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Article

Geochemical Analysis to Determine the Quality of Limestone in the Mario Riaja Area, Soppeng Regency, South Sulawesi Province

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Abstract: Indonesia is a country rich in natural resources, one of which is limestone. The village of Mario Riaja in Soppeng Regency is one of the areas with potential limestone resources; however, to date, there have been few studies analysing its quality against relevant utilisation standards. This study aims to determine the chemical composition of limestone using the X-Ray Fluorescence method, as well as to evaluate its suitability against quality standards for several industrial applications. The results of the chemical analysis show that sample ST 1 contains 53.32% calcium oxide (CaO), 1.04% silica (SiO_2), 0.36% aluminium oxide (Al_2O_3), 0.70% magnesium oxide (MgO), and other oxides below 1 %. Sample ST 2 contains 53.60% CaO, 0.85% SiO_2, 0.40% Al_2O_3, 0.59% MgO, and other oxides below 1%. Meanwhile, ST 3 contains CaO 53.59%, SiO_2 1.14%, Al_2O_3 0.47%, MgO 0.52%, and other oxides in relatively low concentrations. Based on classification against the Cement Data Book standard as cement raw materials, all samples meet the criteria. Based on the Domestic Literature Standard by TT-PERHAPI XXVIII as a flux material for iron ore processing, all samples were also found to meet the criteria. However, based on SNI 02-2804-2005 as a raw material for dolomite fertiliser, none of the three samples met the minimum MgO content requirement (18%). This study shows that limestone from the Mario Riaja area is suitable for use as a raw material in the cement and metallurgical flux industries, but is not yet suitable for use as a raw material for dolomite fertiliser.

Keywords: Limestone, Raw Materials, the Cement Industry, the Metallurgical Industry, the Fertiliser Industry.

1. Introduction

Indonesia is a country blessed with abundant natural resources. One such abundant natural resource is limestone [1]. Limestone is easily found and used in industry as a raw material. The quality of limestone as a raw material is influenced by the presence of various chemical compounds. These chemical compounds have a significant impact on the quality of limestone as a raw material [2].

Limestone is one of the industrial minerals with high economic value and is widely utilized across various sectors, including the cement industry, construction materials, agriculture, and the chemical industry. Limestone is formed organically, mechanically, or chemically. Limestone that occurs naturally through organic processes consists of the sedimentation of shells, snails, and algae derived from coral skeletons [3].

The Mario Riaja area in Soppeng Regency, South Sulawesi Province, is known to have a distribution of carbonate rocks that are believed to contain limestone in fairly abundant quantities. However, to date, scientific information regarding the quality of limestone in this region remains limited. In fact, the quality of limestone is a key determinant of its suitability and intended use. This quality can

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be determined based on geochemical characteristics, such as the content of calcium carbonate, magnesium, silica, and others [4, 5]

Geochemical analysis serves as an effective approach for quantitatively evaluating rock characteristics. Through this analysis, it can be determined whether the limestone in the Mario Riaja region meets the quality standards required by specific industries, such as the cement industry or the production of lime raw materials. This information is crucial not only for the development of local economic potential but also for the responsible and sustainable management of natural resources. The results of this study are expected to serve as a scientific reference and a basis for consideration by relevant parties in the management and utilization of limestone resources in the region, particularly in the cement and dolomite fertilizer industries.

2. Research and Methodology

The research methodology began with a literature review of previous studies, followed by the collection of primary data obtained directly in the field regarding the research subject, such as data describing outcrops and sampling coordinates [6]. The type of sample collected was three rock chip samples, each weighing approximately 2 kilograms (Figure 1).

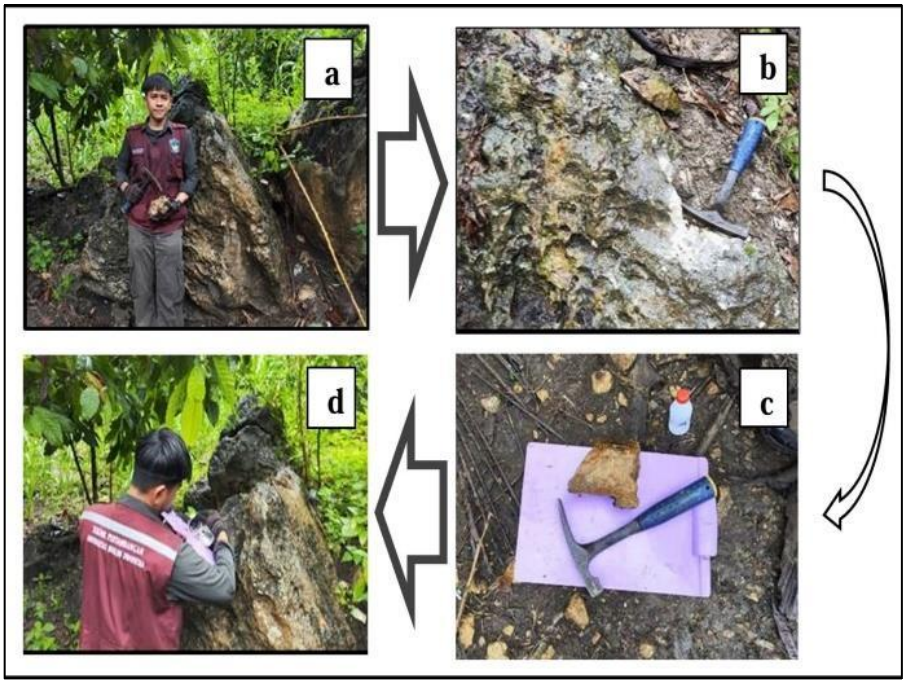

Figure 1. Sample Collection

Field sampling was conducted using hand-collected specimens [7]. In addition to sampling at several points, the geological conditions around the study area were also observed, and rock samples were described to obtain information regarding rock position, distribution direction, outcrop coordinates, and macroscopic mineral content [8]. Limestone sampling using this technique was conducted selectively and representatively from several locations in the Mario Riaja area, Soppeng Regency. The samples obtained in the field were then prepared for shipment to the laboratory to conduct chemical composition analysis using X-ray fluorescence (XRF) analysis [9,10,11]. The stages of this research are summarized in the following figure (Figure 2).

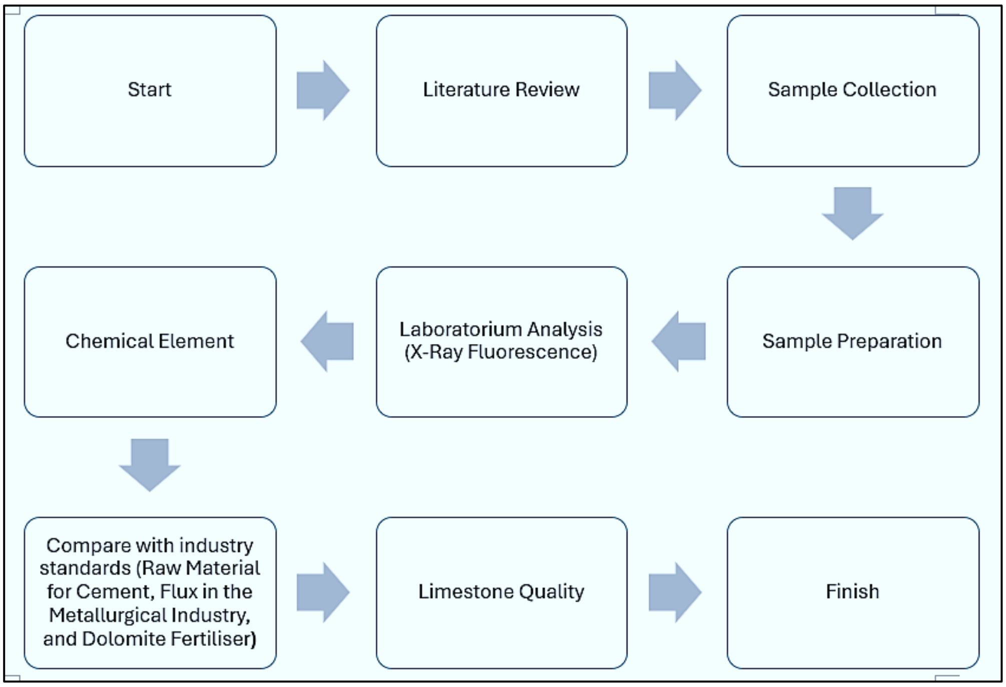

Figure 2. research flowchart

Subsequently, sample preparation and analysis were conducted at PT. Sucofindo Makassar using X-ray fluorescence (XRF) techniques. This analysis aimed to determine the calcium oxide (CaO) content and other compounds in the limestone samples to obtain quantitative data. The analysis results will be compared with several applications of limestone.

2.1. As Cement Raw Material

The chemical specifications for cement used in this study refer to the Cement Data Book, which summarizes international cement industry practices and standards [12]. If the Ca content is high and the Mg content is low, the quality is good; conversely, if the Ca content is low and the Mg content is high, the quality is poor. High Mg content will interfere with the hardening process. The quality requirements are shown in Table 1.

Table 1. Requirements for cement raw materials.

No	Chemical Compound	Cement Raw Material Standards (%)
1	SiO_2	0.76 - 4.75
2	Al_2O_3	0.71 - 2.00
3	Fe_2O_3	0.36 - 1.47
4	CaO	48% - 55.6
5	MgO	< 2

2.2. As a Raw Material for Cement

In the steel production process, limestone is used as a material to bind impurities present in iron ore into slag. The reference standard used refers to the 28th Annual PERHAPI Meeting (TT-PERHAPI XXVIII) regarding quality standards for limestone as a flux material in the metallurgical industry [13], as shown in Table 2.

Table 2. Requirements for flux raw materials.

No	Chemical Compound	Specification (%)
1	CaO	Min. 51
2	SiO_2	Max. 1.2
3	Al_2O_3	Max. 1
4	Fe_2O_3	Max. 0.65
5	MgO	Max. 3.5
6	Sulfur	Max. 0.05
7	**Phosphorus**	**Max. 0.05**

2.3. As a Raw Material for Dolomite Fertiliser

The use of dolomite minerals found in Indonesia is limited to the production of dolomite fertiliser and dolomite bricks for use in construction. The standard applied is SNI 02-2804-2005 [14]. The requirements are set out in Table 3.

Table 3. Requirements for dolomite fertiliser raw materials

No	Chemical Compound	Specification (%)
1	MgO	Min. 18
2	CaO	Min 29
3	$Al_2O_3 + Fe_2O_3$	Max. 3
4	**SiO_2**	**Max. 3**

3. Results and Discussion

3.1 Chemical Composition of Limestone at Mario Riaja

The limestone sampling site is located in Mario Riaja Village, Mario Riwawo Sub-district, Soppeng Regency, South Sulawesi Province. Samples were collected at ST 1, ST 2 and ST 3 within the Soppeng Formation; the geological map of the study area is shown in Figure 2.

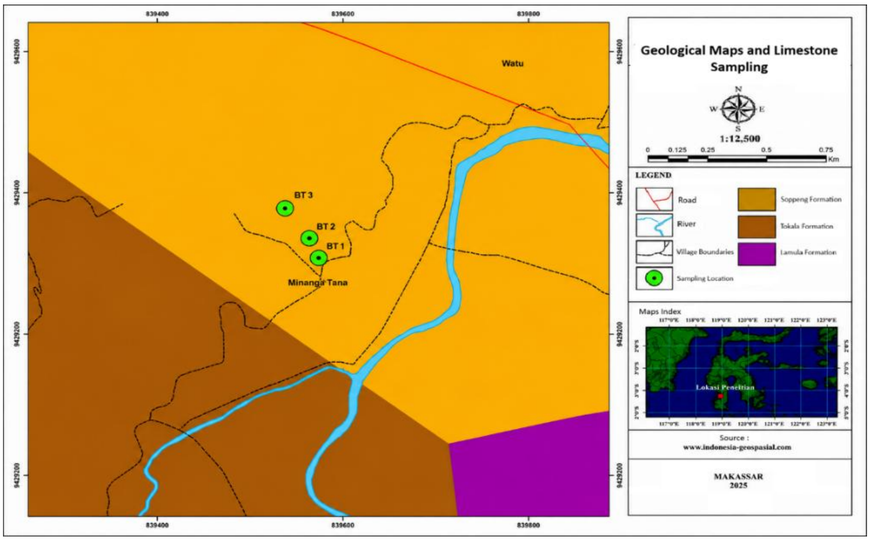

Figure 2. Geological map and sampling locations [15]

The appearance of samples ST 1, ST 2, and ST 3 can be seen in Figures 2, 3, and 4.

3.1.1. Sample 1

The sample consists of a sedimentary rock with a fresh yellowish-brown colour and a weathered greyish-brown colour, a non-clastic texture, a massive structure, moderate sorting, and a closed-grained texture (figure 3). It comprises calcite, which is well-crystallised, and is situated at N 268°E/30°. Located at coordinates X: 119.882432 and Y: 4.503576205, at an elevation of 190 mdpl.

Figure 3. Sample Appearance at ST 1

3.1.2. Sample 2

The sample consists of a sedimentary rock with a fresh grey-green colour and a weathered brownish colour, a non-clastic texture, a massive structure, moderate sorting, and a closed-grained texture (figure 4). It comprises calcite, which is well-crystallised, and is situated at N 325°E/32°. Located at coordinates X: 119.8820775 and Y: 4.502701181 at an elevation of 190 mdpl.

Figure 4. Sample Appearance at ST 2

3.1.3. Sample 3

The sample consists of a sedimentary rock with a fresh, greyish-white colour and a weathered, yellowish-brown colour; it has a non-clastic texture, a massive structure, poor sorting, and an open texture (figure 5). The mineral composition is calcite, and the minerals are well-crystallised, with a bearing of N 270°E/44°. Located at coordinates X: 119.8811269 and Y: 4.501376749 with an elevation of 204 mdpl. The results of the chemical analysis processed by the laboratory using X-Ray Fluorescence (XRF) are shown in Table 4.

Figure 5. Appearance of the Sample at ST 3

Following the macroscopic analysis, XRF analysis was carried out on three limestone samples. The results of the XRF analysis are shown in the table below (Table 4).

Table 4. XRF analysis results.

Composition	**Sample Code**		
	ST 1	**ST 2**	**ST 3**
Na_2O	0.0000	0.0000	0.1246
MgO	0.7064	0.5986	0.5230
Al2O3	1.0459	0.4016	0.4716
SiO2	0.0634	0.8511	1.1444
P_2O_5	0.0634	0.0691	0.0731
SO_3	0.0807	0.0819	0.0136
Cl	0.0155	0.0076	0.0732
K2O	0.0627	0.0518	0.0732
CaO	53.3257	53.6010	53.5936
TiO2	0.0437	0.0000	0.0199
V_2O_5	0.0000	0.0336	0.0084
Cr_2O_5	0.0283	0.0055	0.0385
MnO	0.1874	0.1765	0.0949
Fe2O3	0.4724	0.5109	0.4851
Co_2O_5	0.0000	0.0000	0.0024
Nio	0.0115	0.0096	0.0038
LOI	43.5200	43.4900	43.2000
Total	**99.7095**	**99.9999**	**99.9388**

Sample ST 1 is high-quality limestone, as evidenced by a calcium oxide (CaO) content of 53.32% and a high loss on ignition (LOI) of 43.52%, indicating a predominance of calcium carbonate ($CaCO_3$). Impurity contents such as silica, alumina, and iron oxide, as well as other minor elements, are all at low levels (below 1%), indicating good chemical purity. Sample ST 2 is also pure limestone with a slightly higher calcium oxide (CaO) content (53.60%) and an LOI of 43.49%. The silica content (0.85%) is lower than that of ST 1, whilst other metallic impurities such as Fe_2O_3 (0.51%) and Al_2O_3 (0.40%) also remain low. Other minor elements are within a narrow range, confirming its purity. Sample ST 3 has a similar calcium oxide (CaO) content (53.59%) to the other samples, as well as a LOI of 43.20%. However, this sample recorded the highest silica content (1.14%) of the three. Nevertheless, the other impurity elements remained at low levels, and the total of all chemical components was close to 100%, indicating consistent analytical results.

3.2. The Quality of Limestone as a Raw Material for Cement

The second objective of this study was to determine whether the limestone deposits in the study area meet the standards for use as a raw material for cement, based on the criteria set out in the Cement Data Book [12]. The classification of the study area's limestone according to the standards for cement raw materials is shown in Table 5. The results of the chemical analysis processed by the laboratory using X-ray Fluorescence (XRF) are shown in Table 5.

Table 5. Comparison of the chemical composition of limestone against the Cement Data Book [12].

Chemical Compound	Concentration (mass%)			Standard Cement Raw Material
	ST 1	ST 2	ST 3	
SiO_2	1,04	0,85	1,14	0,76% - 4,75%
Al2O3	0,36	0,40	0,47	0,71% - 2,00%
Fe2O3	0,47	0,51	0,48	0,36% - 1,47%
CaO	53,32	53,60	53,59	48% - 55,6%
MgO	0,70	0,59	0,52	< 2%

Sample ST 1 meets the requirements for use as a cement raw material. The calcium oxide (CaO) content of 53.32% falls within the standard range, and the levels of the main impurities—such as magnesium oxide (MgO), silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3)—are also within the specified limits. Sample ST 2 also meets the requirements for use as a cement raw material. The calcium oxide (CaO) content of 53.60% and the magnesium oxide (MgO) content of 0.59% both comply with the standards. The silicon dioxide (SiO_2) content and the combined aluminium and iron oxide content are also within the permitted limits. Sample ST 3 shows that all its main elements meet the standards and can be used as raw material for cement. The calcium oxide (CaO) content of 53.59% and the magnesium oxide (MgO) content of 0.52% are within the required range. Similarly, the silicon dioxide (SiO_2) content and the combined aluminium and iron oxide content are within the tolerance limits.

3.3. The Quality of Limestone as a Flux in the Metallurgical Industry

The assessment does not refer to the Indonesian National Standards (SNI) as there is currently no SNI specifically regulating the standards for limestone as a flux material in metallurgical processes. Therefore, the reference used in this study is derived from the Domestic Literature Standards published by TT-PERHAPI XXVIII [13]. This standard was not published by a single individual but is a compilation of several standards used by various companies in the cement industry. The results of the chemical composition analysis of the limestone obtained were then compared with the limits of these standards, as shown in Table 6.

Table 6. Results of the comparison of the chemical composition of limestone against domestic literature standards by TT-PERHAPI [13].

Chemical Compound	Concentration (mass%)			National Literature Standards by TT-PERHAPI XXVIII
	ST 1	ST 2	ST 3	
CaO	53,32	53,60	53,59	Min. 51 %
SiO_2	1,04	0,85	1,14	Maks. 1,2 %
Al2O3	0,36	0,40	0,47	Maks. 1 %
Fe_2O_3	0,47	0,51	0,48	Maks. 0,65 %
MgO	0,70	0,59	0,52	Maks. 3,5 %
SO_3	0,08	0.08	0.07	Maks. 0,5 %
P_2O_5	0,06	0,06	0,05	Maks. 0,5 %

Sample ST1 has a CaO content of 53.32%, which exceeds the minimum limit of 51%. The SiO_2 content of 1.04% is close to the maximum limit of 1.2%, whilst Al_2O_3 (0.36%), Fe_2O_3 (0.47%), MgO (0.70%), SO_3 (0.08%), and P_2O_5 (0.06%) are all below the specified limits. With this composition, ST1 is deemed to meet the standards as a flux material in iron ore refining. In ST2, the CaO content reached 53.60% and all impurity elements such as SiO_2 (0.85%), Al_2O_3 (0.40%), Fe_2O_3 (0.51%), MgO (0.59%), SO_3 (0.08%), and P_2O_5 (0.06%) remained within the maximum limits. Therefore, ST2 also meets PERHAPI's standard criteria and is suitable for use as a flux material in the metallurgical industry. Sample ST3 contains 53.59% CaO, exceeding the minimum requirement, with SiO_2 (1.14%), Al_2O_3 (0.47%), Fe_2O_3 (0.48%), MgO (0.52%), SO_3 (0.07%), and P_2O_5 (0.05%) all of which are below the threshold limits. This standard-compliant elemental composition confirms that ST3 is suitable for use as a flux material in iron ore refining.

3.4. Quality of Limestone as a Raw Material for Dolomite Fertiliser

This assessment is based on the chemical parameters specified in Indonesian National Standard (SNI) 02-2804-2005 regarding the specifications for dolomite fertiliser raw materials. The results of the chemical analysis of the limestone at the study site will subsequently be compared with this standard to assess the suitability of the material as a raw material for dolomite fertiliser, as shown in the classification table in Table 7.

Table 7. Comparison of the chemical composition of limestone against SNI 02-2804-2005 [14].

Chemical Compound	Concentration (mass%)			Standards for Dolomite Fertiliser Raw Materials
	ST 1	ST 2	ST 3	
MgO	0,70	0,59	0,52	Min. 18%
CaO	53,32	53,60	53,59	Min. 29%
Al2O3 + Fe2O3	0,83	0,91	0,95	Maks. 3%
SiO_2	1,04	0,85	1,14	Maks. 3%

Sample ST1 contains 53.32% CaO, which meets the minimum requirement of 29%, with Al_2O_3 + Fe_2O_3 at 0.83% and SiO_2 at 1.04%, both of which remain below the maximum limit of 3%. However, MgO is only 0.70%, well below the minimum requirement of 18%, and therefore does not meet the standards for dolomite fertiliser. ST2 shows a CaO content of 53.60%, which meets the requirement, with Al_2O_3 + Fe_2O_3 at 0.91% and SiO_2 at 0.85%, both still within the maximum limit. However, the MgO content of 0.59% remains well below the 18% requirement, meaning this sample is also unsuitable as a raw material for dolomite fertiliser. In ST3, the CaO content reached 53.59%, in line with the standard, with Al_2O_3 + Fe_2O_3 at 0.95% and SiO_2 at 1.14%, both still within the maximum limits. However, the MgO content was only 0.52%, far below the minimum requirement, meaning ST3 also fails to meet the dolomite fertiliser standard. Based on the analysis results, all samples (ST1-ST3) fail to meet the dolomite fertiliser standard due to very low MgO content (0.52–0.70%), far below the minimum requirement of 18%. Conversely, the CaO content is quite high (over 53%), indicating a predominance of calcite. Although the Al_2O_3 + Fe_2O_3 and SiO_2 content still meets the maximum limits, the low MgO content is the main factor rendering the samples unsuitable.

4. Conclusion

The chemical composition of the limestone samples (ST1, ST2, and ST3) namely, calcium oxide (CaO) above 53% and a loss on ignition (LOI) value above 43%-indicates a high proportion of calcium carbonate. Impurity content, such as silica, alumina and iron oxide, remains low and within acceptable limits, whilst other minor elements such as magnesium oxide, phosphate and other metals are below 1%, indicating good and consistent chemical purity for industrial purposes. All samples (ST1, ST2, and ST3) meet the quality standards for cement raw materials according to the Cement Data Book (Duda, 1987), as evidenced by high calcium oxide content (53–54%), low magnesium oxide (<2%), and total aluminium and iron oxide levels below the maximum limits. The silicon dioxide content in all three samples also remains within the required range. All samples (ST1, ST2, and ST3) meet the requirements for use as flux materials in the metallurgical industry in accordance with the PERHAPI Literature Standards. The calcium oxide (CaO) content of all samples is above the minimum limit, whilst the SiO_2 and Al_2O_3 contents remain below the maximum limit. Impurities such as Fe_2O_3, MgO, SO_3, and P_2O_5 are also within permissible limits. With a suitable composition of major elements and low impurity levels, all three samples are deemed suitable for use as flux materials in the metallurgical industry. 4. The three samples (ST1, ST2, and ST3) do not meet the requirements for use as raw material for dolomite fertiliser according to SNI 02-2804-2005, as the magnesium oxide content in all samples is well below the minimum limit of 18%, although other elements such as calcium oxide, silica, aluminium oxide, and iron oxide are within the permitted standard limits.

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