Identification of Phase CaCO₃/MgO in Bangkalan Dolomite Sand as An Antibacterial Substance

L Rohmawati*, S P Sholicha¹, S Holisa SP¹ and W Setyarsih¹
¹Department of Physics, Universitas Negeri Surabaya, Surabaya, Indonesia

*e-mail: lydiarohmawati@unesa.ac.id

Abstract. Dolomite sand has several ingredients such as CaCO₃ and MgO which have the potential as an antibacterial substance. The making of this antibacterial substance uses the heating/calcination method of dolomite powder with a variation of holding time from 0.5 to 2.5 hours at a temperature of 700°C. The nanoparticles produced from the calcination process were then characterized by XRD to identify the formed phase. This study aimed to determine the effect of holding time on phase formation on dolomite. The results of this study are identified as forming four phases namely calcite (CaCO₃), periclase (MgO), calcium hydroxide (Ca(OH)₂) and lime (CaO) with different percentages in each variation of holding time. The Ca(OH)₂ and CaO phases include the impurity phase with a lower percentage than the CaCO₃ and MgO phase percentages. The most dominant phase is CaCO₃ and the MgO phase formed optimally at 1 hour holding time with a percentage of 47.1% CaCO₃ and 35.9% MgO.

1. Introduction

Dolomite is limestone which is mostly found in Indonesia, especially in the regions of Java, such as Tuban, Lamongan and Bangkalan. Each region has different dolomite content. The dolomite content of Tuban include: 92.40% Ca, 6.5% Mg, 0.45% Fe, 0.055% Mn, 0.54% Yb and 0.073% Cu [1]. Dolomite from the Lamongan area has several elements as 35.7% CaO, 16.7% MgO, 2.19% SiO₂, 0.02% Al₂O₃ and 0.01% Fe₂O₃ [2]. The content of Bangkalan Madura dolomite as 63.42% CaO, 26.39% MgO, 5.93% Na₂O, 1.20% SiO₂, 0.86% Al₂O₃ and 0.74% Fe₂O₃ [3]. Both of CaO and MgO elements are optimal content of dolomite, especially in Tuban and Bangkalan areas. But the MgO element from Bangkalan is greater compared to the MgO from Tuban. MgO has an important role as an antibacterial agent that is good and safe to use in humans [4] [5]. So, in this study, the dolomite used is from Bangkalan Madura. CaCO₃/MgO composite in dolomite can be formed in a simple calcination process.

Calcination of dolomite at 700°C for one hour produced optimum CaCO₃/MgO phases using analysis on match software of XRD characterization and obtained a percentage of 42.4% MgO (periclase), 55% CaCO₃ (calcite) and 2.6% CaO (lime) [6]. In that research, dolomite was calcined at 600°C, 700°C, and 800°C for one hour. Yamamoto reported that heating dolomite at 800°C formed CaCO₃/MgO composites which can be known from the results of XRD characterization. CaCO₃/MgO composites have the good antibacterial potential for the bacteria Staphylococcus aureus and Escherichia coli [7]. Jannah about CaCO₃ composites from shellfish and MgO with a composition of 80 wt% CaCO₃ and 20 wt% MgO have the best inhibitory properties as an antibacterial material in S.
The extraction of dolomite in this study was carried out using a simple calcination method at a temperature of 700°C [6] with a holding time variation of 0.5 to 2.5 hours. The calcination results were characterized by XRD and the results were analysed using match software to identify the optimum CaCO$_3$/MgO phase, which can later be used as a reference for application as an antibacterial material.

2. Materials and Methods

2.1. Materials and tools

The material used in this study is dolomite lime from Jaddih Hill, Bangkalan-Madura. The tools used for dolomite extraction include mortar and pestle, 200 mesh sieve and furnace with type L5 / 11 / B170. The characterization tool used was XRD Bragg-Brentano Philips X’pert Diffractometer with Cu-Kα radiation, range 2θ = 15-90º, data step = 0.02º/minute, detector zero position = 0.023. Match software is used to analyse data resulting from XRD characterization.

2.2. Preparation of CaCO$_3$/MgO

Referring to the research of Sholicha et al. (2019) [6] preparation of dolomite powder containing CaCO$_3$/MgO was carried out by smoothing dolomite powder which had an average particle size of about 7μm using mortar and pestle. Then dolomite sieved using a 200-mesh sieve, then weighed using a digital balance sheet of 5 grams and calcined at a temperature of 700°C at a heating rate of 10°C / minute with a holding time variation of 0.5 hours, 1 hour, 1.5 hours, 2 hours and 2.5 hours. After reaching 700°C, the powder is cooled to room temperature. Furthermore, the XRD characterization is performed to identify the optimum phase from the holding time variations in the calcination of dolomite.

3. Result and Discussions

XRD characterization results show the phases formed with some data obtained, namely diffraction intensity (I), diffraction peak position data (2θ) and distance between fields (d) or miller indices. The data obtained is used to determine the optimum phase formed in the sample. The sample tested was Bangkalan dolomite powder. Analysis of XRD characterization is done using software Match! that is to match the ICSD database data with the XRD characterization data. Dolomite was calcined at 700°C with a variation of holding time 0.5 to 2.5 hours then XRD was tested which showed four phases formed namely phase CaCO$_3$, MgO, Ca(OH)$_2$ and CaO (Figure 1).
Phases formed in dolomite powder have different percentages (Table 1). The phase of CaCO$_3$ (calcite) is formed at the highest diffraction intensity which is at $2\theta = 29.42^\circ$ with the miller index (104), according to [15], which revealed that the phase of CaCO$_3$ was formed at $2\theta = 29^\circ$ with the miller index (104). Other diffraction peaks for the CaCO$_3$ phase are formed at the miller index (012), (006), (110), (113), (202), (024), (018), (116), (211), (122), (010), and others that are in accordance with PDF cards number 96-900-9669. The diffraction peak in the MgO (periclase) phase is formed at $2\theta = 42.96^\circ$ with the miller index (200). Other MgO diffraction peaks are formed at the miller index (111), (202), (311) and (222), according to PDF cards number 96-101-1118. At a holding time of 1.5 hours, the intensity of the CaCO$_3$ phase is lower when compared to other holding times, such as at an angle of $2\theta = 57.44^\circ$ which shows the percentage of CaCO$_3$ phase of 25.8% (Table 1). Besides that, the intensity for the MgO phase is also formed minimum in samples with holding time 0.5 and 2 hours, which is at an angle of 37.38°, 42.94°, 62.29°, 74.66° and 78.60°.

The other two phases other than the phase of CaCO$_3$ and MgO are the phases of CaO and Ca(OH)$_2$ which are impurities. Lime phase (CaO) is formed at an angle of $2\theta = 32.26^\circ$, 37.40°, 54.31°, 64.72° and 67.37° with the miller index (111), (200), (202), (311), (222), (400) and (331) according to PDF cards number 96-101-1096. Phase Ca (OH) 2 is formed at an angle of $2\theta = 18.05^\circ$, 28.70°, 34.11°, 36.97°, 47.46°, 50.83°, 54.31°, 56.61°, 62.35°, 63.80°, 64.72° 71.82°, 77.08°, 79.04°, 81.59°, 84.83° and 86.29° with miller indices (001), (100), (011), (102), (012), (110), (111), (003), (200), (201), (013), (013), (022), (004), (113), (121), (104) and (023) which are suitable for PDF cards numbers 96-100-8782. The two impurities were formed at holding time 0.5 to 2.5 hours with different percentages according to Table 1, but at holding time 1 hour the phase of CaO and Ca(OH)$_2$ was formed with a low intensity at an angle of $2\theta = 32.26^\circ$ and 37.40° for the CaO phase and angles $2\theta = 63.80^\circ$ and 79.04°.

The highest percentage of CaCO$_3$ phase is formed at 0.5 hour holding time, while the highest MgO phase is formed at 1 hour holding time (Table 1). In this case, the highest percentage MgO holding time at 1 hour was chosen compared to the highest CaCO$_3$ composition at 0.5-hour detention because the MgO phase can be used to inhibit antibacterial activity while CaCO$_3$ is only used to remove stains and plaque on teeth [16], [17]. With a low percentage of the phase of CaO and Ca(OH)$_2$ at 1 hour holding time, so the phase of CaCO$_3$ and MgO becomes the dominant phase with a percentage of 47.1% CaCO$_3$ and 35.9% MgO.
The presence of impurities such as CaO and Ca(OH)$_2$ provides its benefits, which have certain functions namely the Ca(OH)$_2$ phase can be used as an antimicrobial and anti-fungal which can kill bacteria because it has a strong alkaline pH (12.3), where bacteria cannot live in an alkaline environment [18], [19], [20]. Calcium oxide (CaO) can be used as an antimicrobial because it has the same superoxide and alkaline pH as Ca(OH)$_2$ which can kill bacteria [21]. The pH value is very influential on antibacterial material in inhibiting the activity of bacteria or microorganisms. The higher the pH value, the antibacterial activity increases as a solvent with alkaline properties mixed into the antibacterial material will increase the pH value and the antibacterial activity [10].

Table 1. Percentage of phase formed in CaCO$_3$/MgO composite using Analysis Match! software

| Holding Time (hour) | Percentage of Phase (%) |
|---------------------|-------------------------|
|                     | CaCO$_3$ | MgO | CaO | Ca(OH)$_2$ |
| 0.5                 | 56.3     | 29.4 | 8.9 | 5.3        |
| 1                   | 47.1     | 35.9 | 0.9 | 16.0       |
| 1.5                 | 25.8     | 35.8 | 17.8| 20.6       |
| 2                   | 49.9     | 29.5 | 17.1| 3.5        |
| 2.5                 | 47.4     | 34.2 | 7.0 | 11.5       |

The phase of CaCO$_3$ and MgO in dolomite which is the dominant and formed phase at 1 hour holding time is used as a candidate for antibacterial material because it has a high percentage compared to other holding times. According to research by [14], the longer holding time cause the fewer phase to form, but in this research with variations in the holding time, forming phase with different percentages and isn’t constant that which the fewer or more formed of phase at dolomite.

4. Conclusion
The optimum phase with the highest percentage of MgO and a low percentage of impurity phases namely is CaO and Ca(OH)$_2$ which are formed at a holding time of 1 hour with a percentage of CaCO$_3$ of 47.1% and MgO of 35.9%. This shows that Indonesia has natural materials such as dolomite which can be used as good antibacterial material, namely at calcination of 700°C with a holding time of 1 hour.

Acknowledgement
Thanks to the Direktorat Riset Pengabdian Masyarakat Direktorat Jendral Penguatan Riset dan Pengembangan Kementerian Riset, Teknologi, dan Pendidikan Tinggi multi-year at UNESA Rector’s decision number 507/UN38/HK/LT/2019. This study has been supported by the Department of Physics Universitas Negeri Surabaya. The study process was being done at the Materials Physics Laboratory of Universitas Negeri Surabaya, Laboratory of Materials and Metallurgy of Institut Teknologi Sepuluh Nopember in Surabaya.

References
[1] Arifin Z, Apriliani NF, Zainuri M and Darminto 2017 Characterization of Precipitated CaCO$_3$ Synthesized from Dolomite IOP Conf. Series: Materials Science and Engineering 196
[2] Febriana E 2011 Kalsinasi Dolomit Lamongan untuk Pembuatan Kalsium-Magnesium Oksida sebagai Bahan Baku Kalsium dan Magnesium Karbonat Presipitat (Depok: Universitas Indonesia)
[3] Solihin S, Arini T and Febriana E 2012 Synthesis of Ultra Fine Grain Magnesium Carbonate Part 1. Calcination Behaviour of Indonesian Dolomite J. Metalurgi 27 (3) 173-178
[4] Stoimenov P K, Rosalyn L K, George L M and Kenneth J K 2002 Metal Oxide Nanoparticles as Bactericidal Agents Langmuir 18 (17) 6679-6686

[5] Sundrarajan M, Suresh J and Gandhi R R 2012 A Comparative Study on Antibacterial Properties of MgO Nanoparticle Prepared Under Different Calcination Temperature Digest J. Nanomaterials and Biostructures 7 (3) 983-989

[6] Sholicha S P, Sabrina G J, Rohmawati L and Setyarsih W 2019 Preparation of CaCO$_3$/MgO From Bangkalan’s Dolomite for Raw Biomaterial IOP Conf. Series: Materials Science and Engineering 1171

[7] Yamamoto O, Ohira T, Alvarez K and Fukuda M 2010 Antibacterial Characteristics of CaCO$_3$-MgO Composites Mater. Sci. Eng. B: Solid-State Materials for Advanced Technology 173 208-212

[8] Jannah Z, Mubarok H, Syamsiyah F, Putri A A H and Rohmawati L 2018 Preparation of Calcium Carbonate (from Shellfish)/Magnesium Oxide Composites as an Antibacterial Agent. IOP Conf. Series: Materials Science and Engineering 367

[9] Royani A, Sulistiyono E and Sufiandi D 2016 Pengaruh Suhu Kalsinasi pada Proses Dekomposisi Dolomit Jurnal Sains Materi Indonesia 18 (1) 41-46

[10] Ohira T and Yamamoto O 2012 Correlation Between Antibacterial Activity and Crystallite Size On Ceramics Chemical Engineering Science 68 (1) 355-361

[11] Asa A, Jorn A, Paster B J, Stokes L N, Olsen I and Dewhirst F E 2005 Defining the Normal Bacterial Flora of the Oral Cavity J. Clinical Microbiology 43 5721-5732

[12] Sharma A and Somani R 2009 Dermatoglypic Interpretation of Dental Caries and its Correlation to Salivary Bacteria Interactions: An in Vivo Study J. Indian Soc. Pedod. Prevent Dent. 27 (1) 17-21

[13] Sabir A 2005 Aktivitas Antibakteri Flavonoid Propolis Trigona sp terhadap Bakteri Streptococcus mutans (in vitro) Dent. J. 38 (3) 135-141

[14] Islam M R, Ogura Y, Asadulghani M, Ooka T, Murase K, Gotoh Y and Hayashi T 2012 A Sensitive and Simple Plaque Formation Method for the Stx2 Phage of Eschericia Coli 0157:H7, which does not Form Plaques in The Standard Plating Procedure Plasmid 67 (3) 227-235

[15] Rahman M A, Halfar J and Shinjo R 2013 X-Ray Diffraction is A Promising Tool to Characterize Coral Skeletons J. Sci: Advances in Material Physics and Chemistry 3 120-125

[16] Yamamoto O, Ohira T, Mohan DJ, Fukuda M, Ozkal B, Sawai J and Nakagawa Z 2008 Antibacterial Characteristics of Carbon Coated CaCO$_3$/MgO Powder Led by The Pyrolysis of Poly (Vinyl Alcohol) - Dolomite Mixture Carbon 46 77-81

[17] Sawai J, Kojima H and Igarashi H 2000 Antibacterial Characteristics of Magnesium Oxide Powder World J. Microbiology and Biootechnology 16 (2) 187-194

[18] Farhad A and Mohammadi Z 2005 Calcium Hidroxide: A Review Int. Dent. J. 55 (5) 293-301

[19] Chai W L, Hamimah H, Cheng A C and Sallam A A 2007 Susceptibility of Enterococcus Faecalis Biofilm to Antibiotics and Calcium Hydroxide J. Oral Sci. 49 161-166

[20] Hapsari C A, Putra L A, Rahma R R N and Irawan R S 2012 Pengaruh Kelembapan, Temperatur, dan pH pada Proses Bioremediasi Menggunakan Bakteri Bacillus sp. Bulking Agent Serabut Buah Bintaro J. Polusi Tanah dan Air Tanah 1 (1) 1-9

[21] Roy A, Gauri S S, Bhattacharya M and Bhattacharya J 2013 Antimicrobial Activity of CaO Nanoparticles J. Biomedical Nanotechnology 9 1570-1578

[22] Efhana D P and Zainuri M 2014 Pengaruh Variasi Waktu Penahanan Proses Kalsinasi Terhadap Prekursor Bahan Katoda Lithium Ferrophosphate (LFP) J. Sains dan Seni Pomits 3 2337-3520