Characterization of Limestone in Pamekasan Madura Island as Raw Material for Producing Nano Precipitated Calcium Carbonate (NPCC)

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Abstract. Characterization of limestone in Pamekasan Madura island was investigated. So far, limestone at Madura island has low economic value as additional building material. Limestone was taken from three mining locations. The chemical composition of limestone was characterized by X-Ray Fluorescence (XRF), the crystalline phase was characterized by X-ray diffraction (XRD) and morphological investigation was analyzed by Scanning Electron Microscope (SEM). The results XRF tests are obtained limestone with very high purity from Blumbungan, Pamekasan, East Java with Ca content 99,25 wt%. Characterization by using XRD and SEM are showed 100% calcite phase with rhombohedral- cubic shape and a particle size of CaCO₃ ranges between 1.594 – 2.503 µm. In conclusion, limestones from Blumbungan are able to material for producing nano precipitated calcium carbonate (NPCC). Furthermore, economic value of limestone in Madura Island are able to advance.

Keyword: limestone, calcite, very high purity, nano precipitated calcium carbonate

1. Introduction
Madura island has a high mineral mining potential. One of them is a mineral potential of carbonate-based mineral such as limestone, calcite and dolomite. Based on the data Energi and Mineral Resources (ESDM) East Java [1], Madura island has reserve of limestone amount ±152,219,027.133,86 ton. Limestone at Madura island has low economic value ie additional building material.

Limestone based calcite will be high value if processed precipitated CaCO₃. Precipitated CaCO₃ (PCC) has widely application in many industries that is used as filler in rubber, paper making, printing ink, cosmetics, toothpaste, food industries, pharmaceutical industries, nutritional supplements, adhesives, sealant and cement [2- 9, 11].

Many researchers have been trying to get smaller PCC or Nano PCC from natural resources [2, 7-10]. PCC is able to provide the desired characteristics by controlling the parameters. Arifin et al have succeeded in producing precipitated calcium carbonate from lime solution with carbonation method [7-9]. Threveni et al have succeeded in producing NPCC with carbonation process through a closed loop reactor [10]. Ramasamy et al have succeeded in synthesizing precipitated CaCO₃ nanoparticles using different natural carbonate sources [2]. NPCC has unique and extraordinary properties, that is
related to the size of less than 100 nm or 100 x 10^{-9} m. The natural resources used are limestone with high purity [2, 7-10].

The research aims were to characterize limestone in Pamekasan Madura island, to obtained limestone with very high purity. It will be used as raw material for producing nano precipitated CaCO_3 (NPCC).

2. Methods

The sampling of limestone was taken from three mining locations in Pamekasan Madura island (East Java, Indonesia), that are Blumbungan, Larangan; Lesong Daya, Batu Marmar and Lebbek, Pakong. Potential data limestone is obtained from ESDM East Java [1]. The limestone was crushed and mashed with the mortar and sieved with 18 mesh and 35 mesh. The chemical compositions of limestone was characterized by X-Ray Fluorescence (XRF) PANalytical Minipal 4 Sulfur, the crystalline phase was characterized by X-ray diffraction (XRD) X-Pert MPD with Cu-K_α radiation (λ = 1,5406 Å) and scanned from 10° to 60°. Morphological investigation was analyzed by Scanning Electron microscope (SEM) FEI Inspect S50 X’pertPRO PANalytical.

3. Results and Discussion

The chemical composition of limestone from three mining locations in Pamekasan Madura island is shown in Tab.1. The highest calcium content in limestone from Blumbungan, Larangan District is 99.25 wt% and impurities have less content than 1%. Limestone from Lesong Daya contains 95.15 wt%, 4.4 wt% magnesium and <1 wt% other impurities. The lowest calcium content found in limestone from Lebbek is only 87.4 wt%, with impurities of magnesium 0.5 wt%, aluminium 1.2 wt% and iron 2.99 wt%.

Table 1. Chemical composition of limestone in Pamekasan Madura island.

| Element (wt%) | Mining Location | Oxide (wt%) | Mining Location |
|---------------|-----------------|-------------|-----------------|
|               | Blumbungan, Larangan District | Lesong Daya, Batu Marmar District | Lebbek, Pakong District | Blumbungan, Larangan District | Lesong Daya, Batu Marmar District | Lebbek, Pakong District |
| Ca            | 99.25           | 95.15       | 87.4           | CaO 99.06 | 93.11 | 82.23 |
| Mg            | 4.4             | 0.5         | MgO 0.7        | -         | 6.5   | 0.99  |
| Al            | 0.5             | 1.2         | Al_2O_3 0.41   | -         | 0.35  |
| Si            | 5.71            | SiO_2       | -              | -         | 9.6   |
| S             | 0.36            | SO_3        | -              | -         | 0.7   |
| K             | 0.41            | K_2O        | -              | -         | 0.34  |
| Ti            | 0.32            | TiO_2       | -              | -         | 0.34  |
| Mn            | 0.042           | MnO         | -              | -         | 0.34  |
| Fe            | 2.99            | Fe_3O_4     | -              | -         | 2.55  |
| Cu            | 0.055           | CuO         | -              | -         | 0.064 |
| Sr            | 0.37            | SrO         | -              | 0.098     | 0.26  |
| Zr            | 0.02            | ZrO_2       | -              | -         | 0.03  |
| In            | 0.6             | In_2O_3     | -              | -         | 0.5   |
| Ba            | 0.09            | BaO         | -              | -         | 0.05  |
| Br            | 0.007           | Br          | 0.006          | -         | -     |
Figure 1 shows the XRD patterns of limestone from Pamekasan. The three limestones have different phases. Based on search and match, the diffraction peaks of limestone from Blumbungan are matched with rhombohedral-cubic phase of calcite (CaCO$_3$) without impurity with reference to JCPDS: 00-005-0586, limestone from Lesong Daya are matched with rhombohedral phase of ankerite (Ca[Fe,Mg][CO$_3$]$_2$) without impurity with reference to (JCPDS: 00-041-0586) and limestone from Lebbek are identified three phases i.e. calcite (JCPDS: 00-005-0586), ankerite (JCPDS: 00-041-0586) and trapezohedral phase of quartz (SiO$_2$) (JCPDS: 00-046-1045). The XRD pattern of limestone from Blumbungan has a calcite phase, similar to that studied by Arifin et al [7,9].

Semiquantitative analysis using MACTH software of limestone diffraction patterns is shown in Tab. 2. Based on table 2, limestone from Blumbungan has 100% calcite phase, from Lesong Daya has 100% ankerite phase and from Lebbek has three phases ie 73.8 % calcite phase, 17.4 % quartz phase and 8.7 % ankerite phase.

![Graph](image-url)

Figure 1. The XRD patterns of limestone (a) Blumbungan, Larangan; (b) Lesong Daya, Batu Marmar and (c) Lebbek, Pakong.

| No  | Mining Location       | Chemical composition | Amount (%) |
|-----|-----------------------|----------------------|------------|
| 1   | Blumbungan, Larangan  | Calcite, CaCO$_3$    | 100        |
| 2   | Lesong Daya, Batu Marmar | Ankerite, Ca[Fe,Mg][CO$_3$]$_2$ | 100        |
|     |                       | Calcite, CaCO$_3$    | 73.8       |
| 3   | Lebbek, Pakong        | Quartz, SiO$_2$      | 17.4       |
|     |                       | Ankerite, Ca[Fe,Mg][CO$_3$]$_2$ | 8.7         |
Table 3 shows limestone purity classification in Pamekasan Madura Island according to British Geological survey [11,12], which is based on XRF and XRD test results of the samples. The limestone from Blumbungan has a very high purity, while the limestone from Lesong Daya and Lebbek has a medium purity and impure, respectively. Therefore limestone from Blumbungan with very high purity has potential as raw material for producing nano calcium carbonate precipitated (NPCC), as previous researchers have done [2,7,9,10].

Table 3. Limestone purity classification in Pamekasan Madura Island according to British Geological Survey [11,12].

| No | Mining Location | CaCO₃ wt% (XRD) | CaO wt% (XRF) | MgO wt% (XRF) | SiO₂ wt% (XRF) | Fe₂O₃ wt% (XRF) | Purity Classification |
|----|-----------------|-----------------|---------------|---------------|---------------|-----------------|----------------------|
| 1  | Blumbungan, Larangan | 100 | 99.06 | - | - | 0.15 | Very high purity |
| 2  | Lesong Daya, Batu Marmar | - | 93.11 | 6.5 | - | 0.16 | Medium purity |
| 3  | Lebbek, Pakong | 42.86 | 82.23 | 0.99 | 9.96 | 2.55 | Impure |

Crystal morphology of natural calcite from limestone Blumbungan with very high purity is shown in Fig. 2. Fig. 2(a) shows the CaCO₃ particles tend to agglomerate. Particle size of CaCO₃ ranges between 1.594 – 2.503 µm. The calcite phase has the rhombohedral-cubic shape (Fig. 2(b)). Similar results have been reported by Arifin et al [7,9], where the limestone from Tuban-East Java also has a rhombohedral cubic shape but with a size of 6 times larger than what we reported i.e. 15 µm.

![Figure 2. Distribution of CaCO₃ particle limestone Blumbungan](image)

(a) magnification of 5000x and (b) magnification of 20000x.

4. Conclusions
Limestone from Blumbungan Pamekasan has very high purity with Ca content 99.25 wt% and pure calcite phase (100 wt% CaCO₃). Morphology of calcite is the cubic shape with a particle size of CaCO₃ ranges between 1.594 – 2.503 µm. Limestone from Blumbungan can be used as raw material for producing nano precipitated calcium carbonate (NPCC).
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