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Utilisation of Carbon Capture and Mineralisation Products: Considering Monohydrocalcite as a Potential Functional Filler

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Abstract

Calcium carbonates, ground and precipitated, have an established role in material engineering where they serve as fillers and pigments. In this study monohydrocalcite (MHC) was produced from artificial industrial waste brines as a means of sequestering CO_2, and assessed as a potential functional filler, where its properties were compared with other minerals used in the industry. The results from the morphological analysis which compared MHC with the shapes and sizes of filler crystallites used in papermaking industry were deemed promising. The critical literature evaluation confirmed the potential of MHC as a functional filler: its density, hardness and RI were in-line with PCC fillers which have a well-established role in papermaking and other industries.

Subject Areas

Functional Materials, Green Chemistry, Inorganic Chemistry

Keywords

Monohydrocalcite, Precipitated Calcium Carbonates, Functional Filler, Pigment, Carbon Capture and Utilisation

1. Introduction

Global population growth, intensified agricultural practices and technological developments have all been contributing towards the ever-growing demand of energy since the industrial revolution in the 1700s (Clark II, Cooke, 2016 [1], Etheridge *et al.*, 1996 [2]). The evolution of manufacturing processes, advancement in transportation and the general industrialisation of our cities has come at a large cost to our environment (Hofmann, Butler & Tans, 2009 [3], Liu *et al*., 2018 [4]). Scientists worldwide agree that the recent climate change is attributed to various anthropogenic activities and is a consequence of the increase of greenhouse gas (GHG) concentrations in our atmosphere (Cook *et al*., 2016) [1]. The proposed mitigation options for the stabilisation of atmospheric CO_2 concentrations include: improvements to energy saving, the minimisation and reduction of offshore drilling, the development of renewable energy solutions, the enhancement of biological sinks (Metz *et al*., 2005), and more recently, CO_2 capture and storage (CCS) and utilisation (CCU) technologies (Chaliulina *et al*., 2021) [5]. In essence, CCS usually describes various methods aiming at preventing the carbon dioxide from entering the atmosphere, usually by storing it underground in depleted oil and gas fields; whereas CCU, refers to a sector which aims at sequestering CO_2 for the production of economically viable materials (Galvez-Martos *et al*., 2021) [6]. Amongst such useful products are precipitated calcium carbonate (PCC) minerals, e.g. calcite ($CaCO_3$).

Precipitated calcium carbonates (PCC) are extremely important, both in fundamental research and industry. Usually, PCC are distinguished from ground calcium carbonate (GCC) by regular morphology and enhanced purity. Whilst published studies identify a high potential of other sources of calcium carbonate such "bio-fillers" e.g. chicken eggshells (Toro *et al*., 2007) [7], PCC and GCC remain the main dominators sources for the market. Generally, PCC is attractive due to its advantageous attributes, such as high porosity, high surface area to volume ratio, alkalinity, non-toxicity and biocompatibility (Boyjoo, Pareek & Liu, 2014) [8]. Amongst many applications, PCC is used as a filler and a pigment in the production of a wide range of traditional materials e.g. plastic, PVC, paint and paper. Furthermore, it has even shown promising signs as a filler for new materials, such as wood/plastic composites (Zhang *et al*., 2017) [9]. Novel and economically viable methods for the synthesis and control of calcium carbonate polymorphs and morphologies are highly sought after. The growing construction activities, and demand from industries, such as paper and pulp, plastic, and automotive in Asia-Pacific is driving the growth of calcium carbonate market (Mordor Intelligence, 2018) [10].

Fillers are particles added to a material (e.g. plastics, concrete) to lower the consumption of more expensive binder material (Sharma, Khatri & Kanoungo, 2014) [11]. Fillers can reduce the cost of production, and often, improve a product's properties. With a market share of 34%, the most commonly used filler on the global market is ground calcium carbonate (GCC). PCC has the third largest sales market (after carbon black). Whilst many properties of PCC are identical to those of GCC, they serve best in different industries, e.g. PCC is most frequently used in the production of paper, whilst GCC in segment plastics and construction (Chaliulina, 2019) [12]. PCC is generally more expensive, however, easier to tailor to a specific purpose and is usually purer and hence whiter. In addition to its superior purity, brightness and opacity, its various crystal habits provide unique properties and advantages that make it a highly desired filler in the papermaking industry (Specialty Minerals Inc., 2018) [13]. The annual world consumption of PCC fillers is over ten million tonnes and growing (Rothon, Paynter, 2014) [14].

While fillers are fine particulate materials that give bulk to a medium, pigments can also alter the receiving medium's colour or opacity (Brown, 1981) [15]. Generally, a pigment changes the colour of the material by reflecting or transmitting light as the result of wavelength-selective absorption, however, some pigments also offer added benefits such as gloss or heat resistance (Mukherjee, 2013) [16]. Global demand of pigments amounts to almost 10 million tonnes every year. The most important sales market is the production of paints and varnishes which account for 45% of total global demand. Processing of pigments in plastics are generally ranked second, followed by construction material, printing inks, and paper. The global pigment market is dominated by TiO_2, carbon black and iron oxides (Ceresana, 2016) [17]. They can be natural or synthetic and vary greatly in their origin and purpose. Pigment selection is based on the tinting strength, staining, dispersion and many others, e.g., a pigment that is used to colour glass must have a very high heat stability due to the nature of glass manufacturing. For other applications, such as artistic paint, toxicity is a great issue, whereas heat stability is less important (Mukherjee, 2013) [16].

Blue pigments have attracted worldwide interest because of their wide application in industry, not only as dyes but also for offsetting an undesired yellow tint in white materials (Johnson-McDaniel *et al.*, 2013) [18]. The majority of blue pigments contain Co, e.g. Co_2SiO_4 (an olivine mineral) (Mason, 1961) [19]. Due to Co being scarce, expensive and toxic, the synthesis of Co-based blue pigments comes at a high financial and environmental cost (Eppler, 1981) [20]. Cobalt content and the mineral performance as a pigment, depend on the host lattice, e.g. gahnite ($ZnAl_2O_4$) or willemite (Zn_2SiO_4) can reduce the content of Co without compromising the pigment quality (Forés *et al.*, 2000) [21]. Blue is not the only colour obtained from metal based pigments; most of the traditional pigments contain heavy metals such as lead, mercury, cadmium and copper (Völz *et al.*, 2006) [22], e.g., barium copper silicate pigments are used as a source of purple (FitzHugh, Zycherman, 1992) [23]. In fact, Cu-doped pigments come in many colours and shades, such as yellow, orange, red and brown. It usually follows that the higher *Cu content*, *the darker the pigment colour* (Wu *et al.*, 2018) [24].

Whilst carbonates can be found in many shades and colours (depending on impurities), they are not usually known to be used as dyes or pigments, with some notable exceptions, e.g. malachite—a common copper carbonate pigment used in artist paints (Robinson, 1999) [25]. Carbonates fillers, especially PCC, can be used as pigments due to their high brightness which contributes towards white colour, but are usually referred to as "functional fillers" (Brown, 1981) [15].

The predominant expense in paper production is the cellulosic fibre cost, therefore producers always seek for ways to reduce its constituent fraction, e.g., to replace a portion of fibre with cost-effective fillers, such as PCC, GCC or kaolin. Printing papers, depending on their grade, contain between 5 and 30 percent of filler by mass (Hubbe, Gill, 2016) [26]. Although it is in the interest of the manufacturer to use as much filler as possible, it must be done without compromising the quality of the product. Some of the most challenging barriers limiting how much filler can be added to paper are 1) the need of maintaining caliper (*i.e.* the thickness of a single sheet of paper) and 2) ensuring the operability of paper machines is unaffected (Bown, 1985) [27].

New York-based Minerals Technologies Inc. produces a broad range of speciality mineral, including PCC which is used in the paper industry (produced PCC polymorphs are not specified) (Minerals Technologies Inc., 2018) [28]. They claim that their products address the following concerns: 1) financial aspect of paper production, 2) paper and print quality, 3) fibre supply and 4) environmental cost. Some of their PCC products include: a) clusters (rosettes) of triangular-shaped crystals emanating from a central core, 1 to 2 μm in diameter, which are used to increase whiteness, brightness, and opacity, as well as maximise caliper, and b) hexagonal shaped crystals—average particle sizes in the range 0.7 to about 2 μm, which in addition to the standard advantages, also helps control the porosity of paper. It must be noted, that the described example is by no means representative of the wider industry standards. Standard grade polymer PCCs are significantly smaller and almost exclusively produced as calcite, with crystals in the range 0.02 - 0.1 μm (Rothon, Paynter, 2014) [14]. In fact, the flexibility of PCC is the greatest advantage of filler production by precipitation, because manufacturers can modify crystallite morphology to suit their requirements by adjusting system conditions, such as temperature, pH, salt concentrations, etc.

Minerals in papermaking have become "functional fillers" that impart specific properties to paper, such as brightness, opacity and smoothness. Another important property which can be affected by fillers is colour. Cellulose fibres are brown in colour and must be bleached for white or light-coloured end products. Once bleached, the colouring takes place either through the addition of dyes/pigments to the pulp, or post-sheet formation where it is sprayed or coated (Blus, Czechowski & Koziróg, 2014) [29]. The main colouring matters used in the paper trade are inks, paints, solvents, rubbers, dyes and inorganic pigments (Doble, Kumar, 2005) [30], however, novel sustainable solutions are highly sought after. This paper investigates the possibility to use carbon capture and utilisation as the means to provide the industry with a potentially eco-efficient functional filler.

2. Literature Review of PCC Properties as a Functional Filler in Papermaking

Considering that all mineral and synthetic fillers come with distinct attributes, selecting the best filler can be complicated. Depending on the paper grade, a filler, or combination of fillers are chosen to improve its performance as well as to reduce the cost of manufacturing (Griggs, 1988) [31]. Blends of different fillers, e.g. 75% PCC and 25% GCC could be used as a means of achieving a favourable balance of optical properties and strength at a reasonable cost (Smith,

1999) [26]. Trial runs and analyses are rarely carried out once the filler is chosen, as the most important characteristics can be anticipated from the filler material itself, with the aid of traditional analytical techniques, e.g. XRD and SEM (Hubbe, Gill, 2016) [26]. **Table 1** displays some of the key characteristics from frequently used fillers.

2.1. Opacity

As the appearance of paper comes high in the manufacturer's priority list, a lot of effort goes into ensuring that filler addition fulfils certain optical standards, such as high opacity. Sheet opacity is dependent on refractive index (RI) contrasts among air, cellulose fibre, and filler (Anderson, 1996) [34]. RI measures light's propagation through a material, *i.e.* a material's ability to bend light as it passes through an interface (Hubbe, Gill, 2016) [26]. PCC fillers can increase the RI contrast, and consequently, paper opacity. Many materials have a well-characterized RI, available on online mineral databases (e.g. webmineral.com).

Whilst TiO_2 has a very high RI (**Table 1**) the cost of TiO_2 can be up to 10 times higher than that of other commonly used fillers (Hubbe, Gill, 2016) [26]. The term "extenders" refers to the production of fillers aimed at achieving the high opacity associated with the use of TiO_2 at a lower cost by formation of various TiO_2 composites (Hubbe, Gill, 2016) [26]. Recent studies have been exploring the advantages of synthetic $CaCO_3$-TiO_2 composites prepared by coating TiO_2 particles on the surface of $CaCO_3$ grains (Ding, Lin & Deng, 2016) [35], the mixing of slurries of the two minerals (Olson, 1977) [36], as well as the particle ultra-fine grinding (Tao, He & Zhao, 2015) [37].

2.2. Density and Hardness

The density of fillers (**Table 1**) tend to be considerably higher than that of cellulosic material (typically around 1.5 g·cm^{-3}) (Hubbe, Gill, 2016) [26]. The higher the contrast between the filler and the fibre density, the more difficult the caliper maintenance at given basis weights (mass per unit of area). Furthermore, perhaps

Table 1. Summarizes typical values for four types of frequently used filler in the papermaking industry (Gill, Hagemeyer, 1983 [32], Wypych, 1999 [33]).

	Hardness (Moh's scale)	Refractive Index	Density (g/cm^3)	Typical Particle Shape	Diameter (μm)
Calcite	2.9 - 3.0	1.66	2.71	Rosette, scalenohedral, rhombohedral	0.8 - 2
Aragonite	3.5 - 4	1.68	2.95	Needle, rosette	1 - 3
TiO_2 (rutile)	6 - 7	2.7	4.23	Spherical/rounded	0.3 - 0.35
Kaolin	2	1.36	2.65	Platy, bookettes	2 - 5

more importantly, dense fillers lower the stiffness of paper. Although a small loss of stiffness is acceptable, the quality of certain types of paper such as paperboard, printing and writing paper can be affected if stiffness is compromised (Seo, 2002) [38].

The hardness of fillers used in papermaking is usually measured in the Moh's scale (based on relative scratch resistance) (Hubbe, Gill, 2016) [26], e.g. calcite has a hardness of 2.9 to 3.0, whereas TiO_2 ranges from 5 to 7 (depending on the polymorph) (Hagemeyer, 1984) [39]. Hardness values are especially useful in assessing a filler's abrasivity; harder materials may damage the equipment. Moreover, hard, non-crushable fillers make it difficult to obtain a smooth finish and consequently affect gloss, which is related to both the smoothness and evenness of a paper's surface (Hubbe, Gill, 2016 [26], Anderson, 1996 [34]).

2.3. Morphology

The morphology of particles plays an important part in the selection of a filler with desirable properties (**Table 2**), e.g. plate-like particles, such as clays, can be used to achieve a high-density paper. More rounded, solid-form particles offer other benefits, e.g. rapid dewatering. Particles with internal voids allow for a better light scattering ability, hence contributing to an improved opacity (Gill, Hubbe, 2004) [40]. "Clustered prismatic" structure, a compromise between a rosette structure and a rounded structure, were found to be the best combination of strength and optical properties even at relatively high filler levels (Fairchild, 1992) [41].

In industry fillers with finer particle size are reportedly associated with better light scattering (Bown, 1981) [42], whereas, relatively larger, three-dimensional filler particles can be used to increase the thickness of paper (Hubbe, Gill, 2016) [26]. However, particle size alone is by no means indicative of quality, as particles of various shapes benefit from different advantages brought on by their dimensions, e.g., it has been reported that blocky rhombohedral PCC particles provide the highest light scattering properties at crystallite size of 0.4 - 0.5 μm

Table 2. A brief summary of examples of PCC morphology influence on papermaking process and products.

Function	An example of a morphological attribute
Increase paper density	plate-like (clay)
Increase paper thickness	larger, three-dimensional filler particles
Improve light scattering/opacity	particles with internal voids blocky rhombohedral (0.4 - 0.5 μm) rosette-shaped (0.9 to 1.5 μm)
Maintain paper stiffness	large-size scalenohedral
Improve dewatering	rounded, solid-form particles
Maintain strength (at high % filler)	clustered prismatic structure

(Zeller, 1980) [43]; whereas rosette-shaped PCC particles provide optimum light scattering in the range of 0.9 to 1.5 μm (Gill, Scott, 1987) [44]. Studies also suggest that, in general, large-size scalenohedral PCC appears more favourable for paper stiffness, compared to fine varieties of calcium carbonate (Gill, 1989) [45].

2.4. Mineral Composition

The compositional analyses of fillers can help the identification of polymorphic constituents present in the powder or slurry as well as the material's purity. While calcite polymorph is the most commonly used PCC filler, aragonite has been reported to have favourable strength results combined with an acceptable standard of optical properties (Hu *et al.*, 2009) [46]. Other benefits of using aragonite instead of calcite include: 1) higher strength (especially when the filler content is above 10%) and 2) relatively high filler retention during formation of paper (based on long aragonite needles) (Chen, Qian & An, 2011) [47]. Furthermore, XRD allows to identify whether the filler contains impurities such as quartz (SiO_2) which are very abrasive and may damage paper machine parts (Haller, Stryker & Janson, 2001) [48].

2.5. Pigment Properties

Various minerals can be used as white pigments to conceal the cellulosic fibre, thereby improving its aesthetic appearance and is generally superior to clay and GCC (Wilson, 2006) [49]. Calcium carbonate is also used as a white pigment in many printing inks. Although it is largely dull white, it can be coated to impart greater gloss to the ink surface. Impurities in mineral compositions may affect the colour and brightness of the pigment. Particle size and shape can determine the pigment smoothness, gloss and uniformity (Gueli *et al.*, 2017) [50]. Spherically shaped particles tend to have higher hiding power, *i.e.*, mask the surface to which pigment is applied. Pigments consisting of coarse grain particles (>10 μm) induce a more saturated colour but have poor hiding power, unlike those with fine grain (<1 μm) (Brill, 1980) [51].

The determination of various listed properties provides useful filler performance indicators when assessing a material. Thus, various techniques were used in the analysis of powders containing Mg, Cu and Co doped MHC to investigate its viability as an alternative filler in industry.

3. Methods

The experiments were all carried out under atmospheric pressure of 1 atm at room conditions in the laboratory, at approximately 25˚C. A rapid addition (under constant and vigorous stirring) of a 100 mL of brine (containing various concentrations of Ca and Mg/Cu/Co salts) to a carbonate solution (1 M, 100 mL) was conducted to achieve a $\left(Ca^{2+} + Me^{2+}\right)/CO_3^{2-}$ ratio of 1, full list of conditions are summarised in **Table 3**. The solutions were subjected to stirring for 2 hours in an open container on the lab bench, a schematic representation of the reactor can be seen in **Figure 1**.

Table 3. A list of conditions at which MHC containing samples was obtained for the filler/pigment analysis.

Stabilizing ion		Mg^{2+}				Cu^{2+}				Co^{2+}			
Precipitation conditions		Conc (M)	t (h)	T (˚C)	pH	Conc (M)	t (h)	T (˚C)	pH	Conc (M)	t (h)	T (˚C)	pH
Sample no.	1	0.2	1	20	8.8	0.24	24	20	7.7	0.2	24	20	8.1
	2	0.24	1	5	8.4	0.28	1	5	7.1	0.28	48	20	7.9
	3	0.2	24	20	8.5	0.24	1	40	7.6	0.28	24	20	6.2
	4	0.24	1	5	8.6	0.28	48	20	7.0	0.24	1	20	7.9
	5	0.32	1	40	8.0	0.16	24	20	6.3	0.2	48	20	7.9

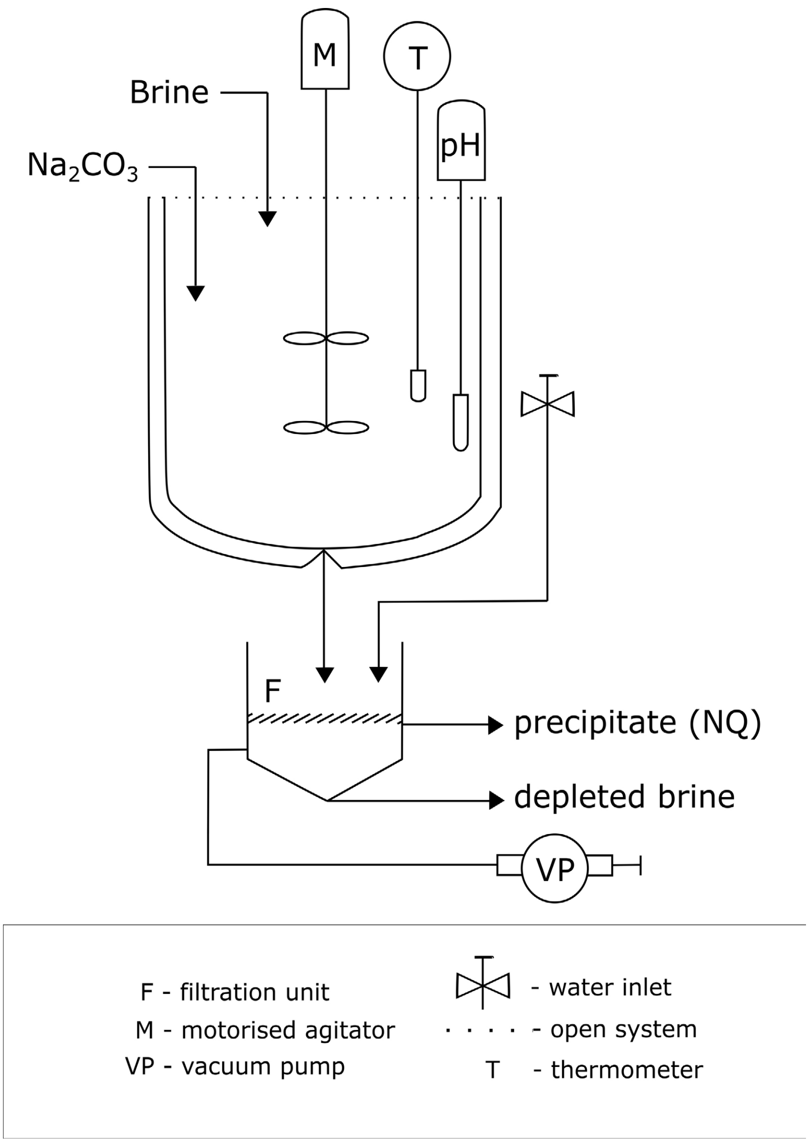

Figure 1. A schematic representation of the reaction apparatus used in the precipitation studies.

MHC accelerated conversion to aragonite was carried out in a heated water bath (8 hours at 80˚C); the slower conversion was obtained by curing MHC powder in a container (desiccator) with approx. 100 RH% atmosphere for 4 weeks.

All samples were analysed by powder X-Ray Diffraction (XRD) using an X'Pert Diffractometer (PANalytical, NL) employing Cu kα radiation (not monochromatic) at 45 kV/40mA. Data were collected over the range 5˚ - 60˚ in 2θ, with a step size of 0.013˚ and a 16.575 s per step. The data obtained from the XRD scans was analysed using the Rietveld method using the EXPGUI application (a graphical user interface for General Structure Analysis System software) for quantitative analysis. Scanning Electron Microscopy (SEM) images were collected on an MA-10 electron microscope (Zeiss, DE) equipped with an energy dispersive X-ray analyser (Oxford Instruments, UK). The analytical instrument used a 10 kV accelerating voltage. Prior to scanning, samples were ground and dispersed on a double-sided sticky carbon disc that was adhered to an aluminium stub and sputter-coated with gold under argon gas atmosphere using SC-500A sputter (EmScope, UK). Colour measurements of the carbonate precipitates were conducted using a Gretag Macbeth Color-Eye 2180 UV spectrophotometer under D65 illumination, in the 360 - 750 nm range. The colour coordinates were identified according to the CIE L*a*b* system evaluation method, by Commission International de l'Eclairage. This method provides a sample's colour and lightness using a three-dimensional plot. In this plot, L* refers to the "lightness" of a sample and operates in the range of 0 to 100, wherein 0 is a black sample and 100 is a white sample. The other two axes of the plot are a* and b* which operate in green-red and blue-yellow gradients respectively and are in the range 0 to 255.

4. Results

4.1. Morphological Analysis

MHC precipitated from a nanoscale amorphous precursor, with significantly smaller particle sizes than the resulting MHC (**Figure 2**). Increasing ageing duration led to larger, more crystalline MHC (1 - 2 μm) and clusters thereof (3 - 4 μm); resulting particle sizes were within the range of the PCC fillers frequently used in the papermaking industry (0.5 - 10 μm) (Roberts, 1996) [52]. The Cu and Co-MHC crystallites were observed to have formed various aggregates (perhaps due to the reduced relative stability with respect to Mg-MHC) or found in clusters with other phases (e.g. amorphous).

4.2. Aragonite from MHC Precursor

Unlike MHC, aragonitic grains are highly common in the PCC industrial production, they are generally valued for their scalenohedral and acicular morphologies. MHC was converted to aragonite in two ways: 1) by curing it in high humidity containers over 4 weeks to achieve spherical aragonite crystals and 2)

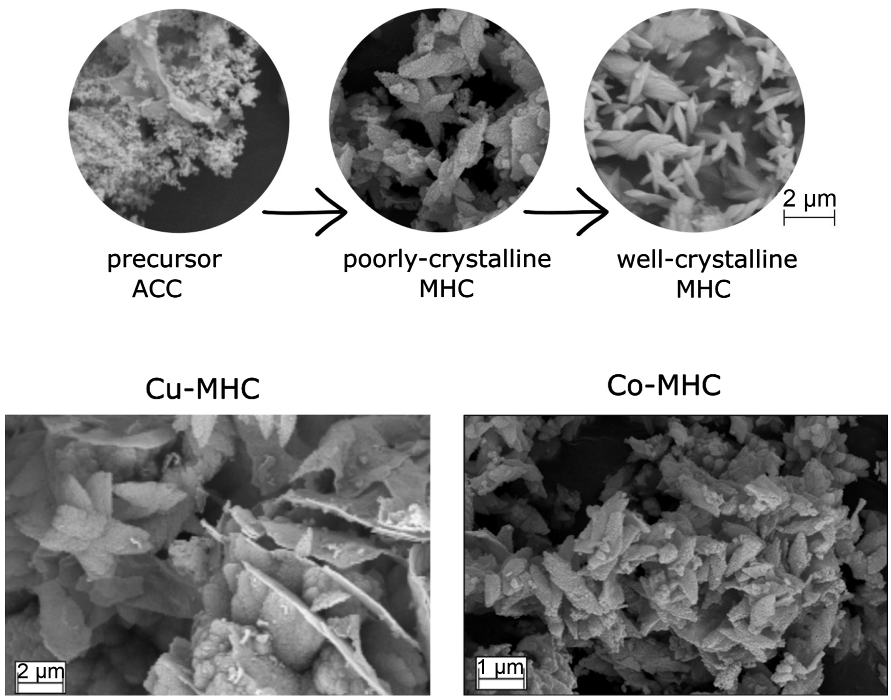

Figure 2. A representation of the frequently observed ACC-MHC morphological evolution, which involves ACC nanoparticle transformation into MHC, followed by further crystal growth and particle aggregation. Below are presented Cu and Co-MHC XRD-phase pure samples displaying clusters of varied morphology, including rice-like MHC and various rosette-shaped aggregates, typically observed in Mg-MHC samples.

by submerging the powder into heated water baths for hours to achieve aragonite rosettes. Two selected samples are displayed in **Figure 3**.

4.3. MHC Colour Analysis

The total of 15 samples were analysed for the colour and brightness. Each containing Mg^{2+}, Cu^{2+} or Co^{2+}, and where XRD identified MHC was the dominant phase (**Figure 4**).

Colour coordinates and brightness of the precipitates were identified according to the CIE L*a*b* system (**Table 4**). The coordinate L* identifies the lightness of the pigment (the higher L*, the lighter), and also acts as an indirect measurement of the brightness or intensity of the pigment (the lower L*, the brighter or more intense the colour) (Llusar *et al.*, 2001) [53]. Mg-MHC displayed high values of brightness (93.21 - 95.54) and fell within the accepted industry standards. Similar studies have identified lab made PCC to have L* = 95 - 97.7 (Llusar *et al.*, 2001 [53], Freeman, Harrison & Lunden, 2000 [54], Scandinavian Pulp, Paper and Board Testing Committee, 2001 [55], Lapnapornwong, Buggakupta & Suvarnakich, 2018 [56]). It was noted that the samples which showed the lowest Ca:Mg ratio had the least crystalline XRD patterns, suggesting that amorphous and less crystalline phases were responsible for the higher Mg content, in agreement with published studies (Rodriguez-Blanco *et al.*, 2014) [57]. Lesser Mg content resulted in powders with higher brightness (L*), the same

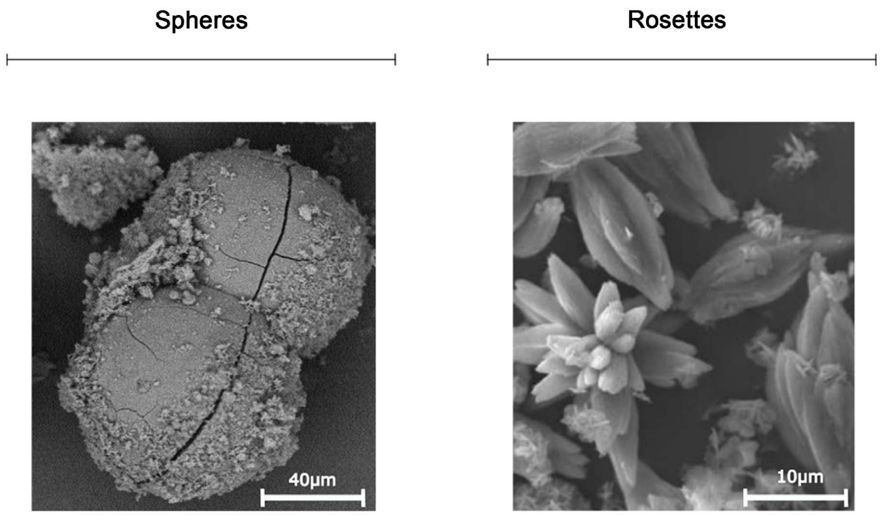

Figure 3. A representative example of two different aragonite morphologies obtained from Mg-MHC precursor (1) spheres and (2) elliptical needles, rosettes.

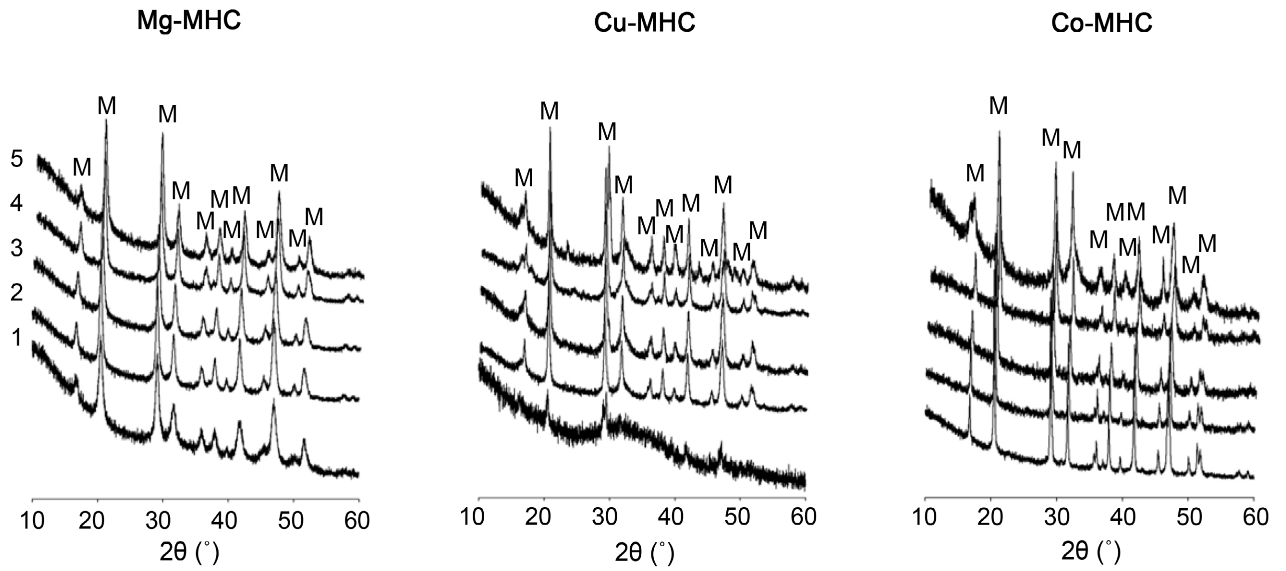

Figure 4. XRD patterns of obtained samples containing MHC used for colour analysis. M-MHC. Numbers 1 - 5 were assigned for sample identification purposes.

pattern was observed with Cu and Co-MHC containing pellets. It must be noted that the atomic calcium to dopant ion ratios cannot quantify the doping ion content within MHC itself, as powders contained other phases, e.g. amorphous.

Cu-MHC containing products yielded powder of various blue and greenish shades, Co-MHC-pink and purple (**Table 4**). In CIE L*a*b* system blue is defined by negative b* coordinates. The yield of green colour is mainly governed by a*: the more negative the a* value, the greener the colour hue. Red and yellow, by positive a* and b*, respectively. MHC colour coordinates were plotted in three dimensional plots (see **Figure 5**). Lower Ca to doping ion ratio led to samples with higher L* values, however, there was no significant correlation between

Table 4. Colour analysis carried on 15 MHC samples synthesised using different doping ions and ionic Ca:ion ratio obtained via EDS analysis. Sample numbers 1 - 5 were assigned for sample identification purposes.

Stabilizing ion		Mg-MHC				Cu-MHC				Co-MHC			
Coordinates		L*	a*	b*	Ca:Mg	L*	a*	b*	Ca:Cu	L*	a*	b*	Ca:Co
Sample no.	1	94.28	−0.12	−0.28	1.6	78.64	−17.21	−8.93	0.28	72.57	9.26	−4.15	9.6
	2	95.48	−0.1	−0.2	3.1	81.72	−14.69	−1.09	7.45	78.42	5.63	−2.54	14.3
	3	95.54	−0.09	0.12	21.1	74.31	−21.01	−9.52	0.59	63.95	11.3	−5.13	2.0
	4	95.63	−0.05	−0.04	24.0	75.18	−19.73	−2.51	3.07	73.72	9.68	−5.28	13.5
	5	93.21	−0.27	0.12	1.7	80.97	−13.84	1.67	7.95	61.93	9.48	−2.46	0.03

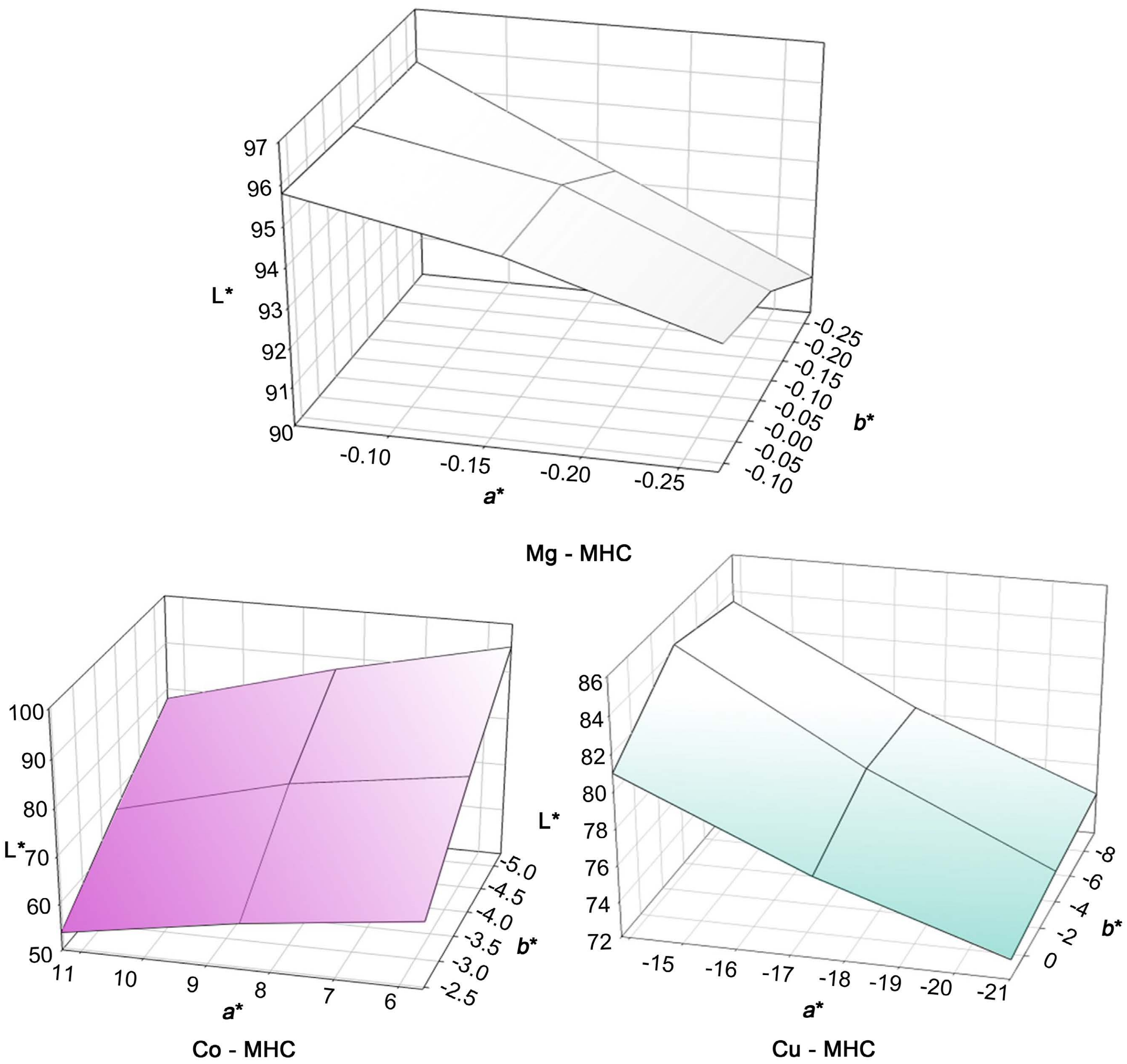

Figure 5. Colour coordinates obtained from a selection of MHC samples stabilised by different ions.

EDS data and other CIE coordinates.

5. Discussion

Scalenohedral morphologies, and especially rosette-shaped aggregates, commonly observed with MHC grains are not uncommon in PCC industrial products. The industry specific advantages of scalenohedral PCC are well-established and widely utilised: narrow, scalenohedral grains are known to improve light scattering and hence paper opacity, and also aid in maintaining caliper (Maloney *et al.*, 2010) [58]. As illustrated in **Figure 6**, a number of industrially available PCC products and MHC grains have comparable scalenohedral morphologies.

Generally, in industrial PCC production the calcium carbonate polymorph used to achieve scalenohedral morphologies is aragonite, although calcite is known to exhibit similar habits too, as seen in **Figure 6**.

As mentioned, scalenohedral particle aggregates often form shapes which may be referred to as rosettes (Gill, Hagemeyer, 1983 [32], Wypych, 1999 [33], Specialty Minerals Inc., 2012 [60]). The observed MHC rosette shapes could be subdivided into a star and flower-like rosettes, based on the shape they resemble (**Figure 7**).

Minerals Technologies Inc. products from ALBACAR® range display morphological similarities to the aforementioned MHC rosettes. ALBACAR® 5970/8101, which resemble star-like aggregates, is said to improve oil absorption

Figure 6. MHC morphology compared to ❶ "EMICAL PCC" produced by General Mineral Industries CO. LLC. (polymorph and particle size not specified) (43) ❷ "CALPREC PA" (aragonite) by Cales de Llierca S.A (44) and ❸ scalenohedral calcite by Omya (Wenk *et al.*, 2018) [59].

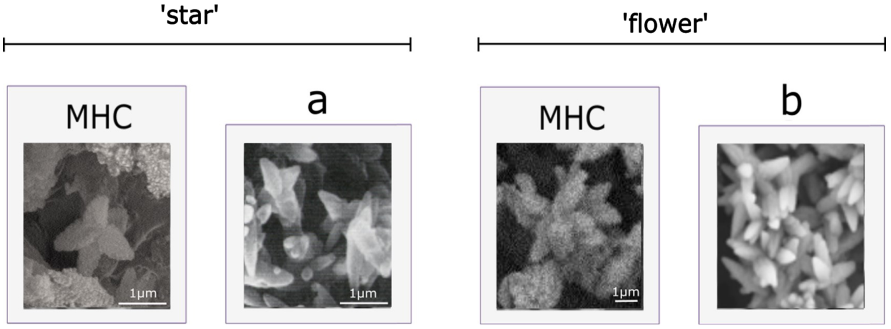

Figure 7. MHC morphologies compared to ALBACAR® by minerals technologies Inc. (a) 5970/8101 and (b) T10 (the scale is absent).

and viscosity and is marketed as a useful filler in plastics, rubber, paints, adhesives, as well as paper (Specialty Minerals Inc., 1998 [61], Specialty Minerals Inc., 2005 [62]). ALBACAR® T10, here compared to a "flower", as described by Minerals Technologies Inc., have a "unique rosette" particle shape which provides excellent light scattering, maintains opacity, gloss and brightness (Specialty Minerals Inc., 2012) [60].

Whilst the morphological assessment of MHC may lead onto a promising start, tests to assess the potential of MHC should be carried out in specialised facilities (e.g., papermaking). Furthermore, the metastability of MHC presents both, potential challenges, and opportunities, therefore the effects of its possible flocculation and transformation into aragonite during the papermaking process must be investigated.

Spherical fillers are utilised within different industries, including papermaking, e.g., amorphous silica, TiO_2 (Hubbe, Gill, 2016) [26] as well as PCC (Vanderheiden, 1987) [63]. The spherical aragonite sample (seen in **Figure 3**) exhibited crystallite sizes significantly larger than those usually associated with paper fillers (up to 10 μm). Further studies should be carried out in order to adjust the particle size to the specific requirements. Whilst MHC and aragonite rosette shapes were somewhat comparable, it is worthy to mention their significant size difference. Aragonite rosettes were between 20 - 30 μm in diameter, which was up to 10 times bigger than MHC. Overall, larger crystals are not necessarily an issue as fillers used in other industrial applications, e.g., asphalt concrete mixes, fire suppression, soil amendment, drilling fluids, glass manufacturing processes and other, which require much larger carbonate particle sizes (up to 100 μm) (Piet Lien and Sons Inc., 2015) [64].

As summarised in the overview of the current paper fillers, morphology alone can provide a sufficient estimation of how well the mineral filler is expected to perform, however, other properties of the mineral must be considered too. MHC density is 2.45 $g \cdot cm^{-3}$, a value which is comparable to that of other carbonate minerals and kaolin (**Table 1**) (Enc. of Minerals, 1990) [65]. In papermaking, lower filler density is often preferred, because it allows easier caliper maintenance (Hubbe, Gill, 2016) [26]. The encouraging signs of MHC as a filler are extended to the RI values: MHC at 1.59 is slightly higher than kaolin (1.36) and is in-line with other PCC, suggesting an acceptable standard for high paper opacity (Zeller *et al.*, 1980) [43]. In terms of hardness, MHC is not known to be significantly different than the other calcium carbonate polymorphs; according to Moh's scale, MHC falls in between gypsum (or kaolin) and calcite (2 - 3). Therefore, both the equipment and the paper quality (smoothness, evenness) (Seo, 2002) [38] should not be compromised with the use of MHC.

Despite the wide use of pigments in manufacture of various materials, there are no known applications for coloured PCC (Chaliulina, 2019) [12]. As already discussed, in other industries, e.g. ceramics, blue pigments can be used to either impart blue colour of various host materials, or to counteract yellow tint and enhance white colour, due to the fact that a blue-white filler generally looks brighter than a yellow-white one (Anderson, 1996) [34]. In order to assess whether blue-coloured Cu-MHC could aid in imparting white or blue colour to a material, e.g., paper, the filler would have to be subjected to specialist tests. The same sentiment extends to pink/purple Co-MHC. Whilst Co containing pigments are known to aid oxidation and consequently hasten the drying of paints (Greenwood, Earnshaw, 1984) [66], it is unknown how utilisation of such fillers would affect paper.

6. Conclusion

Monohydrocalcite, which can be precipitated from various industrial brines, currently has no known industrial applications. A literature evaluation and a number of tests were carried out in order to assess MHC's potential as a filler.

- The results from the morphological analysis which compared MHC with the shapes and sizes of filler crystallites used in papermaking industry were deemed as promising.
- The critical literature evaluation confirmed the potential of MHC as a functional filler: its density, hardness and RI were in-line with PCC fillers which have a well-established role in papermaking and other industries.
- A selected number of MHC samples were subjected to colour analysis: white Mg-MHC containing samples exhibited high brightness, sufficient for paper filling, and coloured samples (Cu and Co-MHC) came in different shades depending on the divalent ion quantities within the powder.
- An MHC conversion product, aragonite, was comparable with fillers which are usually produced at a much higher environmental and economical compromise.

Conflicts of Interest

The author declares no conflicts of interest.

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