Physicochemical Comparison of Precipitated Calcium Carbonate for Different Configurations of a Biogas Upgrading Unit.

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Abstract

BACKGROUND: This paper presents a physicochemical comparison of the solid products obtained from two alternative processes that recycle waste sodium carbonate

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(Na_2CO_3) solution, which is produced following the absorption of CO_2 in a biogas-upgrading unit. Chemical regeneration processes offer an attractive alternative to the energetically demanding standard physical methods. In the first process, sodium hydroxide (NaOH) is regenerated as a precipitate from the chemical reaction of Na_2CO_3 with calcium hydroxide ($Ca(OH)_2$). The second process shows a path to obtain a valuable sodium chloride (NaCl) and Calcium carbonate ($CaCO_3$) rich brine from calcium chloride ($CaCl_2$) acting as a precipitant agent. In both processes, Precipitated Calcium Carbonate (PCC) is obtained as the most valuable by-product, but with varying properties due to the different origin.

RESULTS: The purpose of this work is to analyse physicochemically both variations of PCCs obtained and examining the differences between these solid samples in order to determine which method produces more desirable characteristics in the final product. To this end, FTIR, Raman, XRD and SEM were employed as characterization methods. The results reflect that both PCCs have a calcite crystal structure, or morph, being as both PCC products originate from $CaCl_2$ that is more similar to commercial calcium carbonate calcite.

CONCLUSION: These results confirmed that a pure $CaCO_3$ valuable by-product can be obtained from a biogas upgrading unit with several industrial applications.

Keywords: Biogas; Carbon Capture; Carbon Utilisation; Chemical Analysis; Green Chemistry; Precipitation

1. Introduction

The need to combine renewable energies with current fossil fuels to reduce pollution is one of the topics most discussed by the scientific community [1–3]. Biogas, mainly composed of carbon dioxide (CO_2) and methane (CH_4), is one of the most studied sources of renewable energy [4–8]. Biogas comes from the anaerobic digestion of different types of biomass. To be used as a substitute for natural gas, biogas should be upgraded to obtain biomethane, which can be injected into the natural gas distribution network. Additionally, biomethane can be used as fuel or as a base material for the synthesis of methanol [9–11]. The major contaminant within biogas that is formed during its synthesis, is CO_2. As such, the removal of this contaminant and the resultant upgrading of biogas is a topic of considerable research by several authors [12–14]. Among these techniques, CO_2 absorption seems to be the most promising since high capture efficiencies can be achieved [15,16]. For instance, some authors employed monoethanolamine (MEA) or piperazine (PZ) as solvents, achieving 90% CO_2 capture efficiency [17–21]. On the other hand, caustics solvents such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) were employed towards carbon sequestration showing similar results [22–25]. NaOH does not present degradation as amines do, which can produce emissions with an elevated toxicity. Moreover the formation and harmful effects of nitrosamines and nitramines known as potential carcinogenic compounds is characteristic of amines, which does not occur by the employed of caustic solvents [26]. Furthermore, caustic solvents are cheaper and more abundant than MEA or PZ, but the main problem with caustic solvents compared to these traditional solvents is the high energy penalty in the regeneration stage via physical methods [11,27]. For this reason, many researchers investigate the regeneration via chemical reaction in a recyclable process, as shown in Figure 1, in order to balance the energy penalty with favorable cost [13,25,28–32]. However, these processes did not achieve technical feasibility due to the relatively low regeneration efficiencies (50-60%) seen by the use of waste solutions with high $Ca(OH)_2$-$Mg(OH)_2$ content [13,22,25,33]. In our previous work [12] a method for biogas upgrading and precipitated calcium carbonate (PCC) production was investigated, obtaining promising results for further research.

Figure 1. Process for biogas upgrading and PCC production.

In this work, CO_2 was removed from biogas through sodium hydroxide (NaOH) absorption in a packed tower, according to equation (1). In order to regenerate the NaOH and make the process economically viable, a precipitation step was undertaken to produce PCC (equation (2)), employing calcium hydroxide ($Ca(OH)_2$) as a precipitating agent, as an improved method against weaker hydroxide waste solutions, that were employed previously.

$$2NaOH(aq) + CO_2(g) \rightarrow +Na_2CO_3 + H_2O \qquad (1)$$

$$Na_2CO_3\,(aq) + Ca(OH)_2(s) \rightarrow 2NaOH(aq) + CaCO_3\,(s) \qquad (2)$$

The aim of our previous study was to optimize the reaction parameters to achieve a reasonable NaOH regeneration efficiency, as well as to obtain a high product quality, which could be sold to improve the overall economic performance of the process. Nevertheless, after studying the psychochemical characteristics of PCC, it was concluded that an impure material was obtained under the conditions imposed. However, to achieve higher purity PCC from the chosen concentration of precipitating agent required higher temperature or pressure that would in turn increase the energy penalty of the whole process. Therefore manipulation of the precipitating agent presents a much more viable solution. In this sense, calcium chloride ($CaCl_2$) is an attractive candidate towards improving PCC purity, since it presents a higher solubility in water than $Ca(OH)_2$. The benefit of this higher solubility is that the co-precipitation of $CaCl_2$ with PCC as it remains in the aqueous solution. The reaction between Na_2CO_3 and $CaCl_2$ is defined by equation (3).

$$Na_2CO_3\,(aq) + CaCl_2(s) \rightarrow 2NaCl(aq) + CaCO_3\,(s) \qquad (3)$$

However, the use of $CaCl_2$ produces NaCl rather than the desired regeneration of NaOH. Since the feed of fresh solvent is crucial to maintain the economy of the process, it could be obtained from caustic waste solutions by means of Bipolar Membrane Electrodialysis (BMED). This technique has been widely studied, reporting promising results; as well as benefitting from a cost effective economic balance and positive life cycle assessment when employing renewable energy [34–38]. Figure 2 represents a schema of the proposed innovative process. In this way, high-purity PCC and sodium chloride (NaCl) brine are obtained as valuable products instead of NaOH, making this a potential process for closing the CO_2 capture and utilization cycle.

Figure 2. Innovative proposed process for biogas upgrading and PCC production.

Therefore, the purpose of this new work was to establish a physicochemical comparison for PCC production between calcium chloride ($CaCl_2$) and/or $Ca(OH)_2$ as precipitants to evaluate if the product obtained meets our hypothesis towards high purity PCC production. To define the physicochemical properties of both types of formed carbonates, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray Diffraction (XRD) and Scanning electron microscopy (SEM) were employed. Should the results prove the production of high purity PCC, this process would allow further research to focus on a potential industrial application of this innovative process.

2. Materials and Methods

2.1 Materials

Chemicals used in the experiments ($Ca(OH)_2$, Na_2CO_3, $CaCl_2$, $CaCO_3$) were provided by PanReac-AppliChem (pure-grade or pharma-grade, 99% purity, Barcelona, Spain).

Table 1. Specifications of the chemicals.

2.2 Process conditions and Physicochemical characterization measurements

The process description was previously addressed in our previous work [39]. In brief, first the reactant solutions and equipment were prepared. After these steps, the precipitation reaction was carried out and once finished the solid products obtained were filtered and separated for analyzing. The reaction conditions were set at 50°C, 1.2 mol Ca per mol Na_2CO_3 and 30 minutes for reaction time. After the precipitation experiments, the solid obtained by filtration was dried at 105°C overnight in order to characterize the samples by means of FTIR, Raman, XRD and SEM.

A Perkin Elmer FTIR BX spectrometer (Waltham, Massachusetts, United States) was used for performing the attenuated total reflection Fourier transform infrared spectroscopy in the powders (ATR-FTIR, uncertainty 2%). Background subtracted spectra of the raw and the treated samples were collected at room temperature by co-adding 32 scans at 4 cm^{-1} resolution in transmittance mode. Data were baseline corrected using Spectrum 5™ software. Raman measurements of the powders samples were recorded using a Thermo DXR2 spectrometer (Waltham, Massachusetts, United States) equipped with a Leica DMLM microscope (uncertainty 1%). The wavelength of applied excitation line was 532 nm ion laser and 50x objective of 8-mm optical was used to focus the depolarized laser beam on a sport of about 3 μm in diameter.

XRD analysis was completed using an X'Pert Pro PANalytical instrument (Malvern, United Kingdom) using a step size 0.05^{o},450 time per step over a range of $10\text{-}90^{o}$ at 40 mA and 45 kV using Cu Kα radiation (λ=0.154 nm, uncertainty 1%).

A JEOL JSM6400 (Akishima, Tokyo, Japan) operated at 20 KV equipped with energy dispersive X-ray spectroscopy (EDX) and a wavelength dispersive X-ray spectroscopy (WDS) system was used for the microstructural/chemical characterization (SEM with EDS and WDS).

3. Results

FTIR spectrum

The first step of the physicochemical comparison was to corroborate the formation of the carbonate phase in the collected samples. For this purpose, Figure 3 represents both FTIR spectrum for PCC from $Ca(OH)_2$ and $CaCl_2$ as precipitant agents in comparison with a commercial $CaCO_3$ solid sample.

Figure 3. FTIR spectra for obtained samples.

Typically, a strong band of $CaCO_3$ spectra appears at around 1400-1500 cm^{-1} as well as a weaker peaks at 876 cm^{-1} and 715 cm^{-1} [40]. These are easily identified in every spectra of Figure 1, so it is possible to conclude that the carbonate phase is presented in both studied samples. According to the vibration bands at 715 cm^{-1} are indicative that calcite is the predominant crystal type in the investigated $CaCO_3$ samples, although it will be confirmed later by XRD [41]. Previously, in [40], FTIR spectra for different $CaCO_3$-$Ca(OH)_2$ mixtures were studied, obtaining strong vibrations at around 3600 cm^{-1} which are characteristic of hydroxyl groups. Indeed, only when pure $CaCO_3$ was measured, the produced spectra did not show this peak, inferring the peak at this value suggests the presence of hydroxide ions from $Ca(OH)_2$. In the Figure 3 inset, the data corroborates that there is no presence of these hydroxides, meaning that the purity of the PCC samples obtained is relatively high. Nevertheless, is not possible by means of this technique to distinguish the complete absence of $Ca(OH)_2$ in the represented spectrum. There may be some remnants of $Ca(OH)_2$ in the samples that would appear also at approximately 1400-1500 cm^{-1}, as in $CaCO_3$ spectra [40]. It is also possible to confirm that there is no $CaCl_2$ remaining in the inset of Figure 3, as there is no peak at 3200 cm^{-1}, characteristic of $CaCl_2$.

Table 2. FTIR vibration bands for the chemicals studied.

Raman measurements

To distinguish possible residual $Ca(OH)_2$, Raman spectroscopy was employed. Furthermore, this technique was useful to corroborate a carbonate phase in the collected samples, which can be seen in Figure 4 that represents both the PCC Raman spectrum from $Ca(OH)_2$ and $CaCl_2$ precipitant agents in comparison with a commercial $CaCO_3$ solid sample.

Figure 4. *Raman spectra for obtained samples.*

$CaCO_3$ shows a monoclinic structure that belongs to the P21/c group [42]. The main characteristic band of $CaCO_3$ polymorphs appears at around 1100 cm^{-1} and *ca.* 700 cm^{-1} and is typically ascribed to this monoclinic type of structure [42,43]. Figure 4 shows that these two peaks are presented in both PCC spectra for PCC from $Ca(OH)_2$ and $CaCl_2$, confirming the successful precipitation process due to the formation of the carbonate phase. The appearance of a band at 400 cm^{-1} and 1086 cm^{-1} are characteristic of $Ca(OH)_2$ that must be due to a small amount of $Ca(OH)_2$ remaining present in PCC from $Ca(OH)_2$ sample as this does not appear in the PCC from $CaCl_2$ spectrum. This was distinguished by the Raman vibration mode at *ca*. 400 cm^{-1}, which belongs to the most characteristic intense band of commercial $Ca(OH)_2$ as confirmation of our previous hypothesis [44]. The absence of this peak in PCC from $CaCl_2$ spectra confirms a pure $CaCO_3$ employing $CaCl_2$ as a precipitant agent, proving that by using this innovative process, it is possible to obtain PCC with a purity of 100% by removing CO_2 from biogas streams.

Table 3. Raman bands for the chemicals studied.

XRD analysis

Once $CaCO_3$ was confirmed as the only species for PCC from $CaCl_2$ and predominant species for $Ca(OH)_2$ by both FTIR and Raman measurements, XRD analysis was carried out to distinguish which crystal morph of $CaCO_3$ has been obtained. The future use of the final $CaCO_3$ obtained depends on the morph, so that makes the crystal structure of the final product extremely important for both precipitant agents. There are three types of $CaCO_3$ crystal morphs: calcite, vaterite, and aragonite [45]. In terms of thermodynamics, the most stable form is calcite, followed by aragonite with vaterite being the least stable [46]. Figure 5 represents XRD patterns of the PCC obtained from both sources in comparison with commercial $CaCO_3$ calcite.

Figure 5. XRD spectra for obtained samples.

The analysis of the obtained XRD patterns, confirms that the calcite morph has been produced, the peaks being in accordance with previous references studied [46,47]. The main peaks of calcite appear at 28°, 39°, 43° and 48°. All of these peaks can be seen in both XRD patterns of PCC from $Ca(OH)_2$ and $CaCl_2$. Nevertheless, it seems that PCC from $CaCl_2$ pattern is more consistent with commercial calcite than PCC from $Ca(OH)_2$, due to the strong presence of $Ca(OH)_2$ within the sample, the peaks for which appear at 18°, 28°, 34°, 51° and 55° [48]. Characteristic $CaCl_2$ peaks appear at 13° and 18° [49] and as can be seen on the relevant XRD plot in figure 5, there is no presence of any residual $CaCl_2$ as the mentioned peaks are not present. These results agree with both Raman and FTIR analyses presented previously in this work.

Table 4. XRD peaks for the chemicals studied.

SEM images

Calcite has five different structural shapes: rhombohedral, rhomboscalenohedral, scalenohedral, scalenorhombohedral, and spheroidal [50]. Rhombohedral or scalenohedral shapes are widely employed as filler in paper industry, due to an enhancement produced in the optical properties of paper sheets [50]. Confirming the different shapes of the obtained samples is therefore very important when considering future applications and is possible through SEM analysis. SEM images are useful to gain further insights on the structure of the samples. Multiple images of the obtained samples were taken to ensure homogeneity. Figures 6 and 7, showcase representative examples of the SEM micrographs. Again the presence of $CaCO_3$ is confirmed with the typical morphology of calcite as previously observed by Altiner et al. [43]. In their study, several PCC structures are shown and strictly compared, obtaining similar results to those presented in this work regarding the morphology of the different solids obtained. As can be seen in Figure 6, PCC from $Ca(OH)_2$ presents a polymorph form with a mixture of different morphologies. On the contrary, Figure 7 shows a rhombohedral form of the particles, again highlighting the purity of the $CaCO_3$ obtained in the form of calcite and making the product very valuable from a commercial point of view discussed above.

Figure 6. SEM image for PCC from $Ca(OH)_2$.

Figure 7. SEM image for PCC from $CaCl_2$.

4. Conclusions and future remarks

After sequestrating CO_2 from a biogas stream by employing NaOH as solvent and later NaOH regeneration or transformation to valuable products via chemical reaction with calcium compounds, in this paper the main psychochemical characteristics of PCC from two different chemicals are studied. The results reveal that a more valuable by-product can be achieve by using $CaCl_2$ as precipitant agent instead of $Ca(OH)_2$. Additionally this innovative process could replace the energetically demanding methods employed to regenerate carbonated compounds after CO_2 absorption.

Raman study shows that a carbonate phase is produced in both solid samples, as well as a small quantity of $Ca(OH)_2$ unreacted when PCC comes from this source. Moreover, these results are confirmed by FTIR analyses. XRD provided information about the type of PCC obtained, being calcite in both materials, but seeming more similar PCC from $CaCl_2$ to commercial calcite than PCC from $Ca(OH)_2$. Finally, SEM images show the majority presence of calcite on the precipitated material, comparing with previous references. Interestingly, it was found rhombohedral form when reacting with $CaCl_2$, while more polymorph structure is shown when employing $Ca(OH)_2$.

Overall this study reveals the suitability of $CaCl_2$ as a precipitating and its advantages over $Ca(OH)_2$ to generate a pure $CaCO_3$ final product. This study has therefore set the basis for future process up scaling. Ongoing efforts in our group are devoted to further explore the impact of the proposed process in biogas upgrading units at commercial and pilot scale.

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Figures

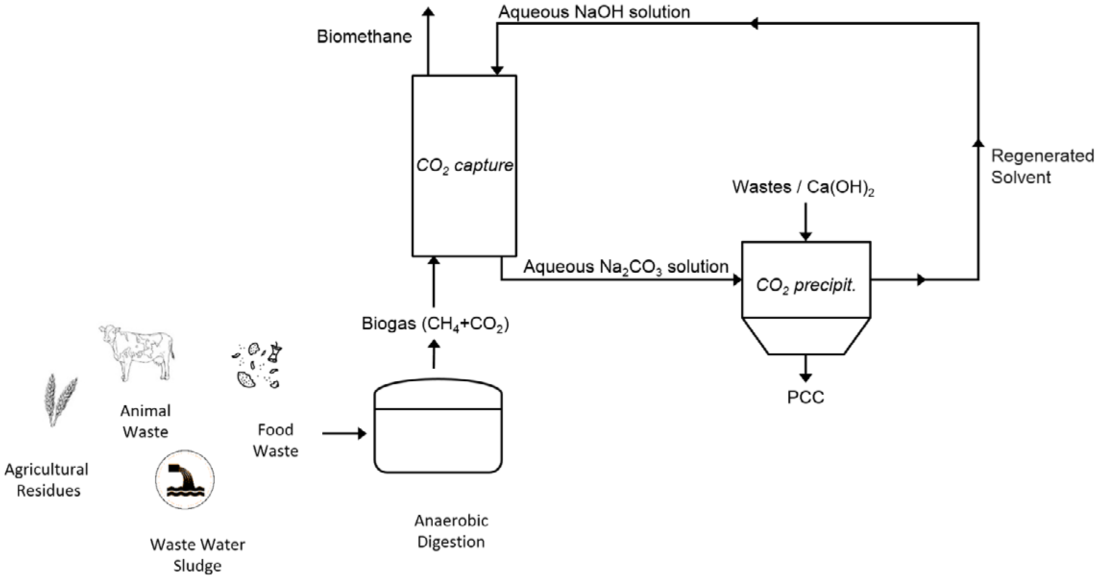

Figure 1. Process for biogas upgrading and PCC production.

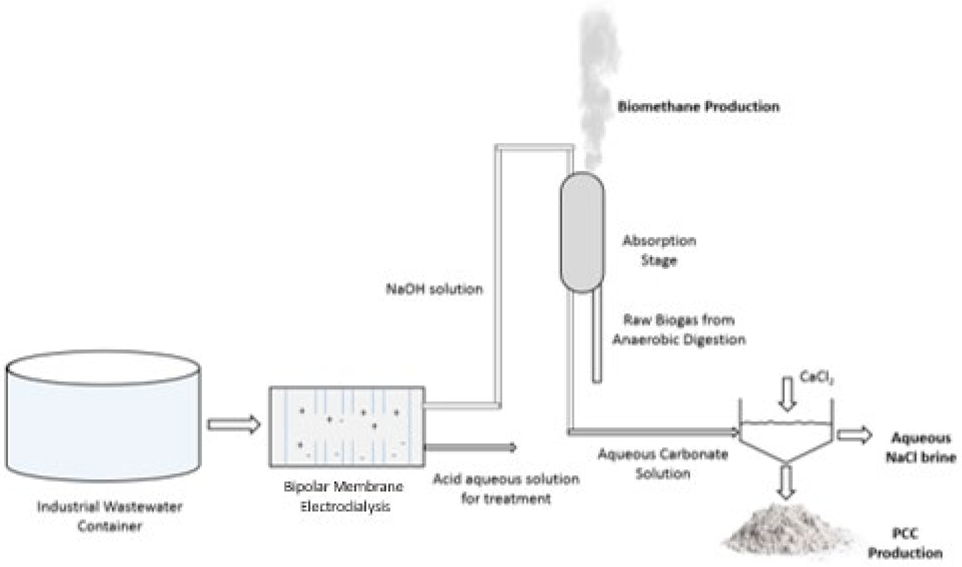

Figure 2. Innovative proposed process for biogas upgrading and PCC production.

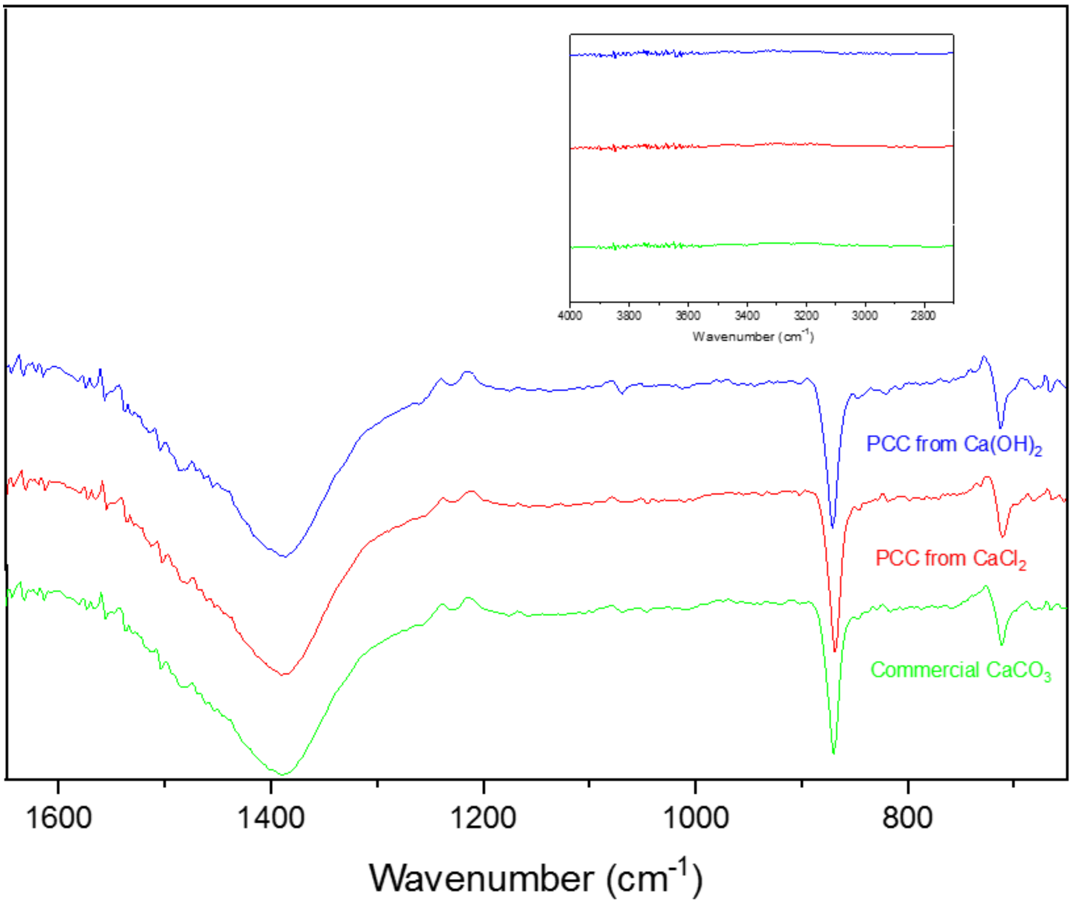

Figure 3. FTIR spectra for obtained samples.

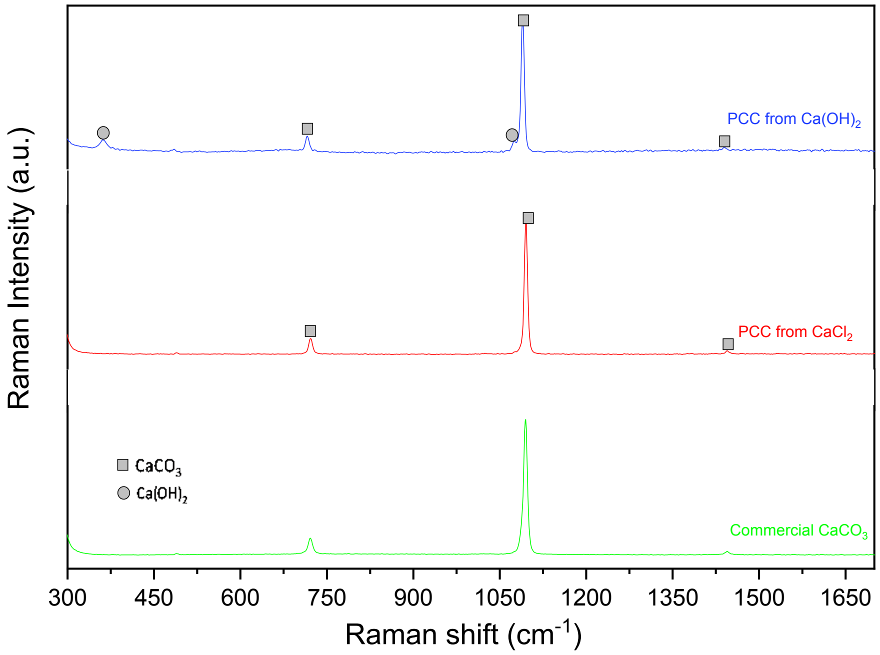

Figure 4. *Raman spectra for obtained samples.*

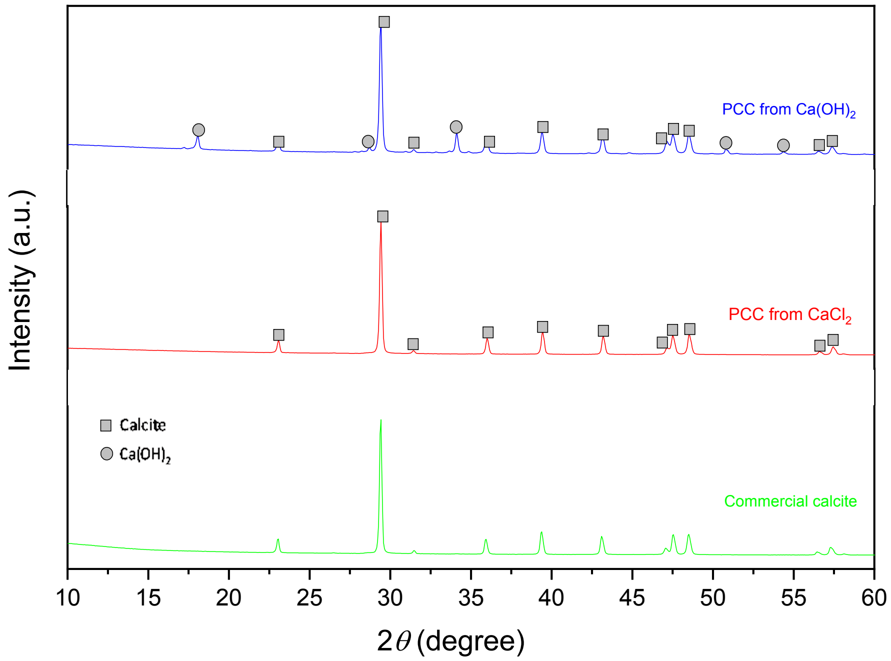

Figure 5. XRD spectra for obtained samples.

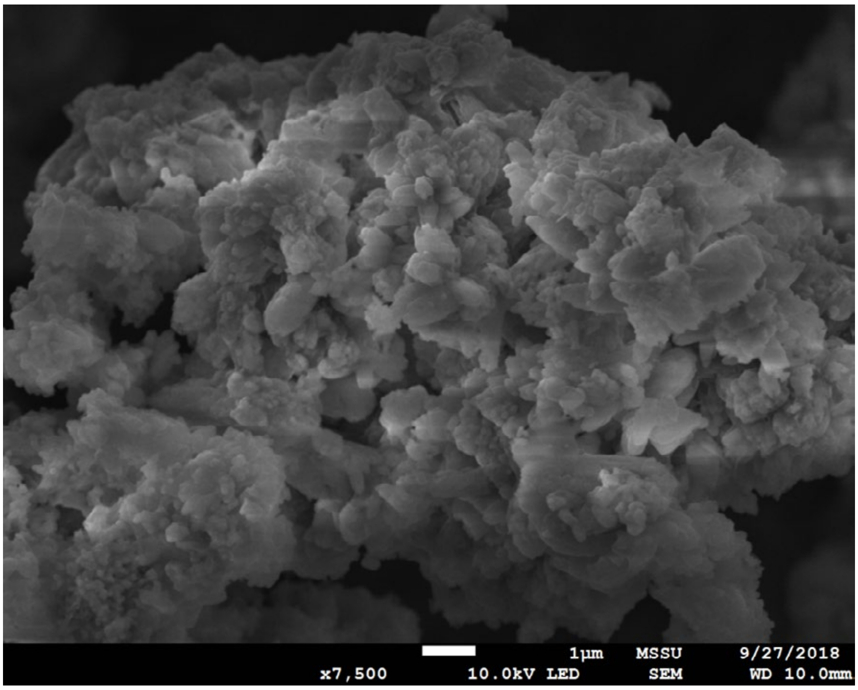

Figure 6. SEM image for PCC from $Ca(OH)_2$.

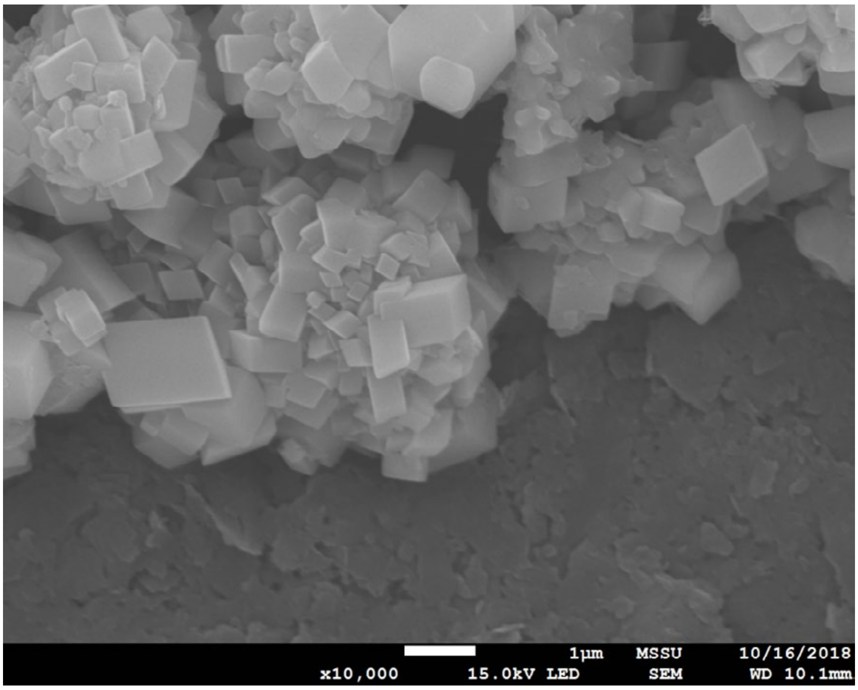

Figure 7. SEM image for PCC from $CaCl_2$.

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Tables

Table 1. Specifications of the chemicals.

Name	CAS no.	Source	Purity (mass fraction)
$Ca(OH)_2$	1305-62-0	PanReac-AppliChem	>0.99
$CaCl_2$	10043-52-4	PanReac-AppliChem	>0.99
$CaCO_3$	471-34-1	PanReac-AppliChem	>0.99
Na_2CO3	497-19-8	PanReac-AppliChem	>0.99

Table 2. FTIR vibration bands for the chemicals studied.

Spectrum	Wavenumber of main bands (cm^{-1})	Uncertainty
PCC from $Ca(OH)_2$	1430, 876, 715	±2%
PCC from $CaCl_2$	1430, 876, 715	±2%
Commercial $CaCO_3$	1430, 876, 715	±2%

Table 3. Raman bands for the chemicals studied.

Spectrum	Raman shift (cm^{-1})	Uncertainty
PCC from $Ca(OH)_2$	400, 732, 1086, 1100, 1435	±1%
PCC from $CaCl_2$	732, 1100, 1435	±1%
Commercial $CaCO_3$	732, 1100, 1435	±1%

Table 4. XRD peaks for the chemicals studied.

Spectrum	Degrees	Uncertainty
PCC from $Ca(OH)_2$	18, 23, 28, 32, 34, 36, 39, 43, 46, 47, 48, 51, 55, 57, 58	±1%
PCC from $CaCl_2$	23, 28, 32, 36, 39, 43, 46, 47, 48, 57, 58	±1%
Commercial $CaCO_3$	23, 28, 32, 36, 39, 43, 46, 47, 48, 57, 58	±1%