Added Value of Limestone Batumilmil and Its Application in Industry

Gustam Lubis, Syed Fuad Said Hasyim, Kamar S Arifin

1School of material and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia
2Department of Geological Engineering, Institut Teknologi Medan Sumatra Utara

*corresponding email: mrsyfuad@usm.my

Abstract. This study explains the added value of the North Sumatra Langkat limestone and its derivative products. Limestone is classified as high calcium, characterized by its high calcium oxide (CaO) content of 38.39% -55.84%, its physical characteristics show dark gray color, dominant calcite, smooth, hard and fossilized texture. So far, the use is in the form of chunks, especially as a raw material for building which gives a low value to the limestone. The 3 limestone samples SK5, SK7 and SK8 were calcined to obtain quicklime and hydrated lime products with different temperatures of 900°C-1100°C. Limestone SK7 and SK8 CaO content increased 59.7% and 66.08% respectively and were light white compared to SK5 55.8% and colored brownish gray. To produce hydrated lime, it is done by adding / soaking with water (H₂O) to the quicklime to produce a heat rate of hydration (slaked). SK8 limestone shows an optimum temperature increase of 74.6°C for 75 seconds compared to SK7 and SK5 limestone 50.2°C and 48°C respectively at 900°C combustion temperature. The heat transfer occurs on the outer side of the limestone, then spreads to the limestone body. The difference in hydrated heat in the limestone is due to the presence of mineral impurities and non-uniform grain size so that the heat obtained is not perfectly distributed. The impurities such as SiO₂, Fe₂O₃, Al₂O₃ and MgO contribute to the product quicklime and reactivity of these samples. Besides the quicklime and hydrated lime products, the added value of Batumilmil limestone is derived by making ground calcium carbonate (GCC). The GCC product is fine mesh size of 60 mesh - 400 mesh ultrafine, with high calcium quality and bright / bright color. The increase in added value added from limestone products contributes to the selling value and various applications in the industrial sector. Keyword: quicklime, hydrated lime, ground calcium carbonate

1. Introduction
Indonesia is enriched with potential limestone deposits in numerous part of this country, scattered from Sumatra, Java, Sulawesi to Papua island. Thus, it is very easy to obtain, cultivate and use it. In North Sumatra, limestone can be discovered in the Alas, Batumilmil and Kuala formations which are Pre-Tertiary (Cameron, at all 1982, Lubis 2011). The limestone is spread along the Bukit Barisan mountain range. According to Lubis (2010) the Pre-Tertiary limestone, in the field, is predominantly composed of calcite minerals with high calcium oxide (CaO) content (48-53%), dark gray, hard, massive and fractured, with different thicknesses. Consequently, limestone can be easily obtained and mined (quarried).
Nowadays limestone is used in the form of boulders, playing around in building foundation material. This is certainly inappropriate limestone utility since it has high quality to produce more valuable product with a higher selling price. The development of the construction and non-construction industries contributes a significant value to the use of limestone. In its application for the limestone industry, it functions as raw material, binder, absorbent material, filler, neutralizer and coating material (Warner, 1998). As a raw material, limestone is used in the cement industry, concrete aggregates, agriculture and carbide. Furthermore, limestone is used as a paper coating, filler in the paint, rubber, toothpaste and cardboard industries. In sewage treatment, water treatment, SOx and NOx gas neutralizers and metal deposition, limestone acts as neutralizing agents. As a binding agent, limestone is applied in soil stabilization, making sand bricks, silica bricks and gypsum. In order to be applied in the industry, the limestone from the quarry, in the form of lumps, is crushed and milled to generate carbonate flour (powder). Limestone in various shapes and sizes with high calcium is ignited at a specific temperature to bring about quicklime, hydrated lime, ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC).

Several attempts have been made to increase the added value of limestone with innovation and technology, such as excavation or mining, breakdown of limestone chunk and burning process with modified furnace system. To generate lime, limestone is normally calcined at a temperature of 850°C - 1000°C to produce hydrated lime, water addition to the lime is required. When the quicklime reacts with water, a hydration heat release process occurs, which is generally equivalent to 1140 KJKG / CaO, (Otcis, 1998). The high concentration of calcium oxide (CaO) obtained during the limestone calcination process becomes a benchmark. To burn limestone, the energy use originate from fuel oil which is relatively high-priced. To save costs, alternative energy uses such as coal, plantation and agricultural waste. Plantation and agricultural wastes such as palm kernel shells and bunches, rice husks and others currently play as a supplier of energy sources for limestone calcination. In the field of application, so far, limestone is used in the form of blocks for building materials with the innovation of increasing the product of grinding limestone to produce natural calcium carbonate flour. Limestone which is high in calcium oxide (CaO> 48%) is ground to produce soil calcium carbonate (GCC). White degree (whiteness) and level of refinement (fine-ultrafine) GCC provide added value that is different from limestone production, especially in its use. Furthermore, GCC is converted into calcium carbonate (PCC) powder which is widely used as a filler and coating for paper which previously used kaolin. The development of limestone processing is in line with the recording of the quality of industrial products, especially having the standards and specifications of limestone or its derivative products.

2. Methodology
In this study, the samples used were the limestone of the Batumilmil Langkat Sumatra Utara formation. A total of 3 limestone samples are coded SK5, SK7 and SK8. They were obtained from different locations. The analysis carried out in this study includes chemical analysis, using X-ray florescence (XRF), thermal analysis (TGA), and X-ray diffraction (XRD) analysis in the USM School Mineral Resources Malaysia laboratory.

Each sample was analyzed chemically to obtain major elements such as CaO, SiO₂, Al₂O₃, MgO, Fe₂O₃, K₂O, Na₂O, Cl⁻, SO₃ and loss on ignition (LOI). Based on the chemical analysis the quality of these limestones can be discovered. Furthermore, to determine the mineral content in limestone, XRD analysis was performed. To measure changes in limestone sample weight as a function of temperature and time, a thermal gravimetry analysis (TGA) is used. The results usually show a continuous diagram. Limestone samples were calcined at chamber temperature of 900°C to 1100 °C with an average combustion soaking time of 5°C/minute. Limestone will lose 38% -44% of its weight during the calcination process as water and CO₂ gas contained in the limestone are lost and evaporate to
release them. Physical analysis, chemical composition and reactivity were then carried out to determine product performance of quicklime. Ground calcium carbonate (GCC) is gained by crushing the limestone Batumilmil, which then milled and sieved to obtain ground calcium carbonate (GCC) with fine-fine grain size.

3. Result and Discussion

3.1. Thermal Gravimetry Analysis (TGA)
Thermal gravimetry (TGA) analysis was performed to determine the change in heat enthalpy from the weight of limestone sample by heat treatment on the function of temperature and time. Based upon the image, curve 1 shows that the limestone samples SK5, SK7 and SK8 with a weight of 100 grams each with an initial combustion temperature of 50°C and multiples for the next temperature. The SK5 sample reduced its weight to 42.5 mg starting at 740°C - 870°C (∆130°C), then the SK7 sample weight decreased 43.6 mg at the combustion temperature 730°C - 890°C (∆160°C) (Figure 1). For SK8 samples the weight percentage was reduced. 25.05% during the combustion at the temperature of 640°C - 820°C (∆180°C). The sample weight reduction during combustion process is due to the exothermic and endothermic heat processes in the limestone, leading the water bond content in the limestone to evaporate with CO₂ together to be decomposed. Furthermore, the sample weight does not change (stable) for the next temperature. The different initial temperature of combustion between SK5 and SK8 can be understood by the presence of mineral impurities in SK5 samples such as quarts and albite so that the initial weight percentage (%) of combustion occurs at 740°C. The chemical analysis, then, results reveal the elemental content of high SiO₂ (14.06%) at SK5 compared to other samples.

![Figure 1. Curve of thermal gravimetry analysis limestone SK5, SK7 and SK8](image-url)
3.2. X-ray fluorescence (XRF)

The content in limestone can be discovered chemically, especially the elements CaO, MgO, Fe₂O₃, SiO₂ and others. The chemical analysis results ensure the quality of the limestone. Based on the results of the chemical analysis of the 3 samples analyzed, it indicates that the chemical composition of limestone Batumilmil CaO (38.39%-55.84%), MgO (0.4%-0.68%), SiO₂ (2.78%-14.068%) and Fe₂O₃ (0.1%-1.38%) (table 1). The high calcium oxide content is SK 7 with CaO 57.76% and SK 5 has a low CaO content among other samples, namely 38.39%. The dominant calcite mineral content in each limestone can be seen in the XRD results, while quartz and clay minerals exist in small amounts. Furthermore, in the sample SK5 the dominant element is SiO₂ (14.068%) compared to SK7 and SK8. According to Kantiranis et all (1999), The complete thermal decomposition of 100% pure calcite theoretically loses 44% of its evolutionary CO₂, known as loss in ignition (LOI). Limestone has a loss on ignition (LOI) of 39.12% - 42.4% which is classified as small and will disappear along with carbon dioxide (CO₂), water and other volatile elements, generating purer limestone.

| Table 1. Chemical analysis result limestone Batumilmil in the Area |
|---|
| Code | Oxide |
| Sample | CaO | MgO | SiO₂ | Al₂O₃ | Fe₂O₃ | Na₂O | K₂O | P₂O₅ | SO₃ | Total |
| SK5 | 38.4 | 0.68 | 14.1 | 4.47 | 1.38 | 0.14 | 0.8 | 0.1 | 0.07 | 99.8 |
| SK7 | 55.8 | 0.4 | 2.78 | 0.23 | 0.1 | tt | 0.03 | 0.01 | 0.05 | 100 |
| SK8 | 52 | 0.4 | 3 | 0.92 | 0.4 | 0.02 | 0.16 | 0.01 | 0.09 | 99.9 |

3.3. X-ray Diffractometri (XRD)

Normally, X-ray analysis is used to determine the crystal structure, type of minerals and grain size of the minerals contained therein. X-ray analysis using X-ray diffraction method was implemented on 3 limestone samples, namely SK5, SK7 and SK8. Based upon the results of the X-rd analysis, it reveals that limestone is composed of calcite and quartz, stishovite and portlandite minerals. Judging from the characteristics of the limestone graphic picking pattern, Batumilmil has a relatively similar picking pattern, beginning with picking at the initial reading of 10.001 0°2 Th and ending at 89.9806 0°2 Th (Figure 2). Mineral calcite is characterized by high picking and shows the similar patterns and picking form as SK5, SK7 and SK8.
3.4. Reactivity Test
Analysis of the reactivity test was carried out for 3 samples, each sample is labelled SK 5, SK 7 and SK 8. Quicklime reactivity analysis was carried out to decide the reaction rate of calcium carbonate (CaO) to water (H₂O) or the rate of heat release from hydration of calcium carbonate (CaO). Hydration heat (slaked) is the amount of heat released when lime (CaO) reacts with water (1,140 KJ/kg/CaO). The combustion temperature varies, 900°C, 1000°C dan 1100°C for the selected samples (SK5, SK7 and SK8) with a variation of the initial time from 10 seconds to 900 seconds (30 minutes). Based on the results of the reactivity test, it shows that the SK8 sample is the most reactive compared to SK7 and SK5 at the same temperature. Limestone/quicklime SK8 is able to release heat when calcium carbonate (CaO) reacts with water (H₂O) 74.6°C with time required of 75 seconds, in which the sample is heated to a combustion temperature of 900°C while SK7 49.1°C and SK5 47°C respectively. (Figures 3a, 3b and 3c). The presence of impurity minerals (purity) affects the combustion temperature and the heat generated. This can be seen in the SK5 sample, which has a lower CaO content compared to SK8 in which it high in calcium. The quicklime products produced have a lower impurity than the SK5 quicklime products.

Figure 2. Picking of XRD analysis limestone SK5, SK7 and SK8

Figure 3. (a) Reactivity test of limestone Batumilmil on SK5
3.5. Limestones Product.

3.5.1. Quicklime

To bring about quicklime, limestone Batumilmil, is calcined in a furnace with different temperature. To do such thing, it must firstly be crushed using jaw crusher to obtain a number of sizes. Megascopically, the sample labelled SK7 and SK8 (dark gray, smooth, hard, compact) are dominantly composed of fossilized calcite mineral, and limestones SK5 (dark, fine-medium, hard, compact, fossilized) consists of calcite mineral. Each limestone sample is calcined at temperature of 900 °C dan 1100 °C.

$$\text{CaCO}_3 (\text{Limestone}) + \text{Heat} \rightarrow \text{CaO} (\text{Quicklime}) + \text{CO}_2$$

The calcination process starts at the edge of the limestone. Then the process continues entering the limestone body. The calcined products obtained reveal that SK 7 and SK 8 samples are bright white and have a dense structure. Meanwhile, the result of SK 5 sample calcined is brownish gray, slightly black color. The difference in the color of the calcined limestone product is caused by the different content of calcium oxide (CaO) from each sample. Sample SK 5 has a lower CaO, 38.39% compared to SK 7 and SK 8, respectively 59.7% and 52.8%. Furthermore, the elements of impurities in the SK 5 sample were higher than those of SK 7 and SK 8, specifically elements of SiO$_2$, Fe$_2$O$_3$ and, Al$_2$O$_3$ (table 2a and 2b). The existence of these impurity minerals affects the quality of the calcined product. Uniform grain size has an impact with an even distribution of combustion temperature to produce a good quicklime.
Generating a better quicklime begins at a combustion temperature of 900°C compared to a combustion temperature of 1100°C. Its purity can be witnessed by the loss of CO\(_2\) content during the calcination process while the water content lost is known as loss on ignition (LOI). This is indicated by the increase of the optimum calcium oxide (CaO) content in each sample, especially SK8 (66.08%) and SK5 (55.8%). Furthermore, impurities such as Fe\(_2\)O\(_3\), Al\(_2\)O\(_3\) dan SiO\(_2\) decreased after calcination during the process. The high content of calcium oxide (CaO) in limestone affects the product color and quality of quicklime. SK8 and SK7 show a bright white in color and the most optimum content of calcium oxide (CaO).

| Table 2. (a) Chemical Analysis of quicklime at temperature 900°C |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Code   | CaO    | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | MnO   | MgO | K\(_2\)O | SO\(_3\) | P\(_2\)O\(_5\) | Na\(_2\)O | LOI |
|SK - 5  | 55.81  | 7.62    | 2.28            | 1.75            | 0.91  | 0.67 | 0.38  | 0.15  | 0.098      | 0.03     | 30  |
|SK - 7  | 59.73  | 2.94    | 0.19            | 0.07            | 0.01  | 0.46 | 0.01  | 0.08  | 0.01       | tt       | 40  |
|SK - 8  | 66.08  | 1.67    | 0.49            | 0.32            | 0.15  | 0.55 | 0.05  | 0.13  | 0.02       | tt       | 30  |

| Table 2. (b) Chemical Analysis of quicklime at temperature 1100°C |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Code   | CaO    | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | MnO   | MgO | K\(_2\)O | SO\(_3\) | P\(_2\)O\(_5\) | Na\(_2\)O | LOI |
|SK - 5  | 48.66  | 12.67   | 3.84            | 2               | 0.78  | 0.71 | 0.64  | 0.13  | 0.14       | 0.07     | 30  |
|SK - 7  | 56.09  | 3.09    | 0.17            | 0.11            | 0.02  | tt   | 0.01  | 0.02  | 0.02       | tt       | 40  |
|SK - 8  | 65.81  | 1.88    | 0.53            | 0.36            | 0.12  | 0.58 | 0.04  | 0.14  | 0.03       | tt       | 30  |

3.5.2. Hydrated Lime

Beside quicklime, other product of limestone is hydrated lime (Figure 4). Hydrated lime is brought about by reacting calcined CaO with amount of water to submerge quicklime in order to gain Calcium Hydroxide (Ca(OH)\(_2\)). The chemical reaction is:

\[
\text{CaO (Quiclime) + H}_2\text{O (Air)} \rightarrow \text{Ca (OH)\(_2\) (Hydrated lime)}
\]

![Figure 4. Illustrate quicklime and hydrated lime process](image)

In this study, hydrated lime is put in a heating bath filled with water was placed on the insulating, then observing the increase of average temperature for a certain time in each sample, namely SK 5, SK7 and SK 8. The product of Hydrated lime is closely related to the raw material of limestone. Based upon the chemical analysis results of the quicklime, each sample of SK8 contained high calcium oxide (CaO), 66.08% and SK5 55.8%. The presence of impurity minerals, silica, affects the formation of hydrated lime, especially during the combustion process and reactivity, specifically from the SK 5 sample.
3.5.3. *Ground Calcium Carbonate (GCC)*

To produce high quality ground calcium carbonate (GCC), Batumilmil limestone must be selected. Furthermore, the limestone obtained from the field was then analyzed to figure out the quality of the limestone, observing the content of major elements of CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO, Na₂O dan K₂O. Based upon the results of chemical analysis using the XRF method, it contains calcium oxide (CaO) in SK7 55.84%, SK8 52.02% and SK5 38.39% respectively (XRF table 1), which are categorized into high quality. The average impurities present were 6.61% silica oxide (SiO₂), 1.87% alumina oxide (Al₂O₃), 0.63% ferric oxide (Fe₂O₃) and 0.5% magnesium oxide (MgO). Furthermore, Batumilmil limestone boulders with a size of 15-20 cm, is crushed by means of a Jaw crushing machine to obtain a size of 3-5 cm. Furthermore, to obtain 0.5-1 cm in size, a smaller raw material, the limestone is crushed by cone crushing (Figure 5). Ground calcium carbonate (GCC) is calcium carbonate flour with a grain size of 60 mesh - 400 mesh. Furthermore, limestone with a grain size of 0.5 - 1 cm is finely ground with a ball mill machine to generate carbonate flour (powder). To meet the standard size of 60 mesh, 200 mesh, 325 mesh and 400 mesh, the calcium carbonate flour is filtered with a sieve with such mesh size.

The ground calcium carbonate (GCC) product is determined by the degree of fineness and purity of the calcium oxide (CaO) content. GCC with a very fine and white mesh has an impact on the higher GCC quality. As the surface area increases and impurities lower during the milling process. In line with the increasing degree of fineness of GCC products, the brighter colors of GCC, the higher economic value it will be.

![Diagram of ground calcium carbonate process](image)

**Figure 5.** Illustrate ground calcium carbonate process
4. Conclusion
Limestone Batumilmil contains calcium oxide (CaO) 38.39% - 55.84%, classified as high quality calcium with a fine-medium, hard and fossilized-textured. So far, the use of limestone in the form of raw material provides low economic value. Efforts were made to add value to the Batumilmil limestone by calcining the limestone to produce quicklime, hydrated lime and ground calcium carbonate (GCC). Calcinations with different temperatures from 900 °C-1100°C were carried out on SK5, SK7 and SK8 limestones. SK8 limestone showed more optimum calcination at 900 °C with 66.9% calcium oxide (CaO) content compared to SK5 55.8% and SK7 59.7% respectively. Furthermore, calcination at a temperature of 1100°C produces a lower content of calcium oxide (CaO) in each limestone. The purity and uniformity of grain size leads SK8 limestone to release 74.5 OC of hydration heat for 75 seconds in comparison with SK5 and SK7 at the same temperature and time. The bright color is obtained due to the SK7 and SK8 limestones are purer compared to SK5 which have relatively high impurity elements. By crushing, then the limestone is ground to generate ground calcium carbonate (GCC). The GCC consists high calcium with light gray color with the size of fine and ultrafine. Purity and grain size become standard and GCC specifications in their application in the industrial sector. The processing of limestone into quicklime, hydrated lime and ground calcium carcobanete (GCC) products is an effort to provide added value and the selling value of the limestone itself.

References
[1] Antonia Moropoulou, Asterios Bakolas, Eleni Aaggelakopoulou., 2001., The Effects of Limestone Characteristic and Calcination Temperatur to the Reactivity of the Quicklime., Cement and Concrete Research
[2] Boynton RS., 1980., Chemistry and Technology of Limestone., 2nd edn (Wiley and Sons, N York)
[3] Cameron, N.R, Aspend, J.A, Bridge, D.McC., Djunuddin, A., Ghazali, S.A., Harahap, H., Hariwidjaja, Johari, S., Kartawa, W., Keats, W., Ngabito, H., Rock, N.M.S. and Whandoyo R., 1982, The Geology of The Medan Quadrangle, Sumatra, Geological Research and Development Centre, Bandung
[4] Hawlett, P.C., Lea’s, 2004., Chemistry of Cement and Concrete, Fourth Edition, Elsivier Science & Technology Books, January
[5] IAR and Dogu G., 2001., Calcination Kinetics of High Purity Limestone., Chem. Eng. J
[6] Ilhs.Com., 2014., Calcium Carbonate, Fine Ground and Precipitated
[7] Kantiranis N, Tsrambides A, Filppidis A, Christians B., 1999., Technological Characteristic of the Calcined Limestone from Agios Panteleimonas Macedonia, Greece., Material and Structures vol 32
[8] Lubis, Gustam, 2012., Geological Map to Raw Material Cement in Langkat Regency, Research Center ITM
[9] Lubis, Gustam, 2013., Drilling Exploration Supervisi to Raw Material Cement in Langkat regency, Research Center ITM
[10] Lubis, Gustam., Syed Fuad S Hashim , Kamar Shah Ariffin., 2017., Geological Investigation On Batumilmil Formation Deposit In Langkat, North Sumatra and Potensial Economic Impact., National Geoscience Conference and Exhibition, Thirty., Kuala Lumpur
[11] Lech R., 2006a., Thermal Decomposition of limestone: Part I- Influence of Properties on Calcination Time., Silic Ind 71
[12] Moropoulou A, Bakolas A, Aaggelakopoulou E., 2001., The Effects of Limestone Characteristics and Calcination Temperature to the Reactivity of the Quicklime, Cement and Concrete Research 31
[13] Oates, JA., 1998., Lime and Limestone Chemistry and Technology, Production and Uses.,
Weinheim: Wiley VCH

[14] Potgieter JH, Potgieter SS, Moja SJ and Mulaba-Bafubiandi A, 2003., An Emperical Study of Factors Influencing lime Slacking, Part II Lime Constituents and Water Composition, Water SA

[15] Potgieter JH, Potgieter SS, Moja SJ and Mulaba-Bafubiandi A, 2002., The Standart Reactivity Test as a Measure of Lime’s Quality, The Journal of the South African Institute of Mining and Metallurgy

[16] Shin K, Kim H, Kim Y, Lee H., 2009, Effect of Reactivity of Quicklime on the Properties of Hydrated Lime Sorbent for SO2 Removal, Journal of Materials Science & Technology

[17] Soltan AM., 2009a., Petrographic Modelling of Egyptian Limestone for Quicklime Production, Arab J Geosci Vol 4

[18] Soltan AM and Hazem M ., 2009b., Quicklime Reactivity as a Function of Limestone Microstructure and Firing Conditions., 87 th Annual Meet of Germani Mineralogy Society (DMG), 238

[19] Soltan AM and Serry MA-K., 2013., Impact of Limestone Microstructure on Calcination Activation Energy., Advances in Applied Ceramics