Effect of Membrane Removal on the Production of Calcium Oxide from Eggshells via Calcination

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In the pursuit of a circular economy and against a background of viable alternative uses of avian eggshells and eggshell membranes, this research investigated the effect of domesticated chicken eggshell membrane separation on the calcination process and quality of Calcium Oxide (CaO) produced. Acetic acid was used to leach the eggshells for 60 min to aid separation of the shell membrane. X-ray diffraction, red green blue colour model, and thermogravimetric analyses were used to characterize the calcined shells. Leached and separated shells produced CaO of comparable quality and crystallinity to unseparated shells after calcination. Results showed that while leaching and membrane separation did not affect calcination temperature, residual ash from the membrane left impurities in the unseparated shells after calcination. It was concluded that leaching and separating the membranes from eggshells prior to calcination serves to upcycle eggshells by facilitating improved CaO production and membrane value extraction.

1. Introduction

The adverse impacts of climate change are arguably the prime focus of the twenty-first century's global dialogues seeking to improve human economic and social wellbeing. Climate change influences almost all human activities demanding urgent and decisive action to address the adverse impacts while simultaneously exploiting any opportunities to advance human wellbeing (Nhamo and Mjimba, 2014). The focus of managing climate change has been and remains two-pronged: learning to live with the adverse impacts of this phenomenon – the essence of adaptation on one hand – and retarding or halting the increase of anthropogenic atmospheric greenhouse gases (GHGs) – the essence of mitigation on the other hand.

A major source of anthropogenic GHGs (also called carbon emissions) is the burning of fossil fuels for direct and indirect energy supply in commercial and social activities. Other sources include farming and waste management practices that rely on the traditional disposal of solid waste in dump areas. In these dumps, the waste decomposes releasing methane - an extremely potent GHG. The contemporary approach to managing waste and (tacitly) climate change encourages recycling, alternative uses of some waste materials (Nhamo and Mjimba, 2014), and ultimately advocating a zero-waste community (circular economy) (Ellen MacArthur Foundation, 2012).

The global awareness for the need to reduce carbon emissions has encouraged investigations on the use of alternative cementitious materials for concrete production (Embong et al., 2016). This focus arises from the realisation that the production of Portland cement clinker emits up to 1.5 Gt CO_2 annually. These emissions account for approximately 5 % of the total person-made CO_2 global emissions (Part et al., 2016). CO_2 in the atmosphere is now above 400 ppm and by far exceeds the pre-industrial benchmark levels (Tan, 2018). Simultaneously, the last few decades have witnessed a tremendous increase in waste generation due to increased industrialization and urbanization (Albino et al., 2015). According to Kaza et al. (2018), global waste generation was estimated at 2.01 Gt in 2016 with a projection of 3.4 Gt by 2050. In South Africa, the Department of Environmental Affairs (2018) reported that 42 Mt of general waste was generated in 2017.

Traditional approaches to the management of waste are disposal in dumpsite or incineration. Both methods contribute to GHG emissions. Modern philosophies of managing waste and the challenges of managing climate change advocates for the continual optimization of resource utilisation in the bid to eliminate waste. One such approach, called the Circular economy, elevates the principles of reuse, sharing, repair, renovation, remanufacturing, and recycling to create a closed system, curtailing the use of virgin inputs and the creation of waste, pollution, and emission (Geissdoerfer et al., 2017). The tenet of the approach is that all "waste" should become "food" for another process (Ellen MacArthur Foundation, 2012).

Currently, the major contribution of CO_2 in the production of Portland Cement is the calcination of $CaCO_3$ to quick lime (CaO), releasing one mole of CO_2 per mole of CaO produced (786 g CO_2/kg CaO produced). A plausible alternative binder to cement is a class of alkali alumino-silicates called geopolymers or alkali-activated materials (AAM) (Ikotun et al., 2017). AAMs presents a dual advantage. Firstly, they help reduce the carbon footprint of the construction industry as a result of their production from agricultural and industrial by-products and secondly, they aid in reducing the cost associated with waste management and disposal. However, because of their low calcium oxide content, geopolymers need to be processed at high temperatures to achieve comparably high early strength to conventional cement used in the construction industry. Where this heating process is fossil fuel-driven, the process directly contributes to GHG emission. It remains necessary to find a means of reducing or eradicating this heating process. Investigations by Ng et al. (2018) showed that CaO is responsible for the early strength development of conventional concrete at room temperature. In the same vein, Ige et al. (2017) opined that the addition of CaO to geopolymers aids early strength development in room temperature.

The production of CaO through the calcination of eggshells makes it a plausible substitute for lime in general. The world production of eggs from domesticated chickens (*Gallus gallus domesticus*) was estimated at 76.7 Mt in 2018 (Shahbandeh, 2020) while the local South African production of eggs in 2018 was 452,000 t (South African Poultry Association, 2019). The calcified eggshell and double layer membrane of the egg makes up approximately 10.2 % of the whole egg (i.e. 7.82 Mt globally and 46,100 t locally in 2018). The average value of quicklime in 2018 was $124.60/t (US Geological Survey, 2020), meaning a potential market value of eggshell derived quicklime of $550 M globally in 2018. The current lime production in South Africa is 1.2 Mt/y (US Geological Survey, 2020), meaning the local production of 452,000 t of eggshells, potentially yielding 252,000 t of lime, has the potential to substitute as much as 21 % of the South African lime market. Currently, the majority of these waste eggshells are landfilled with a high associated management cost (Faridi and Arabhosseini, 2018). However, research works involving the calcination of eggshells have often been done by calcinating the entire shell (Mohadi et al., 2016), including its constituent proteins and membrane (Tangboriboon et al., 2012).

Eggshells consist of about 98 % calcium carbonate and other trace elements such as magnesium and phosphorus. The remaining mass consists of the shell membrane comprising of 69.2 % protein, 2.7 % fat, 1.5 % moisture and 27.2 % ash. The membrane protein consists of about 10 % collagen (King'ori, 2011). Eggshells have been used as fine aggregate in concrete (Raji, 2015), fertilizer in agriculture, soil stabilizer in construction, and calcium supplements in health and medicine. Likewise, extracted shell membrane collagen has diverse uses in medicine, biochemical, pharmaceutical, food, and cosmetics industries. Collagen is a tough protein that connects and supports bodily tissues, such as skin, bone, tendons, muscles, and cartilage. Collagen has primarily been extracted from swine or bovine skins, hooves, and bones. However, following the outbreaks of bovine spongiform encephalopathy, foot and mouth disease, and autoimmune and allergic reactions, restrictions on collagen usage from these sources were enforced. Eggshell membrane collagen is very low in autoimmune and allergic reactions as well as high in biosafety and is of similar characteristics to other mammalian collagens (King'ori, 2011). Eggshells and its membrane can be separated by a wide variety of techniques including chemical, mechanical, steam, microwave, and vacuum processes (Hussain, 2009).

Against the backdrop of the importance of CaO to the construction industry and alternative use of eggshell membranes, this research seeks to evaluate the potential of producing CaO from eggshells via acetic acid leaching and calcination, simultaneously upcycling the eggshell by separating its membrane for other uses before calcination. The process was evaluated and characterized by pH, X-ray diffraction (XRD), red green blue colour model- (RGB), and thermogravimetric (TGA) analyses to assess how membrane separation and leaching affects the calcination and subsequent CaO quality.

2. Materials and Methods

2.1 Experimental Methods

Eggshells were collected from eateries within the Hatfield campus of the University of Pretoria and the Hatfield Plaza mall, in Pretoria, South Africa. To decontaminate the shells, they were washed repeatedly in ultra-pure water, dried at 60 °C for 60 min in an EcoTherm oven and stored within 24 h of collection.

For the leaching rate experiments, 20 g of eggshells were leaching in 13 sacrificial reactors containing 500 mL of 1 mol Acetic acid each. After pH measurement, the entire contents of each reactor were sieved and washed with distilled water and dried to constant weight at 60 °C. The pH of a 14th reactor was measured in parallel for 180 min to monitor the $CaCO_3$ loss over time.

For the calcination experiments, 1 mol of acetic acid was used to leach the shells and aid membrane separation using 250 g of eggshells in 1,000 mL of the solution under gentle stir in a plastic jug. Leaching was carried out for 60 min at room temperature. The membrane separation was done by removing the membrane from its shell by hand. Samples of 20 g shells (unseparated and separated by leaching for 60 min) were calcined using a Carbolite CWF1100 furnace in the presence of oxygen at 700 °C and 900 °C for 30 min, 1 h, 3 h and 5 h. Unseparated shells and shells separated after 60 min are hereafter referred to as US, and S60.

2.2 Analytical Methods

The pH was measured instantaneously using GOnDO software (GOnDO Electronic) with a special purpose pH probe connected to an Ezodo PL-700PC meter. The change in mass was determined by the difference in the initial and final mass for each sacrificial reactor. Thermal analysis was conducted with the use of TGA5500 thermogravimetric analyzer. The change in mass was measured with an increase in temperature from room temperature to 950 °C at a heating rate of 10 °C/min in the presence of nitrogen.

RGB colour analysis was performed using Image J software to observe the colour change in the samples due to change in temperature. A 13-megapixel digital camera was used to take pictures of the samples after calcination at constant distance and lightning condition. The software separated the images into their red, green, and blue colour spectrum. The red component was used for the analysis due to the additive nature of the colours; a value of 255 indicates a pure white sample.

The raw shells and samples calcined for 5 h at 900 °C was subjected to X-ray diffraction (XRD) analysis to determine the mineralogy of the shells before and after calcination. The samples were prepared according to the standardized Panalytical backloading system, which provides a nearly random distribution of the particles. The samples were analyzed using a PANalytical X'Pert Pro powder diffractometer in θ–θ configuration with an X'Celerator detector and variable divergence - and fixed receiving slits with Fe filtered Co-Kα radiation (λ=1.789Å). The mineralogy was determined by selecting the best–fitting pattern from the ICSD database to the measured diffraction pattern, using X'Pert Highscore plus software. The relative phase amounts (weight% of the crystalline portion) were estimated using the Rietveld method using Autoquan/BGMN software employing Fundamental Parameter Approach.

2.3 Chemical Model used to Estimate $CaCO_3$ Mass Leached

The model assumed that all reactions in the leaching process were limited by the rate of $CaCO_3$ dissolution to the medium (reaction 1):

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \tag{1}$$

It was assumed that the interactions between the carbonic species, the acetic species, and the medium were at pseudo equilibrium conditions (Eq 2-4):

$$HAc \rightleftharpoons H^+ + Ac^-, pK_A = 4.76 \tag{2}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}, pK_A = 10.25 \tag{3}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-, pK_A = 3.60 \tag{4}$$

The system of equations used to predict the amount of $CaCO_3$ leached at each time step are shown in equations:

$$\frac{[Ac]}{[HAc]} = 10^{-4.76+pH} \tag{5}$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.25+pH} \tag{6}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{-3.60+pH} \tag{7}$$

$$[Ca^{2+}] = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \tag{8}$$

The concentration of calcium in solution would be equivalent to the amount of $CaCO_3$ leached (in molar units) and was used to determine the mass of $CaCO_3$ leached from the eggshells.

3. Results and Discussion

As expected, 1M Acetic acid leaches $CaCO_3$ from the shell into the solution and this results into an increase in pH and mass loss in the eggshell. The mass loss was measured over 60 min and plotted with the change in pH as seen in Figure 1a. This reveals that after 60 min of leaching, about 6 g (30 %) of $CaCO_3$ was dissolved into the solution. The predicted amount of $CaCO_3$ lost using Eq(5) – Eq(8) correlated well with the measured values as shown in Figure 1b. The pH and predicted $CaCO_3$ mass loss Eq(5) – Eq(8) from the measured pH values are shown in Figure 1c revealing that about 15 g (75 %) of $CaCO_3$ was dissolved in the solution after 180 min of leaching. These results show that one of the most potentially significant limitations of the leaching method for membrane removal would be the amount of $CaCO_3$ lost to the solution as a result of the leaching.
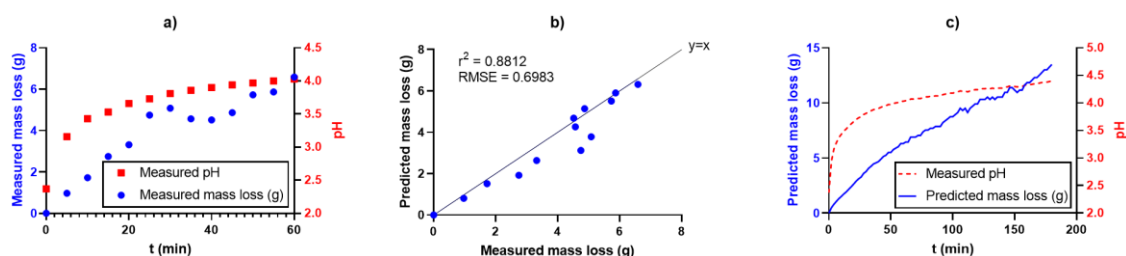

Figure 1: a) Change in pH and measured mass loss of eggshell in acetic acid, b) Parity plot of the measured mass loss and the predicted mass loss using Eq(5) to Eq(8), c) Predicted mass loss estimated from the measured pH using Eq(5) to Eq(8)

Thermal analysis plots comprising of the TG spectra of US and S60 shells, as well as the membrane, are seen in Figure 2. US and S60 samples began with a linear reduction in weight due to loss of moisture up to 300 °C after which US samples records a nonlinear reduction due to the volatilization of its membrane constituent. Both shell samples continued the linear path until about 650 °C. All water, protein, and carbon constituents of the shells are evaporated, and actual calcination sets in. As seen in the plot, separated shells were fully calcined at 720 °C while unseparated shells became fully calcined at 735 °C. On the other hand, the shell membrane which is less dense than the shells turn completely into ash after 300 °C, leaving approximately 10 % weight at > 700 °C. A potential source of impurities in the US samples.
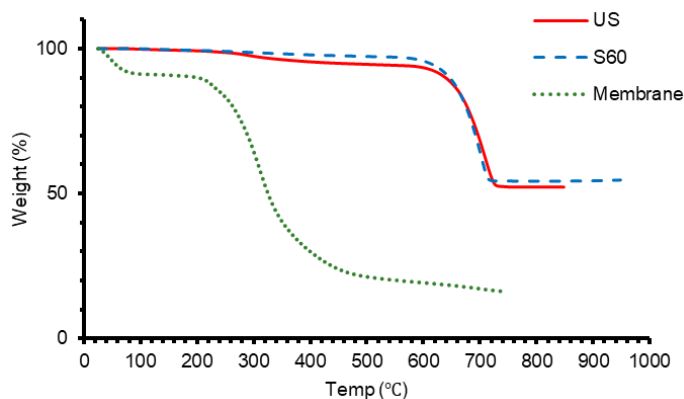

Figure 2: Thermogravimetric analysis of the US, S60, and membrane only in the presence of nitrogen

RGB results in Figure 3 shows the trend of the colour change of the calcined US shells from light brown (242) to dark brown (127), grey (148), and finally, light grey (245) at 900 °C; the carbon in the samples undergo carbonization during the initial stages of calcination (darkening) followed by combustion to CO_2 (whitening). In contrast, it was observed that the samples leached for 60 min did not get as dark as the US samples at either 700 °C or 900 °C. This can be due to the reduced carbon content of the S60 samples. Both US and S60 eventually attained a "white" colour spectrum at 900 °C; S60 had an RGB value of 253 while US samples measured 248 after 5 h at 900 °C. The observation that neither samples became "white" at 700 °C indicates incomplete calcination (supported by Figure 2).

The XRD qualitative results in Figure 4 demonstrates that before calcination, US and S60 shells indicated only the presence of $CaCO_3$. After calcination, shells leached for 60 min had slightly higher CaO intensity compared to the unseparated shells. Quantitative results in Figure 5 reveals that both separated and unseparated shells had about 99 % CaO content after calcination. This implies that leaching and membrane separation did not impact the quality of CaO product. It should be noted that the US samples showed significantly more additional peaks, potentially the result of residual impurities from membrane ash remaining in the sample.
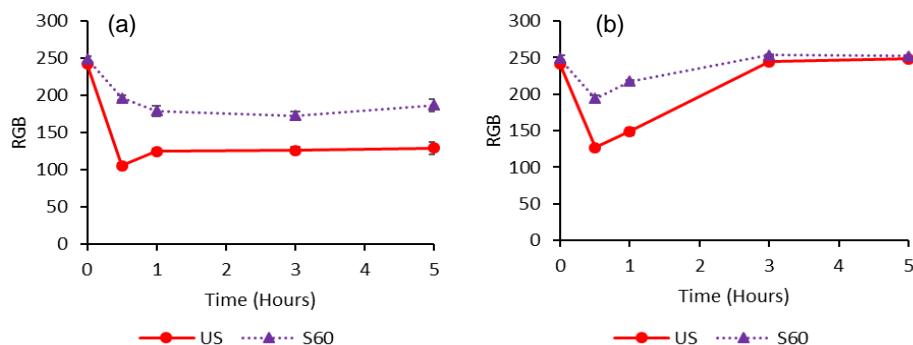

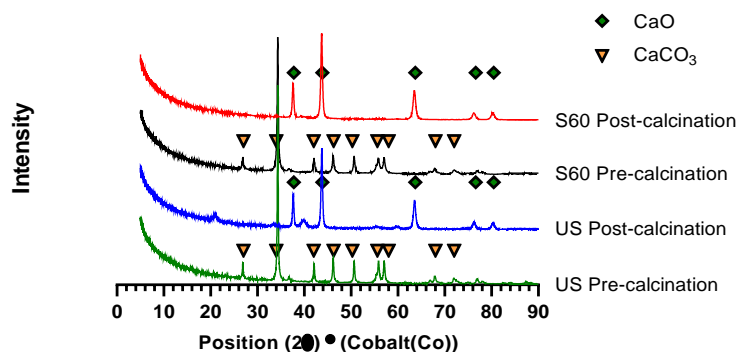Figure 3: RGB colour analysis of calcined eggshells. (a) at 700 ℃; (b) at 900 ℃.

Figure 4: XRD pattern of eggshell after calcination at 900 °C
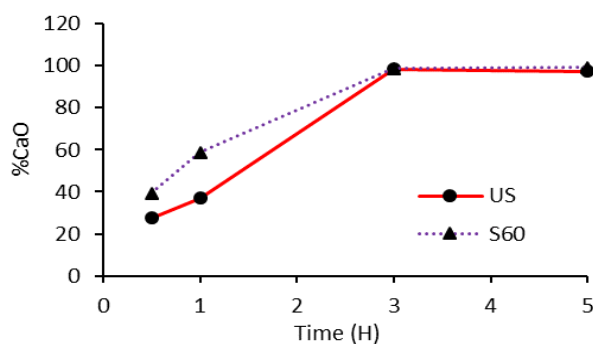

Figure 5: XRD quantitative analysis of calcined eggshells at 900 °C

4. Conclusions and Recommendation

From the experimental results and analysis carried out, it was concluded that acetic acid effectively weakened the bond between eggshells and its membrane aiding separation of the membrane and valorization of the eggshells to CaO facilitating the profitable use of shell membrane and constituent protein. Additionally, the separation of the eggshell membrane before calcination does not harm the quality of CaO produced. Results revealed that both separated and unseparated shells yielded CaO of similar purity and crystallinity at a similar

temperature. It should be, however, noted that eggshell membrane turns to ash above 300 °C consequently becoming an impurity (<1 %) in the CaO produced from the unseparated shells.

Further research is recommended to optimize the process for maximum $CaCO_3$, membrane, and constituent protein recovery. Besides, the optimized process should be costed to assess the economic scalability.

Acknowledgement

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