

PRODUCTION OF PRECIPITATED CALCIUM CARBONATE FROM MARBLE
WASTES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

NURETTİN SEZER

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
MINING ENGINEERING

SEPTEMBER 2013

Approval of the thesis:

**PRODUCTION OF PRECIPITATED CALCIUM CARBONATE FROM MARBLE
WASTES**

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ABSTRACT

PRODUCTION OF PRECIPITATED CALCIUM CARBONATE FROM MARBLE WASTES

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September 2013, 42 pages

The aim of this study was to investigate the production of precipitated calcium carbonate from marble wastes. Limestone is used as the source for the production of precipitated calcium carbonate. Marble wastes primarily constitute of CaCO_3 . As the major content of the marble waste and limestone are the same, marble wastes can be used as an alternative source for the production of precipitated calcium carbonate. By this way, both the adverse environmental effects of marble wastes can be prevented and the wastes can be used as a cheaper source for precipitated calcium carbonate manufacturing industry. Waste samples were dissolved in pure water in an autoclave of 1 liter capacity by addition of CO_2 gas. Contained aqueous carbonates were precipitated by evaporation of the CO_2 in the solution. Concentration of dissolved carbonate species was examined for each test. Microstructure of the marble wastes used in the experiments and the precipitated calcium carbonate obtained from the experiments was investigated by Scanning Electron Microscopy, and their chemical analyses were carried out. The results of the chemical analysis were comparatively evaluated. The studies revealed that the precipitated calcium carbonate can be produced from marble wastes. By the experimental studies, the required conditions for production have been determined. In general, the experimental results in different conditions revealed that high CO_2 pressure, lower ambient temperature and high stirring speed had positive effect in the dissolution of waste samples. The best result was obtained as 4.73 g/L dissolved CaCO_3 under the conditions of -250 +106 μm particle size, 1400 rpm stirring speed, at 2 h, 8 °C and 10 atm CO_2 pressure. The study recommends marble wastes as an alternative resource to manufacture precipitated calcium carbonate with sufficient quality to meet the industrial requirements.

Keywords: Marble wastes, carbonate-water system, calcium carbonate dissolution, precipitated calcium carbonate (PCC).

ÖZ

MERMER ATIKLARINDAN ÇÖKTÜRÜLMÜŞ KALSİYUM KARBONAT ÜRETİMİ

Sezer, Nurettin

Yüksek lisans, Maden Mühendisliği Bölümü

Tez Yöneticisi: Prof. Dr. Ali İhsan Arol

Eylül 2013, 42 sayfa

Bu çalışmanın amacı mermer atıklarından çöktürülmüş kalsiyum karbonat üretiminin araştırılmasıdır. Çöktürülmüş kalsiyum karbonat üretiminde hammadde olarak kireçtaşı kullanılmaktadır. Mermer atıklarının ana içeriği kalsiyum karbonattır. Mermer atıklarının ve kireçtaşının ana içeriği aynı olduğundan mermer atıkları, çöktürülmüş kalsiyum karbonat üretiminde alternatif hammadde olarak kullanılabilir. Böylelikle hem mermer atıklarının çevresel olumsuz etkileri önlenebilir, hem de bu atıklar çöktürülmüş kalsiyum karbonat üretiminde daha ucuz kaynak olarak kullanılabilir. Yapılan deneysel çalışmalarda atık numuneleri CO₂ gazı ilavesiyle, 1 litre kapasiteli bir otoklav hücresinde saf su içinde farklı koşullarda çözüldürülmüştür. Hücredeki çözünmüş karbonatlar çözeltide çözünmüş CO₂ gazının buharlaştırılması ile çöktürülmüştür. Her deneyde çözünmüş karbonat türlerinin derişimi hesaplanmıştır. Deneylerde kullanılan mermer atık numunelerinin ve deneylerden elde edilen çöktürülmüş kalsiyum karbonatın kimyasal analizleri yapıp karşılaştırmalı olarak değerlendirilmiş ve mikro ölçekli yapıları Taramalı elektron mikroskobu ile incelenmiştir. Çalışmalar mermer atıklarından çöktürülmüş kalsiyum karbonatın üretilebileceğini ortaya koymuştur. Yapılan deneyler ile üretim için gerekli koşullar belirlenmiştir. Farklı koşullarda gerçekleştirilen deney sonuçları genel anlamda yüksek CO₂ basıncı, düşük sıcaklık ve yüksek karıştırma hızının atık numunelerinin çözünmesini pozitif yönde etkilediğini ortaya koymuştur. En iyi sonuç, -250 +106 µm tane boyu, 1400 rpm karıştırma hızı, 2 saat süre, 8 °C sıcaklık ve 10 atm CO₂ basıncında 4.73 g/L çözünmüş CaCO₃ olarak elde edilmiştir. Çalışmalar endüstride istenen kaliteye sahip çöktürülmüş kalsiyum karbonat üretimi için mermer atıklarının alternatif kaynak olarak kullanılabileceğini ortaya koymuştur.

Anahtar kelimeler: Mermer atıkları, karbonat-su sistemi, kalsiyum karbonat çözünümü, çöktürülmüş kalsiyum karbonat (PCC).

To My Family

ACKNOWLEDGEMENT

I would like to express my special thanks to my advisor Prof. Dr. Ali İhsan Arol for his enthusiastic guidance and patience throughout this study. I am also so grateful to my advisor for encouraging me in this fascinating field and for letting me benefit from his profound mind and knowledge.

I would like to thank technical staff of the department, especially, Tahsin Işıksal, Caner Baytar, and Aytekin Arslan for their support, research assistants in Mining Engineering Department, especially Mustafa Çırak for their technical support in experimental period of this thesis.

I also wish to express my gratitude to my family especially, to my parents Gülseven and Mustafa Sezer, whom I can not thank enough for their patience, support, and encouragement to finish master of science study and this thesis.

Lastly, my greatest gratitude goes to my dear wife Büşra Sezer for her unbelievable patience, support, and love while I was writing this thesis.

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CHAPTER 1

INTRODUCTION

The most common organic compound, accounting for more than 4 % of the earth's crust is calcium carbonate (CaCO_3). It occurs in three crystal forms as calcite, aragonite and vaterite and they are among the most important rock forming minerals. CaCO_3 is found in varieties of places like sea shells, calcitic rocks, coral reefs, stalactites and stalagmites formations in the caves. These natural resources are linked by calcium carbonate cycle [1].

Dissolved CaCO_3 is absorbed by animals and plants in water. These living creatures use CaCO_3 to build up their skeletons and shells. After their death, mussels, corals, algae, and coccoliths form sedimentary deposits on sea beds. Thus, the rock forming process starts. The first stage is the sedimentation process, from which chalk or limestone originates. If the process occurs in magnesium containing water, dolomitization may result and lead to formation of dolomite [1].

CaCO_3 rocks occur throughout the world and are readily available. But, the required qualities of the CaCO_3 are different according to various industries. For the production of top quality natural CaCO_3 , the purity, whiteness and homogeneity of the rock should be appropriate and even then intensive treatment may be required. Precipitated CaCO_3 is a synthetic CaCO_3 , which is produced industrially by recarbonization [1].

CaCO_3 is an important chemical compound in several industries. Construction industry is the major CaCO_3 consumer, which use the CaCO_3 as a building material; the iron industry use it for purification; the oil industry uses CaCO_3 as an ingredient in drilling fluid. CaCO_3 neutralizes stomach acid, it is also used for neutralizing the acidic soil and water [2].

CaCO_3 is used as filling agents. Ground and precipitated CaCO_3 are used as fillers in the papermaking industries. High quality papers are manufactured by using CaCO_3 products as fillers. CaCO_3 is also used in other industries as a filler, including sealant, plastic and paint [2].

1.1 Limestone

Limestone is a common type of sedimentary rock which primarily constitute of CaCO_3 . Limestone is formed by the accumulation of sea animal shells or by crystallization from water. In the seas, when the shelled animals died, they fall to the bottom of the sea. Because these shells are composed of CaCO_3 , in time, thick layers of CaCO_3 are formed and transformed to solid rocks at the bottom of the seas. Crystallization process occurs by combination of calcium ions in the water with CO_2 dissolved in water or from the atmosphere to produce insoluble CaCO_3 . Then the CaCO_3 precipitates down in the water. By this process, calcium carbonate layers are formed in thousands of years. These layers are transformed to solid rocks through compression generated by overlying materials [3].

If the compression, which the CaCO_3 layers are exposed to, is high, then the crystallization process is better and limestone is formed. If it is poor, little crystallization occurs and soft chalk results [3].

Pure calcite, dolomite, and aragonite present in the limestone are white in color. With impurities, the color of limestone can change from white to tan or gray. High pressure, heat and time cause limestone to metamorphosis. As a result of this process, marbles with different colors and characteristics are formed [3].

Limestone and marble are widely used for constructions, in different forms, such as dimensional stone, crushed stone or aggregate for building, in roadbeds and as a component in concrete, respectively. At elevated temperatures, limestone decomposes into CaO (lime) and CO_2 gas. CaO has a wide use area in industry, including precipitated calcium carbonate production [3].

Limestone is also the source of ground CaCO_3 . Ground CaCO_3 can be in different size ranges. They can be manufactured from 1- 2 mm down to 1 to 5 μm particle size intervals in accordance with industrial demands [3].

1.2 Marble

Marble is a term derived from “marmaros” meaning shining stone. It is a metamorphic rock formed by the alteration of limestone or dolomite rock by heat and pressure, over thousands of years. Due to the subduction of a limestone, heating may be regional or it may be originated from contact metamorphism where the magma intrudes into a limestone, resulting in partial melting [4]. As a result of this process, marble stones with a very tight crystalline structure and small but definite porosity are formed [5].

Marbles have high reactivity with acids so they readily decompose in contact with even weak acids, and will strongly boil in the presence of strong acids. Marble is also a relatively soft rock, having a hardness degree of 3 in Mohs hardness scale, it can be scratched by most of the materials [4].

Marble is made of more than 90 % calcite (calcium carbonate). It is the remaining percentage of "impurities" which give many different varieties of colors and characteristics to marbles. Marble can be translucent, white, brown, red, green, grey and even black. It can have a uniform color and texture or have spots, swirls or veins [6]. Marbles can be used for statuary, ornamental and architectural purposes, based on the aforementioned properties.

One of the important properties of marble is its ability to achieve a natural glasslike polish without the need of waxes or any other chemical compounds. Marble is polished only by abrasion and it eventually reaches its natural glossy luster. And as long as it is well cared for, this luxurious finish can last even for centuries [6]. Marble is proven to be the most heat resistant natural material available on the earth [7]. Owing to this, it is a natural air conditioner when used in the houses.

Many famous monuments all over the world like Taj Majal and el Alhambra were built by using marble. In Greek architecture, marble had a great importance and was the principal building material for the Parthenon and the Acropolis [6].

Many rich marble deposits in countries like Portugal, Spain, Italy, Greece, Turkey, Iran and Pakistan are all located in Alpine-Himalayan belt. As a result of its geological location, Turkey has very rich and natural stone reserves in wide variety of colours and patterns [8]. Types of marble produced in Turkey and well known in international markets are, Suprene, Elazığ Cherry, Akşehir Black, Manyas White, Bilecik Beige, Tiger Hide, Denizli Travertine, Aegean Burgundy, Milas Lilac, Gemlik Diabase and Afyon Sugar [8].

In Turkey, there are 2100 marble mines, 1500 plants in small and medium scale and 7500 workshops where nearly 250000 individuals are employed, in the marble sector. Almost all of the production is made by the private sector. While the production of natural stone in Turkey in 2009 was nearly 4 million m³ in 2010 nearly 5 million m³ production was carried out and the existing processing facilities have a total plate production capacity of 6.5 million m³. In 2009, Turkey is ranked as the 3rd in the marble and travertine production in the world [9].

Marble is exported either in blocks or cut and polished material. In natural stone exports, the products with the highest added value have always been processed marble and travertine. The export potential of the sector is developing quickly parallel to investments. Between 2004 and 2010, our exports of natural stone had risen from 2.6 million tons to 6.6 million tons, displayed an increase by 154 %. By this way, export income increased by 152 % from 621 million dollars to 1568 million dollars. Majority of the 2010 natural stone exports consists of processed products [9].

1.3 Marble Wastes

One of the most extensively used aesthetic stones is marble [10]. Turkey has approximately 3872 million m³ of worthwhile marble reserve [8]. On the other hand, marble manufacturing industry produces high amount of waste [11]. Waste generation continues from mining process to finished product and is about 50% of marble mined [12].

The process of quarrying the marble stones is performed in order to produce slabs and tiles, which are widely used in the construction industry for high quality flooring and wall cladding purposes. In the process of converting in-situ stone deposits to the final product, significant amount of waste is generated in both the mine site and processing and polishing plant. The waste is generated at two stages, first is in the form of fragments, Figure 1, and shapeless blocks, Figure 2, which have no commercial value. Second is generated in the form of fine powder during cutting of in-situ stone and the production of polished slabs and tiles from commercial sized blocks Figure 3.



Figure 1 Rock fragments deriving by cutting and sawing of stone [13]



Figure 2 Shapeless blocks deriving by quarrying operation [13]

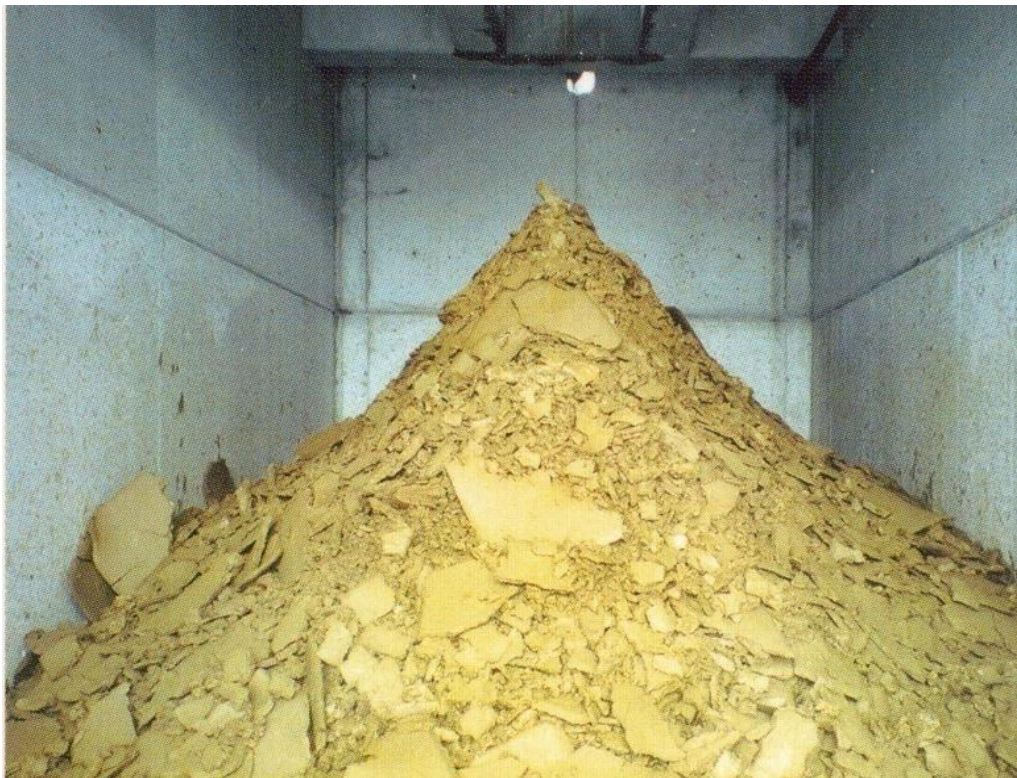


Figure 3 Muds produced by sawing and polishing operations on slabs (Air dried filter-pressed mud) [13]

During the processing of marble, the raw stone block is cut to desired dimensions either into tiles or slabs of various thicknesses (usually 2 or 4cm), by using synthetic diamond blades. Water is sprayed on blades while stone blocks are cut into sheets to cool the blades and absorbs the dust produced during the cutting operation. The amount of waste water from this operation is rather great. It is not recycled as the water so highly alkaline that, if re-used, it can dim the slabs to be polished [14]. In large factories, where the blocks are cut into slabs, the cooling water is stored in pits until the suspended particles settle (sedimentation tanks), then the slurry is collected in trucks and disposed of on the ground and left to dry. This water carries large amounts of stone powder. Eventually, the sludge dries in the sun and its particles become airborne [14]. This causes air pollution problems for the surrounding area. Another solid waste generated by the marble units is the cutting waste which results from cutting slabs into the required dimensions [14]. Chemical analysis, physical properties and particle size distribution of a marble slurry are specified in Tables 1 - 3.

Table 1 Physical properties of a marble slurry [13]

Property	Result
Bulk Density (g/cm ³)	1.3 - 1.5
Specific Gravity	2.83 - 2.87
Particle size (µm)	Less than 363.5

Table 2 Chemical analysis of a marble slurry [13]

Test Carried Out	Test Value %
CaO	49.07
SiO ₂	1.69
Al ₂ O ₃	1.04
Fe ₂ O ₃	0.21
MgO	4.47
Na ₂ CO ₃	Less than 0.01
K ₂ SO ₄	Less than 0.01
Loss on ignition	43.46

Table 3 Particle size distribution of a marble slurry [13]

Particle Size (μm)	% Finer by Volume
- 363.1	100
193.0 - 205.8	90
130 - 140	80
81.0 - 94.7	70
54.5 - 62.51	60
37.5 - 43.1	50
23.9 - 28.1	40
14.24 - 15.2	30
5.9 - 7.15	20
1.23 - 1.69	10
0.321	0.00

Unless stored properly in sedimentation tanks, the fine particles can cause more pollution than other forms of marble waste. The fine particles can be easily dispersed after losing humidity, under atmospheric conditions, such as wind and rain. The white dust particles usually contain CaCO_3 , thus it can visually pollute the environment [14].

Waste piles are usually used to store all the marble wastes of large and small sizes generated during quarrying and fabrication, Figure 4. They alter topography, occupy land, degrade surface and subterranean water, pollute the environment visually and the air and they have negative impact on the agriculture and health [8]. These wastes also cause certain economic losses. Consequently, utilization of the marble wastes; i.e. slurry, powder, rock fragments, shapeless blocks has many benefits on the protection of the environment and will contribute economically.

There have been various studies on utilization of marble wastes. Some of them are; as a filler material for roads and embankments, for bricks manufacturing, for the manufacture of portland cement and ceramic tiles [13]. The primary aim of all these studies were to eliminate the adverse environmental effect of marble wastes.



Figure 4 Examples to views of marble waste piles [13]

1.4 Precipitated Calcium Carbonate

Calcium carbonate (CaCO_3) is abundantly present on the earth. Natural, ground or synthetic CaCO_3 is widely used in various industries. The product, produced by a controlled synthesis to fulfill the desired properties is called precipitated calcium carbonate (PCC). It is also called as synthetic, refined or purified CaCO_3 . PCCs have the same chemical formula as of its natural resources limestone, chalk and marble; CaCO_3 . PCCs gain advantages over natural and ground CaCO_3 with their unique properties of submicron particle size, regular crystal shape, narrow particle size distribution and high purity. Unlike ground CaCO_3 , PCCs can be produced in different crystal shapes and in ultrafine particle sizes. PCC is increasingly used in industries such as paper, rubber, paint, textile, plastic, sealant, cosmetic, tooth paste and food mainly as a filler product, Table 4, [15-17].

Commercial PCCs have been produced since 1841 [18]. PCC was first produced by an English company, John E. Sturge Ltd., by treating the residual CaCl_2 from their KClO_3 production unit with Na_2CO_3 and CO_2 to produce PCC. In 1898, the first milk of lime process was practised in Birmingham [18].

Table 4 PCC global consumption rates [19]

Industry	Consumption %
Paper	72.0
Paints	8.0
Plastics	5.0
Rubber	4.5
Food, cosmetics and pharmaceuticals	4.0
Textile packing	2.5
Putties, caulks, sealants	2.5
Adhesives	1.0
Printing ink	0.5

In 2011, filler grade PCC consumption was 14 million tonnes in the world, with Asia account for more than 50 % of the total consumption. The largest markets for CaCO_3 are the paper and plastics industry. They constitute 26 % of total PCC consumption in 2011 [19].

The major benefit of paper made by adding PCC is the expectancy of much longer life than that of traditionally manufactured paper, i.e. more than 1000 years for the best paper and 500 years for average life time [20].

PCC can be obtained in three main crystal polymorphs: calcite (rhombohedral), aragonite (orthorhombic), and vaterite (hexagonal) depending on the reaction conditions and impurities in the process. Of these, calcite, which forms rhombohedral crystals, Figure 5, is the most thermodynamically stable under ambient conditions [22]. Aragonite is more soluble and denser than calcite. Aragonite usually forms needle-like orthorhombic crystals and is favoured at high temperatures and pressures. It is metastable, converting slowly to calcite [22]. Vaterite is the thermodynamically least stable polymorph, and its hexagonal crystals are rarely seen in the naturally occurring mineral [22]. Since different polymorphs impart different properties, control over the crystal form is important to end users [22]. Typical product specifications of a PCC product is given in Tables 5 - 6, but the desired properties of it generally varies according to its field of application.

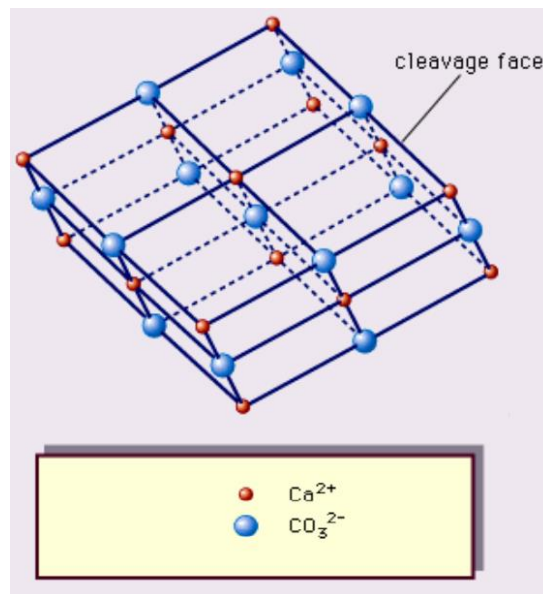


Figure 5 Crystal structure of calcite [25]

In paper, PCCs enhances the smoothness, brightness, and opacity of paper. It also increases receptivity of the ink [21]. In paint, CaCO_3 is used as the primary extender compound to reduce consumption of higher cost pigments, like TiO_2 . Fine sized and narrowly ranged PCC grains provide gaps among TiO_2 particles and improve their hiding power [19]. By this extension, the opacity is improved. CaCO_3 consumption in this market was 8.8 Mt in 2011, with GCC accounting for 7 Mt and PCC for 1.8 Mt [19].

The usual product specifications for PCC is purity of more than 99 %, density of 2.7 g/cm^3 , particle size for filler pigments of $70 \% < 2 \text{ }\mu\text{m}$, and the specific surface area of about $10 \text{ m}^2/\text{g}$. The particle size has a significant effect on smoothness, gloss and printing characteristics of the paper. Characteristics of printing are also in relation to the particle size range and particle shape of PCC, which also directly affects the consumption of chemical additives in papermaking. The brightness of the PCC filler pigments should be higher than 93 %, and the pH of 1 mol of PCC in 1 L solution should be 9. Average particle size of PCCs as coating pigment should be in 0.4 to $2 \text{ }\mu\text{m}$ size range, refraction index of $1.49 - 1.67$ and a specific surface area of $4 - 11 \text{ m}^2/\text{g}$. Narrower particle size ranges and higher refraction indexes of PCCs improves light scattering of the sheets. The ISO standards for brightness of PCCs as a coating pigment is 95 %, which necessitates a CaCO_3 source with a high purity in order to be used as a raw material [27].

For PCC manufacturing industry, raw material should contain low manganese and iron as mineral impurities because these elements have detrimental effects on the brightness of the product [27].

Table 5 Typical chemical specifications of a PCC product [23]

Chemical Properties	
Color	Bright White
Hunter Whiteness	97 % Min.
CaCO₃ % by Weight	98.5 Min.
Lead as Pb	Traces
Copper as Cu	Negligible
Arsenic as As	NIL
Sulphate as SO₄	0.2 % Max.
Soluble alkali as Na₂O	0.15 % Max.
Silica as SiO₂	0.07 % Max.
Iron as Fe	0.01 % Max.
pH	9.0 to 10.5
Phosphate as PO₄	0.05 % Max.
Chloride as Cl	Traces
Magnesium as MgO	0.7 % Max.
Flouride as F	Traces
Manganese (Mn)	0.005 % Max.
Solution in 5N HCL	Clear
Aluminum, Iron, Phosphate and other matter insoluble in HCL – IS 918/1985	0.5 % Max.

Table 6 Typical physical properties of a PCC product [23]

Physical Properties	
Crystal Structure	Calcitic
Water Absorption	80 to 85 ml/100 g
Oil Absorption	60 to 65 ml/100 g
Loss on Drying at 105 °C	0.8 % Max.
Specific Gravity	2.6 to 2.7
Bulk Density	0.45 to 0.50 g/cm ³
Average Particle Size	3 to 5 μm
Residue on 300 mesh	0.2 % Max.

PCC exhibits a regular and controlled crystalline shape and ultrafine particle size, and also synthetic PCCs gain advantages in point of narrowness of particle size distribution and high purity (since impurities are removed in the production process) over natural and ground calcium carbonates (GCC). Therefore, in the literature, the CaCO₃ precipitation methods have attracted great attention [24].

1.4.1 Synthetic PCC Production Methods

There are three common processes for the production of synthetic PCC:

- Lime soda process (Kraft pulping method);
- Calcium chloride process (Mixing of solutions);
- Carbonation process.

These methods are outlined in Figure 6 and explained in the following sections.

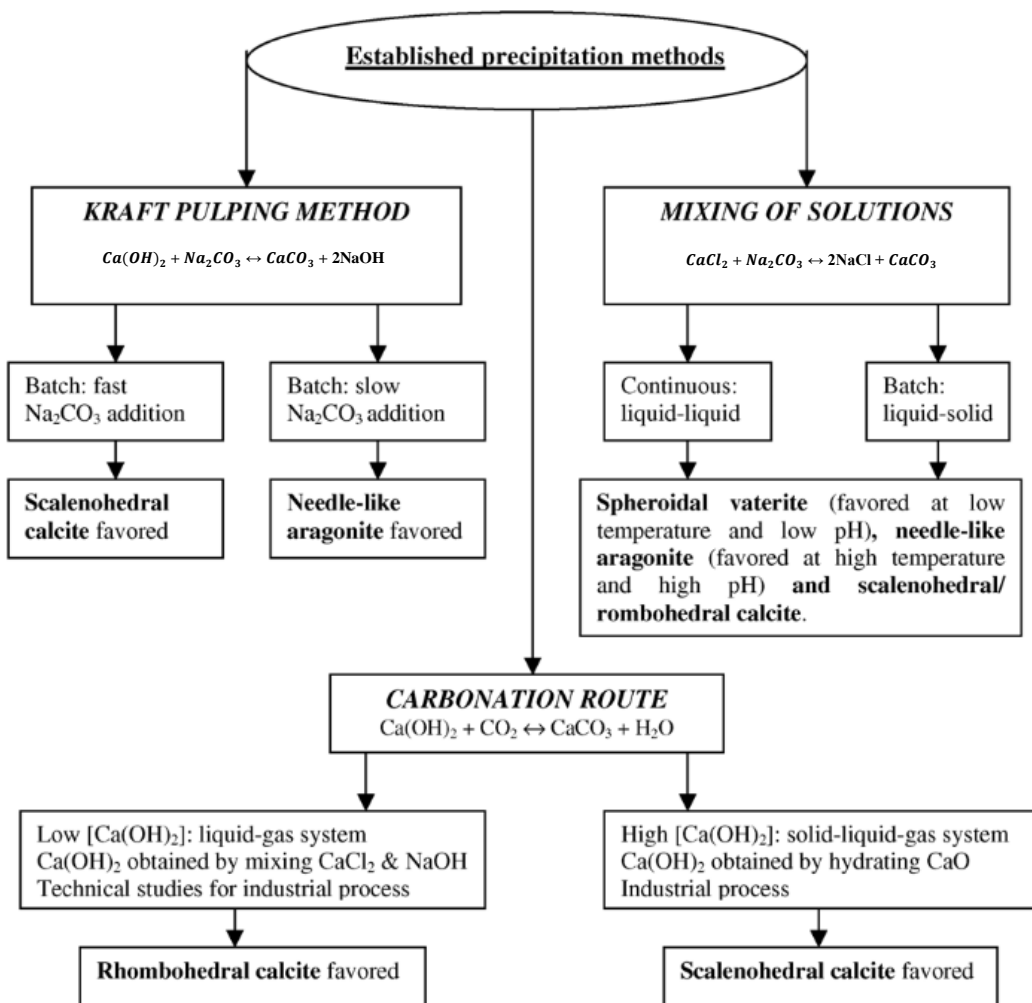


Figure 6 Some of the PCC production methods and their final products [26]

1.4.1.1 Lime Soda Process (Kraft pulping method)

In the lime soda process, a sodium hydroxide solution is obtained by the reaction of calcium hydroxide with sodium carbonate. Then the calcium carbonate is precipitated from the sodium hydroxide solution as a by-product. Alkali manufacturers commonly use this process. Their primary aim is to recover sodium hydroxide. The PCC, produced by this process has coarse particle size [27].

1.4.1.2 Calcium Chloride Process (Mixing of Solutions)

In the calcium chloride process, ammonia gas and calcium chloride solution are obtained by the reaction of calcium hydroxide with ammonium chloride. After purification stage, calcium carbonate precipitate and sodium chloride solution are formed by the reaction of calcium chloride solution with sodium carbonate. This method is the simplest one but it necessitates calcium chloride source with a low cost in order to be economically feasible [27].

1.4.1.3 Carbonation Process

Carbonation process is the most widely used process because it uses relatively cheap material; limestone as a source of raw materials. In the carbonation process, limestone lumps are burned in a lime kiln at 1000 °C for calcination purpose. To provide a grade of high purity, the calcination process is practised using natural gas. In the kiln, lime decomposes into calcium oxide (solid) and carbon dioxide (gas). Calcination becomes possible when the temperature reaches over 894 °C for 1 bar CO₂. Figure 7 presents the calcination reaction as a function of temperature and CO₂ pressure. This reaction is given in Equation 1 [27]. In the kiln, the temperature, flow rate of fresh air and natural gas has to be strictly controlled to ensure the high quality solid CaO .

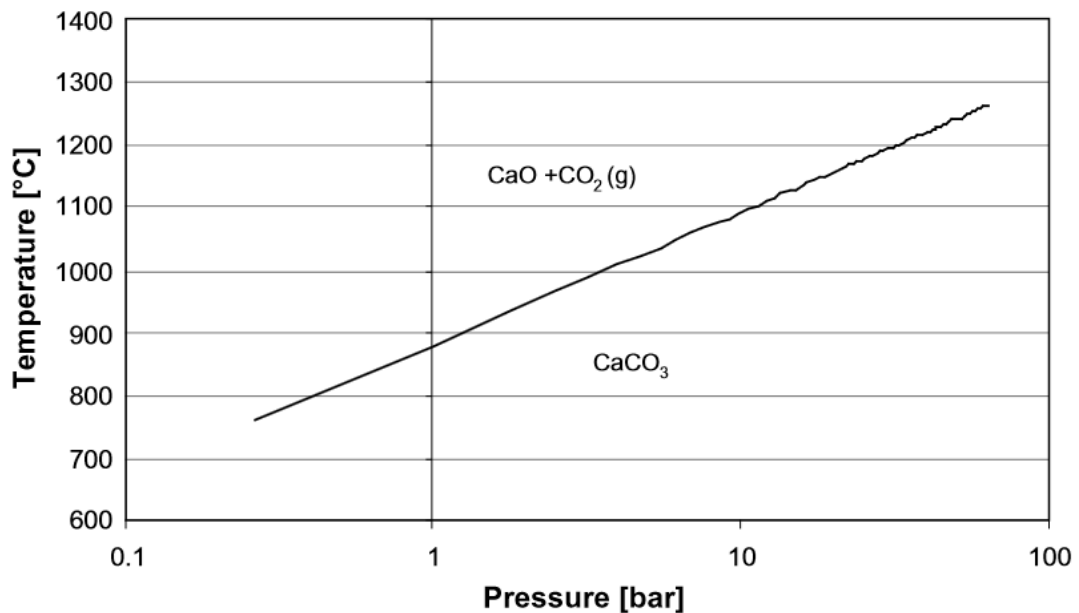


Figure 7 Dependency of calcination reaction on temperature - pressure values [27]



Dry solid calcium oxide is slaked (hydrated) by water at temperatures of 30 - 50 °C and a Ca(OH)₂ slurry is obtained. In industry, slurry formation is provided in slake making tanks, which have agitators, provided by mixing of lime and water at desired temperature. Equation 2 shows this reaction [24].



Slaked slurry (milk of lime) is first screened to remove unburnt and overburnt lime and impurities originated from limestone for purification. Then the slurry is fed to the stirred reactors, where it reacts with CO₂ for carbonation purpose. In industry, carbonation is carried out by bubbling CO₂ through Ca(OH)₂ suspension. This reaction is given in the Equation 3 [24].



In the carbonation process, calcium carbonate precipitate is formed. By controlling the operational parameters, PCCs with desired chemical and physical properties can be obtained.

Crystal shape of the PCCs can be controlled by setting the temperature to a required value at carbonation stage. Cool temperatures favor particles to crystallize in rhombohedral (blocky) shape, while warm temperatures favor scalenohedral (rosette-shaped) shape.

In the PCC manufacturing process, CO₂ is used for carbonation purpose. Carbonation is practised by injecting CO₂ gas through the solution, this process is also called as bubbling. CO₂ gas continuously flows through the solution. Some of the CO₂ is consumed in solution and the remaining bubbles burst when reached to the top of the solution which is open to the atmosphere. Therefore in the carbonation step, there is a considerable amount of CO₂ emission to the environment. CO₂ is one of the primary greenhouse gases, abundance of which influences the greenhouse effect and the quality of breathing air.

Recently, there have been some studies on PCC production from waste materials in order to reduce the adverse affects of industrial wastes. Mattila et al. has studied PCC production

from calcium containing steel-converter slags in two steps and constructed a chemical kinetic model [28].

1.5 Dissolution Chemistry of CaCO₃ in CaCO₃-H₂O System with Externally Fixed Pressure of CO₂

An alternative to the established PCC production methods could be direct dissolution of CaCO₃ in water with externally fixed pressure of CO₂. In this section, theoretical explanation of dissolution and precipitation of CaCO₃ is presented.

Dissolution and precipitation of CaCO₃ is controlled by the reactions taking place among a three phase ternary system H₂O – CO₂ – CaCO₃. In the case of a CaCO₃ – H₂O system with externally fixed CO₂ pressure, the following chemical reactions are responsible for the dissolution and precipitation of CaCO₃:



In the first reaction (4a), the dissociation of water into hydrogen and hydroxyl ions is shown. The second reaction (4b) presents CO₂ dissolution in pure water. In reactions 4b - 4c, CO₂ transforms to bicarbonate and hydrogen dependent on the pH of the solution. In reaction 4d, bicarbonate dissociates into hydrogen and carbonate ions and the rest of the reactions (4e – 4h) are responsible for the dissolution of CaCO₃ [30]. The equilibriums and equilibrium constant values for these reactions are presented in Table 7.

The steps mentioned in equations 4a-4h can be summarized as equation 5:



1.6 Possible Production Route of PCC from Marble Wastes

In the Section 1.5, the dissolution and precipitation mechanism of the CaCO_3 is explained. In this section, how much CaCO_3 can be dissolved under the conditions of 25 °C and 10 atm CO_2 pressure is explained.

The equation for electro-neutrality is shown in Equation 6 [31].

$$2m_{\text{Ca}^{2+}} + m_{\text{H}^+} = 2m_{\text{CO}_3^{2-}} + m_{\text{HCO}_3^-} + m_{\text{OH}^-} \quad (6)$$

Five equations in Table 7 are given to enable calculations for concentration of ionic species, and then to put these derived values into equation 6 in order to calculate the dissolution rate of CaCO_3 , theoretically. Effects of the partial pressure of CO_2 on the concentrations of all the ionic species in the solution are presented in Figure 8-9. Increase in the partial pressure of CO_2 enables dissolution of more CO_2 gas in the water, thus results in increase of carbonic acid (H_2CO_3) concentration in the solution. Then the concentration of H^+ and HCO_3^- ions increase and pH of the solution decreases.

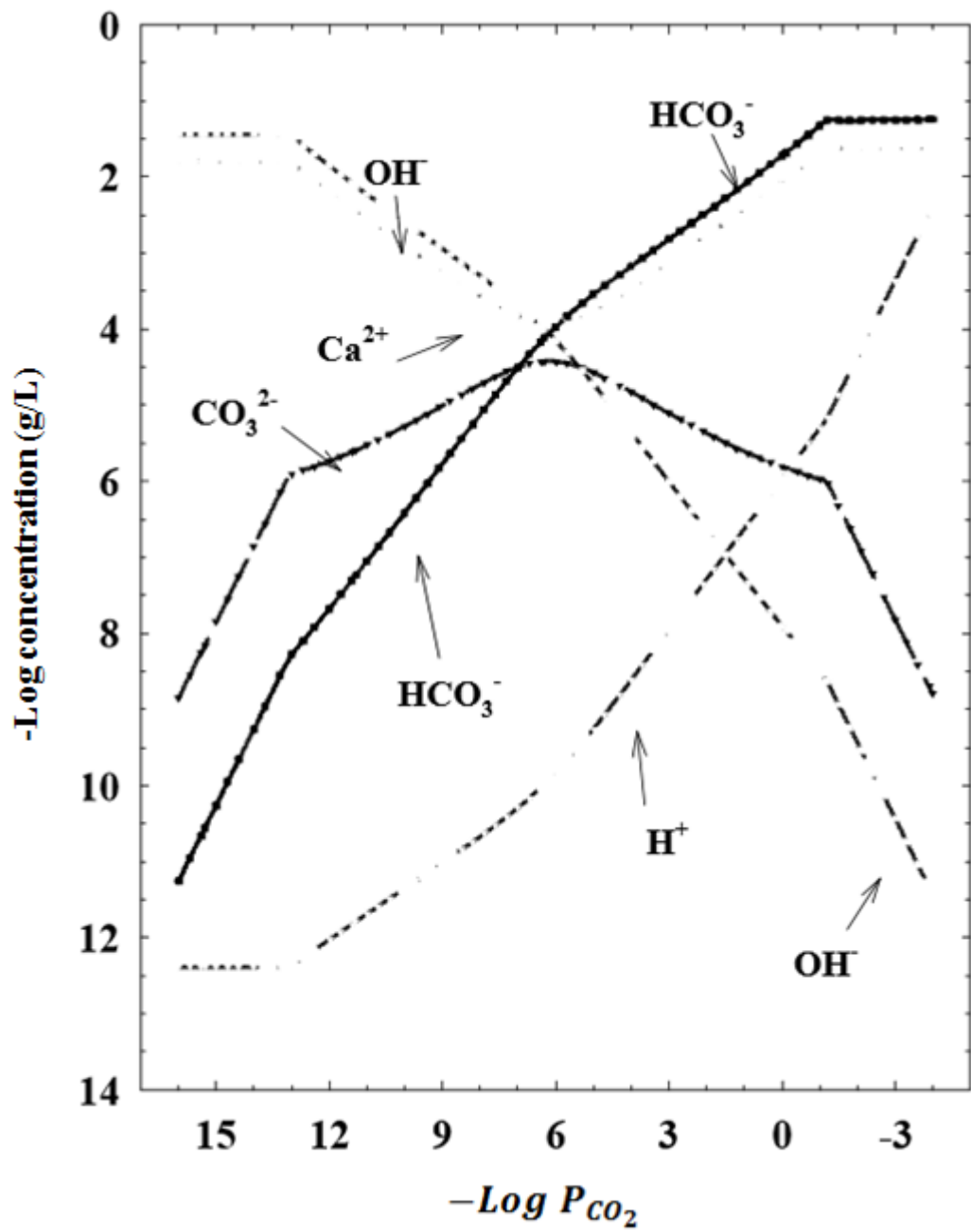


Figure 8 Concentrations of Ca^{2+} and carbonate species in the solution originated from $CaCO_3$ as a function of P_{CO_2} [32]

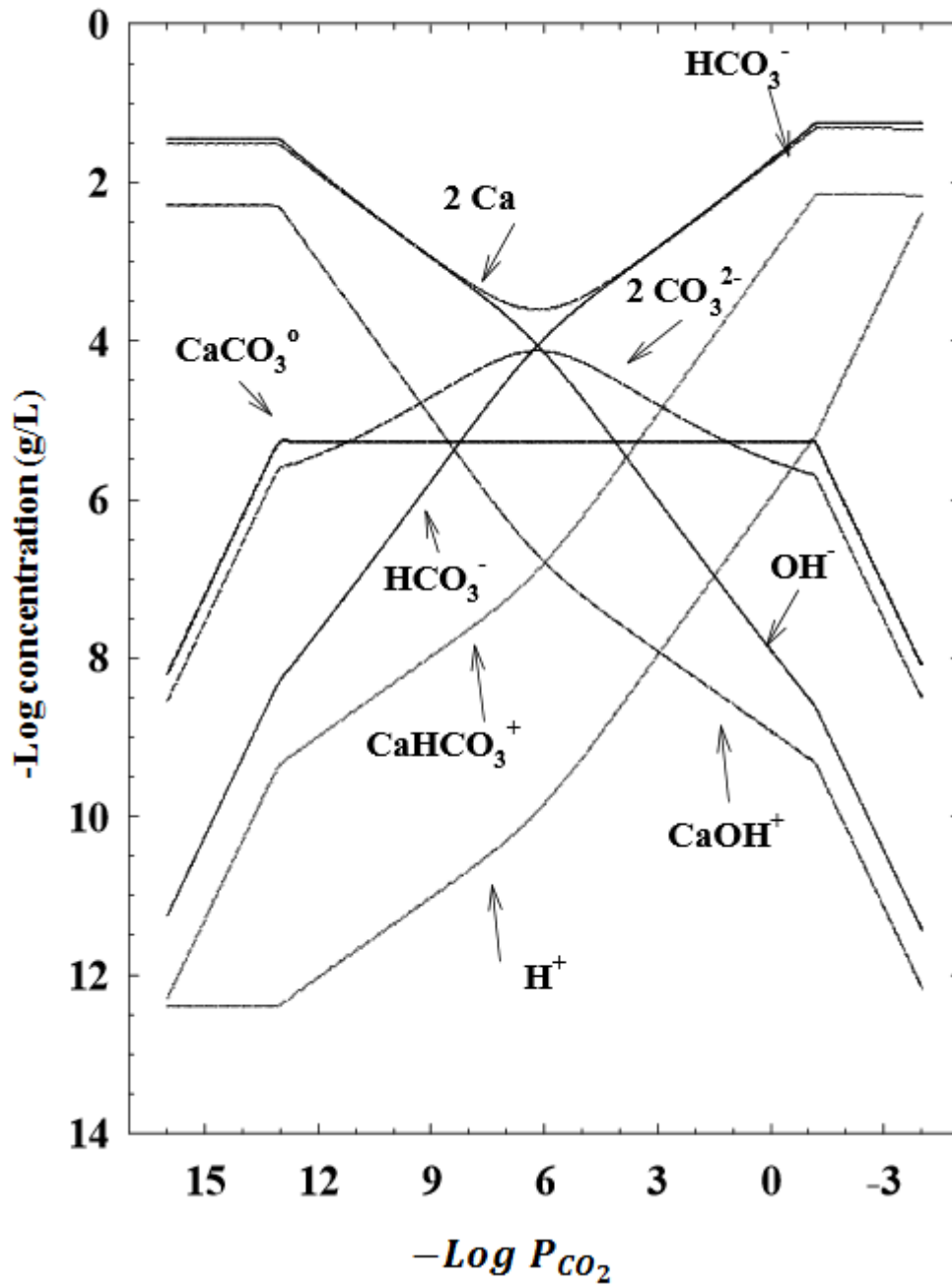


Figure 9 Concentrations of Ca^{2+} and carbonate species in the solution originated from CaCO_3 as a function of P_{CO_2} including complexes and ion pairs [32]

Table 7 Equilibriums and equilibrium constant values for carbonate systems [31]

Equilibrium	Equilibrium constants (K) at 25 °C
$[\text{H}_2\text{CO}_3] = K_{\text{CO}_2} * P_{\text{CO}_2 \text{ g}}$	$K_{\text{CO}_2} = 10^{-1.47}$
$[\text{H}^+][\text{HCO}_3^-] = K_{\text{H}_2\text{CO}_3} * [\text{H}_2\text{CO}_3]$	$K_{\text{H}_2\text{CO}_3} = 10^{-6.4}$
$[\text{H}^+][\text{CO}_3^{2-}] = K_{\text{HCO}_3^-} * [\text{HCO}_3^-]$	$K_{\text{HCO}_3^-} = 10^{-10.3}$
$[\text{H}^+][\text{OH}^-] = K_{\text{H}_2\text{O}} * [\text{H}_2\text{O}]$	$K_{\text{H}_2\text{O}} = 10^{-14}$
$[\text{Ca}^{2+}][\text{CO}_3^{2-}] = K_{\text{CaCO}_3} * [\text{CaCO}_3 \text{ c}]$	$K_{\text{CaCO}_3} = 10^{-8.3}$
Not - In the above equations all of the species are to be taken as dissolved in water, except those designated otherwise, i.e., $\text{CaCO}_3 \text{ c}$ and $\text{CO}_2 \text{ g}$.	

Substitute five values, obtained from equations in Table 7, into equation 6, and solve this equation by trial and error method;

$$P_{\text{CO}_2} = 10 \text{ atm}$$

$$[\text{H}_2\text{CO}_3] = 10^{-1.47} * 10$$

$$[\text{H}_2\text{CO}_3] = 10^{-0.47}$$

$$[\text{H}^+][\text{HCO}_3^-] = 10^{-6.4} * 10^{-0.47}$$

$$[\text{H}^+][\text{HCO}_3^-] = 10^{-6.87}$$

$$[\text{HCO}_3^-] = 10^{-6.87} / [\text{H}^+]$$

$$[\text{H}^+][\text{CO}_3^{2-}] = 10^{-10.3} * 10^{-6.87} / [\text{H}^+]$$

$$[\text{CO}_3^{2-}] = 10^{-17.17} / [\text{H}^+]^2$$

$$[\text{OH}^-] = 10^{-14} / [\text{H}^+]$$

$$[\text{Ca}^{2+}] * 10^{-17.17} / [\text{H}^+]^2 = 10^{-8.3}$$

$$[\text{Ca}^{2+}] = 10^{8.87} * [\text{H}^+]^2$$

Substituting the values into equation 6;

$$2 \cdot 10^{8.9} \cdot [\text{H}^+]^2 + [\text{H}^+] = 2 \cdot 10^{-17.2} / [\text{H}^+]^2 + 10^{-6.9} / [\text{H}^+] + 10^{-14} / [\text{H}^+]$$

$$[\text{H}^+] = 10^{-5.18}$$

$$[\text{Ca}^{2+}] = 0.0347 \text{ mole/L}$$

$$[\text{Ca}^{2+}] = 1.3869 \text{ g/L}$$

1 mole of Ca is 40 g and CaCO_3 is 100 g, so;

$$[\text{CaCO}_3] = 1.3869 \cdot 100/40 \text{ (g/L)}$$

$$[\text{CaCO}_3] = 3.4673 \text{ g/L.}$$

Theoretically it is possible to dissolve 3.47 g/L CaCO_3 in $\text{CaCO}_3\text{-H}_2\text{O}$ system under the conditions of 25 °C and 10 atm CO_2 pressure.

1.7 Aim of This Study

The purpose of this study was to investigate the production of precipitated calcium carbonate from marble wastes. Marble stone quarrying and processing industries generate a great amount of waste in various forms and these wastes are known to have negative impacts on the environment. In addition to the more common utilization routes of marble wastes, it could be useful to utilize these wastes for the production of PCC. The study was focused on determining the most suitable conditions for the parameters, such as particle size, temperature, CO_2 pressure, stirring speed etc. which affect the dissolution rate of CaCO_3 .

There are various studies on utilization of marble wastes by using in different fields and there are also studies on alternative sources like steelmaking slags for producing PCC. But the study in this thesis is unique with regard to use of marble wastes as a source for production of PCC with sufficient quality to meet the industrial requirements.

In industry, most widely used method for production of CaCO_3 precipitate is the carbonation of slaked lime. In this method, mostly the limestones are used as a source of raw material. In our system, to contribute economically and to make it environmentally friendly, the lime calcination and slaking stages were eliminated and marble wastes were used as the source of raw material. Recycling the CO_2 gas in the production stages was proposed to prevent CO_2 emission to the environment and so greenhouse effect.

In industry, solid waste material can be dissolved directly in an autoclave without calcination by addition of CO₂ gas. Then the solution is screened to remove undissolved solid particles (mineral impurities) derived from marble wastes for purification purpose and it is transported to a deaeration tower to recover CO₂ gas, which is dissolved in the solution, for recycling. In the deaeration tower, the main stream is splitted to many smaller streams to reveal CO₂ gas, then the CO₂ gas is vacuumed through an hose which is connected to the top of the tower. Streams continuously flow and release the CO₂ gas contained in. CO₂ gas is recycled to autoclave in order to reuse in the next stages of the process. After deaeration, the stream is poured in a settling pool and waited for complete precipitation of dissolved CaCO₃. At a certain period, clarified water is taken from overflow, and precipitates are taken from underflow as a finished product. This process is illustrated in Figure 10.

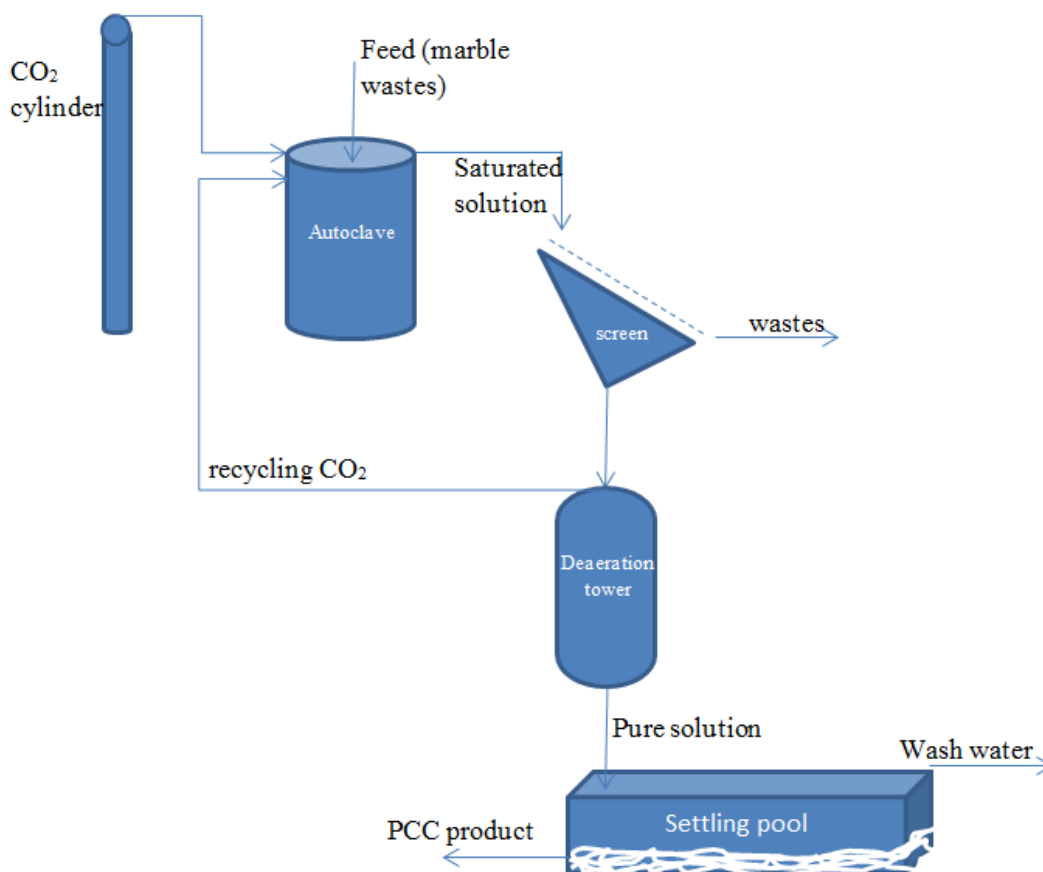


Figure 10 A hypothetical flowsheet of the PCC production process

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

Marble lump wastes from Oğuz Marble Ind. Trade. Co. Ltd. waste storage areas were used as raw material.

CaCO₃ content of marble waste samples was determined by wet analysis. According to the analysis result, the waste contains ≥ 99.5 % CaCO₃.

Chemical analyses were carried out on the raw material (marble wastes) and the PCC product. Samples were prepared to -53 μm particle size. Because the samples were oxidised, they were digested in aqua regia on the hot plate. Then the undissolved solid particles were separated by filter papers. The contents of the solutions were measured by ICP- AES. The analyses results of marble waste and the PCC product are given in Table 8 and Table 9, respectively.

Table 8 ICP analysis results of marble waste sample

Element	Na	P	Pb	S	Al	As	Cu	Mg	Mn	Fe
Unit	%	%	ppm	%	%	ppm	ppm	%	ppm	%
Detection Limit	0.01	0.01	2	0.01	0.01	3	0.01	0.01	2	0.01
Marble Wastes	< 0.01	< 0.01	< 2	< 0.01	< 0.01	< 3	0.02	0.13	23	0.02

2.2 Methods

In this study, a laboratory scale autoclave was used. It had a Teflon cell with 1 liter capacity. A CO₂ cylinder was directly connected to it. It had gauges for monitoring both the temperature and pressure.

A hot plate was used to evaporate H₂O in order to determine the concentration of dissolved CaCO₃ in the solution samples taken from the autoclave cell by a time period of half an hour in a 10 ml beaker during the experiments.

In each test, 50 g ground marble wastes were used. In the tests, effects of time, particle size, CO₂ pressure, stirring speed and temperature on dissolution rate of marble waste were examined.

In each test, 10ml samples were collected in a 10 ml glass beaker after each half an hour time cycle from sample collection port of the autoclave. Then they were placed on hot plate at 135 °C to evaporate CO₂ and precipitate CaCO₃ contained in the solution. The amount of PCC produced was determined from dry matter remaining in the beaker.

2.2.1 Sample Preparation

Samples were blended and then divided into 8 parts by using a laboratory riffle. 5 of the 8 parts were crushed and ground separately to the required particle sizes by a jaw crusher and a roller mill. After size reduction, the material was dried at 70 °C in an electrical furnace. Crushed, ground and dried material was sieved to obtain required size ranges for the experiments. Raw material was classified to the following size ranges:

- + 500 μm - 2 mm;
- + 250 μm - 500 μm;
- + 106 μm - 250 μm;
- + 75 μm - 106 μm;
- - 75 μm.

For each size interval, 50 grams of ground waste samples were prepared and packed and they were kept for the experiments.

2.2.2 Test Apparatus

In this study, a laboratory scale autoclave of 1 L capacity was used. Figure 11 shows the experimental set up. A CO₂ gas cylinder was connected to the autoclave, Figure 12, in order to give required CO₂ pressure to the cell. CO₂ pressure of the gas cylinder was manually controlled and monitored by a valve and a manometer, respectively. Materials were stirred in the cell by a speed-controlled motor drive, actuating mechanism of which was consisted of a belt and pulley system. Different stirring speeds were attained by controlling the speed of the motor. Low temperatures were achieved by cooling the autoclave cell through an external system which consist of a container, filled with cold water and a recirculating pump in it. To examine the effect of temperature on dissolution, cold water was continuously recirculated through the autoclave in a spiral tube immersed into the teflon cell. By this way temperatures of 18 °C, 12 °C and 8 °C were achieved, separately.

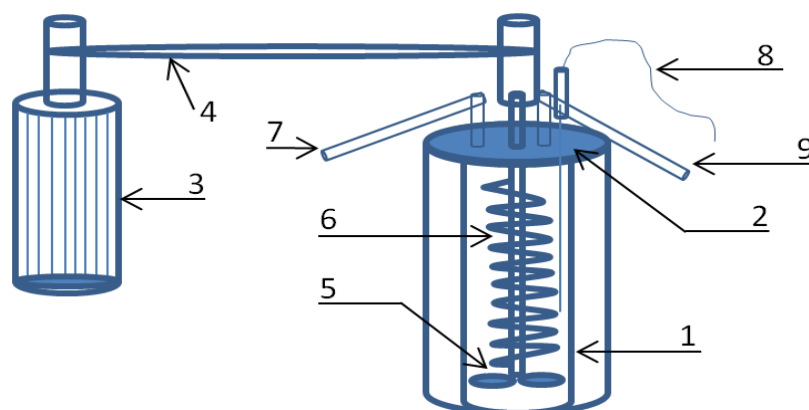


Figure 11 Experimental set up for a batch run. A vessel of teflon (1) is sealed by a lid (2). The lid carries a pulley which is connected to the motor (3) by a belt (4). The pulley has a shaft and a stirrer (5) on it. Teflon cell can be cooled by recycling a cool water in the spiral (6) immersed in this vessel. CO₂ gas is given to the system by a hose (7) which is connected to the autoclave. Temperature inside the closed vessel is measured by a thermometer (8) immersed in the cell and the product samples are taken from the sampling discharge (9) of the unit



Figure 12 The autoclave and the CO₂ cylinder connected to it

SEM analysis was carried out to observe the crystal shapes and sizes of the marble wastes sample and the PCC product. For the analysis of marble waste and the PCC product, NANOSEM 430 was used at 10 kV. Firstly, the samples were coated under vacuum by platinum of 10 nm thickness. Then the microstructural images of the samples were taken.

CHAPTER 3

RESULTS AND DISCUSSION

In order to investigate the effects of conditions on the dissolution of marble wastes, a series of tests were conducted. Systematically, first the required time, and then particle size, CO₂ pressure, stirring speed and temperature were determined, respectively.

In the experiments, two steps were followed which are dissolution followed by precipitation. After dissolution, the quantity of dissolved species was determined by complete drying of samples withdrawn from the autoclave on a hot plate. Particular attention was given to the dissolution stage to produce as much CaCO₃ as possible.

3.1 Effect of Time on Dissolution

In the experiment, time from 1 h to 9 h was allowed to investigate the change in the concentration of dissolved species in water with time, Figure 13, under the conditions of particle size: - 250 + 106 μm; P_{CO_2} : 10 atm; stirring speed: 1400 rpm; temperature: 25 °C. It was found that the amount of dissolved CaCO₃ reached to 2.9 g/L in 15 min. and did not change much thereafter in 2 h. At the end of 9 h, the dissolution was 3.2 g/L. This indicated that 1 to 2 h dissolution time is enough to dissolve CaCO₃. Based on this objective, maximum duration for dissolution was kept constant at 2 h in the following experiments.

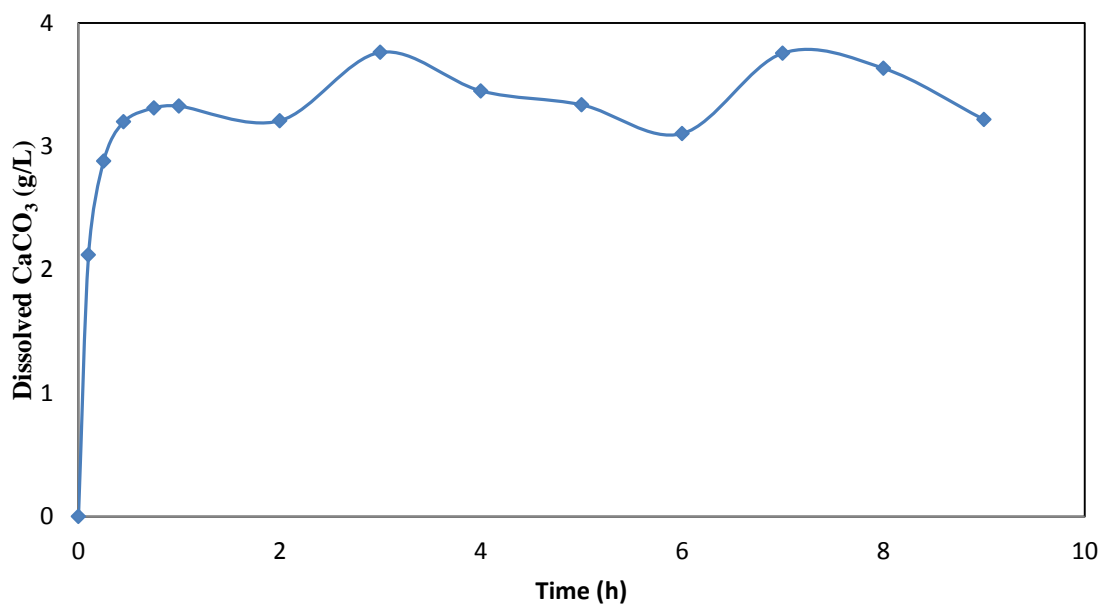


Figure 13 CaCO₃ formation as a function of time, under the conditions: particle size: - 250 + 106 μm; P_{CO_2} : 10 atm; stirring speed: 1400 rpm; temperature: 25 °C

3.2 Effect of Particle Size on Dissolution

In order to investigate the influence of particle size on dissolution, tests were conducted on wastes of different particle sizes under the conditions of P_{CO_2} : 10 atm; stirring speed: 1400 rpm; temperature: 25 °C. Raw materials (marble wastes samples) sieved to five different size intervals, from 2 mm down to 75 μm, were dissolved separately in the autoclave. Samples were collected for half an hour at each test and contained water was evaporated to precipitate dissolved species in the sample. Concentrations of dissolved ions were calculated. Concentrations versus time curves were plotted for each experimental group. Results are shown in Figure 14. The experimental results show that, as expected, the dissolution rate, at constant temperature, CO₂ pressure and stirring speed, increases with decreased particle size. This is because solid CaCO₃ particles with wider surface areas get more chance to come in contact with CO₂ and H₂O in the system, therefore the dissolution rate of CaCO₃ increased with decreasing the size of the particles. At the end of 2 h, minimum dissolution was observed in - 2 mm + 500 μm size interval which was notably different from the others, whereas maximum was in - 106 + 75 μm. - 500 + 250 μm sample has shown the greatest increase in dissolution from 2.09 g/L to 3.36 g/L through the experiment. In the size range of - 250 + 106 μm, dissolution rate was not changed so much through the experiment. - 250 + 106 μm size interval was chosen as the most favored size to continue the experiments at constant size range.

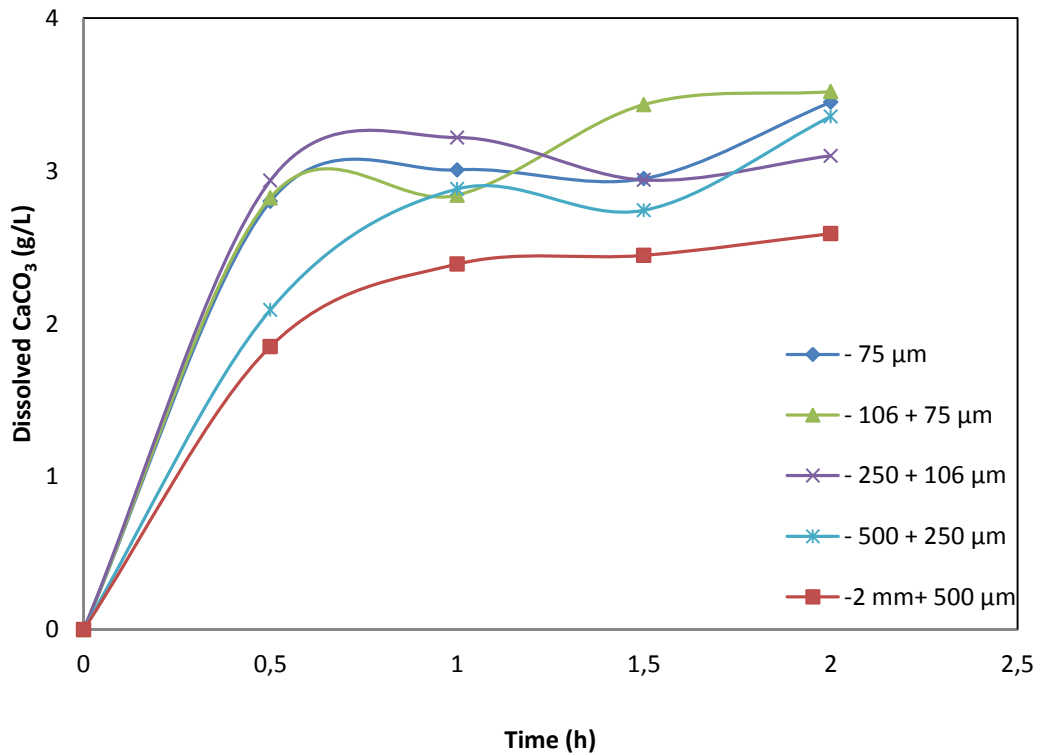


Figure 14 CaCO_3 formation as a function of particle size of starting material, under the conditions: P_{CO_2} : 10 atm; stirring speed: 1400 rpm; temperature: 25 °C

3.3 Effect of CO_2 Pressure on Dissolution

It is known that increased partial pressure of CO_2 increases the amount of CO_2 dissolved in water, so increasing the solubility of CaCO_3 . Although, pressure alone does not affect the solubility of CaCO_3 as much as the effect of temperature [29]. In the experiment, CO_2 gas with a constant pressure was given to the system. Four experiments were conducted at CO_2 pressures of 2 atm, 10 atm, 15 atm and 32.5 atm under the conditions of particle size: -250 +106 μm ; stirring speed: 1400 rpm; temperature: 25 °C. The experimental result shows that, as expected, the dissolution rate, at constant particle size, temperature and stirring speed, increases with increased CO_2 pressure, Figure 15. The concentrations were not changed in two hours, significantly. In practice, it could be difficult to achieve high pressures, higher than 10 atm, economically therefore 10 atm CO_2 pressure was chosen as a favorable value.

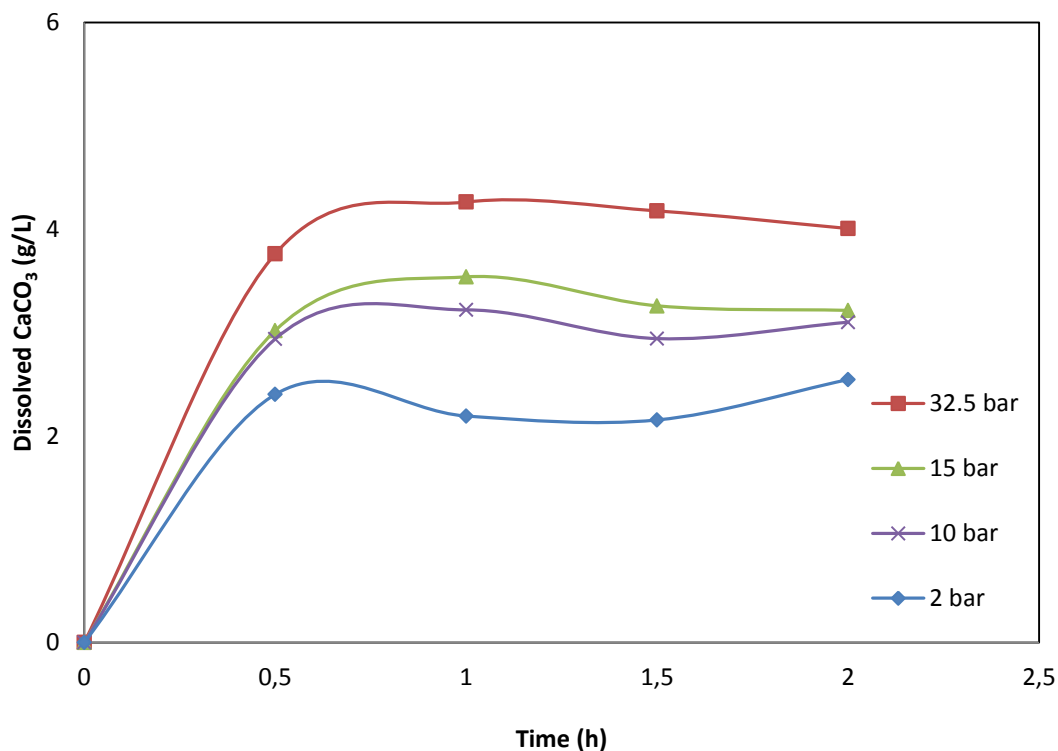


Figure 15 CaCO₃ formation as a function of CO₂ pressure under the conditions: particle size: -250 +106 μm; stirring speed: 1400 rpm; temperature: 25 °C

3.4 Effect of Stirring Speed on Dissolution

Stirring speed has a significant effect on the dissolution rate. In order to demonstrate this, stirring speed was examined by experiments at four different stirring rates from 250 rpm to 1400 rpm under the conditions of particle size: -250 +106 μm; P_{CO_2} : 10 atm; temperature: 25 °C. Functions of stirring were to keep the solids in suspension to prevent settling of the particles and to enable interaction of particles and water to improve dissolution. Accordingly, in the experiments, dissolution rate was improved by higher stirring rates. It is clearly seen in Figure 16 that the maximum dissolution was obtained as 3.54 g/L at 1400 rpm at 1.5 h. Thus 1400 rpm stirring speed was chosen to be the most favoured speed among all the tests for the currently used stirrer design.

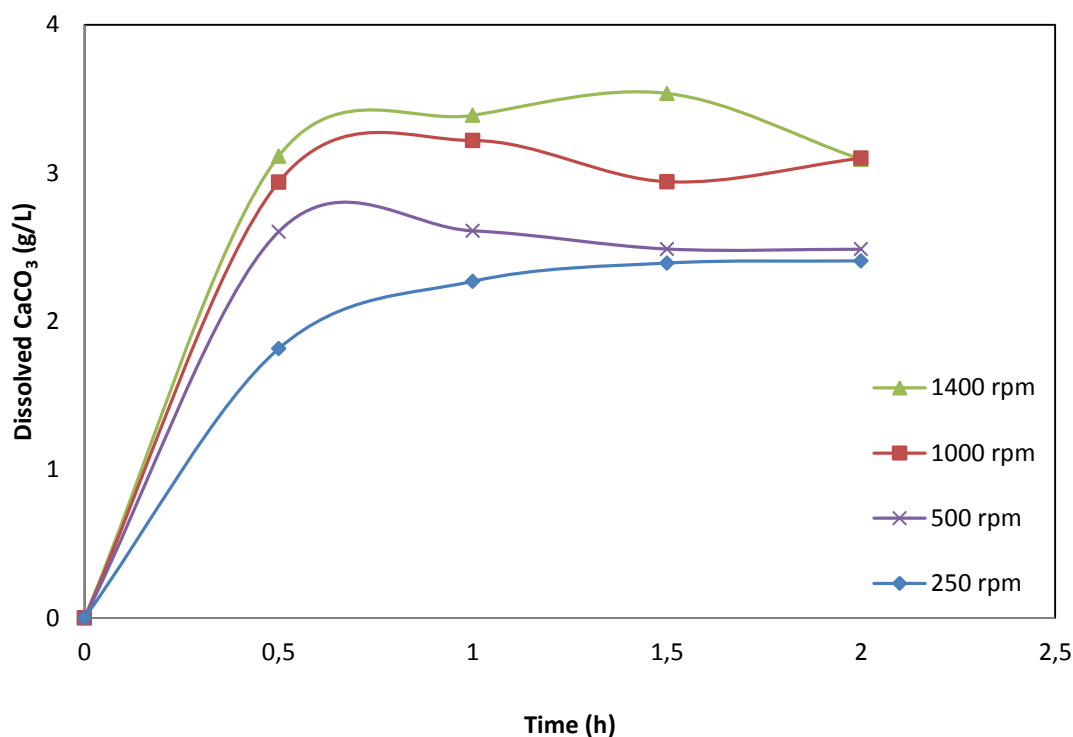


Figure 16 CaCO_3 formation as a function of stirring speed, under the conditions: particle size: $-250 +106 \mu\text{m}$; P_{CO_2} : 10 atm; temperature: 25 °C

3.5 Effect of Temperature on Dissolution

Effects of temperature on dissolution were investigated by conducting experiments at standard and lower temperatures. In most cases, solubility of the minerals typically increases with increase of temperature. In contrast to this, many carbonate minerals get more soluble in cold water. For example, the K_{sp} value for calcite at 0 °C and 50 °C is $10^{-8.02}$ and $10^{-8.63}$ respectively. This is because the dissolution reaction of the carbonate minerals is exothermic, which results in higher temperatures favoring the solid phase over dissolved ions [29]. Four temperature levels were investigated to observe the influence of temperature on dissolution rate of CaCO_3 under the conditions of particle size: $-250 +106 \mu\text{m}$; P_{CO_2} : 10 atm; stirring speed: 1400 rpm. The first was performed at room temperature (25 °C). Other three experiments were conducted by cooling the system. By this system, temperatures of 18 °C, 12 °C and 8 °C were achieved, separately. As can be clearly seen in Figure 17, concentration of dissolved CaCO_3 increased with decreasing temperature. Maximum dissolution was achieved as 4.73 g/L in the experiment conducted at 8 °C, at the end of 2 h.

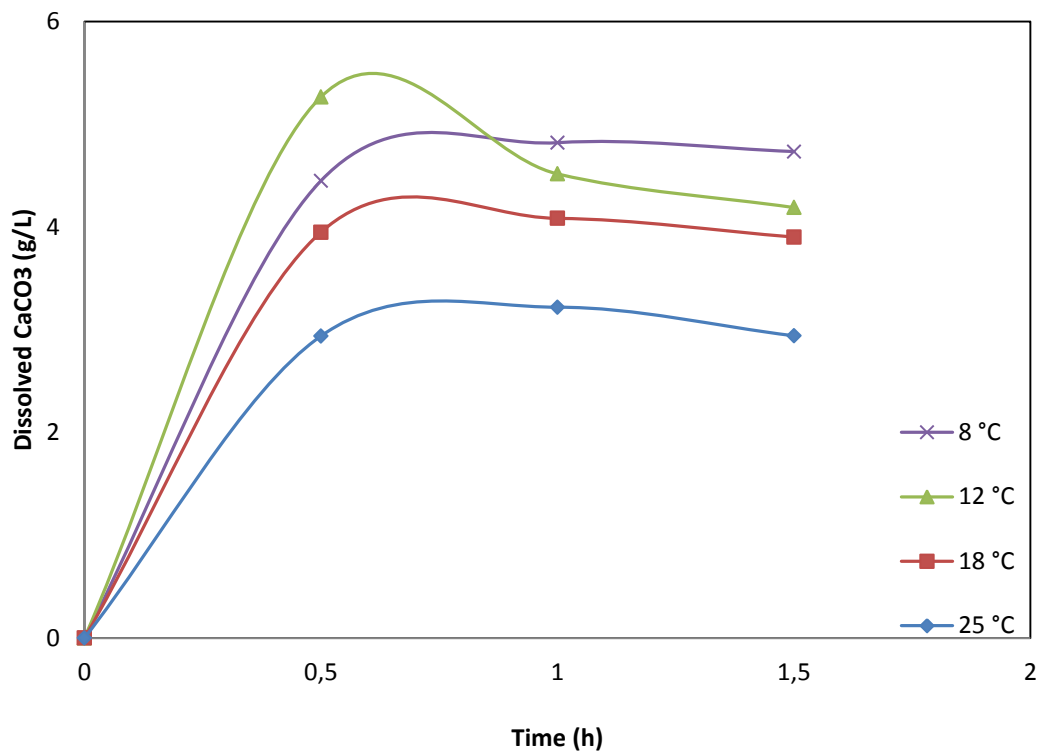


Figure 17 CaCO_3 formation as a function of temperature, under the conditions: particle size: $-250 +106 \mu\text{m}$; P_{CO_2} : 10 atm; stirring speed: 1400 rpm

3.6 Morphological Study

In order to observe the microstructure of the marble waste particles and the PCC crystals, the samples were analysed by Scanning Electron Microscope. SEM images of the waste sample are seen in Figure 18. This figure reveals that at the experiments, the starting material (ground marble wastes) consists of nonuniform, shapeless particles with broader size distribution. On the other hand, the PCC product sample, obtained from the test at 8 °C reveals submicron crystals in narrower size range with uniform rhombohedral shapes having sharp steps, Figure 19.

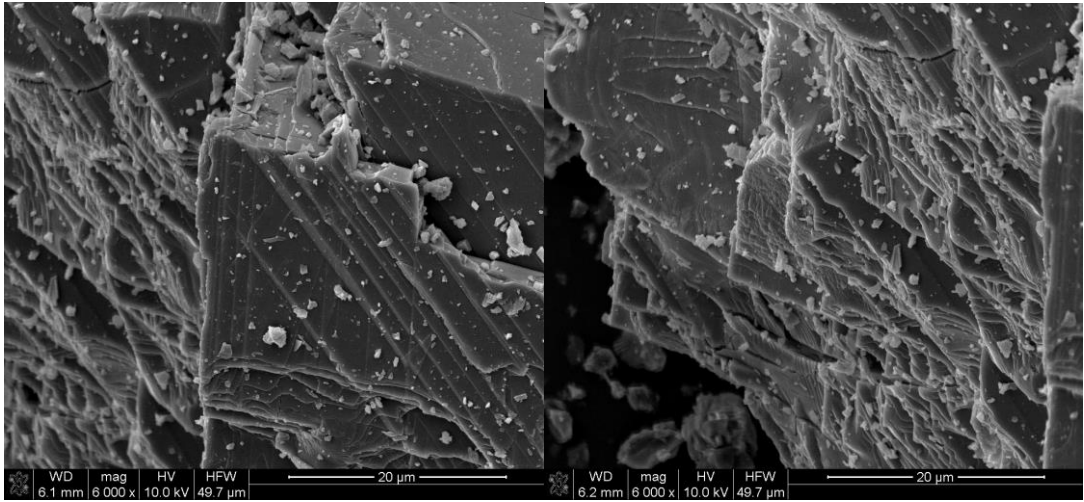


Figure 18 SEM images of the waste sample

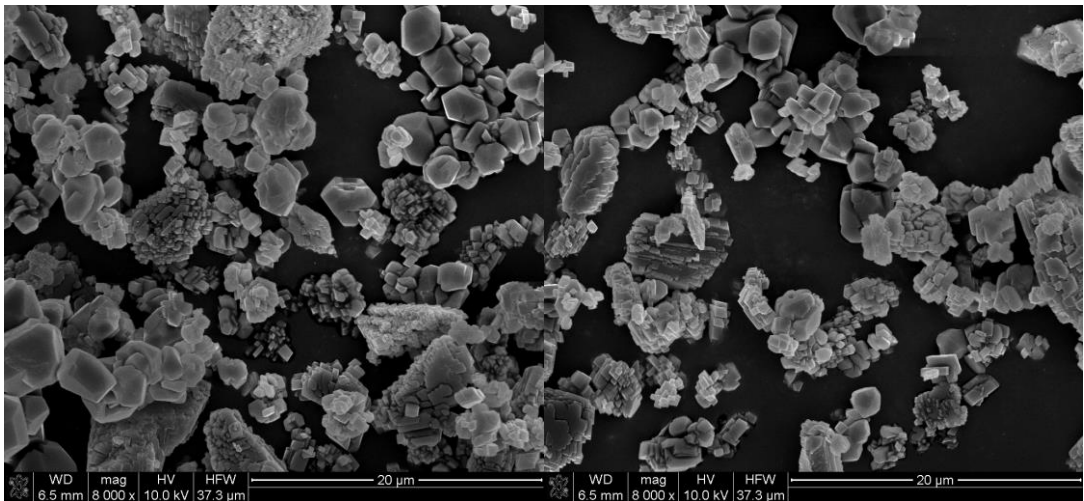


Figure 19 SEM images of the PCC sample obtained at 8 °C

3.7 Chemical Analysis of the PCC Product

In order to evaluate the chemical content of the PCC product, ICP analysis was carried out. In the analysis, 10 elements were measured to characterize the samples, Table 8. The results show that 5 elements; phosphor, lead, sulphur, aluminium and arsenic are out of the given detection limits, 3 elements; sodium, copper and iron are near the lower detection limits and the remaining 2 elements are magnesium and manganese. Because 3 elements are near the lower detection limits, it is possible that they were misread. The iron content should be lower than 0.01 % in PCC product. In the analyses, the lower detection limit for iron was 0.01 and the samples were measured as containing 0.02 % Fe. Because the measured values were too close with the lower detection limit, it may be an experimental error, otherwise further works should be carried out to reduce the iron content in the PCC product. Another possibility in the presence of these elements in the PCC product is that, the cooling system in the experimental set up is made of metal, thus the acidic environment during experiments can cause dissolution of little amount of metallic ions and transfer of them into the solution. According to the ICP results, copper, manganese and magnesium contents are below the allowable limits for PCC. In summary, preliminary investigation shows that the PCC product obtained in this study confirms the PCC specifications, except iron. This matter has to be further studied in detail.

Table 9 ICP analysis results of PCC product

Element	Na	P	Pb	S	Al	As	Cu	Mg	Mn	Fe
Unit	%	%	ppm	%	%	ppm	ppm	%	ppm	%
Acceptable Limit	0.15	0.05	Traces	0.2	0.5	NIL	Negligible	0.7	50	0.01
PCC Product	0.01	< 0.01	< 2	< 0.01	< 0.01	< 3	0.02	0.12	16	0.02

CHAPTER 4

CONCLUSIONS & RECOMMENDATIONS

4.1 Conclusion

Studies on “utilization of marble wastes” were conducted to investigate possibilities of PCC production from marble wastes under different conditions and the following conclusions can be drawn from this study:

- Decreasing the particle size has positive effect on dissolution rate of CaCO_3 , but it is unnecessary to achieve particle sizes below 106 μm . Because even smaller sizes cannot be cost effective and their effect on dissolution is insufficient.
- Increasing the CO_2 pressure has positive impact on dissolution, however, in practice; it is advisable to work up to 10 atm CO_2 pressure.
- Stirring speeds lower than 1000 rpm cause sharp decrease in concentration of dissolved species in the solution. Working at 1000 – 1400 rpm stirring speeds are both practically and economically significant.
- Temperature has a detrimental effect on waste dissolution. Materials were dissolved more readily at lower temperatures. Cooling the solution seems to be very advantageous, from the point of rate of dissolution. It has to be evaluated for its application on the side of economy and applicability in industry.

Result of the studies demonstrate that utilization of marble wastes for the production of PCC may be an alternative route by introducing the wastes with pressurized CO_2 gas has benefits for removing the negative impact of marble wastes to the environment and supplying cheaper raw material to the PCC manufacturing industry. Also this novel PCC production method combined and eliminated some of the conventional PCC production process steps.

4.2 Recommendations

In order to produce a PCC product in commercially acceptable limits, mineral impurities should be eliminated to the acceptable limits during production cycle. Further works should be carried out to investigate the dissolution and precipitation of mineral impurities derived from marble wastes, thus present in the solution, in PCC production cycle. To evaluate the feasibility of the given production method for PCC in industry, a continuous production cycle should be studied in a lab scale set up. PCC product obtained from the experimental studies should be further analysed to evaluate its suitability to the industrial requirements, such as, opacity, brightness, whiteness, specific surface area, specific gravity, particle size distribution, refraction index, etc. Lastly, lower temperatures should be attempted to further investigate the increase in the dissolution rate of CaCO_3 with decreasing temperatures.

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