Physicochem. Probl. Miner. Process. 53(1), 2017, 57−68

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received October 27, 2015; reviewed, accepted February 9, 2016

PRECIPITATED CALCIUM CARBONATE PRODUCTION, SYNTHESIS AND PROPERTIES

Necmettin ERDOGAN, Haci Ali EKEN

Aksaray University, Department of Mining Engineering, Aksaray, Turkey
Email: nerdogan@aksaray.edu.tr

Abstract: Calcium carbonate ($CaCO_3$) is the most widely used filler material in paper, paint, plastic, food, ceramic, cosmetic, medicine and other industries. In the present paper, precipitated calcium carbonate (PCC) has been produced from waste marble powder (WMP) by the Calcination-Dissolution-Precipitation (CDP) method. Calcination, dissolution and precipitation experiments were carried out under various conditions including : calcination temperature (800, 850, 900, 950 and 1000 °C), dissolution time (2.5, 5.0, 7.5 and 10.0 min) and precipitation time (2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 min). Then, XRF, XRD, SEM, particle size, whiteness, brightness and yellowness analyses were performed for the characterization of the produced PCC materials. The analyses showed that the precipitate was mainly micrometer-sized (d_{50} = 1.682 µm) rhombohedral calcium carbonate crystals with 54.5% CaO. The whiteness, brightness and yellowness tests of the precipitates, conducted by Datacolor Elrepho 450x spectrometer, were determined to be 91.28, 98.2 and 1.99%, respectively. It was finally concluded that the produced PCC material reasonably meets Turkish Standards (TS 11653/1995) and can be used in paper industry.

Keywords: *precipitated calcium carbonate, waste marble powder, whiteness*

Introduction

Limestone is a common type of sedimentary rock in the earth crust which primarily constitute of $CaCO_3$ (Kilic, 2015; BGS, 2006). As a limestone, marble is 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 (Sezer, 2013).

Chalk and limestone are relatively soft and easily ground to a fine powder that is non-toxic and usually white in color. These properties ensure that limestone powders are extensively used as fillers in a diverse range of products where the primary purpose is to add low cost bulk. Some limestone powders also make use of the

http://dx.doi.org/10.5277/ppmp170105

chemical properties of the stone. Examples include acting as a source of calcium in animal feeds, and as an acidity regulator in some agricultural and pharmaceutical products. Powder made from chalk is usually known as ‘whiting’ (BGS, 2006).

Calcium carbonate ($CaCO_3$) is the most widely used filler (Karakas and Celik, 2012) and/or extender material in paper (Lopez-Periago et al., 2010), paint, plastic, sealant, adhesive, food, ceramic, textile (carpet), cosmetic, medicine (Dogan, 2007), and several other industries (Koltka and Sabah, 2012). Each industry requires specific product characteristics in terms of chemical purity, particle size distribution, shape and surface area, whiteness, and rheological behaviour etc. (Kilic, 2015). Calcium carbonate was also found superior to other pigments in light-induced ageing experiments (Fjellstrom et al., 2007).

There are two sources of calcium carbonate, namely ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) in the world (Kilic, 2015). GCC is extracted from the earth, and is present in varying quantities in the form of calcite, aragonite, vaterite, limestone, chalk, marble or travertine. Following its extraction, GCC is ground either under dry or wet conditions depending on the final product requirements (Kilic, 2015).

On the other hand, 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 (Sezer, 2013). Calcite is the most thermodynamically stable under ambient conditions, but other polymorphs can form under specific kinetic conditions. Aragonite is more soluble and denser than calcite. It usually forms needle-like orthorhombic crystals and is favored at high temperatures and pressures. It is metastable, converting slowly to calcite. Vaterite is the thermodynamically least stable polymorph, and its hexagonal crystals are rarely seen in the naturally occurring mineral (Piskin and Ozdemir, 2012).

Commercial PCCs have been produced since 1841. It 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 practiced in Birmingham (Sezer, 2013).

There have been many studies on the production of PCC from different sources. Calcium hydroxide for the PCC production was recovered from slaked lime of automobile welder’s carbide sludge was explored by Chukwudebelu et al. (2013). Bilen (2010) investigated the recovery conditions of high purity calcium carbonate by injection of carbon dioxide into the leach solution in which Ca^{2+} ions were selectively extracted from the steel making slags of Iskenderun Iron and Steel Works Co. Precipitation of calcium carbonate from hydrated lime of variable reactivity, granulation and optical properties was also studied by Kemperl and Maček, (2009). Dogan and Yildirim (2008) studied that precipitated calcium carbonate from Afsin – Elbistan power plant fly ashes. Teir (2008) studied the possibility of reducing CO_2 emissions by producing calcium and magnesium carbonates from silicate materials for the long-term storage of CO_2 using multi-step processes. Huijgen (2007), Kodama et al. (2008) and Lim et al. (2010) have investigated mineral carbonation with carbon dioxide gas. Teir et al. (2007) investigated dissolution properties of steelmaking slags in acetic acid for precipitated calcium carbonate production. Effect of limestone characteristic properties and calcinations temperature on lime quality was studied by Kilic and Anil (2006). Bunger et al. (1998) was able to recover slaked lime from carbide sludge into solution with subsequent reacting of the solution with carbon dioxide to form calcium carbonate.

There are three common processes for the production of synthetic PCC (Sezer, 2013; and Bilen, 2010): 1) lime soda process (Kraft pulping method, Eq. 1); 2) calcium chloride process (Eq. 2), and 3) carbonation process (Eq. 3):

$$Ca(OH)_2 + Na_2CO_3 \leftrightarrow CaCO_3 + 2NaOH \tag{1}$$

$$CaCl_2 + Na_2CO_3 \leftrightarrow 2NaCl + CaCO_3 \tag{2}$$

$$Ca(OH)_2 + CO_2 \leftrightarrow CaCO_3 + H_2O. \tag{3}$$

The usual product specifications for PCC is purity of more than 99%, density of 2.7 g/cm^3, particle size of 70% <2 μm for filler pigments and the specific surface area of about 10 m^2/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 mole of PCC in 1 dm^3 solution should be approximately 9. Average particle size of PCCs as coating pigment should be in 0.4 to 2 μm size range, refraction index of 1.49–1.67 and a specific surface area of 4–11 m^2/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 (Teir et al., 2005)

It is well-known that, the presence of PCC enhances the smoothness, brightness and opacity of paper. It also increases ink receptivity of paper. Titanium dioxide (TiO_2) due to its high refractive index is widely used in paint industry as a white pigment, but it is expensive mineral. Therefore, $CaCO_3$ is used as the primary extender compound to reduce consumption of higher cost pigments, like TiO_2 (SPO, 2001; Karakas et al., 2015). Fine sized and narrowly ranged PCC grains provide gaps among TiO_2 particles and improve their hiding power (Stratton, 2012).

The effect of various grades of precipitated and ground calcium carbonate on the tensile strength and Charpy impact energy of extruded PVC profile confirm that ultra-fine precipitated calcium carbonate (PCC) can give rise to large improvements in single notch impact strengths (Fernando and Thomas, 2008). PCC possesses superior specifications over ground calcium carbonate (GCC) with high $CaCO_3$ ratio, low impurities, availability in different morphologies and finer sizes (Dogan, 2007; Kilic, 2015).

Experimental

Waste marble powder used in this study was sampled from a marble processing factory in Aksaray, Turkey. The samples were characterized by X-ray Fluorescence spectrometer (XRF) Model Pan Analytical - Axios Max WD-XRF and Scanning Electron Microscope (SEM) Model FEI - Quanta FEG 250 at Central Laboratories of Aksaray University. They results were presented in Table 1 and Fig. 1, respectively. XRF results showed that the samples mainly constituted of CaO (54.5%).

Table 1. XRF analysis results of WMP (waste marble powder) and PCC product

Content	CaO	LOI	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MnO	Na_2O	P_2O_5	$CaCO_3$
WMP (%)	54.5	42.85	0.9	0.8	0.2	0.4	<0.7	<0.1	<0.1	<0.1	<0.1	97.35
PCC (%)	54.5	43.25	1.1	0.7	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	97.35

Fig. 1. SEM image of the waste marble powder (WMP)

The calcinations-dissolution-precipitation (CDP) method was utilized for the production of precipitated calcium carbonate (PCC). The experimental flow sheet and evaluated parameters for the production are given in Fig. 2 and Tables 2–4, respectively.

Calcination of calcite results in its decomposition as CO_2 gas and water-soluble CaO that was used in PCC production. The waste marble samples were calcined at five different temperatures between 800–1000°C, while keeping the sample amount and calcination time constant as 11.7 g and 20 min, respectively. The remained material (CaO) after calcination was weighted to determine the optimum calcination temperature, above which no further mass loss (due to release of CO_2 gas) took place. Determination of optimum temperature is considered to be critical since higher temperatures accelerate sintering of CaO, and causes lower water-solubility and carbonation conversion of CaO.

After calcination of waste marble sample at optimum conditions, CaO was subjected to dissolution tests in distilled water to obtain $Ca(OH)_2$ under specified conditions (Table 3). The amount of CaO, water amount, mixing speed and dissolution temperature was kept constant, as 5.0 g, 0.09 dm^3, 100 rpm, 25°C, respectively, as seen in Table 3. The effect of dissolution time was tested in the range of 2.5–10 min. Since the continuing CaO dissolution changes (increases) pH of the solution, pH measurement was considered critical and recorded during dissolution tests. It was noticed that the complete dissolution was achieved in 5 min, when the solution pH increased to 12.5 and remained constant with further dissolution time.

After completion of dissolution, the non-dissolving fraction was removed by sieving with 100 μm sieve and discarded. Then, the remaining $Ca(OH)_2$ solution was reacted with carbon dioxide (CO_2) gas in the autoclave to produce PCC. The experimental conditions are given in Table 4. The precipitation time was varied between 2.5 and 15 min at fixed pressure (0.05 MPa) and volume (2 dm^3) of CO_2 gas. The optimum precipitation time was determined by measuring pH of the solution during precipitation tests, knowing that the reaction between $Ca(OH)_2$ and $CO_{2(g)}$ changes (decrease) the pH. Moreover, starting pH of the $Ca(OH)_2$ solution (pH 12.5) was expected to decrease to the natural pH of $CaCO_3$ solution (pH 8.0) in the completion of the precipitation.

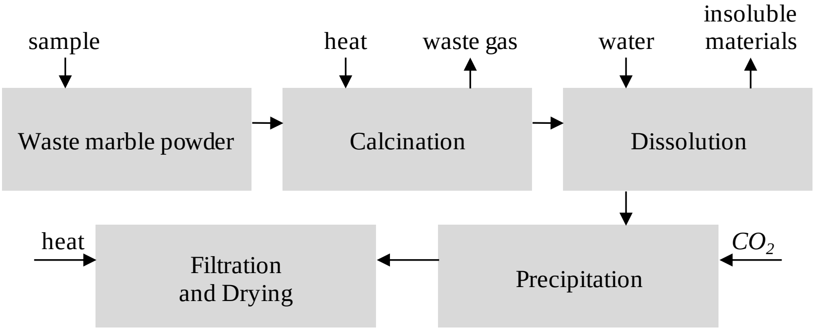

Fig. 2. Schematic representation of PCC production experiments

Table 2. Experimental conditions in calcination of $CaCO_3$

Parameters	C800	C850	C900	C950	C1000
Sample ($CaCO_3$) amount (g)	11.7	11.7	11.7	11.7	11.7
Calcination time (min)	20	20	20	20	20
Calcination temperature (°C)	800	850	900	950	1000

After precipitation, the produced PCC was filtered and dried in an oven. Eventually, the produced PCC was prepared for characterization (i.e. XRF, XRD, SEM, particle size, whiteness, brightness and yellowness analyses).

Table 3. Experimental conditions in dissolution of CaO obtained from calcination of $CaCO_3$ at 950°C (experiment C950)

Parameters	D2.5	D5	D7.5	D10
Dissolution time (min)	2.5	5.0	7.5	10.0
Solid (CaO) amount (g)	5.0	5.0	5.0	5.0
Water (H_2O) amount (dm^3)	0.09	0.09	0.09	0.09
Solid-liquid ratio (%)	5.6	5.6	5.6	5.6
Normality (mol/m^3)	1.0	1.0	1.0	1.0
Mixing speed (rpm)	100	100	100	100
Dissolution temperature (°C)	25	25	25	25

Table 4. Experimental conditions in precipitation of $Ca(OH)_2$ obtained from dissolution of CaO for 5 min (experiment D5)

Parameters	P2.5	P5	P7.5	P10	P12.5	P15
Precipitation time (min)	2.5	5.0	7.5	10.0	12.5	15.0
Gas (CO_2) pressure (MPa)	0.05	0.05	0.05	0.05	0.05	0.05
Amount of CO_2 (dm^3)	2	2	2	2	2	2

A series of tests, namely XRF, whiteness, X-ray Diffractometer (XRD) Model RIGAKU D/Max 2200 PC at Department of Material and Metallurgy of Sakarya University, grain size by model Microtrac S3500 and SEM were performed to characterize the PCC, and the results were presented in Table 5, Table 6, Fig. 3, Fig. 4 and Fig. 5, respectively. Whiteness, brightness and yellowness analysis were conducted using a Datacolor ELREPHO 450x device. The PCC product were compared with standard calcite (TSI, 1995) used in the paper industry and calcites from Hisar Mining (GCC) (URL, 2015a), Cihatsan AŞ (GCC) (URL, 2015b) and Gür Mine (GCC) (URL, 2015c). SEM image of PCC product was also presented (Fig. 5) for comparison with original waste marble powder (Fig. 1).

Table 5. Comparison of the PCC product with TS 11653/1995 (TSI, 1995)

Particle size distribution	TS 11653/1995, Class I (coating calcite) weight %	TS 11653/1995, Class II (filling calcite) weight %	PCC product weight %
-45µm	100.0	100.0	92.5
-45+10µm	max 5.0	max 20.0	12.5
-10+2µm	max 25.0	max 40.0	25.0
-2µm	max 70.0	max 40.0	55.0

Table 6. Comparison of the whiteness, brightness and yellowness features of the PCC product with TS 11653/1995 and commercial firm's calcites

	Whiteness %	Brightness %	Yellowness %
PCC product	91.28	98.2	1.99
TS 11653/1995	≥ 91	≥ 96	< 2
Hisar Mining calcite (GCC)	97-99	96.40	1.54
Cihatsan As calcite (GCC)	97-99	95.25	1.62
Gur Mine calcite (GCC)	99.50	94.50	1.75

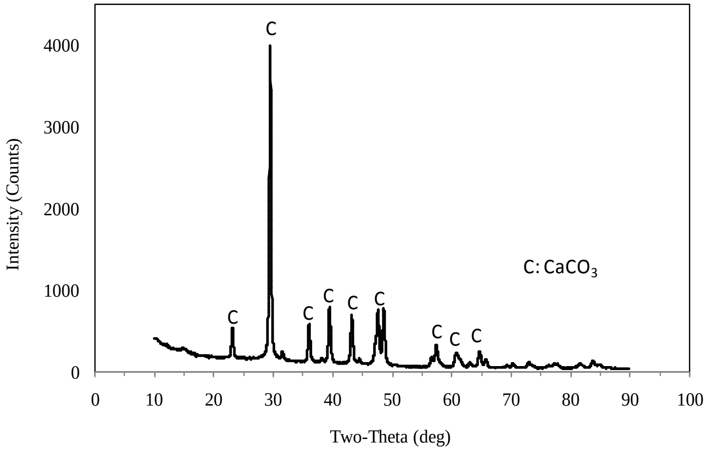

Fig. 3. XRD graph of the PCC product

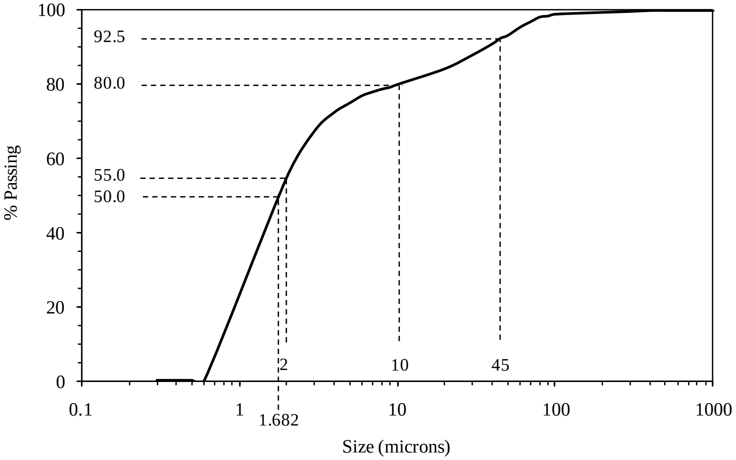

Fig. 4. Particle size analysis results of the PCC product

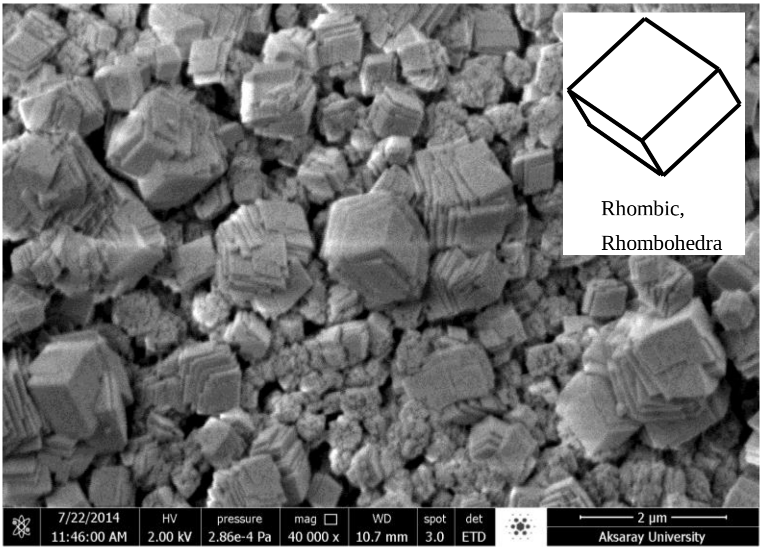

Fig. 5. SEM image of the PCC product

Results and discussion

XRF analysis of original WMP and the produced PCC samples were presented together in Table 1 for comparison. It is seen that the WMP contains mainly $CaCO_3$ (54.5% CaO) and small amounts of SiO_2 (0.9%), Fe_2O_3 (0.4%) and other impurities. It can be seen that the impurities in the sample are insignificant in amount and harmless in nature. XFR analysis of the produced PCC sample exhibited very similar results to that of original WMP, with 54.5% CaO, 0.7% SiO_2 and 0.1% Fe_2O_3.

The calcination experiments were carried out at varying temperatures between 800 and 1000 °C at fixed sample amount (11.7 g) and calcination time (20 min) as explained in Table 2. The mass loss, due to CO_2 gas release, during calcination process was recorded and the results are plotted in Fig. 6. The figure shows that mass loss increased steadily from 24.6% to 50.8% with increasing calcination temperature up to 950°C, above which it remained constant. Based on the calcination results, 950°C was selected as optimum calcination temperature. Hence, the subsequent dissolution and precipitation experiments were carried out only on the samples obtained at optimum calcination conditions (C950 experiment in Table 2).

The dissolution of 5.0 g calcined sample in 0.09 L distilled water at 25°C were investigated for varying dissolution time in the range of 2.5–10 min, while mixing the solution at 100 rpm. The pH of the solution, expected to vary with dissolution of CaO, was recorded during dissolution and the obtained results were plotted in Fig. 7. The figure exhibits clearly that the pH increased with increasing dissolution time up to 5 min, but remained constant at 12.5 with further dissolution time. The results depicted that 5 min should be enough (optimum) for dissolution of the samples. Therefore, the subsequent precipitation experiments were carried out only on the samples obtained at optimum dissolution time (D5 experiment in Table 3).

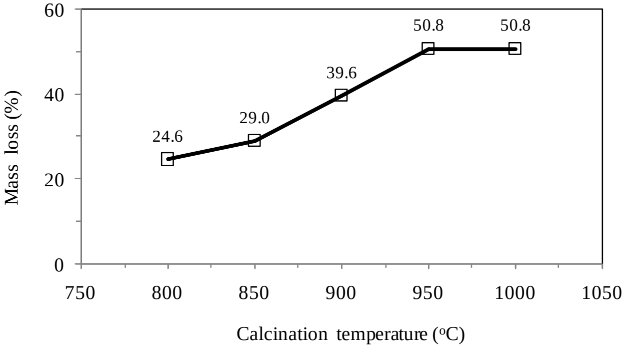

Fig. 6. Calcination of WMP samples at different temperatures

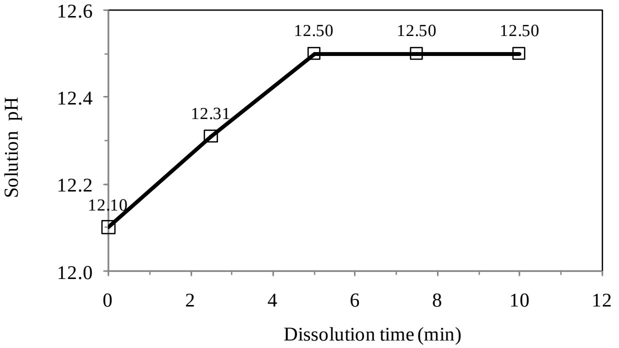

Fig. 7. Effect of dissolution time on dissolution of calcined samples and pH of the solution

The precipitation of the dissolved solids in autoclave were investigated in the presence of 2 L CO_2 gas at 0.05 MPa constant pressure for different precipitation time of 2.5, 5.0, 7.5 and 10 min. The precipitation data are plotted in Fig. 8 which shows that the pH of the solution decreased with precipitation time. When the figure is examined carefully it can be noticed that the pH of the solution decreased markedly (to pH 8.0) in 5 min of precipitation after which, the pH decreased slowly. The slow decrease in pH was explained by the formation of carbonic acid in the autoclave during precipitation and hence 5 min was selected as the optimum precipitation time. The PCC produced at optimum conditions (P5 experiment in Table 4) was considered as the optimum PCC and prepared for characterization.

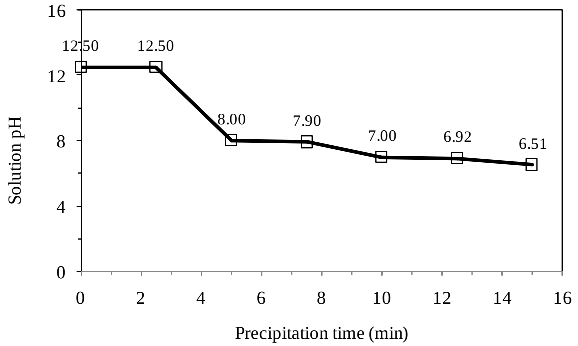

Fig. 8. Effect of precipitation time on formation of PCC and on pH of the solution

Characterization of produced PCC was conducted on dried samples. The XRD results presented in Fig. 3 depicts that the calcium carbonate crystals with a rhombohedral morphology was synthesized successfully. Particle size distribution plotted in Fig. 3 shows that the PCC has a 1.682 µm average grain size. Calcite standards (TSI, 1995) required in various applications and the specifications of produced PCC are presented together in Table 5 for comparison. It is seen that Class I (coating calcite) and Class II (filling calcite) require, respectively, max 70 and 40% particles below 2 µm in size. Since the produced PCC contains 55% particles below 2 µm in size, it can be considered that it can be used as coating calcite, but not as filling calcite.

Whiteness, brightness and yellowness of the PCC samples were determined and the results are presented in Table 6. Calcite standard (TSI, 1995) and the specifications of commercial calcites produced by three local companies are given in the same table for evaluation of the results. It can be seen that the whiteness of PCC is 91.28% and is higher than TS 11653/1995 but lower than the commercial calcites. On the other hand, the brightness of the PCC (98.2%) is higher than the commercial calcites and satisfactorily meets the TS 11653/1995 standard (≥96%). Even though yellowness of the PCC (1.99%) can meet the TS 11653/1995 standard (<2%), it is slightly higher than the commercial calcites. Based on the obtained results, it is concluded that the produced PCC can be satisfactorily used in paper production.

SEM images of WMP and PCC samples are given in Fig. 1 and Fig. 5, respectively. The WMP sample appears to be very heterogeneous in terms of particle size and shape. Unlike to WMP, PCC particles exhibit a narrow size range and rhombohedral crystal shape. It is consequently considered that a paper production quality PCC could be successfully produced from WMP.

Conclusions

The primary aim of the current study was synthesis of finer size and homogenous PCC from impure and heterogeneous WMP by the CDP method. The second phase of this study included the characterization of synthesized PCC. In order to achieve that aim, experimental parameters (calcination temperature, dissolution and precipitation time etc.) and experimental procedure were selected and planned carefully. Optimum calcination temperature, dissolution time and precipitation time were determined as 950°C, 5 min and 5 min, respectively.

XRD and SEM data indicated that calcite crystals with rhombohedral morphology could be synthesized by the proposed method. Further analysis by XRF showed that the PCC is mainly calcite with 54.5% CaO. Particle size analysis revealed that the PCC particles have a narrow size range distribution with an average size of 1.682 μm.

Whiteness, brightness and yellowness analysis showed that the produced PCC meets TS 11653/1995 Class II (filling calcite) standard and can be used in paper industry. Comparison of the products revealed that the produced PCC had certain advantages and disadvantages over commercial calcites produced by the local companies.

References

BGS, 2006, *Limestone,* British Geological Survey. United Kingdom.

BILEN M., 2010, *Recovery of precıpıtated calcıum carbonate from steelmaking slags by leach – carbonatıon process*. Ph.D. Thesis, Cukurova University, Turkey.

BUNGER J.W., COGSWELL D., WISER J.W., 1998, *Process for purifying highly impure calcium hydroxide and for producing high-value precipitated calcium carbonate and other calcium products*. Patent no. 5846500.

CHUKWUDEBELU J.A., IGWE C.C., TAIWO O.E., TOJOLA O.B., 2013, *Recovery of pure slaked lime from carbide sludge: Case study of Lagos state, Nigeria*. Afr. J. Environ. Sci. Technol. 7, 490-495.

DOGAN O., 2007, *The investigation of recovery conditions of precipitated calcium carbonate from afsin/elbistan powder plant fly ashes*. Ph.D. Thesis, Cukurova University, Turkey.

DOGAN O., YILDIRIM M., 2008, *The investigation of recovery conditions of precipitated calcium carbonate from Afsin – Elbistan power plant fly ashes*. Cukurova Univ. J. Sci. Inst. 17, 95-102.

FERNANDO N.A.S., THOMAS N.L., 2008, *Effect of precipitated calcium carbonate on the mechanical properties of poly (vinyl chloride)*. J.Vinyl Addit. Technol. 13, 98-102.

FJELLSTROM H., HOGLUND H., FORBERG S., 2007, *Inhibition of light-induced brightness reversion of high-yield pulps: The UV-screening properties of coating layers containing kaolin or calcium carbonate pigments*. Nord. Pulp Pap. Res. J. 22, 350-355.

HUIJGEN W.J.J., 2007, *Carbon dioxide sequestration by mineral carbonation*. Ph.D. Thesis, Energy Research Centre of the Netherlands, Netherlands.

KARAKAS F., CELIK M.S., 2012, *Effect of quantity and size distribution of calcite filler on the quality of water borne paints*. Prog. Org. Coatings 74, 555-563.

KARAKAS F., VAZIRI HASSAS B., CELIK M.S., 2015, *Effect of precipitated calcium carbonate additions on waterborne paints at different pigment volume concentrations*. Prog. Org. Coatings 83, 64-70.

KEMPERL J., MAČEK J., 2009, *Precipitation of calcium carbonate from hydrated lime of variable reactivity, granulation and optical properties*. Int. J. Miner. Process. 93, 84–88.

KILIC O., 2015, *Cycle of limestone-lime and precipitated calcium carbonates*. 12th Mining and Geotechnology Scientific Conference at "44. jump over the leather". Ljubljana, Slovenia, 1-5.

KILIC O., ANIL M., 2006, E*ffects of limestone characteristic properties and calcination temperature on lime quality*. Asian J. Chem. 18, 655-666.

KODAMA S., NISHIMOTO T., YAMAMOTO N., YOGO K., YAMADA K., 2008, *Development of a new pH-swing* CO_2 *mineralization process with a recyclable reaction solution*. Elsevier Energy 33, 776-784.

KOLTKA S., SABAH E., 2012, *Paint industry and Precipitated Calcium Carbonate (PCC)*. Uluslararası Endustriyel Hammaddeler Sempozyumu. Istanbul, Turkey, 47-56.

LIM M., HAN G.C., AHN J.W., YOU K.S., 2010, *Environmental remediation and conversion of carbon dioxide (CO2) into useful green products by accelerated carbonation technology*. Int. J. Environ. Res. Public Health 7, 203-228.

LOPEZ-PERIAGO A.M., PACCIANI R., GARCIA-GONZALEZ C., VEGA L.F., DOMİNGO C., 2010, *A breakthrough technique for the preparation of high-yield precipitated calcium carbonate*. J. Supercrit. Fluids 52, 298–305.

PISKIN S., OZDEMIR O.D., 2012, *Effect of process conditions on crystal structure of precipitated calcium carbonate (CaCO3) from fly ash:* Na_2CO_3 *preparation conditions*. Int. J. Biol. Ecol. Environ. Sci. 1, 192-195.

SEZER N., 2013, *Production of precipitated calcium carbonate from marble*. Master Thesis, The Graduate School of Natural and Applied Sciences of Middle East Technical University, Turkey.

SPO, 2001. *Mining Specialization Commission Report*. Ankara, Turkey.

STRATTON P., 2012, *An overview of the north american calcium carbonate market*. Quebec, Canada.

TEIR S., 2008, *Fixation of carbon dioxide by producting carbonates from minerals and steelmaking slags*, Ph.D. Thesis, Department of Energy Technology, Helsinki University of Technology, Helsinki, Finland.

TEIR S., ELONEVA S., FOGELHOLM C.J., ZEVENHOVEN R., 2007, *Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production*. Elsevier Energy 32, 528–539.

TEIR S., ELONEVA S., ZEVENHOVEN R., 2005, *Production of precipitated calcium carbonate from calcium silicates and carbon dioxide*. Elsevier Energy Convers. Manag. 46, 2954-2979.

TSI, 1995, *TS 11653/1995: Calcite Standards Used in the Paper Industry*. Ankara, Turkey.

URL, 2015a, *Hisar mine product catalogue*. 14.10.2015

URL, 2015b, *Cihatsan as calcite product catalogue*. 14.10.2015

URL, 2015c, *Gür mine product catalogue*. 14.10.2015