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Synthesis and Regeneration of Sustainable CaO Sorbents from Chicken Eggshells for Enhanced Carbon Dioxide Capture

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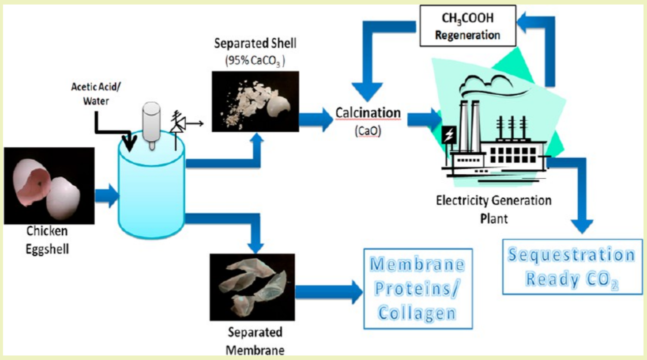
Supporting Information

ABSTRACT: Eggshell waste, which contains 95% calcium carbonate ($CaCO_3$), presents itself as an inexpensive calcium-based sorbent for removal of carbon dioxide (CO_2) in combustion streams used to generate electricity. The utilization of eggshell waste in CO_2 capture via cyclic carbonation-calcination reactions (CCR) was investigated in this work. Using thermogravimetric analysis, the CO_2 capture capacity for multiple acetic acid pretreated eggshell samples was studied. This pretreatement generates a mesoporous structure, allowing the eggshell-derived sorbent to reach higher conversions over more CCR cycles while also removing the eggshell's protein-rich membrane. Six acetic acid treatments were also explored for regeneration of spent sorbents after multiple cycles. The regeneration of spent sorbents with acetic acid provided a 38% improvement in CaO conversion over untreated shells after ten cycles. The eggshell membrane contained highly valuable Type X collagen, which can be recovered through the course of shell pretreatment to increase process feasibility. This scheme allows for sustainable generation of CaO sorbents while also transforming a current waste material into a value-added product.



KEYWORDS: *Carbonation, Calcination, Eggshell, CaO sorbents, CO_2 capture, Sustainable engineering*

INTRODUCTION

In an age where environmental concerns have become increasingly prevalent, efficient and carbon neutral methods for satisfying the global energy demand have become a necessity. Increasing levels of greenhouse gases are widely regarded as a key factor in the shifts observed in global climate patterns.[1] The U.S. alone accounted for 18% of worldwide CO_2 emissions in 2009 where roughly 95% of these emissions were due to the combustion of fossil fuels, predominantly for electricity generation and transportation.[2] Since it is predicted that a majority of the U.S. energy needs will be satisfied by fossil fuels in the near future, development of cost-effective and highly efficient carbon mitigation technologies has generated wide interest.[3]

In recent years, special emphasis has been placed on developing carbon neutral processes that are suitable for retrofitting existing coal-fired power plants, which supply approximately 40% of the nation's electricity and account for one-third of its CO_2 emissions.[3] Capturing and sequestering the carbon from coal or natural gas combustion can produce a more carbon neutral electricity source. Currently, CO_2 capture via physical and chemical absorption using solvents like selexol, rectisol, and monoethanolamine (MEA) is a mature technology. However, research has indicated that when a retrofit MEA system is used to capture 90% of the CO_2 in flue gas, the plant efficiency is derated by almost 30%.[4,5] Among emerging processes, high-temperature solid sorbent looping is very promising due to the potential of reducing energy penalties and CO_2 capture costs through process integration.[6] Within this category, calcium oxide (CaO) has presented itself as a very strong candidate.[6,7] In a typical calcium sorbent-based CO_2 capture process, the carbonation of CaO by reaction with the CO_2 in flue gas results in the formation of calcium carbonate ($CaCO_3$), and the calcination reaction, which occurs in a separate vessel, regenerates the CaO, releasing a sequestration-ready, pure stream of CO_2. Studies conducted at pilot-scale have confirmed the merit of this scheme.[8,9]

Carbonation

$$CaO + CO_2 \rightarrow CaCO_3 \qquad (1)$$

Calcination

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (2)$$

Besides natural precursors like limestone and dolomite, CaO is available from wastes including chicken eggshells. In total, the U.S. consumed approximately 76 billion eggs in 2008. These eggs generate an estimated 50 000 to 200 000 tons per year of shell that is currently treated as waste and can readily be

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collected from commercial processing facilities and hatcheries.[10−12] Preliminary research by our group indicated that $CaCO_3$ obtained from eggshell shows promise in capturing CO_2,[13] while others have shown that removal of heavy metals by eggshells also has merits.[14]

The shell stratum, which is typically referred to as the "eggshell", is largely composed of $CaCO_3$ (~95%). For the utilization of eggshell-derived CaO for CO_2 capture, the eggshell membrane needs to be removed. This membrane, which is present on the inner surface of the egg, contains many proteins including collagen types I, V, and X.[15] Since collagen and other eggshell membrane proteins have additional applications for cosmetic products, as nutritional supplements,[16] and as cell growth scaffolds,[17] separation of waste eggshell membranes is expected to be a beneficial biproduct to repurpose a current waste material. This study focuses on utilization of eggshell-derived CaO in a high-temperature CO_2 capture scheme for application in a model fossil fuel combustion stream. It has been reported that CaO derived from eggshell has a larger macropore volume than that of CaO derived from commercially available $CaCO_3$.[18] However, a systematic investigation of eggshell pretreatment and regeneration for CO_2 capture has yet to be reported in the literature. Herein is reported a novel method for greenhouse gas reduction in which eggshells are subjected to acetic acid pretreatment to remove the membrane and alter the pore structure. The effect of this pretreatment on CO_2 capture has been investigated in addition to the ability of these sorbents to be regenerated with acetic acid solutions to regain and even surpass initial activity after pore collapse.

■ MATERIALS AND METHODS

Treatment of Eggshells. The CO_2 capture capacity of calcium-based sorbents decreases over multiple cycles of carbonation and calcination due to sintering.[19,20] This can be remedied through the generation of a more porous surface structure.[21] A previous study into the treatment of waste oyster shells showed that when CaO derived from oyster shells was reacted with water to form calcium hydroxide ($Ca(OH)_2$), an increase in recyclability of the shell was observed over many cycles.[22] Another method by which the initial particle pore structure can be expanded is through treatment with acetic acid. The reaction of acetic acid with $CaCO_3$ results in the formation of calcium acetate, which has a larger molar volume than $CaCO_3$ and CaO.[23] This leads to an expanded pore structure and better performance over multiple carbonation-calcination reaction (CCR) cycles. Prior studies also report that CaO derived from calcium acetate displays the highest carbonation conversion among different CaO precursors tested.[24] Additionally, due to the low cost and ability to sustainably produce acetic acid via oxidation of biomass-derived ethanol, a pretreatment employing the use of acetic acid was used in this study. The formation of calcium acetate is also accompanied by the release of CO_2. Previous work in our group has shown that the production of CO_2 enhances the membrane's removal.[25]

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O \tag{3}$$

For the preparation of eggshell samples, acetic acid solutions of several strengths were prepared by mixing glacial acetic acid (99% pure, Fisher Scientific) and deionized water in a Pyrex 1.000 L bomb flask. The eggs were obtained from a local supermarket. The samples were prepared by adding the shell of one egg (~5.5 g) to a beaker containing 200 mL of the acetic acid solution. The mixture was then magnetically stirred. After the desired reaction time, the sample was immediately filtered and rinsed with deionized water to halt the reaction of the acid with the shell. The separated shell (200−300 μm in thickness) and membrane were then combined in another beaker containing deionized water. The buoyancy difference between the denser shell and neutrally buoyant membrane allowed for the membrane to be removed from solution more easily. The separated shell was then dried in air and pieces approximately 1−5 mm in size (~20 mg per sample) were retained for thermogravimetric analysis. BET analysis of uncalcined eggshell samples was performed on a Micromeritics Tristar BET after degassing for 14 h at 120 °C.

Regeneration of Spent Eggshell. For use in multiple CCR cycles, the spent sorbent which had undergone pore collapse would require regeneration. Regeneration was performed using deionized water and acetic acid solutions −0.5, 2.0, 5.0 M, 50%, and glacial acetic acid. For the regeneration, the solution was added dropwise to the calcined eggshell until the entire eggshell was saturated. The samples were not soaked in the solution due to the solubility of calcium acetate in water, which can cause the samples to partially dissolve. The samples were then dried overnight in air at 125 °C. While some physical attrition does occur leading to particle size reduction during cycling and regeneration, it has been shown previously that CaO sorbents in the particle size range and temperature range of those tested in this study do not exhibit significant intraparticle diffusion limitations that would provide differences in carbonation conversion or recyclability.[26,27]

Thermogravimetric Analyses. To study the reactivity of the eggshells, a Perkin-Elmer Pyris 1 Thermogravimetric Analyzer (TGA) was used. A detailed description of this equipment is available elsewhere.[28] A TGA cycle consisted of 30 min of calcination and 30 min of carbonation. Pure N_2 and CO_2 (>99.9% purity) were used for these runs, and a total gas flow rate of 120 mL/min was maintained throughout the testing to model the boiler flue gas stream. The system was heated at 50 °C/min from 25 °C up to reaction temperature and held for the duration of the experiment. During calcination, 100% N_2 was fed through the reactor while carbonation was performed in 10% CO_2 (balance N_2). To perform multiple cycles, a multiposition actuator (Valco Instrument Company, Inc.) was used. At the end of the 30 min calcination/carbonation reaction time, the actuator automatically toggled the flow of the gases. A simplified schematic is shown in the Supporting Information. In all of the TGA runs, the carbonation and calcination were performed at 700 °C. Repeated testing of eggshell samples that had undergone the same pretreatment established the standard error in conversion by thermogravimetric analysis to be 4.0%.

Experimental Design. Experiments were conducted to achieve two specific goals—to explore which pretreatment resulted in optimal carbon capture over multiple cycles and to determine the best mode of regeneration. In each case, five CCR cycles were used as a basis to judge the effect of different pretreatments on carbon capture in the first cycle and for longer term recyclability. The strength of the acid solution during pretreatment and the duration of pretreatment were the two variables altered to examine the effect of pretreatment on performance. Since a significant decrease in sorbent conversion was observed after five cycles, a regeneration step was performed after the fifth cycle. Only the effect of the medium was investigated during regeneration. To discover the long-term implications of regeneration on sorbent performance, selected samples that had undergone 20 cycles were regenerated a fourth time and subjected to 30 additional cycles of testing.

Proteomic Testing. In order to verify the stability of collagen in the eggshell membranes, the samples were tested at The Ohio State University (OSU) Mass Spectrometry and Proteomics Facility. The acetic acid solution used in the shell pretreatment was tested before and after being concentrated using a spin filter to ensure that eggshell collagen was not digested during eggshell pretreatment. Gel electrophoresis was used to test for protein presence. The "bands" on these gels that appeared to line up with appropriate molecular weights for collagen were then tested in a SwissProt Unlimited protein analyzer for identification.

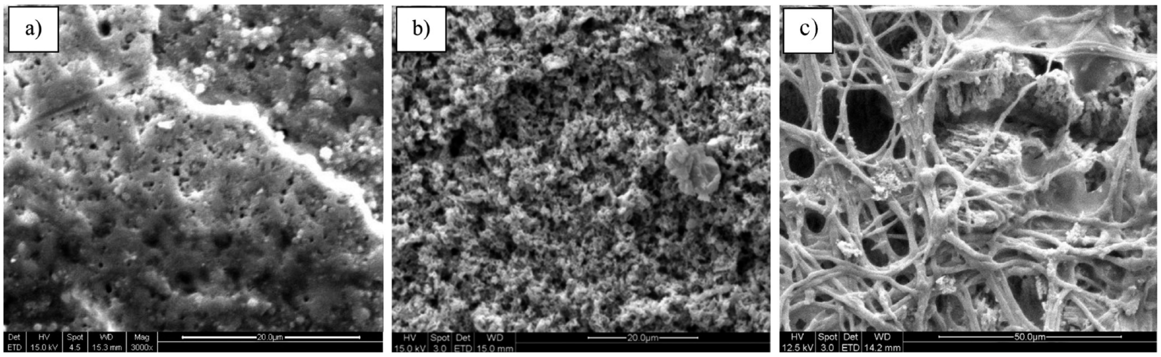

Figure 1. (a) Image of untreated shell. (b) Image of shell treated with 2 M acetic acid for 30 min. (c) Inside portion of the shell treated with 2 M acetic acid for 30 min.

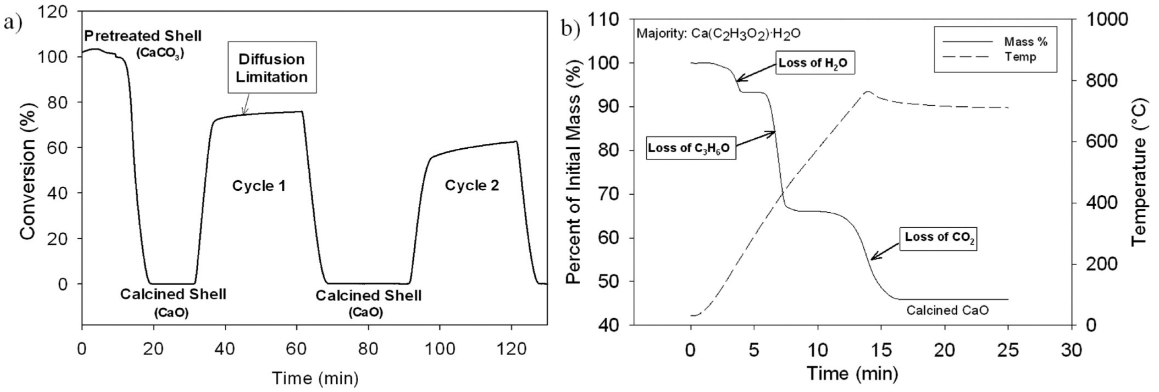

Figure 2. (a) TGA run conducted on the eggshell pretreated with 1 M acetic acid for 30 min with initial calcination and two complete CCR cycles. Temperature was increased at 50 °C/min to 700 °C. (b) Thermal decomposition of calcium acetate obtained from calcined eggshell treated with glacial acetic acid.

RESULTS AND DISCUSSION

Effect of Pretreatment on CO_2 Capture Capacity. To understand the effect of acetic acid pretreatment on the surface of the eggshell, the samples were imaged using a Quanta 200 scanning electron microscope (SEM). The images of the fresh eggshell and eggshell pretreated with acetic acid are shown in Figure 1. The difference is clearly visible—the acid-treated eggshell exhibits a more porous, open structure. Though some cracks can be seen on the surface of the untreated eggshell, CO_2 diffusion into the sorbent can be expected to be less favorable than for the more highly porous pretreated structure. This is further supported by the BET surface area measured for the samples. The untreated eggshell had a BET surface area of <0.02 m^2/g while the shell treated with acetic acid had a surface area of 0.12 m^2/g prior to calcination.

Due to the partial solubility of calcium acetate in water, some of the calcium acetate formed during the pretreatment step is carried away from the surface of the shell into the solution. This was corroborated by measuring the mass of the shell before and after treatment. It is believed that the dissolution of calcium acetate helps to generate "pockmarks" in the shell surface. The inside portion of the shell was also imaged and is shown in Figure 1c. It can be observed that some of the membrane fibers, which were identified using previous imaging of membrane fibers in hen eggshells,[16] remained attached to the inner surface of the eggshell. This indicates that the acetic acid treatment cannot remove all the fibers, but removes a large enough fraction for the resulting material to be useful as a sorbent.

Figure 2a illustrates the weight change over time when the eggshell pretreated with 1 M acetic acid for 30 min was calcined and carbonated in the TGA. The shell calcines at 700 °C, forming CaO. At a time of 30 min, CO_2 is introduced and the initial, rapid carbonation occurs. The reaction rate-limited carbonation is followed by diffusion-limited carbonation, where the CO_2 must diffuse deeper into the pores of the sorbent.[26] Figure 2a also shows that the sample at the start of the run was essentially pure $CaCO_3$. If the sample contained significant amounts of calcium acetate, it would undergo several decompositions during the temperature rise. To illustrate this, Figure 2b shows the thermal decomposition of calcium acetate formed during regeneration by treating the calcined eggshell with acetic acid. This data coincides well with findings reported elsewhere for the atmospheric pressure thermal decomposition of calcium acetate.[24,29] Further, a differential thermogravimetric analysis (DTG) plot is included in the Supporting Information showing that, with the exception of desorption of small amounts of water, a single peak is observed for the decomposition of the pretreated eggshell sorbent to CaO. To quantify the extent of CaO utilization, conversion of the substrate will be defined in eq 4:

$$\text{conversion} = \frac{n_{\text{CaCO}_3,30\text{min}}}{n_{\text{Cao,initial}}} \times 100\% \tag{4}$$

where "n" indicates moles of the species.

To explore the effects of different pretreatments, experiments were carried out with acid solutions of different strengths with varying time for pretreatment. To assess the best first cycle reactivity and multicyclic reactivity, five CCR cycles were performed for each pretreated shell. The results are presented in Figure 3. It can be seen that the best conversion in the first cycle occurs for the eggshell treated with 1 M acetic acid for 30 min. However, the 2 M acetic acid treatment for 15 min provides the best performance after five cycles. It can also be seen that the difference between the conversion of this eggshell and the raw (untreated) eggshell, which had the membrane removed manually instead of chemically, is close to 15% after five cycles.

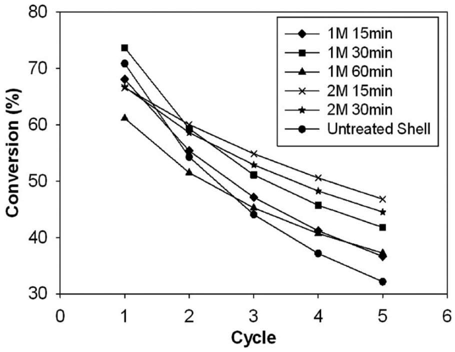

Figure 3. Conversion obtained in five CCR cycles for varying eggshell pretreatments.

Effect of Regeneration on CO_2 Capture Capacity. Previous work by Lu and co-workers has shown that the pore volume and surface area is significantly higher for CaO derived from calcium acetate or $Ca(OH)_2$ compared to materials derived from $CaCO_3$.[24] Later work in which limestone was treated with 50% acetic acid prior to calcination also showed dramatic increases in pore volume due to calcium acetate formation, even after cycling.[30] Regenerations were carried out using pure water, and 0.5, 2, 5 M, 50%, and glacial acetic acid. The regenerations were screened for two separate pretreatments—1 M, 15 min and 1 M, 30 min—to study the effect of pretreatment on multicyclic sorbent regeneration. The regenerations were performed at 25 °C after every 5 cycles up to a total of 20 CCR cycles. To account for small material transfer losses after each regeneration, the mass of CaO was updated in eq 4 following the first calcination after regeneration. While higher temperature regeneration of CaO has also been explored using water and was found to be effective,[21] the present study is limited to regeneration at ambient conditions rather than at reaction conditions to prevent the known high temperature dehydration and decarboxylation of acetic acid which would hinder regeneration. The results are shown in Figure 4. It can be observed that pure water provides the least effective regeneration when compared to regenerations involving acetic acid at ambient conditions. This can be attributed to the fact that calcium acetate has a higher molar volume than $Ca(OH)_2$. While it may be expected that glacial acetic acid would perform the best due to the argument of its molar volume alone, having some water helps the structure to reorganize to increase porosity in the first several regenerations due in part to the solubility of calcium acetate in the water. Without the presence of water, the acetic acid may not be able to reach the entirety of the CaO pore network.

By screening intermediate acetic acid strengths, it was found that 2 M acetic acid offered the best regeneration of those tested. Hence, the effect of different pretreatments was investigated using 2 M regeneration to establish how the initial pretreatment of the shell affects long-term recyclability after regeneration. The results are shown in Figure 5a. It is clear that all the samples converge to similar conversion after three regenerations, which implies that acetic acid regenerations tend to renew the initial porosity of the sorbent while also causing the sorbent performance to be more dependent on the regeneration than the initial pretreatment. It is also observed that both the first and last cycle carbonation conversion increase on average after each subsequent regeneration. These results indicate that periodic regeneration can effectively increase the reactivity of the spent sorbent. This effect occurs as the material begins to increasingly take on the properties of the calcium hydroxide and calcium acetate formed upon regeneration.

Effects of Multiple Regenerations on Long-term Recyclability. To investigate long-term sorbent reactivity, 30-cycle tests were carried out for selected acetic acid regenerations. The samples that had undergone 20 cycles and three regenerations from the prior tests were regenerated for a

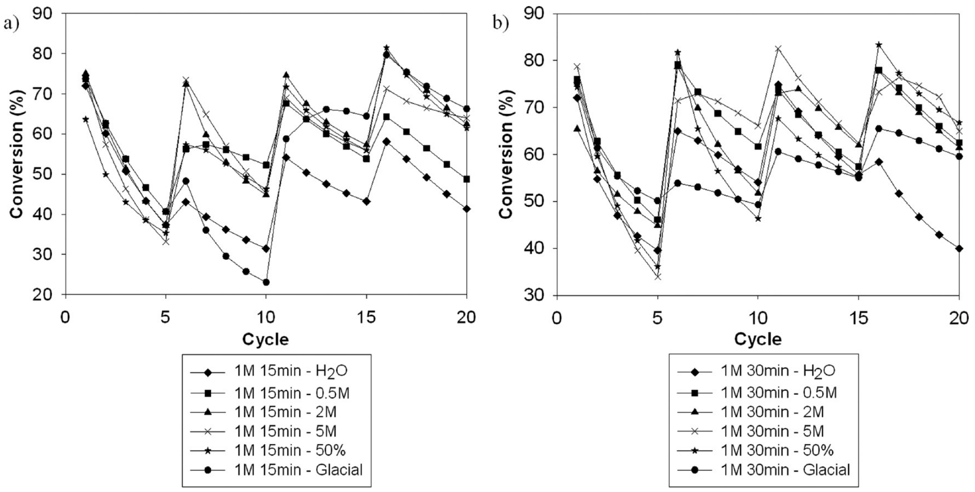

Figure 4. (a) Conversion obtained with different regenerations for a 1 M, 15 min pretreatment (b) and a 1 M, 30 min pretreatment. Nomenclature for samples is the pretreatment conditions (strength and exposure time) followed by the strength of acetic acid used for regeneration.

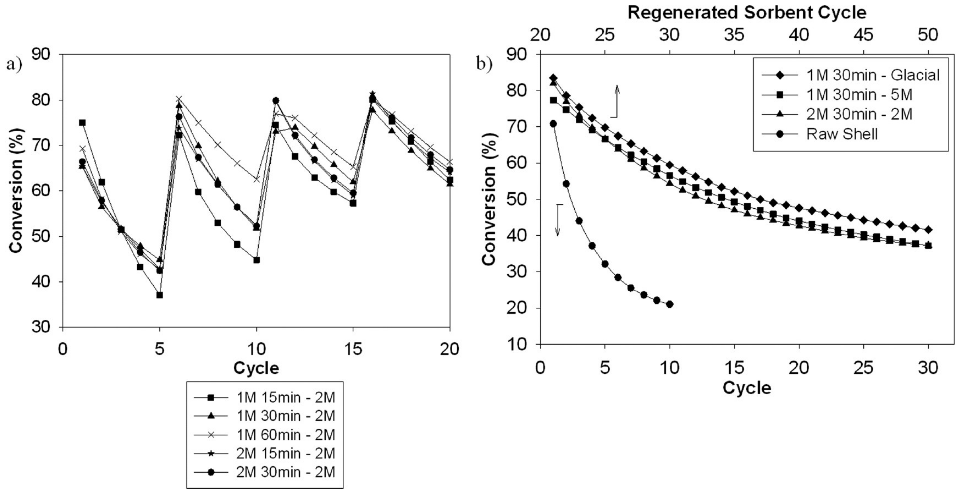

Figure 5. (a) Conversion obtained with different pretreatments for 2 M acetic acid regenerations. (b) Long-term performance of the regenerated eggshells—cycle 21 to 50 (4th regeneration performed after cycle 20) compared to unpretreated (raw) shell subjected to 10 CCR cycles. Nomenclature for samples is the pretreatment conditions (strength and exposure time) followed by the strength of acetic acid used for regeneration.

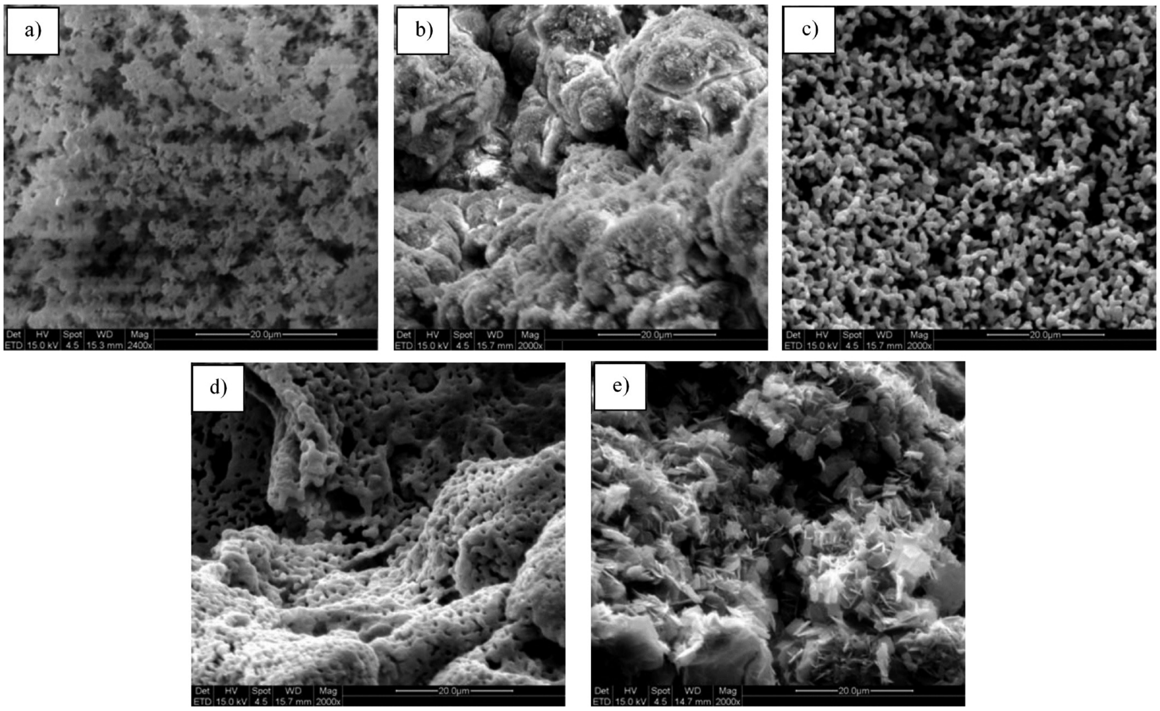

Figure 6. (a) Eggshell after one calcination. (b) Calcined eggshell after three 2 M regenerations and 20 cycles. (c) Calcined eggshell after three glacial acetic acid regenerations and 20 cycles. (d) Regenerated eggshell after five 2 M regenerations and 50 cycles. (e) Regenerated eggshell after five glacial acetic acid regenerations and 50 cycles. (Regenerations performed after cycle 5, 10, 15, 20, and 50 for each sample).

fourth time and allowed to undergo 30 additional CCR cycles without intermediate regeneration. As shown in Figure 5b, all regenerated samples in their 21st through 50th cycles performed similarly with glacial acetic acid treated CaO slightly outperforming the rest. The recyclability of these sorbents also compares quite favorably to Linwood Carbonate fines tested previously at OSU (36% conversion after 25 cycles).[28] Figure 5b also depicts the conversions achieved using untreated eggshell as compared to the acetic acid-regenerated eggshell in cycles 21−50. As can be readily observed in Figure 5b, reactivity even in excess of what can be achieved initially can be gained by regeneration of spent eggshell with acetic acid. While the conversion of the untreated shell drops to approximately 38% in just 4 cycles, the regenerated eggshell takes over 30 cycles to drop as low. This shows how sorbent recyclability is greatly enhanced in the provided scheme.

To best illustrate the effect of regeneration, SEM images are shown in Figures 6. Sorbents regenerated with 2 M and glacial acetic acid that had undergone three regenerations were imaged and compared to the shell that underwent only one calcination. From Figure 6, it can be seen that the surface morphology is different depending on the treatment and regeneration. The treated shell that is calcined only once shows a fairly open surface structure. This structure is found to undergo agglomeration to form a less porous sorbent after 20 CCR cycles, which includes three regenerations with 2 M acetic acid.

This coincides with the well-known sintering of CaO sorbents upon recycle. When the regenerating medium is changed to glacial acetic acid, the resulting surface structure is still remains uncollapsed, even after 20 cycles. The observed, porous macrostructure of regenerated sorbents is consistent with previous SEM observations in which increasingly "fluffy" and porous looking surfaces also correlated with increased pore volume and higher CCR conversion for calcium acetate derived CaO.[24] The significant change in molecular volume for calcium acetate to decompose to CaO causes fracturing of the macrostructure of the material in addition to increased formation of the macro- and mesopore volume, as studied previously.[24,30]

Figure 6 also shows the images of the regenerated eggshells that had undergone 50 CCR cycles and 5 regenerations—after cycles 5, 10, 15, 20, and 50. When regenerated with 2 M acetic acid, the structure formed is much more porous and is able to restructure into a much different surface with numerous openings through which CO_2 can diffuse once the sample is calcined. This is due to the formation of calcium acetate in the presence of water. On the other hand, regeneration with glacial acetic acid results in the formation of calcium acetate crystals, clearly visible in the Figure 6e. When the calcium acetate is calcined to CaO, the large decrease in molar volume opens up the pore structure of the sorbent providing good reactivity over numerous cycles, as has been explained by BET and BJH analysis previously.[24]

Comparison with Previously Published Results. Smirniotis and co-workers have investigated CO_2 capture by CaO derived from different organometallic precursors.[24,31] Most relevant for comparison with the present work is the data obtained using calcium acetate-derived CaO—they report ~80% conversion at the end of 30 min, using 30% CO_2 at 600 °C.[31] A higher conversion of 90% has been reported for CaO derived from calcium acetate-monohydrate.[24] For all the different regeneration and pretreatment conditions studied in our work, it was found that the conversion lies between 70 and 80% in the first cycle. While the present work has used waste eggshells and acetic acid treatment, reagent-grade high-purity chemicals have been used as CaO precursors in the other works, in addition to higher CO_2 concentrations.[24,31] Our work focuses more closely on the 10 mol % concentration of CO_2 that is likely to be found in the flue gas of a typical power plant. Further, the intermittent acetic acid regeneration technique employed here restores the conversion to the original value (>70%). The carbonation conversions are, however, also dependent on the calcination conditions employed. For harsher calcination conditions (900 °C), Liu et al. report a drop to 50% conversion after only 10 cycles for calcium acetate-derived CaO.[32]

Our previous work reports a comparison of the multicyclic performance of CaO derived from different precursors.[28] CaO derived from commercially available Linwood carbonate and Rockwell dolomite exhibits 45% and 41% conversion in the 10th cycle, respectively.[28] Comparing with the untreated eggshell (Figure 5b), a low conversion of 21% is obtained. Hence, the pretreatment and regeneration techniques shown here, which provide a conversion of 53−60% ten cycles after regeneration (Figure 5b), provide an attractive alternative not only when using waste eggshells as sorbents in a CO_2 capture process, but for other CaO materials as well.

Proteomic Testing. As described previously, the availability of collagen in the eggshell membrane was also investigated. It was believed that since proteins, including collagen, are often dissolved in acetic acid solutions along with a digestive protease such as pepsin for further analyses,[33,34] a significant yield of collagen could be lost during the membrane pretreatment phase. Type X collagen, specifically, has been found to act as an inhibitory boundary on the eggshell membrane and has previously been detected even without pepsin digestion.[35] Hence, the acetic acid used in pretreatment was tested for the presence of type X collagen in addition to the membranes themselves. After concentrating the acetic acid used in pretreatment, no significant amount of collagen was detected. This indicates that the amount of collagen lost in the pretreatment stage is negligible compared to the amount of collagen present in the membrane largely due to the lower contact times, relatively low acidity, and the absence of proper digestive aids compared to typical collagen dissolution techniques.[34] When testing the membranes themselves, Type X collagen was identified after it was isolated via gel electrophoresis, indicating stability of the collagen under pretreatment conditions.

Pretreatments of 1−2 M acetic acid generate eggshell sorbents with exceptional initial chemisorption reactivity while providing sufficient membrane removal on both lab and bench scale. Regenerations using 2 M acetic acid also led to significantly increased sorbent recyclability due to formation of calcium acetate. This regeneration technique will help eggshells become sustainable, recyclable sorbents for CO_2 capture in carbon neutral and carbon negative technologies. Finally, the collagen and proteins in the eggshell membrane can either be separated and purified using standard techniques for differential salt precipitation[34] to create numerous value added products or the membrane can be dissolved and sold as a cell-culture scaffold,[17] allowing waste eggshells to be repurposed for both biological and environmental benefits.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Description of the experimental apparatus in addition to a differential thermogravimetric analysis plot for the thermal decomposition of calcium acetate formed from eggshells. This information is available free of charge via the Internet at http://pubs.acs.org/

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Notes

The authors declare no competing financial interest.

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