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Carboxylic ligands to enhance material recovery from construction waste to produce CaCO₃ for carbon utilization†

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The decarbonization of the built environment is a pressing issue to achieve CO₂ reduction targets in the concrete industry. Carbon mineralization of construction and demolition waste (C&DW) is an attractive pathway to capture of CO₂ as stable carbonates which can be re-utilized and upcycled in a circularized fashion through the creation of new building blocks. Material recovery from the C&DW is often performed in hydrometallurgical leaching using acidic media; however, this process is often hindered by solubility issues and passivation. To ensure high recoveries of these elements, ligands can be used to enhance dissolution. Carboxylic acids are used in conventional hydrometallurgical mineral processing, such as leaching, floatation, and solvent extraction, and are desired due to their affordability and stability. In this study, we explore the dissolution of waste cement pastes in acidic conditions under the presence of four carboxylic acid ligands: formate, acetate, glutamate, and citrate. The leaching kinetics are categorized and the pseudo-rate constants are established, demonstrating the advantages of these agents to enhance reaction rates in the general order of citrate ≫ formate > acetate > glutamate > control. The characterization of the post-extraction reactor residue (PERR) revealed a significant increase in Si-content. Finally, the leachate was carbonated to produce calcium carbonate, which was characterized for its use based on morphology and size. Glutamate demonstrated distinct advantages compared to other ligands, with a dual function of not only improving leachability of cement but promoting and stabilizing vaterite during crystallization. Overall, this study motivates the use of sustainable ligands to enhance material recovery during the dissolution of alkaline wastes for carbon mineralization.

Keywords: Carbon mineralization; Material recovery; Leaching; Ligands; Carboxylic acids; Calcium carbonates; Carbon capture utilization and storage.

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1 Introduction

1.1 Material recovery from built environment wastes for decarbonization and upcycling potential

The utilization of alkaline wastes rich in Ca and Mg (*e.g.*, steel slag, mine tailings, construction debris, *etc.*) is posited to contribute to a significant portion of *ex situ* carbon

mineralization as a method of carbon dioxide removal (CDR).^{1–4} This is especially relevant for the built environment, where 25% of construction and demolition waste (C&DW) is directly landfilled without further processing (U.S.);⁵ by 2050, estimates report that global C&DW waste could reach 27 billion tonnes.⁶ On-site sorting and pre-processing of the C&DW will allow for enhanced downstream separation and will ensure different fractions of waste can reach their upcycling centers at lower CO₂-footprints.⁷ Previous studies have demonstrated that the dissolution of waste HCP to recover elements such as Ca, Si, Al, and Fe is a viable method to sequester carbon in the form of calcium carbonates and produce upcycled materials.^{8,9} This aqueous dissolution and carbonation process could sequester between 100–150 kg CO₂ per tonne of C&DW waste; however, this could in fact be lower when considering the distribution, shipping, milling, and comminution carbon impacts.^{6,9} The replacement of clinker through upcycled materials, such as calcium

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carbonates and recovered silica residues, could reduce the CO₂-burden of cement without compromising the structural integrity of the materials.¹⁰ Recent works by Zhao *et al.* have highlighted the ability for the three anhydrous polymorphs of CaCO₃ (vaterite, aragonite, and calcite) produced from the dissolution of waste cement pastes to replace clinker and enhance its hydration during curing.^{11,12} Additionally, numerous studies have demonstrated that the use of silica-bearing compounds from industrial wastes such as fly ash, steel slag, and other alternatives to fumed silicon could be used as pozzolanic SCMs in new cement mixtures.^{13–17} The tandem capture of CO₂ and production of new built environment materials through hydrometallurgical carbon mineralization processes offers additional advantages which motivates the implementation of carbon capture and utilization (CCU).¹⁸

1.2 Carboxylic ligands for enhanced material recovery from alkaline wastes during carbon mineralization

During conventional hydrometallurgical processes involving elemental and metal recovery, complexing agents and ligands are often used to enhance extraction and recoveries.^{19,20} The use of ligands during aqueous dissolution can also reduce the necessity for pyrometallurgical roasting or smelting, which can lower the overall environmental impact of such processes.²¹ Classically, cyanide (CN⁻) has been utilized in gold leaching to form water soluble cyanide salts; however, due to cyanide's environmental toxicity, thiourea (CH₄N₂S) and thiosulfate (S₂O₃²⁻) are being studied as alternative ligands.^{22–24} Carboxylic acids and carboxyl derivatives can also

be utilized during dissolution to recover valuable metals, such as ethylenediaminetetraacetic (EDTA), oxalic acid, citric acid, malic acid, and nitrilotriacetic acid (NTA).^{25–27} In certain cases, these organic species are preferable to their inorganic counterparts (*e.g.*, cyanide, ammonia), due to their reduced toxicities. Carboxyl species are also utilized during other hydrometallurgical processes, such as flotation, solvent extraction, and precipitation. Fig. 1 demonstrates the wide variety of uses for these carboxylic species across a wide variety of relevant processes.

Renewed interest into the utilization of CO₂ as a green solvent and source of carbonate ions for hydrometallurgical precipitation has occurred, especially in the context of carbon mineralization to capture CO₂ itself and to recover energy critical metals, rare earth elements (REEs), and platinum group metals (PGMs) from waste sources.^{28–31} Carboxylic acids and carboxylic acid derivatives can be readily produced through bio-based, electrochemical, and thermochemical processes and are currently utilized in a myriad of industries.^{32,33} The simplest carboxylic acids, formic and acetic, are mostly produced through reactions of methanol and carbon monoxide, both of which stem from syngas produced from methane reformers.^{34,35} Formic acid is generally produced from the hydrolysis of methyl formate while acetic acid is produced through the well-known Monsanto or Cativa processes.³⁴ Useful higher order carboxylic acids with large market shares include citric acid, which is mainly produced from fermentation systems using certain fungi, such as *Aspergillus niger*.³⁶ Certain amino acids also contain valuable carboxylic acid groups, such as glutamic acid, unique as it is one of two amino acids with



Fig. 1 Schematic demonstrating classical hydrometallurgical processes which utilize carboxylic chemistry including, but not limited to, leaching, solvent extraction, flotation, and precipitation.



a negatively charged side chain. Similar to citric acid, it is primarily produced *via* fermentative bioprocesses.³⁷ Unfortunately, the current carbon footprint of these carboxylic acids is quite high, and thus the net carbon impact of applying them to carbon mineralization methods today is not highly beneficial. However, with the growth of CO₂ to chemicals and CO₂ utilization, the production of these species in a more renewable fashion could be attainable in the future. For instance, formic acid can be produced *via* the thermochemical hydrogenation of CO₂ or the electrochemical reduction of CO₂ in aqueous electrolytes.^{38,39} Catalysts can also be utilized to convert CO₂ into useful molecules, such as cyclic carbonates.^{40,41} These thermo/electrochemical methods are more popular for lower order carboxylic acids (*e.g.*, formic *vs.* decanoic acid) due to decreased C–C bond formation required and enthalpy considerations.⁴²

Aqueous dissolution generally occurs at low pHs to ensure protons can hydrolyze metals from the mineral particles *via* metal oxide (M–O) bond cleavage; moreover, most mineral and industrial wastes are highly alkaline due to the abundance of Mg and Ca hydroxides/carbonate species.⁴³ While there are a variety of previous studies examining the effect of carboxylic ligands, especially citrate, on the recovery of metals from industrial wastes, these are generally limited to electronic residues, spent batteries, slags, fly ash, and certain minerals.^{44–48} The target elements in these studies include more monetarily valuable species, such as Cu, Pb, Fe, Ni, and even rare earth elements (REEs).^{46,49–51} There are limited studies in the literature focused on the utilization of carboxylic ligands with respect to Ca-rich heterogenous alkaline wastes, such as hydrated waste cement paste.⁵² Additionally, these analyses are generally focused only on the chemistry and metal recovery during leaching, and do not consider the full process

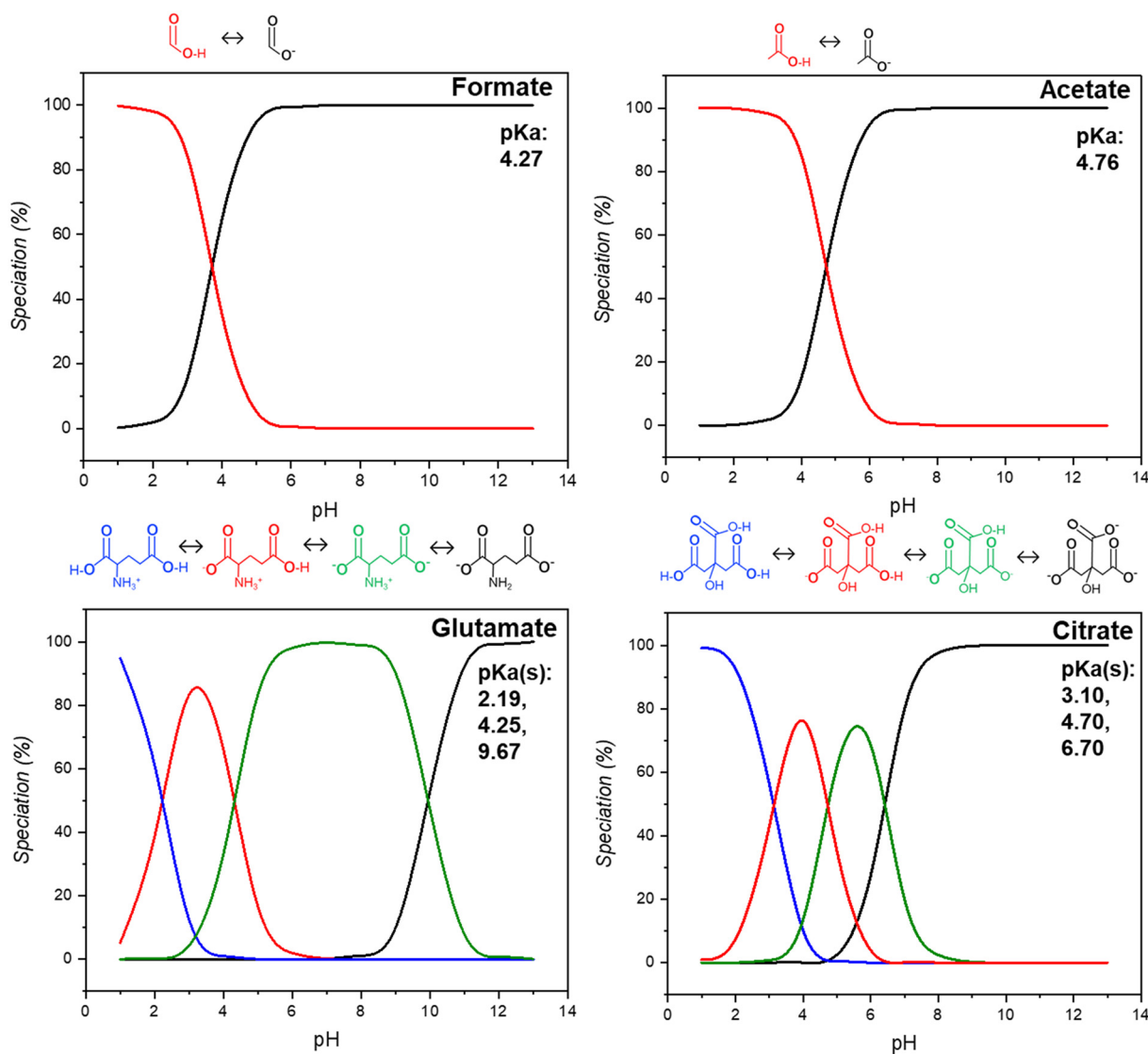


Fig. 2 Speciation and calculated $pK_a(s)$ for salts of formate, acetate, glutamate, and citrate using visual MINTeq at different pH values. Inserts show the removal of protons from the structures of the molecules at different $pK_a(s)$.



engineering production of CaCO_3 for CCUS applications which follows through multiple process steps. These coordinating molecules not only have interesting properties in terms of leaching, but they may also affect the crystallization of CaCO_3 during carbon mineralization downstream as surface modifiers or nucleation inhibitors. Thus, the combined and systematic use of these materials for both leaching and crystallization control within carbon mineralization processes for carbonate formation is both timely and needed.

In this study, we examine the dissolution of waste HCP from the built environment in acidic media in the presence of four representative carboxylic acid salts, formate, acetate, glutamate, and citrate, chosen for their respective industrial relevance and current production market share. The main functionalities which contribute to their differences arise from their protonation potentials at different pHs, as show in Fig. 2. For formate and acetate, one proton is available, as represented by a single pK_a being present between 4.2–4.8. Glutamate has two carboxyl groups and one amino group whereas citrate has three carboxyl groups, both species with three available groups for

deprotonation. Glutamate can exist as a zwitterion over the majority of the studied pH range. The leaching behavior, kinetics, and reaction rates were analyzed for all four ligands after leaching, the post-extraction reactor residue (PERR) was characterized for its properties and a pH swing was employed to precipitate out non-Ca ions in the solution from pH 3–9. These precipitated metal oxides (PMOs) were characterized for their morphology and elemental composition to assess their potential uses. Finally, the dissolution liquor was reacted with CO_2 to produce calcium carbonates and assess the degree of CO_2 capture which is afforded by the enhanced material recovery using these carboxylic ligands.

2 Results and discussion

2.1 Kinetic analysis of ligand-assisted leaching of waste hydrated cement pastes

2.1.1 Leaching kinetics. Fig. 3a–d shows the leaching kinetics over the course of the dissolution experiment for



Fig. 3 Leaching kinetics as measured by ICP-OES for (a) Ca^{2+} ; (b) Si; (c) Al; and (d) Fe for HCl, acetate, formate, citrate, and glutamate leaching cases over the course of 60 min extraction.



Table 2 Best of fit R^2 values for the kinetic data obtained for Ca, Si, Fe, and Al in the presence of the four ligands studied. The data was fit to models describing chemical control, diffusion control, and a combination of the two

| Best of fit (R -value) | | | | | |
|------------------------------|--------------|--------------|--------------|--------------|--------------|
| Element of interest | Ca | | | | |
| Ligand | Control | Acetate | Formate | Citrate | Glutamate |
| Chemical reaction control | 0.979 | 0.990 | 0.984 | 0.966 | 0.989 |
| Diffusion control | 0.985 | 1.000 | 0.997 | 0.985 | 0.999 |
| Chemical + diffusion control | 0.983 | 0.996 | 0.991 | 0.977 | 0.995 |
| Element of interest | Si | | | | |
| Ligand | Control | Acetate | Formate | Citrate | Glutamate |
| Chemical reaction control | 0.891 | 0.968 | 0.959 | 0.934 | 0.958 |
| Diffusion control | 0.913 | 0.991 | 0.983 | 0.963 | 0.978 |
| Chemical + diffusion control | 0.892 | 0.973 | 0.965 | 0.945 | 0.961 |
| Element of interest | Fe | | | | |
| Ligand | Control | Acetate | Formate | Citrate | Glutamate |
| Chemical reaction control | N/A | 0.942 | 0.965 | 0.984 | 0.910 |
| Diffusion control | N/A | 0.942 | 0.982 | 0.999 | 0.905 |
| Chemical + diffusion control | N/A | 0.943 | 0.966 | 0.991 | 0.909 |
| Element of interest | Al | | | | |
| Ligand | Control | Acetate | Formate | Citrate | Glutamate |
| Chemical reaction control | 0.776 | 0.972 | 0.996 | 0.987 | 0.909 |
| Diffusion control | 0.696 | 0.898 | 0.990 | 0.995 | 0.883 |
| Chemical + diffusion control | 0.773 | 0.969 | 0.999 | 0.993 | 0.908 |

dissolution process, which is consistent with previous studies. It should be noted that this is diffusion-limited reaction regime in reference to the diffusion through and within the solid cement paste and no liquid-liquid dissolution or the diffusion of species within the bulk. Fig. 4a demonstrates an example of this fitting using the diffusion-controlled model (eqn (1)) with the calcium dissolution kinetics over the desired time range of about 420 s (7 min). Shorter time frames are utilized for the kinetic analysis to avoid the saturation region of mass

transfer limitations which generally occurs after 10–15 min of dissolution. Ca and Si extraction fit this model the best of all the elements profiled, whereas there are slight deviations in the case of Al and Fe. While part of this could be due to higher error associated with these elements which are present in less than 3% of the starting cement feedstock, it could also be indicative of additional factors controlling the extractive processes of Al and Fe. For the case of citrate, the affinity of iron and aluminum towards citrate is quite high; thus, increased solubility of the formed



Fig. 4 (a) Example of the data fitting using the calcium extraction kinetics up to about 7 min for all five test cases using the diffusion-limited model and (b) calculated rate constants (k_d) for diffusion-controlled shrinking-core reaction regime Ca, Si, Al, and Fe dissolution from the waste hydrated cement paste (HCP). Control case refers to HCl dissolution only.



complexes will have strong implications for the apparent rate constants. In the case of Al, the leaching kinetics suggest that saturation is not reached within the dissolution time tested whereas the high affinity of iron towards citrate and its increased solubility is the main mechanism active in the Fe leaching kinetics. Additional studies using these same ligands with other alkaline wastes (*e.g.*, steel slag, waste to energy ashes, *etc.*) that contain greater amounts of Al and Fe should be conducted to provide additional mechanistic insights.

Fig. 4b shows the rate constants for dissolution as calculated for the five leaching cases for Ca, Si, Al, and Fe. Correspondingly, it can be observed that the increase in rate constants follows a similar trend observed in the kinetic data shown in Fig. 3a–d, where elemental extraction rates for citrate \gg formate \sim acetate $>$ glutamate $>$ HCl only. Based on this analysis, it is clear that thermodynamics is dominating the enhancement effects observed by the carboxylic ligands in these reactions. Utilizing these chemicals has altered the apparent solubilities *vis-à-vis* the observed apparent rates. Calcium extraction rates were more or less similar between the species; however, in the case of citrate Fe rates were increased by 4 orders of magnitude (OOM), Al by 3 OOM, and Si by 2 OOM. Based on kinetic data, apparent rates, and the particle size data (section 3.2) obtained from the samples after the reaction, it is theorized the improvement in the rate of reaction offered for Ca is present at the surface of the dissolving particles, since the Ca extent of extraction is the same for all ligands within the reaction timeframe. Citrate-Ca enhancement could also be a function of 3 \times greater presence of ligating groups with respect to the other ligands studied. In the case of Si, it seems that there are different Si-ligand species coming to different equilibriums over the course of the dissolution reaction. In reference to the Al and Fe, the ligand enhancement in extraction is likely a result of increased solubilization of these poorly soluble ions, increasing their

concentration in the bulk and preventing their reprecipitation of the dissolving particles. Al seems to be pore-controlled, as the kinetics never fully reach saturation. These carboxylic ligands may provide benefits at scale, when mass transfer and solubility limitations can become more pronounced.

2.2 Characterization of the post-extraction reactor residue (PERR)

The characterization of the unreacted residue accumulated during the single pass leaching provided insights into the dissolution behavior of the hydrometallurgical processing system in addition of the potential downstream uses of these materials. Fig. 5a shows the percentage of feedstock dissolved compared to HCl only and Fig. 5b shows the individual elemental dissolution percentages as a function of the elemental mass of the feedstock itself calculated by eqn (4):

$$\text{Elemental Dissolution (\%)} = 100 \quad (4)$$

$$\times \frac{\text{Mass of element dissolved (g)}}{\text{Mass of element in Feedstock (g)}}$$

The ligands all enhanced the solubilization of the bulk material itself, with citrate leaving only 8% of the cement remaining in the reactor (Fig. 5a). As demonstrated earlier, the total recovery of calcium was not enhanced much by these salts; however, significant improvements in Fe, Al, and Si total yield were observed, especially in the case of acetate and citrate. XRF analysis of the PERR complemented the mass balance results, showing an increase in SiO₂ content and decrease in CaO content for all the samples tested with respect to the original cement itself (Fig. 6). Increased Fe₂O₃ was observed in the acetate, formate, and glutamate PERR as shown by XRF relative to the acid only. This could be due to the reprecipitation of certain iron species on the undissolved particles during leaching. Visually, the PERR in these three cases looked red compared to the raw feedstock and acid



Fig. 5 (a) Total feedstock dissolved and (b) elemental dissolved mass balance for the carboxylic acid ligands after the hydrometallurgical leaching of waste HCP.





Fig. 6 XRF solids mass balance of the PERR showing the remainder of the residual elements present after leaching.

only cases (Fig. S1†), alluding to the presence of iron. Optical microscopy provided additional visual insights into the characteristics of the PERR (Fig. 7 and S2†). In the case of the ligand PERR, the particles appeared smaller and more fragmented than the HCl control (Fig. S2†). The acetate and formate PERR had a red hue due to the presence of iron species, while the glutamate and citrate PERR looked translucent (Fig. 7), likely a result of the high elemental extraction from the dissolved cement matrix.

Sulfur was detected (SO₃) in the HCP sample, present mainly as ettringite, which originated from the reaction of gypsum (CaSO₄·2H₂O) with aluminates in cement.⁶² No or minimal sulfur was detected in the PERR residues, suggesting that the reaction conditions were adequate to dissolve the ettringite into free sulfate. Previous studies with waste HCP at high slurry densities revealed a reprecipitation of gypsum on the PERR itself, but at low slurry densities sulfate was not observed.⁶ FTIR data of the PERR revealed similar spectral patterns for all five leaching cases (Fig. 8a). Notably, the disappearance of the OH⁻¹ peak at about 3630 cm⁻¹ from the waste HCP was observed. Additionally, the formation of increased Si-O-Si bonding can be seen through the shift (condensation) of the silanol (Si-O) peak from 950 cm⁻¹ in the raw HCP to about 1030 cm⁻¹ in the PERR samples.⁶³⁻⁶⁵ This peak shift has been attributed to the breakage of lower energy Fe-O-Si and Al-O-Si bonds

compared to SiO₂ bonding, allowing for the condensation of silanol groups after removal of other ions, such as Fe and Al.⁸ The peak shift in this region is the most pronounced for citrate, which is supported by the observed mass balance and kinetic data. Correspondingly, the particle size data from the PERR (Fig. 8b) shows a similar trend, with particle size reduction following the order of citrate ≫ formate ~ glutamate ~ acetate > acid only ≫ raw HCP. The increased reduction in PSD, especially for citrate, supported the observed mass of the residue obtained, with very little remaining.

2.3 pH-Swing to concentrate ancillary ions present in the leach liquor

Following the dissolution reactions, a pH swing process was employed to precipitate certain species, such as Al, Si, and Fe, which would otherwise contaminate the PCC downstream during carbonation.⁶¹ Fig. 9 shows the titration data for the disappearance of Ca, Si, Fe, and Al as a function of increasing pH through NaOH addition. Generally, as the pH increased, the precipitation of Fe and Al species was hindered through the presence of carboxylic ligands. Citrate was the most resistant towards the precipitation of Fe and Al, followed by glutamate, acetate, and formate. The amount of NaOH used for titration also scaled with the potential strength and degree to which the ligand was able to recover material during leaching (Fig. S3†). This is likely due to the increased concentration of ions present in the leaching liquor, especially Si, Al, and Fe, which will require additional base to titrate out. Formate and acetate actually assisted in the precipitation of Si, even at high pHs where it would be thermodynamically more soluble.⁶⁶

Unfortunately, the presence of the carboxylic ligands also allowed for the loss of calcium from the aqueous phase, which was upwards of 60% in the presence of citrate. This behavior could be due to the precipitation of the corresponding calcium salt of the ligand material (*i.e.*, calcium acetate, calcium citrate, *etc.*) or increased gelation of Si-Fe-Al hydroxides due to higher absolute concentrations (Fig. 3b-d) which precipitate and can trap calcium within *via* an occlusive process.⁶¹ While citrate allows for enhanced material recovery during leaching due to its strength as a chelator, its downside is the subsequent trapping of ions during PMO precipitation. Swinging the pH



Fig. 7 Optical microscopy at 40× magnification of the PERR samples after the dissolution process.



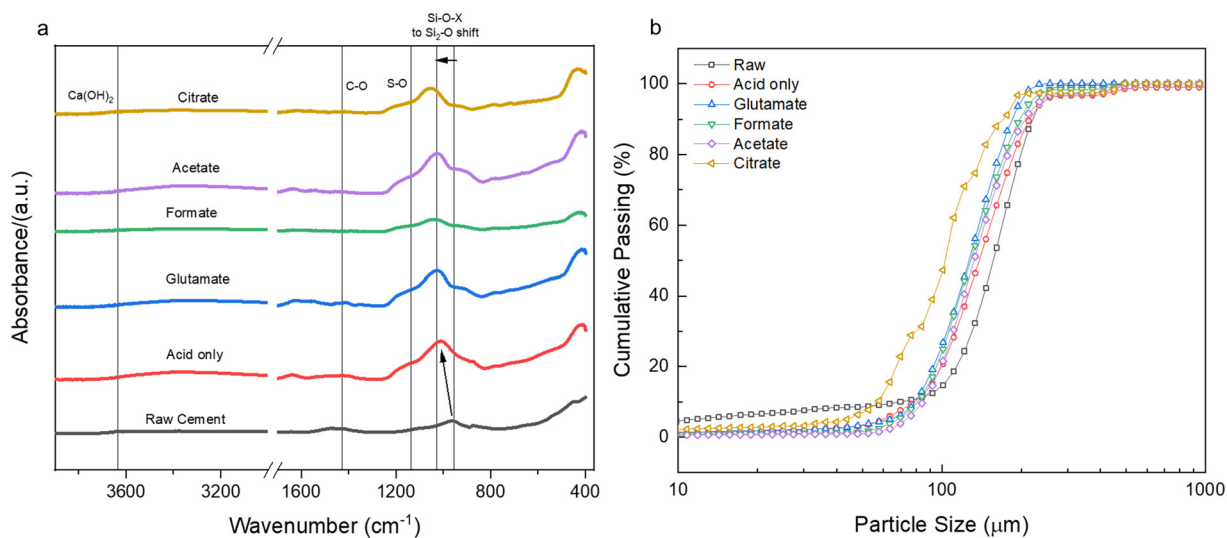


Fig. 8 (a) FTIR spectral data for the post-extraction reactor residue (PERR) for the five leaching cases studied in comparison to the raw cement paste; (b) cumulative passing particle size distribution (PSD) of the same PERR.



Fig. 9 ICP-OES data at various pH points for Ca, Si, Fe, and Al during the pH-swing process for different carboxylic salts used during the dissolution of the HCP.



to as high as 12 could potentially aid in fully precipitating the citrate salts, however a fraction of calcium will also be lost. In a similar study assessing PMO recovery from iron slag leaching, Hong *et al.* (2023) report similar losses of calcium from the aqueous phase during a pH-swing processing using NaOH;⁵³ thus, sequential PMO redissolution, purification, and precipitation to recover wash out excess calcium might be warranted. This behavior is not seen to the same extent in the cases of formate, acetate, and glutamate, demonstrating that for the production of high-purity carbonates for paper making, food and beverage, and paint applications, other ligands could be more advantageous. However, low-purity carbonates can be produced in high yields even if a PMO-precipitation is not employed and these materials can still have use within the built environment or for long-term carbon storage as carbonates.⁹ Al, Fe, and Si can act as supplementary cementitious materials (SCMs) and thus there may even be benefits for their incorporation within carbonates for CCU applications.^{67,68}

Characterization of the PMO revealed much similarity between the precipitates from each ligand case studied. All of the PMO samples had roughly the same composition of Ca, Al, Si, and Fe present as shown by XRF analysis (Fig. 10a) and were amorphous, as confirmed by Q-PXRD (Fig. 10b). Distinct differences in morphology were observed between the PERR, which after leaching appeared quite porous, and the PMO which looked quite smooth in all cases studied (Fig. S4†). ²⁷Al (Fig. 11a) and ²⁹Si (Fig. 11b) MAS solid-state NMR was performed on the control case PMO to assess its phase differences compared to the raw HCP, specifically in the changes of the Al and Si bonding networks. The raw HCP shows a large peak at 4.9 ppm in the ²⁷Al spectra which could be correlated with the presence of an Al-O_{5/6} bonding regime, akin to those found in the tricalcium aluminate (celite) and tetracalcium aluminoferrite (felite) clinker phases.^{69,70} The

PMO contained a slightly downshifted version of this same peak (4.9 shifted to 9.9 ppm) and the growth of a peak at 64 ppm, which could be attributed to Al-O₄ bonding or the bonding of Al to Q₃-Q₄ Si structure (Fig. 11a). The bonding of Al with Si during the precipitation with NaOH is a likely outcome of the PMO swing process. In terms of the Si-NMR analysis, a shift from Q₀-Q₁ silica in the raw HCP towards a broader distribution of Q-structures, with a greater percentage of Q₃-Q₄ Si bonding in the PMO can be observed (Fig. 11b).⁶ The presence of the Q₀-Q₁ structures are indicative of the C-S-H hydrated clinker phases present in the cement itself.^{8,71} After dissolution and PMO precipitation the growth of Q₃-Q₄ Si-structures is indicative of the reprecipitation of SiO₂ bonding to itself and also other elements, such as Al and Fe.

The differences in the structure and phases of the PERR and the PMOs could allow for different uses if they are upcycled within the built environment. These PMOs, which contain calcium, could be useful as pozzolanic materials in new cement hydration.⁷² The PMOs material is amorphous, which generally means it could react during cement hydration to form new phases.^{73,74} Cement hydration data is shown in Fig. 12. As observed, the replacement of PMO in OPC considerably enhanced the hydration kinetics of the cement in the first 8 h (Fig. 12a), and also resulted in a similar cumulative heat release as the OPC-only sample (Fig. 12b) over the course of the 168 h curing time. These results indicate that PMO had a strong accelerating effect on cement hydration at the early age, and the amounts of hydrated phases generated after 7 d were quite similar between OPC and PMO10. It can be potentially used as SCMs to replace cement without compromising its engineering properties. In another study, the placement of cement with 10 wt% PMO even improved the compressive strength of cement mortar, similar to commercial SCMs like silica fume.⁷⁵ This suggests that the PMO materials recovered during the hydrometallurgical processing of

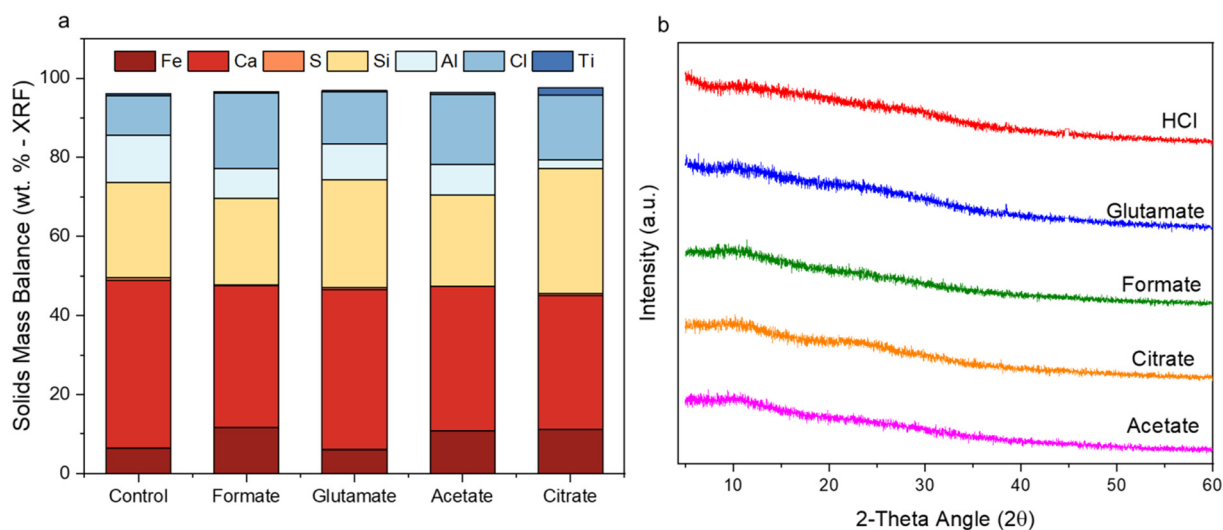


Fig. 10 (a) Pure elemental balance of the precipitated metal oxides (PMOs) as determined by XRF; (b) PXRD spectral data of the same PMO species for all five cases studied.





Fig. 11 ^{27}Al (a) and ^{29}Si (b) MAS solid-state nuclear magnetic resonance (NMR) testing of the raw HCP material before leaching and a representative sample of PMO produced during the pH-swing process. The PMO used for the tests was obtained from the HCl only leaching process.

alkaline wastes could indeed be used as upcycled materials within the build environment.

2.4 Carbonation to produce pure precipitated calcium carbonate (PCC) polymorphs

The carbonation of the leachate liquor was performed after PMO removal to produce pure PCC through carbon mineralization.

The morphology of the carbonates was analyzed to probe at the various crystalline phases present. Fig. 13a shows the refined Q-PXRD data with the wt% of the crystalline phases of the PCC produced at all five leaching cases. The main anhydrous and most common forms of CaCO_3 observed are vaterite, aragonite, and calcite, listed in order of thermodynamic stability.^{76–78}

Calcite is the most widely used polymorph globally and is the main constituent of limestone. However, there is growing



Fig. 12 (a) Heat flow of OPC and OPC replaced 10 wt% by PMO over 48 hours; (b) cumulative heat release for the same samples over 168 hours of curing and hydration.





Fig. 13 (a) Refined Q-PXRD data of the PCC produced showing the polymorphs of CaCO_3 , vaterite, calcite, or aragonite, present in the samples; (b) FTIR spectral data of the carbonates produced showing characteristic CO_3^{2-} out-of-plane vibrational bending near 873 cm^{-1} , with vaterite characteristic peaks at 742 cm^{-1} and calcite in-the-plane bending at 712 cm^{-1} .^{81–83} Table S2† shows the Rietveld refinement data and Fig. S6† shows the raw PXRD spectral data.

interest and research in the production of vaterite and aragonite, the metastable phases of CaCO_3 , for industrial applications based on their distinct morphologies, with vaterite being spherical and aragonite being needle-like.^{12,78–80} In this study, the control experiment produced a 50–50 wt% mixture of vaterite and calcite after 30 min carbonation. Due to the relatively dilute amount of Ca present ($\sim 3000\text{ ppm}$, 0.075 M), the calcite observed is likely a result of the precipitation of vaterite and recrystallization into calcite, which has been reported one of its main synthesis pathways by other researchers.⁸¹ The presence of formate, acetate, and citrate seemed to favor the production of calcite over vaterite, and could have decreased the nucleation rate of vaterite itself while promoting that of calcite. Interestingly, glutamate stabilized vaterite and resulted in a vaterite phase purity of the product of almost 97 wt% (Fig. 13a).

FTIR analysis confirmed the presence of vaterite in this sample though a peak at 744 cm^{-1} which corresponds with vaterite CO_3^{2-} symmetrical vibration (Fig. 13b).⁸² Calcite peaks in the other samples can be clearly seen at $710\text{--}713\text{ cm}^{-1}$, demonstrating the usefulness of FTIR to fingerprint the polymorphs of CaCO_3 .^{82,83} Fig. 14 shows the morphology of the produced carbonates for all the samples obtained during the carbonation reaction, further corroborating the presence of vaterite and calcite. The D_{50} of all the PCC produced was less than $10\text{ }\mu\text{m}$ (Fig. S5†), however the presence of glutamate and citrate resulted in the greatest degree of particle size reduction, with citrate PCC having a D_{50} of roughly $3.5\text{ }\mu\text{m}$. The ability for certain ligands to control the PSD of the PCC during carbonation could be useful if the end use requires smaller carbonates based on size.

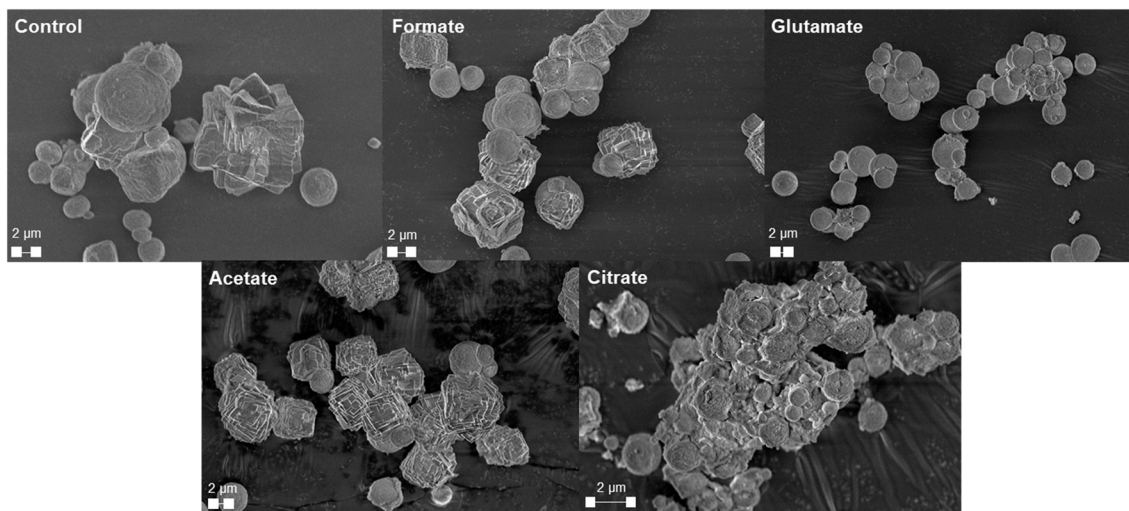


Fig. 14 SEM micrographs of the produced precipitated calcium carbonates showing the distinct morphologies present for the various ligands utilized during the hydrometallurgical leaching process.



to both the dissolving cement particles and the crystalizing carbonates. Overall, this study presents a compelling look into the use of carboxylic acid ligands which can be derived from CO₂ to enhance both material recovery and carbon capture during the *ex situ* carbon mineralization of C&DW for the decarbonization of the built environment.

4 Experimental section

4.1 Materials

The cement paste studied was produced from ordinary Portland Cement in-house and hydrated with a water to cement ratio of 0.4. Hydrated cement samples were crushed, milled, and sieved to a particle size range of 125–210 μm. In order to provide an accurate basis for assessing the degree of elemental extraction, the composition of the hydrated cement paste was assessed by ICP-OES. First, the samples were fused with lithium metaborate and then a solution of this product was analyzed *via* ICP. The major recoverable elemental composition of the cement was determined to be 44.0 wt% Ca, 14.0 wt% Si, 1.3 wt% Al, and 2.3 wt% Fe.⁹ The Ca and Si content is much smaller than ordinary Portland cement (OPC), due to the fact that this is hydrated cement paste; thus, to ensure proper material balance the ICP basis is preferred.⁶ The carboxylic ligands were all sourced from Sigma-Aldrich Chemicals, USA (>99% purity) and were sodium formate (NaCHO₂), sodium acetate (NaC₂H₃O₂), sodium glutamate (NaO₄NH₃C₅), and sodium citrate (Na₃C₆H₅O₇). CO₂ for carbonation was obtained from AirGas (Allentown, PA, USA) at 100% anhydrous. HCl for the leaching experiments was procured at 37 wt% (Sigma-Aldrich Chemicals, USA) and diluted to 5 M prior to use. Stock solutions of 25 wt% (w/v) NaOH (Alfa Aesar, MA, USA) were used for the pH swing process and to maintain the pH within the carbonation reactor during PCC production. Deionized water (MilliQ Grade, Millipore Sigma, USA) was used throughout the entire process, including leaching, washing, and stock solution creation.

4.2 Methods

4.2.1 Leaching reactor design. The dissolution of the waste HCP was carried out in 500 mL ChemGlass (Vineland, NJ, USA) stirred-tank, temperature-controlled reactors in a reaction volume of 300 mL. A slurry-density of 1 wt% (solids/liquid mass ratio) was utilized to properly assess the dissolution kinetics. The reactor was maintained at 25 °C for the duration of the 60 min leaching process which was performed at 900 rpm through overhead agitation. In the case of carboxylic ligand leaching, a 0.05 M solution of the corresponding salt (*i.e.*, formate, acetate, glutamate, and citrate) was made with MilliQ deionized water. This concentration was chosen based on previous studies and preliminary results suggesting an optimal low concentration window of 0–0.1 M for these ligands. The pH was then adjusted to 3 with 5 M HCl prior to leaching in all cases. pH was continually monitored and kept at 3 *via* HCl addition throughout the entire duration of the experiment. Afterwards,

the mixture was quickly filtered through a Buchner apparatus (Whatman, GE, USA) and the post-extraction reactor residue (PERR), or the undissolved portion of the cement matrix, was rinsed with 70% EtOH (v/v) prior to drying overnight in a vacuum oven at 80 °C until the samples reached a constant weight to ensure all water was removed.

4.2.2 pH-Swing process. In an effort to purify the leaching liquor prior to PCC production during carbonation, a pH swing process was employed to precipitate the major ancillary ions present, such as Si, Al, and Fe. The leaching liquor at pH 3 was slowly titrated with 25 wt% (w/v) NaOH towards pH 10, stopping before appreciable amounts of Ca²⁺ began to precipitate as Ca(OH)₂. The system was allowed to equilibrate at each whole-step pH for approximately 30 minutes before moving to the next. At pH 10, the reactor liquors were filtered and washed thoroughly with EtOH prior to drying the precipitated metal oxides (PMOs) in a vacuum oven at 80 °C overnight until the samples reached a constant weight to ensure all water was removed.

4.2.3 Carbonation reaction. The carbonation reaction was carried out in the same 500 mL ChemGlass stirred tank reactor systems at a temperature of 25 °C and a stirring rate of 600 rpm. Carbonation was performed over the course of 30 min and CO₂ was sparged into the reactor using a ceramic micro-sparger to ensure adequate solvation and absorption of the CO₂ itself. The CO₂ flowrate used was 150 mL min⁻¹. The pH of the reactor was maintained at 10 through the continuous addition of NaOH to ensure carbonate ions were present for carbonation. After carbonation finished, the solution was quickly filtered using a Buchner apparatus as described above, and the carbonates were washed with EtOH to ensure removal of trapped water. Finally, the PCC was dried overnight in an 80 °C oven until the samples reached a constant weight to ensure all water was removed prior to characterization.

4.2.4 Characterization techniques. Aqueous species analysis for both the leaching kinetics and the titration during pH swing was performed using an Agilent 5110 inductively coupled plasma optical emissions spectrometer (ICP-OES). Samples were taken and quickly filtered using a 0.22 μm syringe filter to remove any residual debris, prior to being diluted 50 to 100-fold and quenched in 2 wt% HNO₃. The following wavelengths were used to track the major elements through the use of the ICP: Ca²⁺: 422.67 nm; Si: 288.16 nm; Al: 237.31 nm; and Fe: 234.35 nm. To facilitate the titration of the dissolution reactor liquor, a Metrohm Titrand potentiometric titrator was used to dose in the base required to raise the pH of each solution. This also allowed for adequate time to collect samples for precipitation analysis *via* ICP-OES.

The three sets of produced solids, the post-extraction reactor residue (PERR), PMOs, and the PCC, were all subject to rigorous solids characterization techniques. A Panalytical X'pert3 (Malvern) powder X-ray diffractometer (PXRD) with a 3 kW Cu X-ray generator was used to study the crystalline phases present in the solids, especially the presence of the



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