*, 1010–1017. [CrossRef]
- 16. Kazikawa, M.; Yamasaki, A.; Yanagisawa, Y. A new CO<sub>2</sub> disposal process via artificial weathering of calcium silicate accelerated by acetic acid. *Energy* **2001**, *26*, 341–354.
- 17. Doucet, F.J. Effective CO<sub>2</sub>-specific sequestration capacity of steel slags and variability in their leaching behavior in view of industrial mineral carbonation. *Miner. Eng.* **2010**, *23*, 262–269. [CrossRef]
- 18. Teir, S.; Elenova, S.; Fogelholm, C.J.; Zevenhoven, R. Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production. *Energy* **2007**, *32*, 528–539. [CrossRef]
- Gunning, P.J.; Hills, C.D.; Carey, P.J. Accelerated carbonation treatment of industrial wastes. *Waste Manag.* 2010, 30, 1081–1090. [CrossRef] [PubMed]
- 20. Muriithi, G.N.; Gitari, M.W.; Petrik, L.F.; Ndungu, P.G. Carbonation of brine impacted fractionated coal fly ash: Implications for CO<sub>2</sub> sequestration. *J. Environ. Manag.* **2011**, *92*, 655–664.
- Uibu, M.; Velts, O.; Kuusik, R. Developments in CO<sub>2</sub> mineral carbonation of oil shale ash. *J. Hazard. Mater.* 2010, 174, 209–214. [CrossRef] [PubMed]
- 22. Uibu, M.; Kuusik, R.; Andreas, L.; Kirsimäe, K. The CO<sub>2</sub>-binding by Ca-Mg-silicates in direct aqueous carbonation of oil shale ash and steel slag. *Energy Procedia* **2011**, *4*, 925–932. [CrossRef]
- Baciocchi, R.; Polettini, A.; Pomi, R.; Prigiobbe, V.; Von Zedwitz, N.V.; Steinfeld, A. CO<sub>2</sub> Sequestration by direct gas-solid carbonation of air pollution control (APC) residues. *Energy Fuel* 2006, 20, 1933–1940. [CrossRef]

- Sanna, A.; Dri, M.; Hall, M.R.; Maroto-Valer, M.M. Waste materials for carbon capture and storage by mineralisation (CCSM)—A UK perspective. *Appl. Energy* 2012, 99, 545–554. [CrossRef]
- 25. 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]
- 26. Wang, X.; Maroto-Valer, M.M. Dissolution of serpentine using recyclable ammonium salts for CO<sub>2</sub> mineral carbonation. *Fuel* **2011**, *90*, 1229–1237. [CrossRef]
- 27. Hemmati, A.; Shayegan, J.; Sharratt, P.; Yeo, T.Y.; Bu, J. Solid products characterization in a multi-step mineralization process. *Chem. Eng. J.* **2014**, 252, 210–219. [CrossRef]
- Béarat, H.; McKelvy, M.J.; Chizmeshya, A.V.G.; Gormley, D.; Nunez, R.; Carpenter, R.W.; Squires, K.; Wolf, G.H. Carbon sequestration via aqueous olivine mineral carbonation: Role of passivating layer formation. *Environ. Sci. Technol.* 2006, 40, 4802–4808. [CrossRef]
- 29. Qafoku, O.; Kovarik, L.; Kukkadapu, K.R.; Ilton, E.S.; Arey, B.W.; Tucek, J.; Felmy, A.R. Fayalite dissolution and siderite formation in water-saturated supercritical CO<sub>2</sub>. *Chem. Geol.* **2012**, *332–333*, 124–135. [CrossRef]
- Geologic Storage of CO2 in Basalts. Available online: https://ieaghg.org/docs/General\_Docs/Reports/2011-TR2.pdf (accessed on 26 June 2019).
- 31. Palandri, J.L.; Rosenbauer, R.J.; Kharaka, Y.K. Ferric iron in sediments as a novel CO<sub>2</sub> mineral trap: CO<sub>2</sub>–SO<sub>2</sub> reaction with hematite. *Appl. Geochem.* **2005**, *20*, 2038–2048. [CrossRef]
- 32. Berger, P.M.; Roy, W.R. Potential for iron oxides to control metal releases in CO<sub>2</sub> sequestration scenarios. *Energy Procedia* **2011**, 4, 3195–3201. [CrossRef]
- 33. Garcia, S.; Rosenbauer, R.J.; Palandri, J.; Maroto-Valer, M.M. Experimental and simulation studies of iron oxides for geochemical fixation of CO<sub>2</sub>-SO<sub>2</sub> gas mixtures. *Energy Procedia* **2011**, *4*, 5108–5113. [CrossRef]
- 34. Murphy, R.; Lammers, K.; Smirnov, A.; Schoonen, M.A.A.; Strongin, D.R. Hematite reactivity with supercritical CO<sub>2</sub> and aqueous sulfide. *Chem. Geol.* **2011**, *283*, 210–217. [CrossRef]
- 35. Lammers, K.; Murphy, R.; Riendeau, A.; Smirnov, A.; Schoonen, M.A.A.; Strongin, D.R. CO<sub>2</sub> sequestration through mineral carbonation of iron oxyhydroxides. *Environ. Sci. Technol.* **2011**, *45*, 10422–10428. [CrossRef]
- 36. Yuen, Y.T.; Sharratt, P.N.; Jie, B. Carbon dioxide mineralization process design and evaluation: Concepts, case studies, and considerations. *Environ. Sci. Pollut. Res. Int.* **2016**, *23*, 22309–22330. [CrossRef]
- 37. Lavikko, S.; Eklund, O. The significance of the serpentinite characteristics in mineral carbonation by "the ÅA Route". *Int. J. Miner. Process.* **2016**, *152*, 7–15. [CrossRef]
- 38. Sanna, A.; Wang, X.; Lacinska, A.; Styles, M.; Paulson, T.; Maroto-Valer, M.M. Enhancing Mg extraction from lizardite-rich serpentine for CO<sub>2</sub> mineral sequestration. *Miner. Eng.* **2013**, *49*, 135–144. [CrossRef]
- 39. Sanna, A.; Dri, M.; Maroto-Valer, M.M. Carbon dioxide capture and storage by pH swing aqueous mineralization using a mixture of ammonium salts and antigorite source. *Fuel* **2013**, *114*, 153–161. [CrossRef]
- Daval, D.; Hellmann, R.; Martinez, I.; Gangloff, S.; Guyot, F. Lizardite serpentine dissolution kinetics as a function of pH and temperature, including effects of elevated pCO<sub>2</sub>. *Chem. Geol.* 2013, 351, 245–256. [CrossRef]
- 41. Arce, G.L.A.F.; Neto, T.G.S.; Luna, C.M.R.; dos Santos, J.C.; Carvalho, J.A., Jr. Influence of physicochemical properties of Brazilian serpentinites on the leaching process for indirect CO<sub>2</sub> mineral carbonation. *Hydrometallurgy* **2017**, *169*, 142–151. [CrossRef]
- Lacinska, A.M.; Styles, M.T.; Bateman, K.; Wagner, D.; Hall, M.R.; Gowing, C.; Brown, P.D. Acid-dissolution of antigorite, chrysotile and lizardite for ex situ carbon capture and storage by mineralization. *Chem. Geol.* 2016, 437, 153–169. [CrossRef]
- 43. Dri, M.; Sanna, A.; Maroto-Valer, M.M. Dissolution of steel slag and recycled concrete aggregate in ammonium bisulphate for CO<sub>2</sub> mineral carbonation. *Fuel Process. Technol.* **2013**, *113*, 114–122. [CrossRef]
- 44. Stopic, S.; Dertmann, C.; Koiwa, I.; Kremer, D.; Wotruba, H.; Etzold, S.; Telle, R.; Knops, P.; Friedrich, B. Synthesis of nanosilica via olivine mineral carbonation under high pressure in an autoclave. *Metals* **2019**, *9*, 708. [CrossRef]
- 45. Oskierski, H.C.; Dlugogorksi, B.Z.; Jacobsen, G. Sequestration of atmospheric CO<sub>2</sub> in a weathering-derived, serpentinite-hosted magnesite deposit: 14C tracing of carbon sources and age constraints for a refined genetic model. *Geochim. Cosmochim. Acta* **2013**, 122, 226–246. [CrossRef]
- 46. Ukwattage, N.L.; Ranjith, P.G.; Yellishetty, M.; Bui, H.H.; Xu, T. A laboratory-scale study of the aqueous mineral carbonation of coal fly ash for CO<sub>2</sub> sequestration. *J. Clean. Prod.* **2015**, *103*, 665–674. [CrossRef]

- 47. Klobes, P.; Klaus, M.; Munro, R.G. *Porosity and Specific Surface Area Measurements for Solid Materials*; National, I., Ed.; NIST—National Institute of Standards and Technology: Washington, DC, USA, 2008.
- 48. Gadikota, G.; Swanson, E.J.; Zhao, H.; Park, A.-H.A. Experimental design and data analysis for accurate estimation of reaction kinetics and conversion for carbon mineralization. *Ind. Eng. Chem. Res.* **2014**, *53*, 6664–6676. [CrossRef]
- 49. Sidhu, P.S.; Gilkes, R.J.; Cornell, R.M.; Posner, A.M.; Quirk, J.P. Dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids. *Clays Clay Miner.* **1981**, *29*, 269–276. [CrossRef]
- 50. Dorman, F.L.; Dawes, P. Chapter 3 column technology open tubular columns. In *Gas Chromatography*; Elsevier: Amsterdam, The Netherlands, 2007; pp. 79–96.
- 51. Hemmati, A.; Shayegan, J.; Bu, J.; Yeo, T.Z.; Sharratt, P. Process optimization for mineral carbonation in aqueous phase. *Int. J. Miner. Process.* **2014**, *130*, 20–27. [CrossRef]
- 52. Georgakopoulos, E.D. Iron and Steel Slag Valorization through Carbonation and Supplementary Processes. Ph.D. Thesis, Cranfield University, Cranfield, UK, December 2016.
- 53. dos Santos Alfonso, M.; Stumm, W. Reductive dissolution of iron (III) hydroxides by hydrogen sulfide. *Langmuir* **1992**, *8*, 1671–1675. [CrossRef]
- 54. Poulton, S.W.; Krom, M.D.; Raiswell, R.A. A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide. *Geochim. Cosmochim. Acta* **2004**, *68*, 3703–3715. [CrossRef]



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