

Assessment of Ammoniacal Leaching Agents for Metal Cation Extraction from Construction Wastes in Mineral Carbonation

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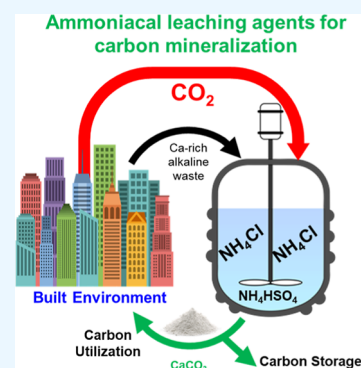


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ABSTRACT: The use of carbon mineralization to produce carbonates from alkaline industrial wastes is gaining traction as a method to decarbonize the built environment. One of the environmental concerns during this process is the use of acids, which are required to extract Ca^{2+} or Mg^{2+} from the alkaline waste to produce carbonates. Conventionally, acids such as hydrochloric, nitric, or sulfuric are used which allow for the highest material recovery but are corrosive and difficult to regenerate as they are utilized in a linear fashion and generate additional process waste. An alternative is to use regenerable protonatable salts of ammonia, such as ammonium chloride (AC) or ammonium sulfate, the former of which is used globally during the Solvay process as a reversible proton shuttle. In this study, we show that regenerable ammonium salts, such as AC (NH_4Cl) and ammonium bisulfate (NH_4HSO_4), can be effectively used for material recovery and the production of calcium carbonate during the leaching of waste cement paste as an alternative to conventional acids such as HCl. Leaching kinetics, postreaction residue, and carbonate characterization were performed to assess the productivity of this system and potential uses of these materials downstream. The stabilization of vaterite was observed in the case of AC leaching, suggesting its importance in the kinetic stability of vaterite and suppression of calcite nucleation. Overall, this study motivates the use of alternative leaching agents, such as salts of ammonia, to facilitate material recovery and carbon capture from alkaline industrial wastes.



1. INTRODUCTION

1.1. Ex Situ Carbon Mineralization as a Pathway for Material Recovery from Construction and Demolition Waste.

Carbon mineralization is a promising pathway for carbon dioxide removal (CDR) from either point-source or atmospheric emissions.^{1–4} It involves the capture of CO_2 by producing a carbonate, generally MgCO_3 or CaCO_3 , which comes from reacting an alkaline material with CO_2 .⁵ The abundance of alkaline wastes from heavy industries, such as steel production (slags), the built environment (construction and demolition waste, C&DW), and combustion processes (fly/bottom ashes), makes ex situ carbon mineralization methods useful for not only CDR but also as a method of waste reduction.^{1,6,7} Considerable amounts of alkaline industrial wastes are bound for landfills, especially in the U.S., which then occupies vast amounts of land; approximately 250 million tons of C&DW is landfilled each year (2018).⁸ The decarbonization of the built environment itself is quite challenging due to the intrinsic nature of the materials used in its construction. Cementitious materials contribute to roughly 8% of the global CO_2 emissions during their manufacture, a result of CO_2 release during both the roasting of limestone from both calcination and process emissions required to maintain a kiln temperature of $>1400\text{ }^\circ\text{C}$.^{9,10} Previous research has shown that two-step dissolution and carbonation are effective ways to recover material from alkaline industrial wastes.¹¹ During dissolution, Ca and Mg can be recovered

along with other useful ancillary elements, such as Fe, Al, Si, Ti, and S. Based on the feedstock, rare-earth elements or platinum group metals could also be recovered;^{12,13} this is especially true for ashes of waste-to-energy (WtE)-type processes.^{14,15} The ancillary elements are generally recovered during a pH-swing step which bridges the dissolution and carbonation processes; the former of which operates at low (<3) pHs and the latter at high pHs (>10).¹² During the carbonation reaction, Mg or Ca carbonates are precipitated through their reaction with CO_2 gas which is sparged into stirred tank reactors.^{16,17} The pH is controlled using a base, such as NaOH or NH_4OH , which helps to promote the dissolution of CO_2 and speciation of carbonate ions in the bulk. This precipitated calcium carbonates (PCCs) have many industrial uses, and its production within the context of carbon capture utilization and storage (CCUS) makes it an attractive commodity.¹⁸ PCC is commonly used as a filler in numerous industrial processes, including papermaking, paint production, and in the built environment.^{19,20} Recent studies have

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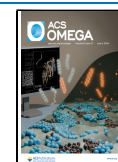


Table 1. Various Acid (Proton) Sources That Are and Could be Used During Hydrometallurgical Leaching Processes for Material Recovery Showing Their Chemical Formulas, $pK_a(s)$, Leaching Effectiveness, and Potential for Regeneration

acid source	chemical formula	$pK_a(s)$	leaching effectiveness	regeneration potential
hydrochloric acid	HCl	-1.74	extremely effective ^{27,28}	low; need external energy (e.g., electro dialysis)
ammonium chloride	NH ₄ Cl	9.24	effective ^{5,43,54}	high; regenerated by weak acid (e.g., CO ₂) ⁴³
ammonium bisulfate	(NH ₄)HSO ₄	~1.9	initially high due to acid strength; free Ca concentration low due to gypsum precipitation ^{45,55}	high; regenerated by heat and weak acid (e.g., CO ₂) ⁵⁶
carbonic acid	H ₂ CO ₃ , HCO ₃ ⁻	3.49; 6.45	poor; Ca-carbonate passivation ⁴¹	N/A; source new CO ₂

showcased the potential uses of the metastable polymorphs of PCC, such as vaterite and aragonite, as new construction materials and fillers reincorporated into the built environment. Vaterite could be used to accelerate the hydration of ordinary Portland cement (OPC), whereas aragonite could be used as a rheological modifier for cement flowability applications.^{21–24} Carbon mineralization to produce useful upcycled materials from C&DW is a promising pathway to facilitate decarbonization of certain areas of the build environment.

1.2. Alternative Leaching Agents for Conventionally Used Inorganic Acids during the Dissolution of Alkaline Industrial Wastes. The dissolution of alkaline waste generally requires a strong acid to facilitate the removal of elements of interest from the waste particles.^{25,26} Previous studies have shown that protons assist in the hydrolyzation or cleavage of X–Si–O bonding networks within the alkaline material, where X can be Ca, Mg, Si, Al, Fe, etc.^{27–29} In the case of Si-rich materials, such as mine tailings, mineral wastes, or even C&DW, the reprecipitation of silica on the surface of dissolving particles or incongruent dissolution of Si vs other elements (e.g., “Si-passivation”) can block the extraction of material of interest.^{30,31} However, abrasive materials, such as internal grinding media, can assist in boosting yields through the disruption of this passivation layer, which was shown by Rim et al. (2020) in the case of serpentine waste.³⁰ The manufacture of conventional inorganic acids, such as HCl, can be carbon-intense. Generally, HCl is manufactured by the chlor-alkali process, which electrolyzes brines to produce H₂ and Cl₂ gas, the both of which are then reacted to generate HCl gas.³² H₂ can also come from steam methane reforming as well. Overall, the process generates approximately 0.5 kg–CO₂/kg product with many hazardous side products being generated, such as caustics.^{33,34} Cheap and abundant renewable energy (e.g., solar and wind) could significantly reduce the intrinsic carbon footprint of its manufacture. The replacement of HCl for conventional hydrometallurgical processes with regenerable salts that can be recycled (e.g., NH₄Cl) is also attractive from a circularity point of view and the reduction of the use of extremely corrosive materials. Organic acids, such as acetic acid, can also be used effectively during the leaching of alkaline wastes. Teir et al. (2007) reported high recovery and production of calcium from steel slag³⁵ using acetic acid during dissolution, whereas Mun and Cho (2013) reported the recovery of calcium from waste cement using the same.³⁶ Organic acids can carry a higher carbon-footprint, with acetic acid, which is conventionally produced through methanol carbonylation, reaching upward of 1.9 kg–CO_{2-eq}/kg material.^{37,38} Organic acids can also pose an issue during the carbonation portion of ex-situ carbon mineralization as some of them, such as citrate and oxalate, are excellent calcium

chelators.^{39,40} This makes their carbon capture and carbonate production potential much lower than those of other inorganic acids, such as HCl and HNO₃. CO₂ itself, as carbonic acid, has previously been shown to also be a potential leaching agent.²⁵ The pCO₂ process uses CO₂ to facilitate both the dissolution and carbonate of Mg- or Ca-rich waste materials.²⁵ Unfortunately, although a green solvent, CO₂ dissolution usually results in low yields due to the weak nature of carbonic acid.^{41,42} Solubility limits of CO₂ in aqueous media as well as potential precipitation of calcite in the dissolution reactor are potential drawbacks to the use of carbonic acid in these systems.²⁵ Salts of ammonia, such as ammonium chloride (AC), have been shown to be effective leaching agents of alkaline wastes. Significant research has been performed on the recovery of metals from minerals and steel slags by using ammoniacal salts. Hall et al. (2014) achieved single-pass Ca extractions of 40% using AC as the leach with blast furnace slag.⁴³ Wang and Maroto-Valer (2011) proposed a regenerable leaching and carbonation process using ammonium bisulfate (ABS) as the proton carrier/leaching agent^{5,44} based on their research, and Highfield et al. (2012) proposed a similar solid–solid ABS flux system based on their work with slags.⁴⁵ Although carbonic acid is more acidic than AC, the precipitation potential of carbonate salts of calcium makes it a poor choice for ex situ carbon mineralization processes (Table 1). Nonconventional sources of acidity could be utilized in CCUS methods, which employ mineralization to produce carbonates if they can be produced through non-CO₂ intensive pathways.

1.3. Utilizing Chloride and Sulfate Salts of Ammonia for Tandem Dissolution of Alkaline Wastes and Control of Calcium Carbonate Morphology during Carbon Mineralization. Another attractive aspect of the use of ammonia salts during dissolution of alkaline wastes is their regeneration potential and mild acidity. Currently, ammonia and AC are already used as a proton looping agent in the Solvay process, and this chemistry has been widely studied and implemented at scale.^{46–48} Figure 1 shows the conventional configuration of the Solvay, or ammonia soda, process used in the production of sodium carbonate (soda ash; Na₂CO₃) from brines (i.e., NaCl) and limestone (i.e., CaCO₃). In this process, lime is roasted to release CO₂, which is used to carbonate brine in the presence of ammonia (NH₃). This generates AC (NH₄Cl) and sodium bicarbonate (NaHCO₃) which are roasted to produce soda ash. The ammonia used for brine carbonation is regenerated by reacting NH₄Cl with the lime (CaO) produced during limestone calcination. This reaction generates calcium chloride (CaCl₂) and NH₃, circularizing the process. This reaction chemistry could be exploited to reutilize the weakly acidic ammonium salts after the dissolution of

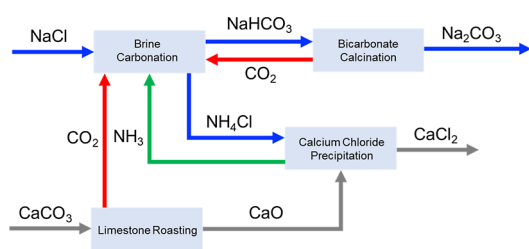


Figure 1. Conventional Solvay or ammonia-soda process which is a method to produce soda as Na_2CO_3 from the carbonation of brine using CO_2 from the roasting of limestones (CaCO_3). Ammonia is used as a reversible proton shuttle, facilitating both carbonation (basic activity) and calcium chloride precipitation (acidic activity).

alkaline wastes for carbon mineralization. Table 1 shows a comparison between the various acids/proton sources that can be used for hydrometallurgical material recovery processes. While HCl generally offers the highest extraction efficiency due to its low $\text{p}K_{\text{a}}$, it is difficult to regenerate, especially in situ or on-site. Although AC is a weak acid, it can readily react with a strong base, in this case the C&DW, to facilitate material recovery. Its regeneration potential is high, especially since the corresponding base could be regenerated via a weak acid (e.g., CO_2). This cycle of green chemistry presents a number of advantages against conventional inorganic leaching methods, especially in the context of C&DW upcycling and cement decarbonization.

Ammonium salts and ammonia have also been shown to be an important component of metastable polymorph control during carbon mineralization, especially in the precipitation of vaterite over calcite.^{49–52} These species are theorized to kinetically suppress calcite nucleation, allowing vaterite to freely nucleate and remain stable in the aqueous crystallization reaction mixture for time scales long enough to be purified.^{19,53} The use of ammonium species upstream in the reactor could be important if calcium carbon polymorph control is desired downstream during carbon mineralization components. The tunability and versatility of these salts make them ideal candidates for upcycling and carbon capture applications in the treatment of alkaline industrial wastes.

In this study, we investigate the leaching of waste hydrated cement paste (HCP) using alternative leaching agents, such as AC and ammonium bisulfate, to examine their effectiveness in replacing conventional acids, such as HCl. Dissolution kinetics are reported and insights into the mechanisms of dissolution are analyzed through comparisons in the rate of Ca extraction vs Si extraction.^{27,28} The unreacted residue recovered from the leaching reactor through filtration is characterized to better understand its material properties and the extent of calcium removal afforded. The dissolution reaction liquors are then carbonated using gaseous CO_2 and the morphology and associated properties of the PCC produced are analyzed for its potential uses. Specific attention is given toward the metastable polymorph control of PCC afforded by the use of ammonium salts, and the isolation of vaterite is observed in the case of AC, while pure calcite is observed when ABS is used. This study extends previous studies involving alternative leaching agents to the processing of construction and demolition waste, which is a growing source of waste and potential for CCUS with tandem material recovery.

2. MATERIALS AND METHODS

2.1. Materials. The C&DW utilized in this project was a 1 yr old waste HCP which was created in-house and used in similar leaching studies.²⁵ The cement paste was analyzed via both inductively coupled plasma-optical emission spectrometry (ICP-OES) digestion and X-ray fluorescence (XRF) analysis which revealed a total Ca, Si, Fe, and Al contents of 44.0, 14.0, 2.3, and 1.3 wt %, respectively. The cement paste was sieved to maintain a tight particle size range of 120–210 μm . Previous work into a similar material revealed that the main crystalline phases present are portlandite, calcium silicate trihydrate/dihydrate (alite, belite), and calcium aluminoferrite. 37 wt % HCl (Sigma-Aldrich Chemicals, USA) and 25 wt % NaOH (Sigma-Aldrich Chemicals, USA) were utilized during the control leaching and the carbonation reactions, respectively. 100% bone-dry CO_2 was purchased from Airgas, USA, and utilized for the carbonation experiment. AC (99.998%, trace metal basis, Alfa Aesar, USA) and ammonium hydrogen sulfate (99.99%, trace metal basis, Sigma-Aldrich Chemicals, USA) were purchased and used as leaching agents.

2.2. Methods. **2.2.1. Dissolution Reactor Design and Operation.** The dissolution of the waste HCP was carried out in a 500 mL jacketed ChemGlass (Vineland, NJ, USA) reactor equipped with overhead magnetic stirring. Leaching was performed at a solid-to-liquid ratio of 1 wt % over the course of 60 min at a temperature of 25 $^{\circ}\text{C}$ for 1 h at a stirring rate of 900 rpm. Deionized water (Millipore) was used as the aqueous solvent for dissolution. In the control case using HCl, the pH was maintained at 3 through the continual addition of acid. In the leaching using AC or bisulfate, 0.1 or 0.5 M stocks were prepared prior to the addition of the waste cement at the beginning of the experiment. When CO_2 was used as the leaching media, deionized water was saturated with 100% CO_2 at either 150 or 1000 $\text{mL} \times \text{min}^{-1}$ for 5 min prior to the addition of waste HCP for leaching. After the dissolution was finished, the reaction mixture was quickly filtered using a 5 μm Whatman (GE, USA) Buchner filter. The postextract reactor residue (PERR) was then washed with 70% EtOH prior to being dried overnight in a vacuum oven at 80 $^{\circ}\text{C}$.

2.2.2. Carbonation of Ca-Rich Leachate Liquor. The recovered dissolution reactor liquid from leaching was pH adjusted using NaOH (25 wt %) to pH 10 to remove any ancillary elements such as Si, Fe, and Al which were also recovered during leaching. This was performed only if the pH of the leaching reactor was below 10 prior to carbonation (e.g., HCl leaching). The range of pHs after leaching can be observed in Figure S1 and is highly dependent on the concentration of ammonium salt or acid utilized. This pH-swing process was performed to cleanse the dissolution liquor prior to carbonation and has been previously shown to boost the purity of the produced PCC. Carbonation was carried out at pH 10 over the course of 20 min at a CO_2 -addition rate of 150 $\text{mL} \times \text{min}^{-1}$ at a stirring rate of 600 rpm. A metal microsparger was used to deliver the CO_2 to the ChemGlass carbonation reactor. After the reaction, the mixture was filtered in a similar manner as the dissolution reaction and the PCC was rinsed with 70% EtOH prior to being dried overnight in a vacuum oven at 80 $^{\circ}\text{C}$.

2.2.3. Characterization Techniques. Kinetic analysis of the dissolution reaction was performed using Agilent 5110 ICP-OES. Samples were isolated at various time points during leaching and quickly filtered using a 0.22 μm syringe filter prior

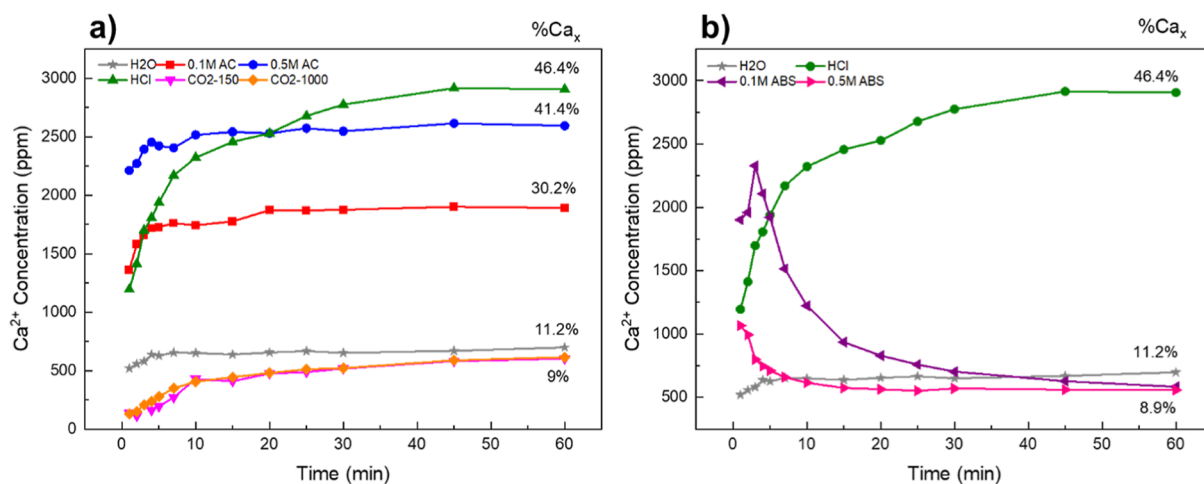


Figure 2. (a) Leaching kinetics for Ca²⁺ and reported extraction yields over 60 min from waste HCP using water, HCl (pH 3), 0.1/0.5 M AC, and CO₂ bubbling at 150 and 1000 mL × min⁻¹. (b) Leaching kinetics for the same using 0.1 M/0.5 M ABS with water and HCl kinetics replotted for clarity. 150 and 1000 denote the CO₂-flow rate (in mL × min⁻¹) used for carbonic acid leaching. The final pH after leaching is shown in Figure S1.

to being diluted 100× and quenched in 2% HNO₃. The ICP-OES was used to track the accumulation of Ca, Si, Fe, and Si present in the leaching liquor. The produced solids from both the leaching reaction, the postextraction reactor residue (PERR), and from the carbonation reaction, the PCC, were subjected to a variety of characterization techniques. Powder X-ray diffraction (PXRD) was utilized to analyze the presence of crystalline phases after leaching and the polymorphs of calcium carbonate, vaterite, aragonite, and calcite present after carbonation. Panalytical X'pert3 XRD (Malvern Panalytical) using a 3 kW Cu X-ray generator with a PIXcel 1d detector was used. The PXRD data was refined with open-source material analysis using diffraction (MAUD) software with relevant crystal structures being sourced from the crystallography open database.

A Quantachrome NoveE Brunauer–Emmett–Teller (BET) analyzer was utilized to study changes in surface area of the produced materials, and Nicolet iSS0 Fourier transform infrared (FTIR) spectrometry was used to exam the surface bonding structure of the residues. The PCC was further analyzed via scanning electron microscopy (SEM) to examine its morphology. A Zeiss Sigma VP SEM was used to collect images from samples that were sputter-coated for 20 s with AuPd before imaging. The particle sizes of the residues and PCC were analyzed with an LS 13,320 Beckman Coulter particle size analyzer. Samples were suspended in ethanol prior to injection into the water column to serve as a dispersant over a 90 s measurement time using three distinct filters. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 TGA instrument. Samples were loaded onto a tared Pt pan and analyzed from room temperature to 1000 °C at a ramp rate of 10 K × min⁻¹. Shimadzu 7200 energy-dispersive X-ray fluorescence spectrometry (ED-XRF) was used to analyze the elemental composition of the residues.

3. RESULTS AND DISCUSSION

3.1. Leaching Kinetics of Demolition Wastes Utilizing Alternative Proton Sources. Figure 2a,b shows the leaching kinetics over the course of 1 h for the waste HCP at a slurry density of 1 wt % using various proton sources. While HCl at pH 3 resulted in the highest percent of Ca extraction at 46.4%, 0.5 M AC was close behind at a single-pass extraction

efficiency of 41.4% (Figure 2a). The final reactor pH of the HCl leachate was 3, while the pH was approximately 9 for the 0.5 M AC case (Figure S1). These results complement those obtained by He et al. (2013), who revealed that ammoniacal agents, such as AC and ammonium nitrate, were able to achieve between 35 and 40% Ca extraction in a single-pass conversion.⁵⁷ The AC leaching curves reached saturation quickly versus the HCl control, which took almost 60 min to reach completion. This phenomenon is due to proton availability; in the former, the pH was not controlled and all the leaching agent was present at the start of the reaction, but in the latter, the pH was continually maintained at 3 (Figure S1). In the HCl leaching cases, 3–14× more protons were present in the reactor than either AC or ABS. Zhang and Moment (2023) explored this behavior with the leaching of waste concrete in 37 wt % HCl, where they observed a similar extraction of Ca regardless of when the acid was added during the process (e.g., all-at-once or continual dosing).²⁷ In the same leaching system using ABS, high initial Ca concentrations of upward of 2500 ppm were achieved within 5 min, but the final aqueous Ca concentration dropped to about 600 ppm, corresponding to a Ca aqueous extraction of 9% (Figure 2b). This is due to the precipitation of gypsum (CaSO₄·2H₂O) which is likely a result of the abundance of sulfate ions that can react with calcium at pH values greater than 2 (Figure S2). Nonetheless, the extraction of Ca from the cement matrix and reprecipitation as gypsum could be a useful method of employing a regenerable system for Ca extraction and conversion, as others such as Ding et al. (2023) and Wang and Maroto-Valer (2011) have proposed.^{44,58} Previous studies in our group have established that the activation energy of this waste HCP with HCl is roughly 20.4 kJ/mol, with increased Ca²⁺ extraction and decreased Si extraction occurring at elevated temperatures.²⁹ In this case, higher extraction temperatures would likely lead to increased Ca recovery due to greater kinetic energy imparted to the system; however, the degassing of ammonia from the aqueous phase could also be increased as this is a function of temperature. Thus, the reactor system needs to be properly tuned in the case of ammonia-based leaching agents to optimize elemental recovery and prevent solvent loss.

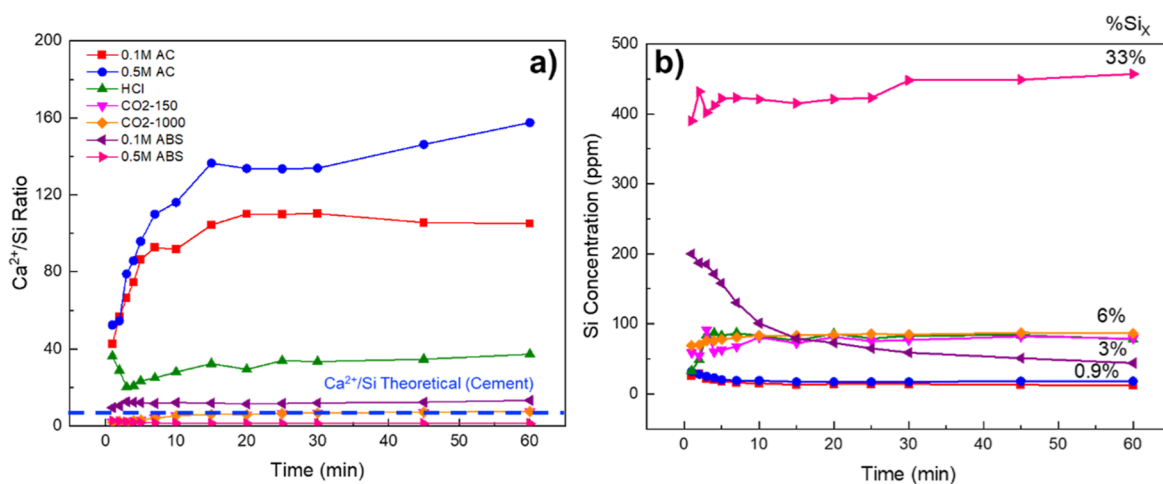


Figure 3. (a) Calcium-to-silica (Ca^{2+}/Si) extraction ratio for the leaching of waste HCP using different leaching agents plotted with the theoretical Ca/Si ratio present in the HCP. (b) Si leaching kinetics for the different leaching agents over the course of 60 min. 150 and 1000 denote the CO_2 -flow rate (in $\text{mL} \times \text{min}^{-1}$) used for carbonic acid leaching.

The use of only water or carbonic acid (H_2CO_3) as a leaching media results in low recoveries of Ca^{2+} into the aqueous phase. Using CO_2 as a leaching media for alkaline waste has been proposed previously but ultimately results in low yields due to the weak acidity of carbonic acid and the inevitable precipitation of CaCO_3 on the surface of the particles undergoing leaching within the dissolution tank.²⁵ The presence of calcite on the surface of cement particles subjected to carbonic acid leaching was observed via both PXRD (Supporting Information, Figure S3) and SEM (Figure S4). The use of water only leads to a rapid increase in reaction pH, and solubility limitations of $\text{Ca}(\text{OH})_2$. In addition, the lack of a source of acidity results in low calcium extraction efficiency. Theoretically, this could potentially be mitigated with alternative reactor designs such as a packed-bed system. This system seems to be more applicable toward minerals rich in Mg, where the MgCO_3 formation kinetics are much slower compared to CaCO_3 .^{5,25,59} Methods to disrupt this carbonate-passivation layer and multiple-pass leaching reactors could boost the overall efficiency of such a concept.^{25,60} Additional release of Ca^{2+} could potentially be realized by subjecting the residues to additional reaction passes, especially in the case of AC leaching.

Figure 3a shows the Ca/Si ratio over the course of the leaching process, which is calculated from the Si concentration in the aqueous phase measured by ICP-OES (Figure 3b). The Ca/Si ratios for HCl and 0.1/0.5 M AC leaching were both higher than the original Ca/Si ratio within the cement, suggesting incongruent dissolution. This type of dissolution has been reported in various silicate minerals and also Ca-rich alkaline wastes and is generally attributed to the weaker metal-oxide bonds which are easier to cleave than the Si–O bonds.²⁵ This behavior allows for the formation of silanol groups on the surface which condense to form a passivating effect (e.g., silica passivation layer), which can dampen removal of metals from the particles.^{30,61} Interestingly, the AC leaching media show the most incongruent dissolution according to the Ca/Si ratio compared to all other proton sources. This could be useful if a high Si-content product is desired for reuse in the built environment and could also be useful to mitigate issues with silica gel precipitation later in this process, which is conventionally done in the case of HCl leaching.^{27,62} This Si

residue could be akin to Si fume or a pozzolanic supplementary cementitious material (SCM).^{63,64} The differences in Si dissolution between HCl and AC could be a result of pK_a and acidity, where HCl has an approximate pK_a of -6.3 and AC has a pK_a of about 9.2 . The stronger acid could release higher energy bonds and access more of the Si than the AC proton source. 0.5 M ABS leaching was able to extract the highest amount of Si at 33% and stabilize it in the aqueous bulk. This behavior was also reported by Bai et al. (2009), who observed that the dissolution rate and quantity of silica is significantly enhanced by the presence of sulfate ions.⁶⁵ They postulate that the adsorption and bonding of sulfate to silica can weaken the silanol bonds, allowing for solubilization of the silica. Thus, ABS could be a good candidate for dissolution systems where a high-purity silica precipitate is desired, which can be recovered during the pH-swing process, which is generally used to precipitate silica and other ancillary (e.g., Al, Fe, etc.) ions. ABS leaching could also be advantageous for systems where gypsum is a desired intermediate or product, or the conversion of gypsum into other products is desired. This could be particularly useful in nonmined gypsum for advanced drywall production or alternatives to gypsum produced from flue gas desulfurization in the future.

3.2. PERR Analysis and Composition. The PERR was characterized to study its composition and crystalline phase composition. This residue was obtained from the undissolved fraction obtained by filtration after the leaching reactor. Figure 4 shows the refined quantitative-PXRD data (raw spectral data are shown in Figure S3) of the raw HCP before leaching and the unreacted residue from each leaching case studied. In almost all cases studied, the predominate phase remaining was calcite. In most cases, the final pH of the leach was above 8, with the exception of HCl and 0.5 M ABS. The high pH can allow any free calcium to react with carbonate ions, some of which are present from dissolving HCP and others from CO_2 naturally dissolving CO_2 in the leaching reactor. As expected after ABS leaching, gypsum was the predominant crystalline phase in the PERR. Interestingly, calcite seemed to be precipitated primarily on the surface of dissolving particles, whereas gypsum was present as distinct and large crystals as shown by SEM (Figure S4). The presence of carbonate and sulfate groups within the PERR was also monitored via

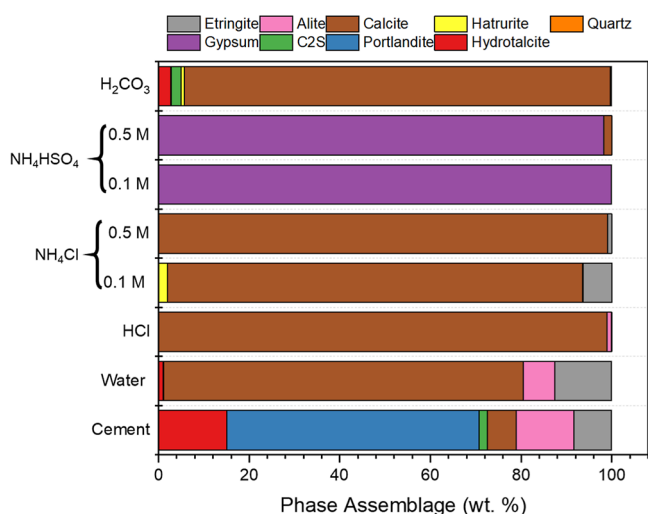


Figure 4. PXRD crystalline phase composition of the PERR. Spectral data was refined using Rietveld refinement in the MAUD software. The carbonic acid leaching case was performed at a CO_2 -flow rate of $1000 \text{ mL} \times \text{min}^{-1}$.

attenuated total reflectance (ATR)-FTIR (Figure 5a). The abundance of SO_4 vibrational signatures can be seen in the case of ABS leaching whereas the presence of CO_3 vibrational signatures can be observed in the carbonic acid and AC leaching cases. Despite the PXRD data, the absence of distinct carbonate vibrations in the HCl PERR showcases the strength of hydrochloric acid to prevent the precipitation of calcite on the surface of the dissolving particles or differences in the surface charge.

BET surface areas (SAs) show that in all cases, the PERR had a higher SA than the starting cement itself owing to the increased internal SA in the particles due to leaching (Figure 5b). The highest SAs reported were HCl and 0.5 M AC leaching, at almost $70 \text{ m}^2 \times \text{g}^{-1}$, nearly 7 \times larger than the waste HCP. Previous studies have shown that SCMs and fillers with high SA can enhance cement hydration and provide favorable mechanical properties; thus, high SA residues could be upcycled in new cement admixtures or make interested

sorbents for separation applications.^{21,22,63,66} TGA analysis complements previous characterization techniques, showing the absence of the calcium-silicate-hydrate (C-S-H) and portlandite peaks in the PERR samples due to destruction during leaching (Figure 6a,b). Gypsum decomposition was not observed due to temperature limitations of TGA ($900 \text{ }^\circ\text{C}$). Derivative thermogravimetric (DTG) shows the presence of a strong carbonate decomposition peak at $700 \text{ }^\circ\text{C}$ in the carbonic acid leaching samples due to precipitating calcium carbonates on the shrinking particles. Carbonic acid has been studied as a leaching media in waste mineral samples (e.g., serpentine) via the pCO_2 process, which is effective due to the low-reactivity of minerals during ex situ carbon mineralization and the slow kinetics for magnesium carbonate precipitation;^{59,67–69} however, for highly reactive Ca-rich alkaline waste, it appears that carbonic acid is not a strong enough acid to overcome carbonate-induced passivation, leading to low Ca extraction.²⁵ XRF analysis was performed to complement the aforementioned observations and shows the effectiveness of HCl in removing a significant amount of Ca in a single-pass leach (Figure 7a). Interestingly, while the composition of the AC PERR is quite similar to that of the HCl PERR, the D_{50} after leaching is much smaller in the former (Figure 7b). This difference could be partly due to the increased incongruent dissolution afforded by the AC system allowing the transformation of the solid cement phases into smaller, more condensed phases (e.g., precipitated silica, silicates, and ammonium salts). Additionally, it could be a result of different concentrations of the acids (e.g., AC, ABS, and HCl) present during leaching, with HCl being present at a molar concentration 3–14 \times higher than that of AC/ABS.

3.3. Carbonation of Ca-Rich Leachate to Produce High-Purity PCC. The collected Ca-rich liquor obtained during leaching was carbonated to produce high-purity calcium carbonates, which were then characterized for their composition. Figure 8 shows refined Q-PXRD data of the major crystalline phases present in the carbonate samples, which was analyzed to probe at the relative concentrations of the three major anhydrous forms of calcium carbonate, vaterite, aragonite, and calcite, listed in the order of thermodynamic

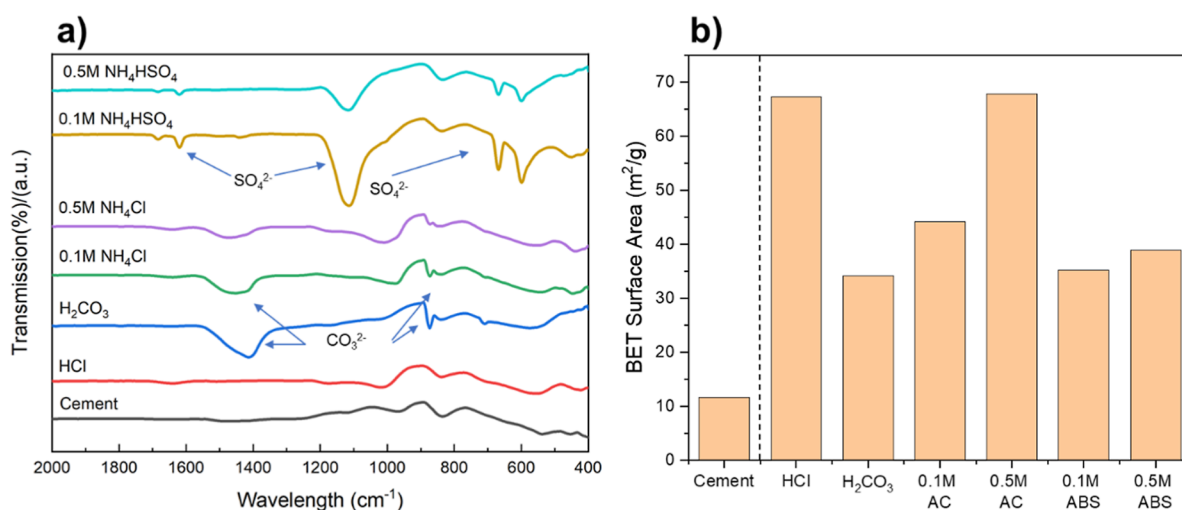


Figure 5. (a) FTIR spectral data of the PERR using various leaching agents compared to raw cement with markings for the most prominent functional group vibrations, such as carbonates (CO_3^{2-}) and sulfates (SO_4^{2-}). (b) BET surface area for the PERR compared to raw cement, as determined by multipoint isotherms. The carbonic acid leaching case was performed at a CO_2 flow rate of $1000 \text{ mL} \times \text{min}^{-1}$.

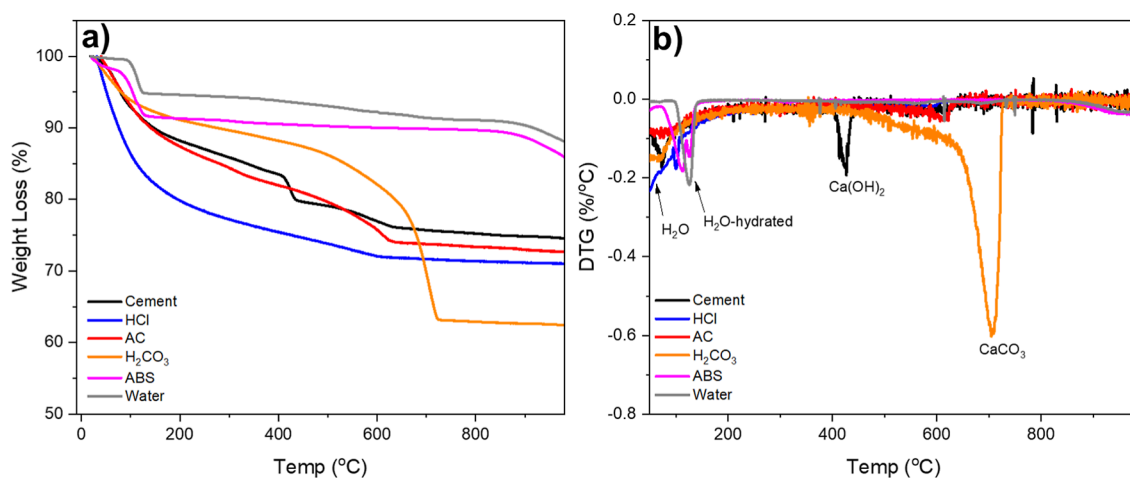


Figure 6. (a) TGA data for weight loss (%) and (b) DTG data ($\% \times \text{°C}^{-1}$) for the PERR using various leaching agents. AC and ABS residues are from the 0.5 M leaching case, and the H_2CO_3 leaching was performed at $1000 \text{ mL} \times \text{min}^{-1}$.

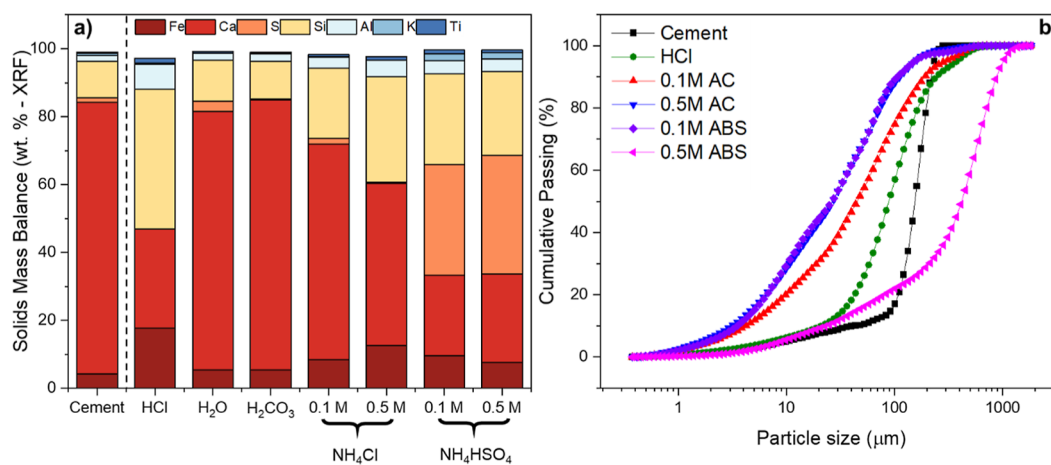


Figure 7. (a) XRF data of the PERR material and (b) particle size data of the same. H_2CO_3 in the XRF data corresponds to a CO_2 -flow rate of $1000 \text{ mL} \times \text{min}^{-1}$.

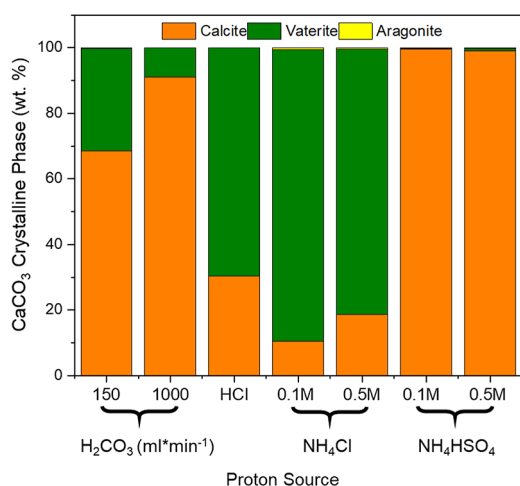


Figure 8. PXRD phase assemblage data for the produced PCC samples using different leaching sources to generate the Ca-rich liquor. Carbonation was conducted at a CO_2 -flow rate of $150 \text{ mL} \times \text{min}^{-1}$.

stability.^{49,70} The product of the HCl leaching was able to form a product with roughly 70 wt % vaterite, whereas the carbonate produced by the AC leaching system was as high as 90 wt %

vaterite. Ammonium has been well studied as an inorganic additive which can preferentially stabilize vaterite on reaction-relative time scales for vaterite isolation.^{51,71} It is theorized that ammonium salts can modify the surface of the vaterite to prevent redissolution and precipitation into calcite, which in turn suppresses the calcite phase from nucleating.^{50,51,72} At high concentrations of ammonium, morphological changes to vaterite, generally the spherical metastable polymorph of CaCO_3 , can be observed (Figure 9). The difference between the 0.1 M AC vaterite and 0.5 M AC vaterite can clearly be observed, with the latter appearing more porous and having a ridged surface structure. While an induction effect imparted by AC could result in slightly higher calcite percentages at the higher AC concentration, further work needs to be undertaken to uncover this. Similar morphologies of vaterite were reported using AC as a calcite nucleation suppressor in a recent study by Williams et al. (2023).⁴⁹ Carbonic acid leaching favored the production of calcite after carbonation, likely due to a seeding effect due to residual calcite (dissolved and undissolved) present in the leachate. ABS leaching produced near 100% calcite regardless of the concentration. Similarly, Liu et al. (2022) observed the synthesis of calcite in the carbonation of gypsum from desulfurization residue. They were only able to synthesize pure vaterite in these sulfate systems if they added

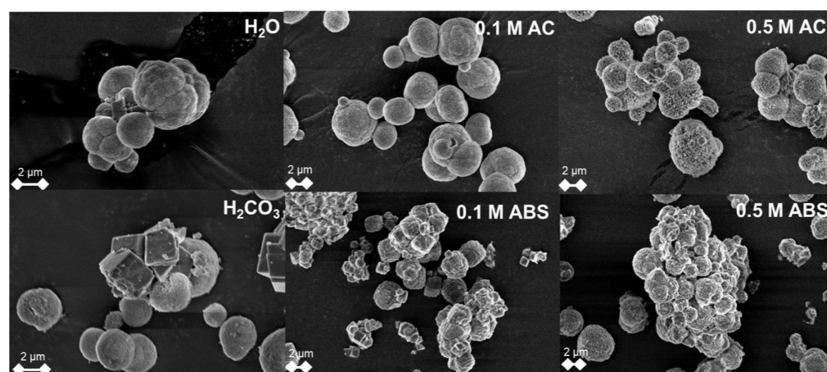


Figure 9. SEM images of the PCC samples generated from the Ca-rich liquor from leaching of waste HCP using various leaching agents.

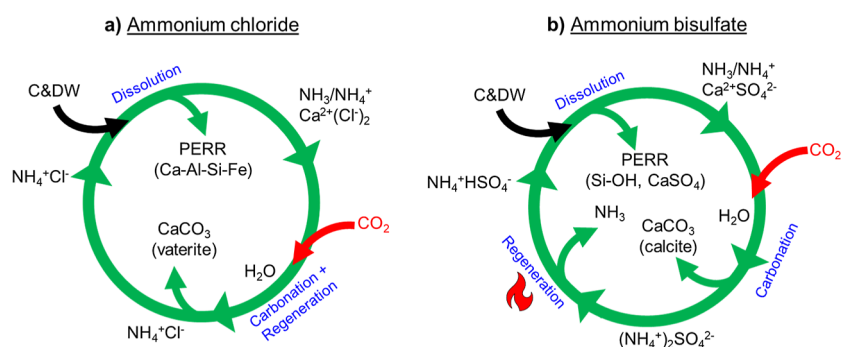


Figure 10. Proposed (a) AC and (b) ABS dissolution and carbonation reactor systems utilizing alternative leaching agents for the creation of PCC for CCUS in addition to the generation of PERR which may have uses as novel materials in new construction building blocks.

ammonium glycine.⁷³ Previous work has shown in some cases that sulfate can stabilize vaterite in addition to ammonium.⁴⁹ Our rationale for the absence of this effect in the case of the carbon mineralization of ABS leachate is that the concentration of Ca^{2+} is nearly a third lower than that of AC and HCl in the aqueous phase. This lower Ca^{2+} concentration also plays a role in crystallization as carbonation will occur much faster and at a lower saturation index, which could favor calcite nucleation over vaterite. Interestingly, the calcite formed in the ABS system seems to be much smaller and more spherical than “classical” calcite, as observed in the case of carbonate leaching (Figure 9). This is likely a result of crystal habit modification due to the presence of sulfate ions, which was observed by Tang et al. (2012), who crystallized CaCO_3 in the presence of sulfate and observed, smaller prism-like calcite as opposed to the cubic shape which is commonly found.⁷⁴

The preferential stabilization of vaterite could be useful toward increasing the value and uses of carbon capture and utilization processes through carbon mineralization. Vaterite is theorized to have potential uses in pharmaceuticals, drug delivery, environmental remediation, catalysis, and as a reactive agent and hydration modifier in cement systems.⁷⁰ Recently, Zhao et al. (2023b) showcased that the metastable polymorphs of CaCO_3 , vaterite, and aragonite could be used to replace OPC in the creation of new admixtures which can impart increased compressive strength and acceleration of cement hydration.²² In a separate study, they show that aragonite could be used as a rheological modifier to improve the settling and pourability of cement (Zhao et al., 2023).²¹ Using ammoniacal leaching agents, especially AC, could be a promising method to facilitate both the leaching of alkaline wastes and subsequent CaCO_3 polymorph control in a single

system. Additionally, high temperatures ($>70\text{ }^\circ\text{C}$) or the use of crystal seeding at lower temperatures ($40\text{--}50\text{ }^\circ\text{C}$) could be useful methods to produce high-purity aragonite, another useful PCC polymorph, from these Ca-rich reaction liquors.²³

3.4. Use of Alternative Ammoniacal Leaching Agents during C&DW Dissolution and PCC Production for Carbon Capture Storage and Utilization (CCUS). Figure 10 demonstrates the proposed and studied process for the use of alternative leaching agents, such as AC and ABS, for the hydrometallurgical dissolution and carbonation of construction and demolitions waste. In this reactor system, the weakly acidic AC or ABS salts are used to extract Ca from the C&DW in the leaching reactor. When AC is used, a filtrate of PERR which is rich in Si is recovered, whereas in the case of ABS, a filtrate of PERR rich in gypsum is recovered. Both of these unreacted residues could have uses within the manufacture of new built environment materials, where the Si-rich residue could function as a viable SCM and the gypsum could be added to cement coming from alkaline waste as opposed to mined rock.^{58,63,75} Previous work has demonstrated that these PERR substances, which are mostly amorphous Si, can be used to replace OPC within new cement mixtures.²⁹ The PERR, which has a high SA, can function in a similar manner to fumed silica and provides sites for enhanced nucleation during cement hydration. The gypsum-rich PERR could have uses as a replacement or filler material in the manufacture of housing structures such as drywall and plasters.

In such processing, pH adjustment or pH swing is done intermittently and as required to precipitate other elements, such as Si, Al, and Fe, which were also extracted during the dissolution step. Due to the weak acidity of salts such as AC and ABS vs HCl, the necessity for this process step is negated,

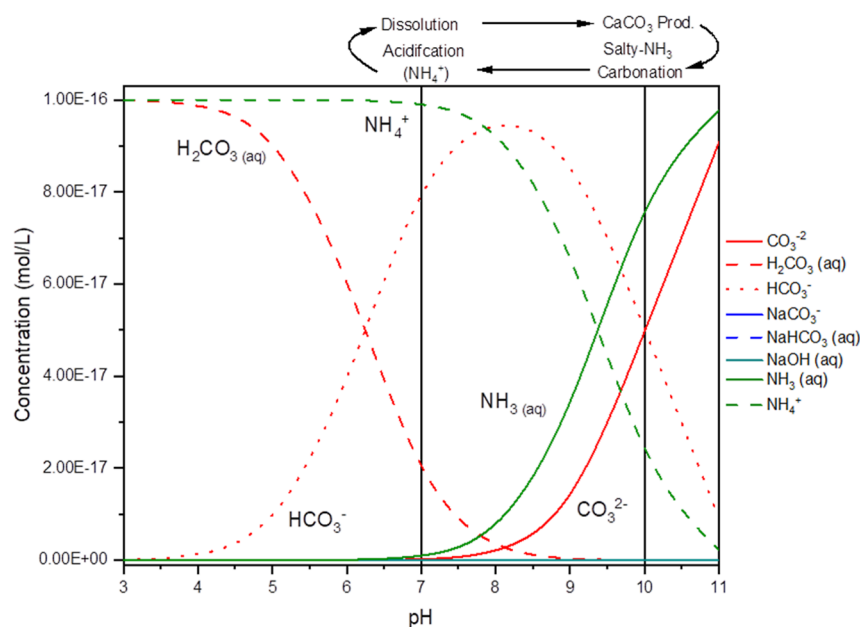
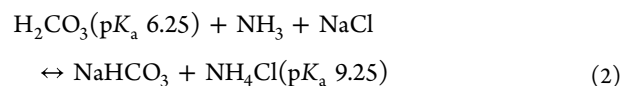
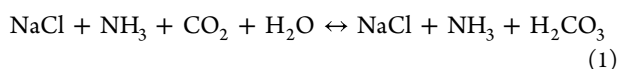


Figure 11. Visual MINTEQ thermodynamic speciation analysis at a fixed total species concentration of 0.1 M representing the regeneration potential of salty ammonia–water with carbonic acid in a manner similar to the Solvay process.

which is another potential advantage of these recyclable salts. The carbon mineralization reactor then allows the precipitation of PCC through the reaction of captured CO_2 with the extraction Ca from the dissolution step. The morphology of the produced PCC will vary based on the salts used during leaching which in turn will allow for a wide variety of uses as upcycled materials.²⁰ After PCC precipitation, the ammonia-rich water/brine (effluent) can be regenerated with CO_2 to the acid side to produce NH_4Cl and can be recycled for subsequent dissolutions. In the case of ABS leaching, after PCC precipitation, ammonium sulfate will likely be the salt present. To regenerate ABS, light heating of the ammonium sulfate will produce ABS and ammonia, both of which can be recycled and recovered.⁷⁶ In this study, we observed the off-gassing of ammonia from the carbonation reactor, which is likely a result of the high pH required for CaCO_3 production. This gaseous ammonia could be recovered and used in the carbonation of brine solutions to produce soda ash, another useful carbonate, and then subsequently used again in the dissolution of C&DW.⁷⁷ Additionally, ammonia could also be used to capture gaseous CO_2 and deliver it for sequestration activities. The general chemistry of ammonium salt regeneration is shown below, whereby salty ammonia–water can first be acidified with CO_2 (eq 1). Afterward, the production of bicarbonate will occur, which in turn generates a protonated ammonia species (eq 2). This chemistry is akin to what is done in the Solvay process. A visual representation of this chemistry was achieved through thermodynamic MINTEQ speciation modeling (Figure 11). After CaCO_3 production, the use of CO_2 can be used to protonate ammonia and shift the pH of the solution back to anywhere between 4 and 7 which can be used to solubilize additional Ca^{2+} from waste HCP in subsequent process cycles. From a process standpoint, the most challenging step is likely to be the separation of sodium bicarbonate and ammonia chloride if excess bicarbonate is present in the solution.



The regeneration of ammonium sulfate salts in the carbonation of Mg-bearing minerals and Ca-rich steel slags have both been heavily studied by numerous research groups, especially Maroto-Valer and Zevenhoven.^{5,44,55,56,76,78–81} Generally, these systems result in an effluent that is rich in ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$. Degassing of ammonia can be facilitated through mild heat, regenerating ABS used in leaching, whereas the gaseous ammonia can then be used as a base or to assist in CO_2 capture.^{44,45} Unfortunately, the strength of strong acids, such as HCl, HNO_3 , and H_2SO_4 , make them much more attractive due to superior extraction efficiencies in these processes.⁶² In the future, systems which allow for the renewable production of acid and bases, utilizing wind or solar for the electrochemical production of acids, are most desired.⁸² Additionally, the utilization of CO_2 to produce organic acids electrochemically, such as formic, acetic, citric, etc., is also a potential candidate process for the dissolution of alkaline wastes in the context of CCUS; however, choice of organic acid is crucial as it will affect carbonation potential if the binding energy between Ca^{2+} and the counteranion (e.g., citrate) is higher than that of calcium and carbonate anions.^{83,84} Previous studies have reported on the dissolution of C&DW and mineral wastes using organic acids. Recently, Hong et al. (2023) showcased the enhancement of metal recovery from iron slag utilizing various organic acids.¹² The proposed system using alternative leaching agents, such as AC and ABS, allows for a reduction in potential safety hazards at-scale through the handling of mildly acidic aqueous ammonium salts versus concentrated HCl (37 wt %). Additionally, the ability to use CO_2 as the acid source to regenerate the weak acid (i.e., NH_4Cl) could provide economic as well as carbon capture benefits. The ability to control the downstream crystallization of PCC and enable the preferential synthesis of the metastable phases of calcium carbonate, such

as vaterite, highly motivates the use of ammonia-based leaching agents for carbon utilization applications.

4. CONCLUSIONS

In this work, the leaching of waste HCP was conducted by using a wide variety of alternative proton sources to conventional inorganic acids (i.e., HCl) for ex situ carbon mineralization. The reactivity and recovery of metals from the cement is reported during the leaching process and the incongruent dissolution behavior is analyzed. Carbonation of the leachate was then performed to generate PCC which were analyzed to understand the distinct morphologies and crystal habits present as a function of which proton source was utilized during leaching. Supporting previously obtained data, we observed the purification of vaterite when AC salts were used in the carbon mineralization reaction system. Pure calcite with a nonobvious morphology, as confirmed by SEM, was observed in the ABS leaching case. Based on the data analyzed and characterizations performed within, the following conclusions can be drawn from this study:

- AC (NH_4Cl , AC) salts yield similar Ca extraction % at about 42% to HCl which yielded 46% Ca extraction in a single-pass conversion.
- ABS (NH_4HSO_4 , ABS) salts lower the concentration of Ca present in the aqueous phase over the course of leaching to roughly 10% at the end due to the formation of insoluble gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) during the reaction.
- Leaching with carbonic acid yielded the lowest extraction of Ca from the cement matrix, presumably due to the weak acidity of H_2CO_3 and the formation of calcite on the dissolving cement particles.
- The PERR mostly contained calcite as the predominant crystalline phase for all samples tested, with the exception of gypsum being present for the ABS leaching salts. Thermal analysis revealed that the degree of calcite present was the highest in the carbonic acid leaching case, as expected due to the reaction with carbonate ions present and the leaching calcium.
- The PERR residue was highest in Si content as confirmed by XRF for the AC and HCl leached cases, making it a potential Si-rich residue which could be reincorporated into new built environment feedstocks. The presence of residual calcium could also be useful in the creation of new reactive phases during subsequent OPC replacement and clinker hydration.
- PCC synthesis revealed the presence of vaterite as the main PCC morphology in the HCl and AC leaching cases, whereas calcite was the main crystalline phase present in all the other carbonates. The presence of calcite is theorized to be a result of calcite seeding in the presence of carbonic acid leaching. Vaterite stabilization by ammonia is likely the reason for the highest percentage of vaterite being present in the AC leaching case at >90 wt %.
- Aqueous AC and ABS are alternative reagents to hydrogen chloride when extracting calcium from cement paste, offering potential advantages including lower reagent use, recyclability, and milder conditions.
- Future works include more detailed kinetic analysis at a broader range of concentrations, elevated temperatures, and the establishment of the activation energy of the system using ammonium salts. Additionally, exploration

into the regeneration potential of the system and recovery of ammonia gas is required to assess the true viability of this system. Finally, assessment of the CO_2 utilization and storage capacity is needed via LCA and TEA.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c03393>.

Recorded pH changes, speciation of sulfate in aqueous media, PXRD spectra of the PERR, and SEM images (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

HCP, hydrated cement paste; CCUS, carbon capture utilization and storage; CDR, carbon dioxide removal; AC, ammonium chloride; ABS, ammonium bisulfate; C&DW, construction and demolition waste; CDS, construction and demolition solids

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