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Cikel apnenec-apno in obarjeni kalcijevi karbonati

Cycle of limestone-lime and precipitated calcium carbonates

PROF.DR. ÖZEN KILIÇ[1]

[1] *University of Çukurova, Faculty of Engineering-Architecture, Department of Mining Engineering, Balcali-Adana, TURKEY*
zenkilic@cu.edu.tr

POVZETEK

Kalcijev karbonat ($CaCO_3$) je eden od najpogostejših mineralov v zemeljski skorji. Osnovni in obarjen kalcijev karbonat (GCC in PCC) sta glavna vira kalcijevega karbonata. GCC se pridobiva z rudarskimi metodami kot apnenec, marmor, dolomit ali kreda v mokri ali suhi obliki odvisno od namena končne uporabe. Obarjeni kalcijev karbonat (PCC) se pridobiva s kemijskimi metodami iz apnenca in ima izvrstne lastnosti z zelo visokim deležem $CaCO_3$ in majhnim deležem nečistoč, možnostjo proizvodnje različnih morfologij in nano velikosti delcev, v primerjavi z osnovnim kalcijevim karbonatom (GCC).

Ključne besede: apnenec, kalcijev karbonat, obarjen kalcijev karbonat

ABSTRACT

Calcium carbonate ($CaCO_3$) is the most abundant mineral in the earth crust. Ground and precipitated calcium carbonates (GCC and PCC) are the two main sources of calcium carbonate. GCC is extracted through mining in the form of limestone, marble, dolomite or chalk, and it is wet or dry ground depending on the final product requirements. Precipitated calcium carbonate (PCC), produced synthetically from limestone, has superior specifications with high $CaCO_3$ ratio and low impurities, availability of production in different morphologies and nano size compared to ground calcium carbonate (GCC).

Key words: Limestone, Calcium carbonate, Slaked lime, PCC

INTRODUCTION

Calcium carbonate ($CaCO_3$) is the most widely used filler and/or extender material in paper, paint, plastic, sealant, adhesive and several other industries, each of which requires specific product characteristics in terms of chemical purity, particle size distribution, shape and surface area, whiteness, and rheological behavior etc.

There are two sources of calcium carbonate, namely ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) in the world. 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. The most commonly used method

of manufacturing PCC is by the carbonation process (eq. 1-3). The carbonation process requires the use of high quality limestone and carbon dioxide gas (CO_2) (Roskill, 2005). According to this process, carbon dioxide is blown into a suspension of calcium hydroxide, and the resulting calcium carbonate is intermittently recovered (Ryu, et al., 2007; Sung-Tsuen and Robert, 2008; Thriveni, et al., 2014). The variable factors include: the reaction temperature, the speed at which carbon dioxide gas is introduced and the agitation rates. These variations affect the PCC's particle size and shape, its surface area and surface chemistry as well as its size distribution.

Burning of limestone	$CaCO_3 + ISI \rightarrow CaO + CO_2\uparrow$	(1)
Slaking of quicklime	$CaO + H_2O \rightarrow Ca(OH)_2$	(2)
Precipitation	$Ca(OH)_2 + CO_2 + \rightarrow CaCO_3\downarrow$ (PCC) $+ H_2O$	(3)

Precipitated calcium carbonate of uniform particle size is produced by contacting a suspension of calcium hydroxide with a carbon dioxide.

In this study, cycle of limestone-lime and PCC (the product from a suspension of calcium hydroxide) was investigated. Çelemli Region limestone was calcined then slaked. Carbon dioxide is blown into a suspension of calcium hydroxide, and the resulting calcium carbonate is recovered. The limestone, lime and synthesized calcium carbonate were analyzed by XRF, XRD, SEM and mastersizer to identify the content, phase and particle size.

MATERIAL AND METHOD

The limestone was taken from large commercial deposit (Çelemli-Adana, Turkey). Limestone was observed macroscopically light-coloured 'dirty white' without any distinguished crystals, microcracks throughout the mass.

Analytical methods and techniques

Analyses were performed on samples by using the following analytical procedures.

- XRF (Siemens SRS 300 X-ray Fluorescence Spectrometer) was used to determine the chemical compositions of the samples.
- X-ray diffraction (XRD) analyses of finely pulverized samples for the identification of the presented crystalline compounds were performed with a Rigaku Minflex 2. The diffraction angle (2θ) interval was 20°–60° with a step of 0.02°.
- The images of the samples were analyzed by scanning electron microscopy (Zeiss Evo 60 EP-SEM)
- Spesific surface area of the samples was determined by Malvern Instruments Mastersizer 2000 Ver. 5.60.
- Lime production: ~30x30x30 mm sized limestone samples were calcined at 135 min, ~950°C (Kılıç, 2005) in the small scale laboratuar furnace (Nabertherm).
- PCC production: The burnt limestone is subsequently mixed with dilute water to produce calcium hydroxide (hydration or slaking). Cooled and purified carbon dioxide gas is then bubbled through the lime in a reactor. The gassing process continues as a batch process until all the calcium hydroxide has been converted to PCC. When this has been completed, the product is screened (or sieved) to further purify the PCC (Potential impurities tend to be coarser than the particle size of the required PCC).

In the experiments: 1 litre of a freshly prepared calcium hydroxide slurry (2,5% solid content) was transferred into a reactor, stirring rate of 400-700 rpm. CO_2 (99,9%) was bubbled into the reactor at a flow rate of 300-700 mL/min. The pH value was measured in a range of 12,4-7. The experiments were also carried out fixed at 50°C temperature and reaction time durations of 15-50 min (ÇÜBAP, 2015).

RESULTS AND DISCUSSION

The limestone, lime and synthesized calcium carbonate were analyzed by XRF, XRD, SEM and mastersizer to identify the content, phase and particle size.

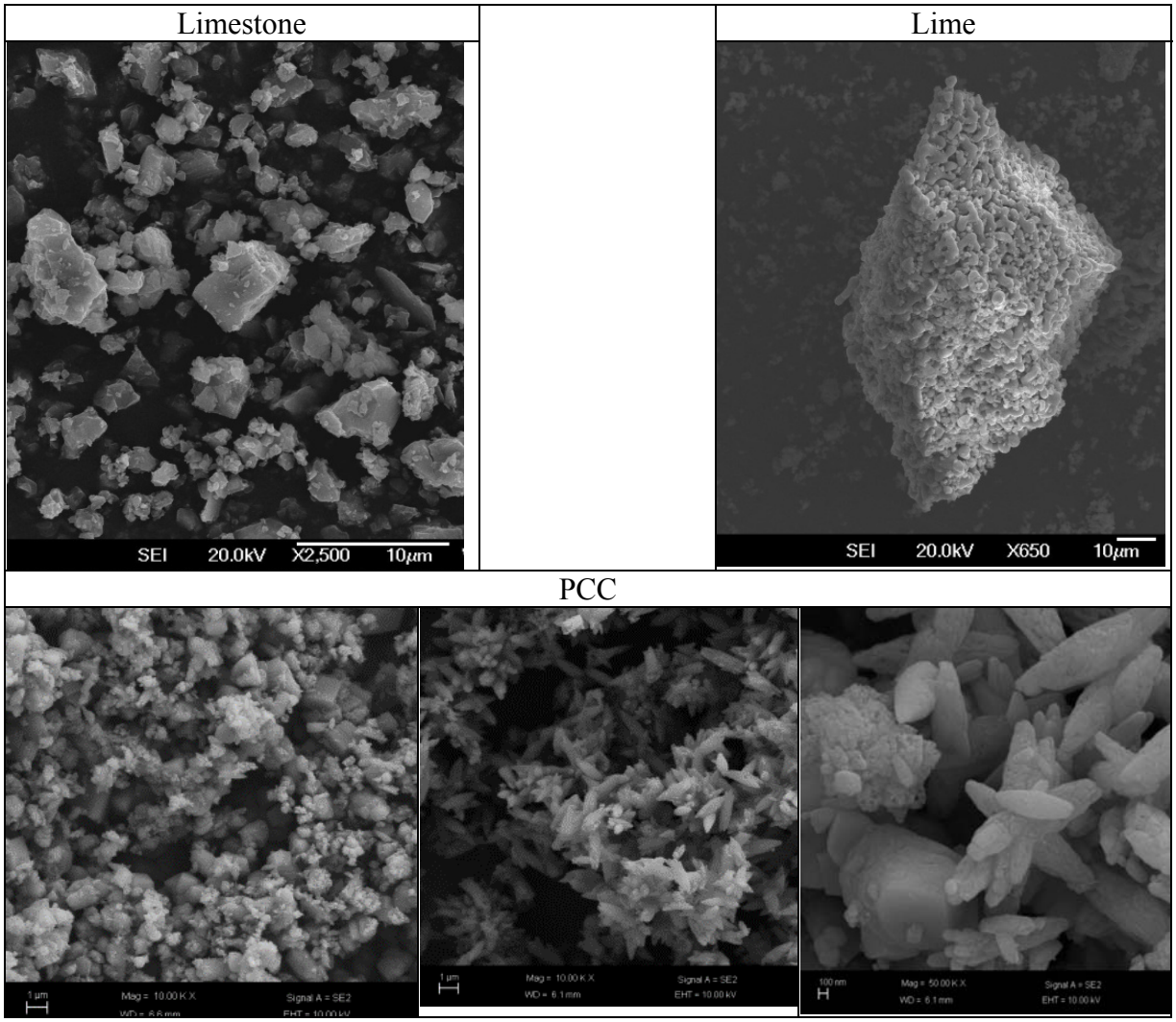

Figure 1.: SEM images of limestone, lime and PCC.

The chemical analyses results of limestone, lime and PCC samples are presented in Table 1. It was found that the limestone is very pure with an average $CaCO_3$ content higher than 97%. The impurities concentrations (MgO, Fe_2O_3, Al_2O_3 and SiO_2) are very low. Lime is

good quality and reactivity, soft burnt type. PCC is very pure with an average $CaCO_3$ content higher than 99%.

Table 1.: Chemical compositions of the samples.

Limestone					Lime				PCC				
SiO_2	Al_2O_3	Fe_2O_3	$CaCO_3$	$MgCO_3$	Total CaO	MgO	LOI	Impurity	Al_2O_3	Fe_2O_3	SO_3	$MgCO_3$	$CaCO_3$
0,51	0,18	0,11	98,24	0,96	93.67	0,51	2,62	1,61	0,11	0,08	0,09	0,42	99,56

The XRD analysis results show that the main component of limestone and PCC is calcite mineral. During the PCC production experiments, metastable crystalline forms of $CaCO_3$ such as aragonite and vaterite were not identified from the XRD pattern. The relative content of carbonate compounds is analogous to attained by XRD and SEM investigation. Both analysis results show that experimental conditions are suitable for obtaining scalenohedral calcite (Figure 1.).

Limestone, lime and PCC of specific surface area are measured 0,7 m^2/g, 2,5 m^2/g and 3,2 m^2/g, respectively. PCC particle size $d_{0,97}$ is more than 5 µm. The particle size of commercially available PCC ranges in general from 0.05.5.0 microns. The particle shapes vary from rhombohedral to acicular (needle like), either in clustered or in single form. Calcitic PCC commonly has a rhombohedral, prismatic or scalenohedral shape, whereas aragonitic PCC is usually acicular or tabular in shape (Roskill, 2005).

CONCLUSION

In this study, cycle of limestone, lime and precipitated calcium carbonate was investigated. Firstly, the properties of Çelemli limestone sample were determined; secondly it was calcined and slaked. Then PCC from a suspension of calcium hydroxide (Çelemli lime) was produced. Precipitated calcium carbonate of uniform particle size and scalenohedral calcite is produced by contacting a suspension of calcium hydroxide with a carbon dioxide.

Cycle of limestone, lime and precipitated calcium carbonate (carbonation process) is shown that calcium carbonate is produced a commercial scale and properties (chemical purity, particle size distribution and shape and surface area).

REFERENCES

1. ÇÜBAP (Çukurova University Scientific Research Projects Coordination Unit), 2015. (Project No: MMF2011BAP12, Investigation of Precipitated Calcium Carbonate Production from Çukurova Region Limestone, Project Manager: Prof. Dr. Özen KILIÇ)
2. Kılıç, Ö., 2005. Comparison of Calcination Parameters of Classic (Eberhart) and Parallel Flow Regenerative Kiln (Maerz) and Applications on Çukurova Region Limestones, PhD Thesis, Department of Mining Engineering, Institute of Natural and Applied Sciences, University of Çukurova, Adana, p. 171.
3. Roskill, 2005. The Economics of Precipitated Calcium Carbonate, PCC Report, 6th Edition, London, 7, 9, 14 p.

4. Ryu, M., You, K., Ahn, J., Kim, H., 2007. Effect of the pH and Basic Additives on the Precipitation of Calcium Carbonate during Carbonation Reaction, Resources Processing, Volume 54, Pages 14-18.
5. Sung-Tsuen, L., Robert M., 2008. Precipitated Calcium Carbonate, United States Patent No 7361324.
6. Thriveni, T., Um, N., Nam, S. Y., Ahn, Y. J., Han, C., Ahn, J., W., 2014. Factors Affecting the Crystal Growth of Scalenohedral Calcite by a Carbonation Process, Journal of the Korean Ceramic Society, 51(2), 107-114.