minerals

MDPI

Article

Accelerated Carbonation of Recycled Aggregates Using the Pressurized Supercritical Carbon Dioxide Sparging Process

Jinyoung Park [1], Jinkyun Lee [1], Chul-Woo Chung [2], Sookyun Wang [3] and Minhee Lee [1,*]

[1] Department of Earth and Environmental Sciences, Pukyong National University, Busan 48513, Korea; jyp@kigam.re.kr (J.P.); leejk9936@hanmail.net (J.L.)
[2] Department of Architectural Engineering, Pukyong National University, Busan 48513, Korea; cwchung@pknu.ac.kr
[3] Department of Energy and Resource Engineering, Pukyong National University, Busan 48513, Korea; sookyun@pknu.ac.kr
* Correspondence: heelee@pknu.ac.kr; Tel.: +82-51-629-6630

Received: 1 May 2020; Accepted: 25 May 2020; Published: 26 May 2020

Abstract: The carbonation of recycled aggregate was accelerated by sparging with supercritical carbon dioxide ($scCO_2$) to reduce the amount of time needed for carbonation, which is necessary for the pH neutralization of recycled aggregate. To accelerate the carbonation process, pressurized $scCO_2$ was sparged into two different types of recycled aggregates immersed in water for 1 h, followed by standstill for 2 h (in total, a 3 h treatment process). The reduction of the pH of the treated aggregates due to carbonation was investigated using batch extraction experiments. A continuous column extraction experiment for the $scCO_2$-sparged recycled aggregate was also performed to identify the effect of pH reduction under the condition of non-equilibrium reaction. From XRD, SEM/EDS, and TG/DTA analyses, much of the portlandite in the recycled aggregates was consumed. In its place, calcite was created as a secondary mineral during only 3 h of treatment (1 h $scCO_2$ sparging and 2 h stationing), indicating satisfactory carbonation of the aggregate. The results of the batch extraction experiments for both of the two recycled aggregate types also showed that the average pH of $scCO_2$-sparged aggregate decreased from 12.0 to <9.8 (the tolerance limit for recycling). The pH of the eluent from the column packed with the $scCO_2$-sparged aggregate also remained as <9.8, suggesting that a 1 h $scCO_2$ sparging process is sufficient to carbonate waste concrete aggregate and to create an alternative construction material resource.

Keywords: carbonation; recycled aggregate; concrete waste; supercritical carbon dioxide; sparging

1. Introduction

As the by-product of industrialization and urbanization, a large amount of construction waste has been produced worldwide. In 2016, 199,444 t of construction waste per day (48% of the total waste) was created in South Korea [1]. Concrete waste accounted for more than 70% of that waste, making it a major pollutant in Korea [2]. In recent decades and in many countries, there is a shortage of concrete waste disposal sites. In response, new technologies are being developed to reuse concrete waste. One of the most popular recycling processes for concrete waste (the production of recycled fine and coarse aggregates from the crushed concrete waste) has been utilized to provide alternative resources using concrete aggregates or other materials disposed as landfill [3,4]. The reuse of concrete waste as an aggregate is considered to be desirable and beneficial as a plan to minimize the high volume of concrete waste [5,6]. Even though the process to manufacture recycled aggregate from concrete waste is relatively simple and mostly involves crushing and screening, only a small portion of the recycled aggregate is being used at construction sites to replace typical concrete aggregate because the recycled aggregate has weaker mechanical properties than normal aggregates have [7,8]. For practical reasons, the recycled fine and coarse aggregates have typically been reused as a landfill material [9,10]. There exists another major problem for even such applications, which originates from the high pH of the recycled aggregates. This alkalinity is due to high content of cement paste and mortar mainly composed of portlandite and calcium silicate hydrates (C-S-H) in concrete [11,12].

The pH of the recycled aggregate is dependent on the amount of portlandite ($Ca(OH)_2$) in the concrete waste, and the pH of the recycled aggregates increases to pH 12 and generally ranges from 11 to 13 due to the dissolution of $Ca(OH)_2$ and the production of OH^- in water [13]. Hence, the high pH of concrete waste threatens the environment when it is exposed to water, and the reuse of the recycled aggregate in areas where it has can influence the pH of water is strictly limited by law [14,15]. In Korea, there was an accident in 2008 related to increase in the pH of an ecosystem by recycled aggregate, in which noteworthy numbers of birds and fish were killed. As a result, the pH level of the recycled aggregate was regulated to be <9.8 in order to reuse it for the road sub-bases and non-structural facilities [16–18].

There are several treatment processes for reducing the pH of concrete waste that could improve its reuse. Carbonation using CO_2 gas is considered one of the most popular processes over the past decade [19]. The CO_2 gas dissolves in water to form carbonic acid and the carbonic acid reacts with the hydrated portlandite and/or the calcium silicate hydrate producing secondary carbonate minerals such as $CaCO_3$, in the process called carbonation [20–23]. The carbonation achieved by dissolved CO_2 can reduce the alkalinity in water and thus the pH of concrete aggregates. From recent research, the CO_2-water-aggregate reaction at atmospheric pressure in the laboratory has been simulated to induce the carbonation of concrete aggregate. The pH reduction of the recycled aggregate by the CO_2-water-aggregate reaction has been effective to a certain point [24,25]. However, because the carbonation with dissolved CO_2 mainly takes place on the surface of the recycled aggregates and because the partial pressure of CO_2 in the atmosphere is relatively low (around 0.05%), the conventional carbonation rate in the CO_2-water-aggregate reaction at atmospheric pressure is slow. This means that the reaction time necessary for sufficient pH neutralization takes too long to achieve a satisfactory pH reduction for recycled aggregates (generally more than 30 d). If enough carbonation time by dissolved CO_2 is not guaranteed, the pH of water extracted from the CO_2-treated aggregate may decrease early in the extraction; then, may go back up to pH 11–12 in the latter stage of extraction. This is because of additional dissolution of the unaltered portlandite remaining in the aggregate. The extent and the rate of carbonation for the aggregate depends on several parameters, including CO_2 diffusivity, and CO_2 reactivity, dissolved CO_2 amount, and infiltration capacity into micro pores. These are proportional to the conditions under which recycled aggregate in water is exposed to dissolved CO_2. With larger contact area and the higher pressure in the $scCO_2$-water-aggregate reaction, the carbonation process is accelerated, and the time needed for carbonation to reduce the pH of the recycled aggregate may decrease. The reduction of the carbonation time for recycled aggregate is unavoidable for its wider commercialization as well as for its use in construction.

As an alternative to accelerate carbonation, liquid CO_2 and supercritical CO_2 ($scCO_2$) could be used instead of CO_2 gas. It can be inferred that the actual solubility of CO_2 in water is high under low-temperature and high-pressure conditions during the CO_2-water-aggregate reactions [26,27]. However, a large amount of calcium carbonate ($CaCO_3$), which is the by-product resulting from CO_2 sequestration in the carbonation process, can precipitate in high-temperature and high-pressure conditions [28–30]. The viscosity and density of $scCO_2$ is more similar to gaseous CO_2 than to liquid CO_2; thus, the mobility of $scCO_2$ in aggregate is much greater than that of liquid CO_2. This accelerates carbonation in the recycled aggregate. For these reasons, $scCO_2$ rather than gaseous CO_2 and liquid CO_2 is more appropriate for use in the carbonation process to neutralize the pH of recycled aggregate. The $scCO_2$-water-aggregate reaction under high-pressure and high-temperature conditions was conducted at laboratory scale by Chung et al. [31] and Costa et al. [32]. The carbonation of the Portland cement matrix and the cement mortar was simulated by inducing undisturbed $scCO_2$-water-material reaction under a supercritical condition (50 °C and 10.0 MPa or 70 °C and 13.8 MPa). The formation of calcite ($CaCO_3$) was identified after the carbonation and the pH of the cement samples declined to 9.8 (the tolerance limit). However, the time needed for carbonation to satisfy the pH tolerance limit (9.8) for the reuse of the recycled aggregate took from 30 to 50 d. This is too long to facilitate its reuse in construction. It is necessary to develop an additional technology to accelerate the carbonation process, thereby minimizing the carbonation time of the recycled aggregate to <1 d.

In this paper, a new treatment process is introduced to minimize the carbonation time needed to reuse concrete aggregate to within a few hours (3 h at most). To overcome the limitation of the conventional carbonation time, the carbonation process of the concrete aggregates was optimized by sparging pressurized $scCO_2$ into recycled aggregate immersed in water under supercritical condition (0.8 MPa and 50 °C). In the case of $scCO_2$ sparging into water-immersed aggregate, the stirred micro water and $scCO_2$ bubbles can penetrate deeply into micro pore spaces inside the aggregate. There, they facilitate the dissolution of the hydrate (portlandite) in the aggregate much more than the undisturbed water would, which quickly increases the pH of the water. However, the sparged $scCO_2$ (micro-bubble type) simultaneously increases the saturation of CO_2 in water and produces plenty of H^+ and carbonic acids (HCO_3^- and CO_3^{2-}) that penetrate much better into the micro pores of the aggregate to neutralize the hydroxides dissolved inside them. This results in decrease of the pH of the water and the precipitation of $CaCO_3$ on the aggregate surface in a relatively short time. The successful reduction of pH in the recycled aggregate can be achieved by this process of accelerated carbonation of hydrated portlandite (or calcium silicate hydrates attached to the aggregates), which is transformed into secondary carbonate minerals such as $CaCO_3$. Batch and column extraction experiments with the $scCO_2$-sparged/untreated recycled aggregate were performed to demonstrate the pH reduction of the recycled aggregate treated with this accelerated carbonation process. The optimal conditions for accelerated carbonation were determined by laboratory experiments and the effect of this carbonation process on the pH reduction of the recycled aggregates was also quantitatively and visually investigated using several kinds of quantitative analysis. The use of the $scCO_2$ sparging process as the accelerated carbonation process has never before been attempted, even in the laboratory, and this study presents a new technology for effectively shortening the time for carbonation of concrete waste to overcome the time limitation affecting its reuse at real construction sites.

2. Material and Experimental Methods

2.1. Materials

Two types of recycled aggregate samples were used in this work. One (hereafter "Type-A"), was made of 1-year old mortar samples (cured in lime-saturated water). Its water-to-cement (ASTM type I) ratio was 0.4 and its cement-to-sand ratio was 1:3 (wt). Each mortar specimen was crushed using an automatic hammer and the aggregate particles (from 10 to 15 mm in diameter) were separated using sieves for the carbonation experiment. The size of the aggregate was controlled to make the particle size similar to that of the second type.

The other type of recycled aggregate sample (hereafter "Type-B") was recycled coarse aggregate produced by a recycled aggregate company (Hana-Ktec, Republic of Korea). The aggregate was composed of granite and andesite, and the average diameter was ≈10–13 mm. To investigate the effect of the $scCO_2$ sparging process on the recycled aggregate carbonation, the authors requested that the recycled aggregate company does not apply their own carbonation process. It should be noted that Type-A was intended to simulate the most difficult case scenario (lowering the pH of recycled aggregate) and Type-B was chosen to investigate whether the suggested test procedure works with general recycled aggregate, or not.

2.2. Accelerated Carbonation Using Pressurized $scCO_2$ Sparging

The carbonation of recycled aggregate was accelerated by the $scCO_2$ sparging process at laboratory scale. The micro bubbles originating from the $scCO_2$ sparging accelerated the dissolution of portlandite and other calcium silicate hydrates that were attached to the recycled aggregate surface and produced OH^- due to the swirling water and bubble currents in the cell. They also cause CO_2 to dissolve quickly into the water in the cell as well as to penetrate deeply into the micro void spaces of the recycled aggregates. The aqueous CO_2 from the sparged $scCO_2$ dissolution produces carbonic acid and H^+ in the water that are very reactive with the minerals in the recycled aggregate. In this study, chemical reactions (dissociation, secondary mineralization, and precipitation) on the aggregates caused lowered pH in extracted solution. These reactions were investigated in laboratory-scale extraction experiments.

A stainless steel-cylindrical chamber (75 L capacity) was designed as the pressurized $scCO_2$ injection source and was filled with the $scCO_2$ at 110 bar (11 MPa) using a high-pressure syringe pump (260D Teledyne Isco). The outer wall of the chamber was covered with a heat jacket maintained at 50 °C to keep the $scCO_2$ fluid in the chamber. Fifty grams of recycled aggregate and 100 mL of distilled water were poured into a highly pressurized stainless-steel cell (150 mL capacity) and the void space of the cell was filled with $scCO_2$ at 80 bar by a high-pressure syringe pump. The top and the bottom of the cell were connected with a stainless-steel tube and a gas regulator was used to control the pressure in the cell. The $scCO_2$ from the chamber was sparged at 90 bar from the bottom of the cell using a gas regulator. The sparged $scCO_2$ quickly mixed with the water-immersed aggregates due to the pressure difference ($\Delta p = 90\ \text{bar} - 80\ \text{bar} = 10\ \text{bar}$) in the cell. By the sparging process, micro and macro bubbles of $scCO_2$ strongly contacted water molecules, much CO_2 was dissolved into water within a short time, and water containing dissolved CO_2 penetrated deeply into the void spaces of the aggregates, thereby consuming the portlandite in them. The sparged $scCO_2$-water-aggregate reaction was maintained for 1 h and the sparged $scCO_2$ was flushed from the top of the cell at 80 bar through a stainless steel tube attached to the regulator. After 1 h of $scCO_2$ sparging, the cell was allowed to reach standstill for 2 h (total 3 h of reaction time). A stationing time of 2 h after the sparging process was given to provide enough time for calcite precipitation. After the sparging process was finished, aggregate samples were taken out and dried for 3 d in an oven at 50 °C for further analyses.

Carbonation was also performed using the $scCO_2$-water-mortar reaction without $scCO_2$ sparging (hereafter "dissolution reaction" with $scCO_2$) and those results were compared with those from the $scCO_2$ sparging process. After fixing a Teflon beaker inside a 150 mL high-pressure stainless-steel cell, 50 g of Type-A aggregate and 100 mL of distilled water were added to the beaker. Then, $scCO_2$ was injected from the top of the cell at 50 °C and 80 bar using a high-pressure syringe pump (260D Syringe pump, TELEDYNE ISCO, USA) and the outer wall of the cell was covered with a heating jacket to maintain 50 °C. The dissolution reaction time was 3 h, similar to the total time of the $scCO_2$ sparging process (3 h). After the dissolution reaction with $scCO_2$, all aggregate samples were dried for 3 d in an oven at 50 °C.

A schematic of the carbonation process with the $scCO_2$-water-mortar reaction without $scCO_2$ sparging, is shown in Figure 1. A schematic of the carbonation process accelerated by $scCO_2$ sparging, and photographs of the recycled aggregates used in the experiment, are shown in Figure 2. SEM (Scanning Electron Microscope; HITACHI S-2700) images of the $scCO_2$-sparged aggregate surface were compared with those of untreated aggregate surface to visualize the carbonation originating from the $scCO_2$ sparging. The XRD (X-Ray Diffractometer; Rigaku, Ultima IV), EDS (Energy Dispersity Spectroscope; HORIBA EX-250), and TG/DTA (Thermo Gravimetric-Differential Thermal Analyzer; Bruker TG-DTA 2020) analyses for recycled aggregate samples before and after the $scCO_2$ sparging process were also performed to identify the mineralogical and compositional changes occurring during the carbonation process.

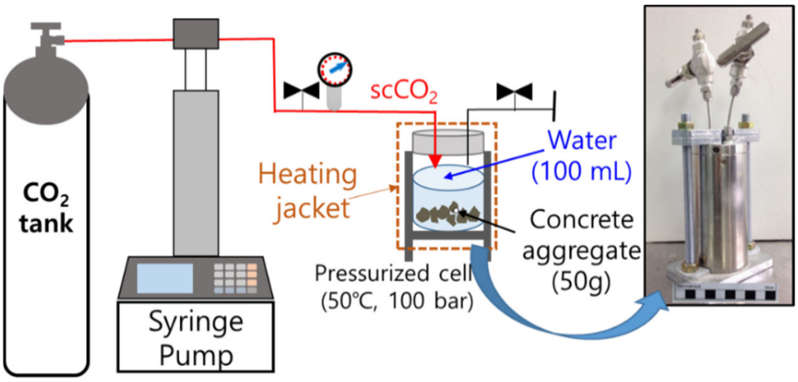


Figure 1. Schematic of the $scCO_2$ dissolution reaction for the carbonation of concrete aggregate.

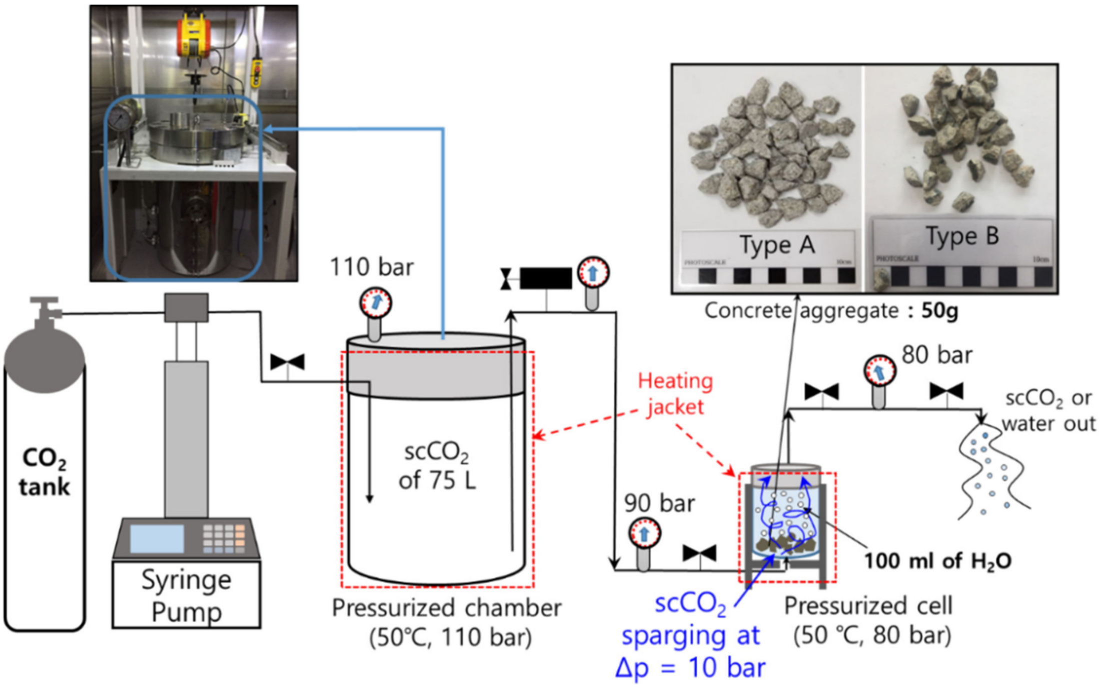


Figure 2. Schematic of the $scCO_2$ sparging process for the carbonation of concrete aggregate.

2.3. Extraction Batch Experiment for Decrease of pH by Carbonation

Aggregate that was either $scCO_2$ sparged or untreated, was used in the extraction experiment to demonstrate decrease of the pH of the aggregate treated with the accelerated carbonation process. The $scCO_2$-sparged aggregates and the untreated aggregates were dried in the oven and 20 g of each aggregate was poured into a glass flask filled with 100 mL of distilled water. The mixed solution in the flask was stirred with a magnetic stirrer for 10 min at 150 rpm. The change in pH of the solution in each flask was measured at different extraction times for 20 d and their results were compared to evaluate the effect of the $scCO_2$ sparging treatment on the reduction of pH in the recycled aggregates.

2.4. Continuous Column Experiment

A continuous column experiment was also performed to identify the pH reduction effect of the carbonation process for massive concrete aggregates (Type-B), considering the non-equilibrium reaction condition in the field. A Kentes glass column (4.8 cm in diameter, 15 cm in length) was gravity-packed with the $scCO_2$-sparged (or untreated) recycled aggregate and 220 L of distilled water (about 20–30 pore volumes of the column) was flushed down into the column from a sprinkler at the top of the column at a constant flow velocity of 1.5 mL/min (the average amount of rainfall in

1 year in Korea was flushed during 24 h). The upper part of the column was covered with glass silica beads (2 mm diameter) in a layer 2 cm thick to maintain the continuous laminar flow at the top of the column. The pH and Ca^{2+} concentrations of the effluent from the bottom of the column were measured at certain time intervals. A schematic of the continuous column experiment is shown in Figure 3. The comparison of pH from the effluent between two columns (one packed with $scCO_2$-sparged Type-B aggregates and one with untreated Type-B aggregates) was performed to investigate the pH reduction of aggregates caused by the carbonation process with $scCO_2$ sparging, and considering the kinetic effect. The column experiment was performed in triplicate and the arithmetic mean was used to investigate the pH reduction of the $scCO_2$-sparged concrete aggregate.

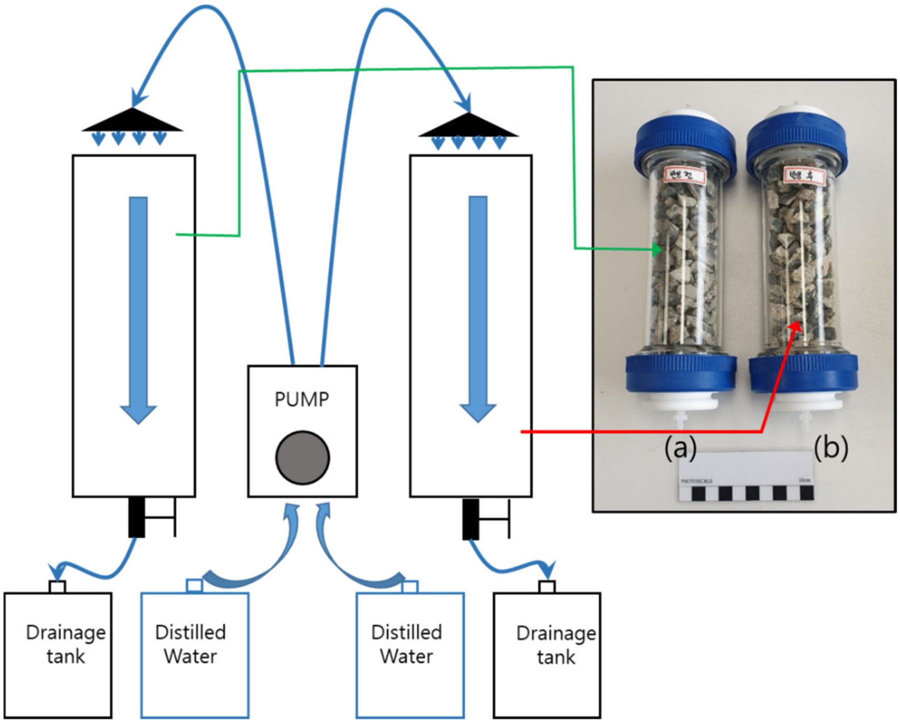


Figure 3. Schematic of the column experiment with Type-B concrete aggregate ((**a**) column packed with untreated aggregates; (**b**) column packed with $scCO_2$ sparged aggregates).

3. Results and Discussion

3.1. Accelerated Carbonation Using Pressurized $scCO_2$ Sparging

The XRD analyses for Type-A aggregate were performed before and after the $scCO_2$ sparging process (1 h for sparging and 2 h for stationing) and the results are shown in Figure 4. Distinct peaks for portlandite ($Ca(OH)_2$) and quartz (SiO_2) were found in the XRD pattern for untreated aggregates. The presence of quartz in Type-A aggregate was from the use of ISO standard sand, which is composed of 100% quartz. After only 1 h of $scCO_2$ sparging, the intensity of the portlandite peaks at 18.09° and 34.09° of 2θ degree, significantly decreased by 80% due to the dissociation of portlandite from the recycled aggregates. Moreover, the intensity of the calcite ($CaCO_3$) peak at 29.40° of 2θ degree increased more than five times. This indicated that the calcite was precipitated as a secondary mineral during the $scCO_2$ sparging process of recycled aggregates. Even the change of XRD peak intensity for a specific mineral did not quantitatively match the change of its amount in the compounds. These results indicate that the transportation of sparged $scCO_2$ and water into the inner parts of the recycled aggregates occurred actively and that they were trapped even in micro pore spaces, where they accelerated the carbonation of the aggregates (dissolution of portlandite and precipitation of carbonate minerals). Even after a significant portion of the portlandite in an aggregate was dissolved and transformed to carbonate precipitate by the $scCO_2$ sparging process, the pH of the water in contact with the treated aggregate might increase when it was exposed to the outside environment later because of the residual portlandite in the treated aggregate. However, continuous carbonation by dissolved CO_2 in a water system can also consume the dissolved Ca^{2+} and OH^-, preventing drastic increase in the pH of treated aggregate after the $scCO_2$ sparging process. The precipitated secondary Ca-bearing carbonates (such as calcites) might also fill up the void spaces produced during the dissolution of portlandite in the aggregate and make the treated aggregate physically more stable (see the next paragraph). They also can act as a buffer medium to maintain the pH of treated aggregate within a certain range by repeating dissolution and precipitation whenever the pH of the water in the external environment changes.

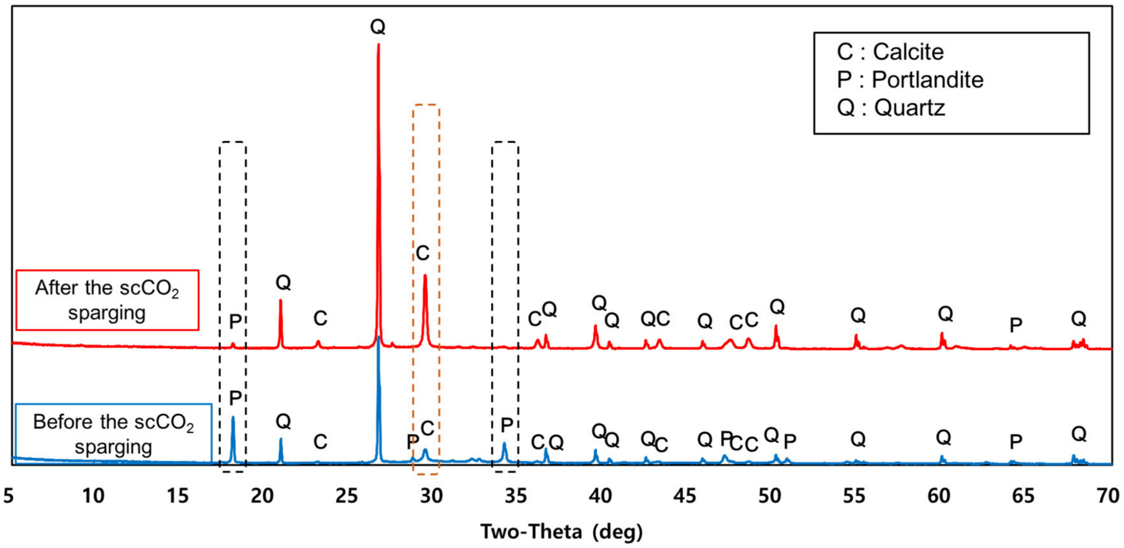


Figure 4. XRD patterns of Type-A concrete aggregate before/after the $scCO_2$ sparging.

The morphology of precipitated calcites on Type-B aggregate after $scCO_2$ sparging was visualized using SEM images, which are shown in Figure 5. Before the $scCO_2$ treatment, the surface of an aggregate cube (10 mm × 10 mm) was polished with sandpaper (200 mesh) and its SEM image showed a preserved mortar surface composed of sand phenocryst and cement groundmass, having void spaces and micro cracks (Figure 5a–c). However, this area was found to be apparently carbonated after only 1 h of $scCO_2$ sparing, and showed the growth of secondary minerals (Figure 5d–g), of which morphology is similar to that of the carbonated region in SEM images of previous carbonation studies [33,34]. In Figure 5c,f, a void space on the aggregate surface (red circle area in Figure 5c) was filled with secondary minerals during the carbonation process (Figure 5f). In many parts of cement matrix pore spaces and phenocryst surfaces, the growth of secondary minerals of various shapes, as well as euhedral calcite crystallites, are observed (Figure 5d,e,g). This is thought to be a direct consequence of making it more stable physically during the carbonation process. From EDS analysis of the secondary minerals upon the $scCO_2$-sparged aggregate, the carbonate minerals identified were mainly composed of Ca, C, and O (Figure 5h,i).

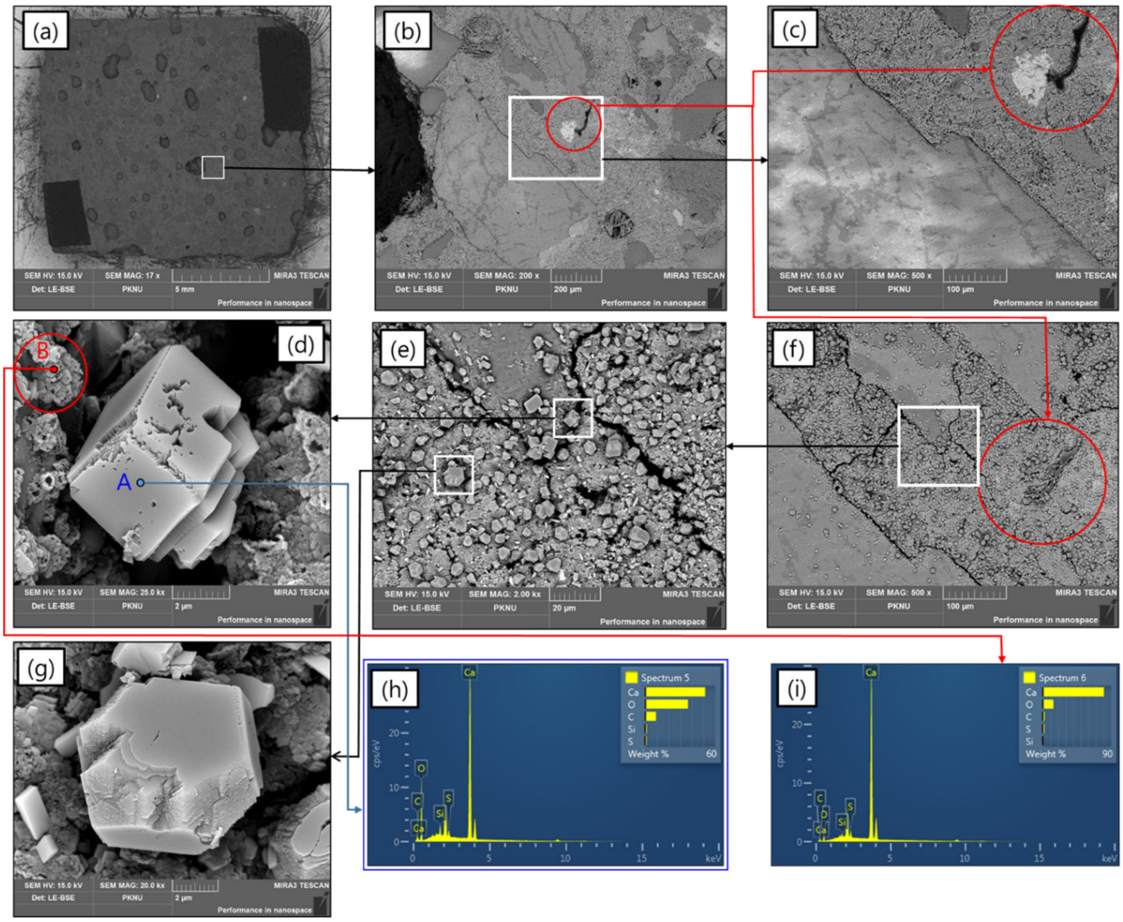
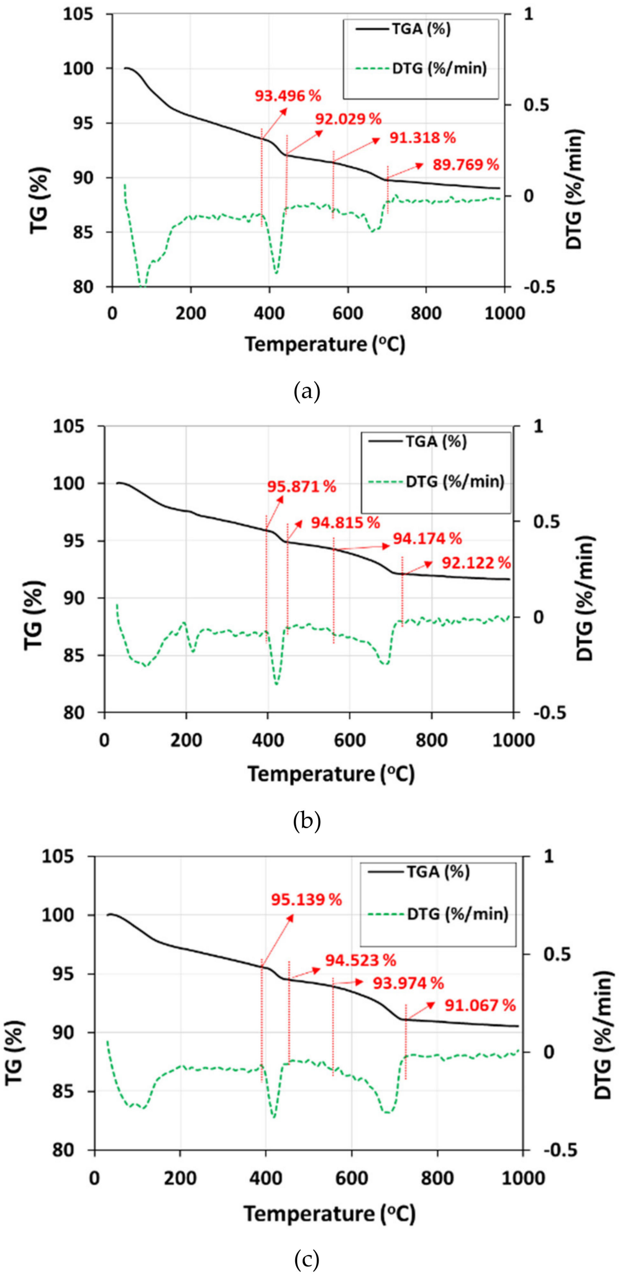


Figure 5. SEM-BSE photomicrographs (**a**–**g**) and EDS peaks (**h**,**i**) of Type-A concrete aggregate surface before/after the $scCO_2$ sparging.

Thermogravimetric analysis of the recycled aggregate before and after $scCO_2$ sparging was also performed to evaluate the weight loss of portlandite and weight gain of calcite due to the carbonation process based on mass loss in certain temperature ranges. Both portlandite and calcite content were determined using weight loss in the range 400–500 °C (portlandite) and in the range 600–800 °C (calcite). This was done using the modified tangential method suggested by [35]. The TG and DTA curves for $scCO_2$-sparged, only $scCO_2$-reacted, and untreated recycled aggregate (Type A) are shown in Figure 6. In the range 50–200 °C, recycled aggregates showed loss of mass originating from the evaporation of free water, decomposition of hydration products (such as ettringite), and dissociation of chemically bound water from calcium silicate hydrates in the micro pores. These occur in both $scCO_2$-treated and untreated aggregates. The untreated aggregate showed greater weight loss in this region than the $scCO_2$-sparged aggregate did (Figure 6a) because ettringite decomposition and disintegration of the calcium-silicate-hydrate structure occurred due to continuous leaching of Ca^{2+} and OH^- ions during the $scCO_2$ sparging process.



(a)

(b)

(c)

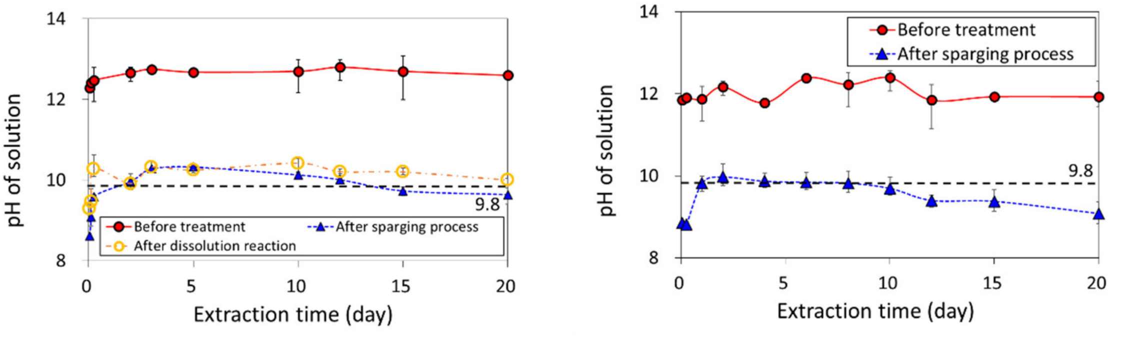
Figure 6. TG/DTA analyses of Type-A aggregates (before treatment (**a**); after the $scCO_2$ dissolution reaction (**b**); after the $scCO_2$ sparging (**c**)).

The mass loss of recycled aggregate between 400 and 500 °C was caused by dihydroxylation from such as decomposition of portlandite ($Ca(OH)_2$) in the cement matrix of the aggregates [35,36]. The untreated Type-A aggregate shows a significant mass loss (1.47% of total mass) at 400–500 °C, the equivalent of 6.03% of the aggregate when it is converted to portlandite molecular ($Ca(OH)_2$) weight (Figure 6a). After 3 h of dissolution reaction with $scCO_2$ and water, the mass loss of aggregate at 400–500 °C was 1.06% of the total mass, showing that the remaining portlandite portion was 4.34 wt% of the total aggregate after the reaction. This suggests that 28.02% of the portlandite in the aggregate was consumed by the dissolution reaction with $scCO_2$ (Figure 6b). However, the $scCO_2$-sparged aggregate presented only 0.62% of mass loss in the same temperature range and the residual portion of portlandite in the aggregate was 2.53 wt%. This suggests that 58.01% of the portlandite in aggregates was depleted after only 1 h of $scCO_2$ sparging (Figure 6c).

The last definite mass loss of aggregates occurred at 600–800 °C, and this was from CO_2 loss due to the decomposition of $CaCO_3$ polymorphs. For the untreated Type-A recycled aggregates, 1.55% of mass loss occurred and this means that the calcium carbonate accounts for 3.52% of Type-A aggregate before the $scCO_2$ treatment. However, after 3 h of dissolution reaction with the $scCO_2$ and water, the mass loss of $scCO_2$-reacted Type-A aggregate at 600–800 °C was 2.52%. Moreover, the $CaCO_3$ covered 4.66 wt% of the reacted aggregate, suggesting that a significant portion of the calcite newly precipitated on aggregates was by the $scCO_2$ dissolution reaction, and that a 32.47% increase of the calcite mass in the aggregate was by the $scCO_2$ dissolution reaction. For 1 h of $scCO_2$ sparging, the greatest loss of $scCO_2$-sparged recycled aggregate in the 600–800 °C range was 2.91% (compared to 1.55% of untreated aggregate). This showed that 87.67% of the calcite mass was precipitated during the 1 h $scCO_2$ sparging process. As a result, the $scCO_2$ sparging process was able to dissolve more than 1.7 times the $Ca(OH)_2$ and to produce more than 1.4 times the $CaCO_3$ compared with only the dissolution reaction with $scCO_2$ and water. From the XRD analysis results, SEM images, and TG/DTA analysis results, the mineralogical transitions, such as the depletion of portlandite and the precipitation of calcite, successfully occurred in recycled aggregate through the carbonation process when using $scCO_2$ sparging. When the $scCO_2$-sparged aggregate is exposed to water outside for a long period of time, the remaining portlandite may start to dissolve, increasing the pH of the water in proportion to the exposure time. However, the portlandite dissolution is no longer active and is limited because of newly precipitated calcite covering the aggregate surface. Moreover, CO_2 is also continuously transported into the water from the atmosphere, which buffers against abrupt increase in the pH of the water. These processes consistently prevent severe increase of the pH of treated aggregate in contact with the water, even after $scCO_2$ sparging. Results from more than 20 d of batch and column extraction experiments also support this assumption (see Sections 3.2 and 3.3).

3.2. Batch Extraction Experiment for pH Neutralization by the Carbonation Process

The change in pH of the solution mixed with recycled aggregate was measured at different extraction times for 20 d and their results are shown in Figure 7. The increase in the pH of the solution comes directly from the dissociation of OH^- from hydroxide minerals such as portlandite in the original recycled aggregates. The average pH of the solution extracted from the original Type-A aggregate abruptly increased from pH 8.6 to 12.7 (maximum of 12.8) within two days of extraction and was maintained at pH > 12.5 since then (Figure 7a). For Type-B aggregate, the maximum pH of the solution was 12.4 and it remained >11.5 because Type-B aggregate includes coarse granite aggregates in concrete blocks and the cement mortar portion (especially portlandite content) in Type-B recycled aggregates is less than in Type-A aggregates (Figure 7b). The average pH of the solution extracted from $scCO_2$-sparged recycled aggregates increases to 10.0 for the first five days of extraction time, of which the trend was similar to that of untreated aggregate. However, the solution pH started to show a downward trend and remained <9.8 for both Type-A and Type-B aggregate after 15 d of extraction time. For Type-A aggregate treated with 3 h of $scCO_2$ dissolution reaction with water, the trend of average pH in the solution resembled that for $scCO_2$-sparged aggregate except when maintained at higher than pH 9.8, suggesting that the $scCO_2$ sparging process is more effective for carbonation of recycled aggregates than the $scCO_2$ dissolution reaction process is (Figure 7a). The results of the extraction batch experiments successfully demonstrated that the 1 h $scCO_2$ sparging was enough to accelerate the carbonation process in concrete aggregates, lowering its pH to <9.8 and allowing them to be safely recycled as subgrade landfill materials and for pavement construction.



(**a**) (**b**)

Figure 7. The pH of extracted solution from concrete aggregate with/without the $scCO_2$ treatment ((**a**) type-A recycled aggregate; (**b**) type-B recycled aggregate).

3.3. Continuous Column Experiment

Two columns packed with Type-B aggregates ($scCO_2$-sparged or untreated aggregates) were designed and a total of 235.0 L of distilled water was used to flush each column. This is similar to the amount of average rainfall for 20 years in South Korea because 2.35 L represents the average rainfall per year in Korea. The pH of the effluent from the bottom of each column was measured at certain time intervals and the results are shown, in Figure 8. For untreated Type-B aggregates, the pH of the effluent increased to 11.8 at the early stages of the flushing and remained above pH 11.0. In the column experiments, the pH of the extraction solution was a little lower than the pH of the solutions in the batch experiments due to the kinetic effect from the non-equilibrium reaction in the column experiments. For untreated recycled aggregates, the pH of the effluent was >9.8, which is the Korean tolerance limit for drainage. Additional pH reduction would be needed to maintain pH <9.8. In the case of 1 h $scCO_2$-sparged aggregates, the pH of the effluent from the column slightly increased early in the extraction process, but remained <9.8 after 15 L of flushing.

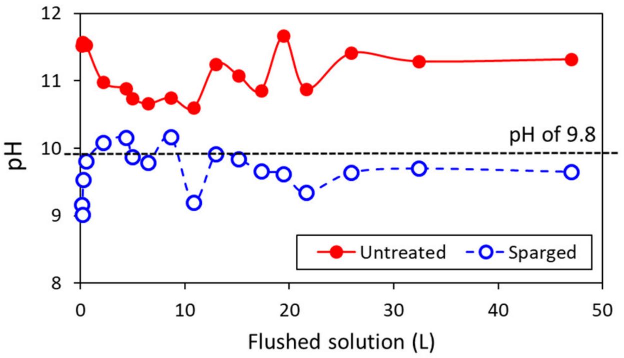


Figure 8. The pH of the effluent from the column packed with untreated and $scCO_2$ sparged Type-B concrete aggregate.

The Ca^{2+} concentration in the effluent from each column was also analyzed during the column experiments and their results are shown in Figure 9. For the untreated aggregates, the Ca^{2+} concentration of the effluent ranged from 20 to 70 mg/L, but for the $scCO_2$ sparged aggregates, it remained below 15 mg/L except for the very early extraction stage (less than three pore volumes). Results suggested that the low Ca^{2+} concentration in the effluent directly resulted in less portlandite remaining in the $scCO_2$-treated aggregate as well as lower Ca solubility of subsequently precipitated silicate or carbonate minerals as secondary minerals other than portlandite [31]. In this study, only 1 h of $scCO_2$ sparging and 2 h of stationing was able to lower the pH of concrete aggregate enough to recycle the concrete waste aggregates at real construction sites exposed to non-equilibrium conditions.

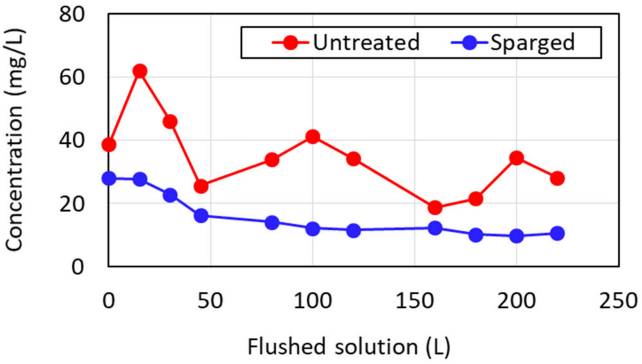


Figure 9. Concentration of Ca^{2+} in the effluent from the column packed with Type-B concrete aggregate.

3.4. Role of Carbonation in the Lowering of pH in Water Contacting $scCO_2$-Treated Aggregate

According to our results shown in Figure 4 (XRD peaks) and Figure 6 (TG results), the presence of portlandite in treated aggregate was clearly observed even after 1 h of $scCO_2$ sparging. When a certain amount of portlandite remained, the pH of water contacting the treated aggregate could rise due to continuing dissolution of the portlandite. However, from our results on the pH measurements in Figure 7 (from batch extraction experiments) and in Figure 8 (from continuous column experiments), the $scCO_2$-sparged aggregate maintained a solution pH <9.8, even after 20 d of extraction time. It is considered that this phenomenon occurred due to the hindering effect of calcite crystals on the abrupt dissolution of the remaining portlandite because a large portion of the surface of the aggregate was covered by carbonate precipitates during the $scCO_2$ sparging process (see SEM images in Figure 5). When CO_2 was continuously dissolved into water from the atmosphere, additional carbonation also occurred that consumed Ca^{2+} and OH^-, ions originating from portlandite dissolution. This buffered the water in contact with the aggregate from increase in pH for a long time. Carbonates formed on the surface of the $scCO_2$-sparged aggregate can also act as the source of HCO_3^-, CO_3^{2-}, and H^+ by additional dissolution, thereby counteracting the increase in pH with OH^-. These results supported the conclusion that only 1 h of $scCO_2$ sparging and 2 h of stationing is enough to maintain the pH of contact-water at pH <9.8, even when some portlandite remains in the treated aggregate.

4. Conclusions

Several previous studies have demonstrated the process of carbonation of concrete using $scCO_2$ treatment, but more than 10 d of treatment time (mostly 30–50 d) was required for successful lowering of the pH of the concrete or the recycled aggregate. In this study, the feasibility of using $scCO_2$-sparging for treating concrete waste to provide a recycled construction resource was evaluated using quantitative results of batch and column experiments, as well as from mineralogical and visualization analyses. Even when using only 1 h of $scCO_2$ sparging and 2 h of stationing, the carbonation of concrete aggregate was significantly accelerated. Moreover, the pH of the aggregate was lowered to <9.8 for a long time. As the main cause of pH lowering, significant mineralogical transition has also been observed on the surface of concrete aggregates, including such as portlandite depletion and the precipitation of calcite. As the operation of $scCO_2$ sparging of recycled aggregates is fairly straightforward and provides superior reactivity, it is hoped that the usage of the $scCO_2$ sparging process will be regarded as one of the most effective technologies for accelerating carbonation, and therefore for maintaining low pH in the recycled aggregate for a long time. This study focused on the rapid carbonation of concrete aggregate to reuse in various environments and further studies are required in areas of the estimation for the CO_2 reduction by carbonation of recycled concrete aggregate in life-cycle scale and quantitatively understanding its carbonation behavior [37].

Author Contributions: M.L. and J.P. conceived and designed the experiments; J.P. and J.L. performed the experiments and the data analyses; C.-W.C. and S.W. contributed materials and data interpretation; M.L. wrote the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Korea Agency for Infrastructure Technology Advancement (KAIA) grant funded by the Ministry of Land, Infrastructure and Transport (Grant 19CTAP-C151965-01) and by the grant (2019002470002) from Korea Ministry of Environment as "The SEM (Subsurface Environmental Management) projects".

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

References

1. Jo, H.; Ji, S.; Shin, H.; Jo, J.; Kim, J.; Bang, J.-H. Study on the Classification of Fine Particles by Using a Multi-step Hydrocyclone for the Recycling of Waste Concrete Slurry. *J. Korean Soc. Miner. Energy Resour. Eng.* **2019**, *56*, 73–78. [CrossRef]
2. Kim, J.; Tae, S.; Kim, R. Theoretical study on the production of environment-friendly recycled cement using inorganic construction wastes as secondary materials in South Korea. *Sustainability* **2018**, *10*, 4449. [CrossRef]
3. Ossa, A.; García, J.L.; Botero, E. Use of recycled construction and demolition waste (CDW) aggregates: A sustainable alternative for the pavement construction industry. *J. Clean. Prod.* **2016**, *135*, 379–386. [CrossRef]
4. Rahman, M.T.; Mohajerani, A.; Giustozzi, F. Recycling of Waste Materials for Asphalt Concrete and Bitumen: A Review. *Materials (Basel)* **2020**, *13*, 1495. [CrossRef] [PubMed]
5. Peng, Z.; Shi, C.; Shi, Z.; Lu, B.; Wan, S.; Zhang, Z.; Chang, J.; Zhang, T. Alkali-aggregate reaction in recycled aggregate concrete. *J. Clean. Prod.* **2020**, *255*. [CrossRef]
6. Tam, V.W.Y.; Butera, A.; Le, K.N.; Li, W. Utilising CO_2 technologies for recycled aggregate concrete: A critical review. *Constr. Build. Mater.* **2020**, *250*, 118903. [CrossRef]
7. Tabsh, S.W.; Abdelfatah, A.S. Influence of recycled concrete aggregates on strength properties of concrete. *Constr. Build. Mater.* **2009**, *23*, 1163–1167. [CrossRef]
8. Tu, T.Y.; Chen, Y.Y.; Hwang, C.L. Properties of HPC with recycled aggregates. *Cem. Concr. Res.* **2006**, *36*, 943–950. [CrossRef]
9. Tam, V.W.Y.; Tam, C.M. A review on the viable technology for construction waste recycling. *Resour. Conserv. Recycl.* **2006**, *47*, 209–221. [CrossRef]
10. Rao, A.; Jha, K.N.; Misra, S. Use of aggregates from recycled construction and demolition waste in concrete. *Resour. Conserv. Recycl.* **2007**, *50*, 71–81. [CrossRef]
11. Taylor, H.F.W. *Cement Chemistry*, 2nd ed.; Academic Press: London, UK, 1997.
12. Moreno-Pérez, E.; Hernández-Ávila, J.; Rangel-Martínez, Y.; Cerecedo-Sáenz, E.; Arenas-Flores, A.; Reyes-Valderrama, M.I.; Salinas-Rodríguez, E. Chemical and mineralogical characterization of recycled aggregates from construction and demolition waste from Mexico city. *Minerals* **2018**, *8*. [CrossRef]
13. Lee, J.C.; Song, T.H.; Lee, S.H. Leaching behavior of toxic chemicals in recycled aggregates and their alkalinity. *J. Mater. Cycles Waste Manag.* **2012**, *14*, 193–201. [CrossRef]
14. Galvín, A.P.; Ayuso, J.; Jiménez, J.R.; Agrela, F. Comparison of batch leaching tests and influence of pH on the release of metals from construction and demolition wastes. *Waste Manag.* **2012**, *32*, 88–95. [CrossRef] [PubMed]
15. De Michelis, I.; Ferella, F.; Beolchini, F.; Olivieri, A.; Vegliò, F. Characterisation and classification of solid wastes coming from reductive acid leaching of low-grade manganiferous ore. *J. Hazard. Mater.* **2009**, *162*, 1285–1291. [CrossRef] [PubMed]
16. Gil, S.W. Long-term master planning for environment-friendly process and recycling promotion of Construction Wastes. *J. Korean Recycl. Constr. Resour. Inst.* **2006**, *2*, 8–12.
17. Lee, W.P.; Lee, C.H. The Use of Recycled Aggregate and Recycled Products Revitalization. *J. Korean Recycl. Constr. Resour. Inst.* **2014**, *9*, 18–28. [CrossRef]
18. Hong, S.W.; Park, S.; Ahn, Y.S. A Research on the Efficient Way and the Analysis of the Actual Condition for Recycling Waste Concrete Discharged as Construction Waste. *J. Archit. Inst. Korea* **2004**, *20*, 97–104.
19. Martín, D.; Flores-Alés, V.; Aparicio, P. Proposed methodology to evaluate CO_2 capture using construction and demolition waste. *Minerals* **2019**, *9*. [CrossRef]
20. Atiş, C.D. Accelerated carbonation and testing of concrete made with fly ash. *Constr. Build. Mater.* **2003**, *17*, 147–152. [CrossRef]

21. Turcry, P.; Oksri-Nelfia, L.; Younsi, A.; Aït-Mokhtar, A. Analysis of an accelerated carbonation test with severe preconditioning. *Cem. Concr. Res.* **2014**, *57*, 70–78. [CrossRef]
22. Cui, H.; Tang, W.; Liu, W.; Dong, Z.; Xing, F. Experimental study on effects of CO_2 concentrations on concrete carbonation and diffusion mechanisms. *Constr. Build. Mater.* **2015**, *93*, 522–527. [CrossRef]
23. Silva, R.V.; Neves, R.; De Brito, J.; Dhir, R.K. Carbonation behaviour of recycled aggregate concrete. *Cem. Concr. Compos.* **2015**, *62*, 22–32. [CrossRef]
24. Zhan, B.; Poon, C.S.; Liu, Q.; Kou, S.; Shi, C. Experimental study on CO_2 curing for enhancement of recycled aggregate properties. *Constr. Build. Mater.* **2014**, *67*, 3–7. [CrossRef]
25. Kou, S.C.; Zhan, B.J.; Poon, C.S. Use of a CO_2 curing step to improve the properties of concrete prepared with recycled aggregates. *Cem. Concr. Compos.* **2014**, *45*, 22–28. [CrossRef]
26. Duan, Z.; Sun, R. An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. *Chem. Geol.* **2003**, *193*, 257–271. [CrossRef]
27. Wiebe, R.; Gaddy, V.L. The Solubility of Carbon Dioxide in Water at Various Temperatures from 12 to 40° and at Pressures to 500 Atmospheres. Critical Phenomena. *J. Am. Chem. Soc.* **1940**, *62*, 815–817. [CrossRef]
28. Mathur, V. Precisely Sized Precipitated Calcium Carbonate (PCC) Crystals of Preselected Crystal Habit, Manufactured Using Pressure Carbonation. U.S. Patent Application NO 09/791,433, 24 January 2002.
29. Declet, A.; Reyes, E.; Suárez, O.M. Calcium carbonate precipitation: A review of the carbonate crystallization process and applications in bioinspired composites. *Rev. Adv. Mater. Sci.* **2016**, *44*, 87–107.
30. Korchef, A.; Touaibi, M. Effect of pH and temperature on calcium carbonate precipitation by CO_2 removal from iron-rich water. *Water Environ. J.* **2019**. [CrossRef]
31. Chung, C.W.; Lee, M.; Kim, S.O.; Kim, J. The pH reduction of the recycled aggregate originated from the waste concrete by the $scCO_2$ treatment. *Econ. Environ. Geol.* **2017**, *50*, 257–266. [CrossRef]
32. De Sena Costa, B.L.; de Oliveira Freitas, J.C.; Santos, P.H.S.; de Araújo Melo, D.M.; da Silva Araujo, R.G.; de Oliveira, Y.H. Carbonation in oil well Portland cement: Influence of hydration time prior to contact with CO_2. *Constr. Build. Mater.* **2018**, *159*, 252–260. [CrossRef]
33. Hidalgo, A.; Domingo, C.; Garcia, C.; Petit, S.; Andrade, C.; Alonso, C. Microstructural changes induced in Portland cement-based materials due to natural and supercritical carbonation. *J. Mater. Sci.* **2008**, *43*, 3101–3111. [CrossRef]
34. Ruiz-Agudo, E.; Kudłacz, K.; Putnis, C.V.; Putnis, A.; Rodriguez-Navarro, C. Dissolution and carbonation of portlandite [$Ca(OH)_2$] single crystals. *Environ. Sci. Technol.* **2013**, *47*, 11342–11349. [CrossRef] [PubMed]
35. Kim, T.; Olek, J. Effects of sample preparation and interpretation of thermogravimetric curves on calcium hydroxide in hydrated pastes and mortars. *Transp. Res. Rec.* **2012**, 10–18. [CrossRef]
36. Moon, H.; Ramanathan, S.; Suraneni, P.; Shon, C.S.; Lee, C.J.; Chung, C.W. Revisiting the effect of slag in reducing heat of hydration in concrete in comparison to other supplementary cementitious materials. *Materials (Basel)* **2018**, *11*, 1847. [CrossRef]
37. Visintin, P.; Xie, T.; Bennett, B. A large-scale life-cycle assessment of recycled aggregate concrete: The influence of functional unit, emissions allocation and carbon dioxide uptake. *J. Clean. Prod.* **2020**, *248*. [CrossRef]