CHARACTERIZATION OF LIMESTONE AND DOLOMITE FILLERS FOR INDUSTRIAL APPLICATIONS

[1]Prof. dr Nedzad Haracic
[2]Prof. dr Nevzet Merdic
Kakanj cement plant
Bosnia and Herzegovina
[4]Adelina Pasalic
Student at Faculty of Engineering and Natural Sciences
Bosnia and Herzegovina

[3]Prof. dr Ilhan Busatlic
[4]Prof. dr Nadira Busatlic
Faculty of Engineering and Natural Science
Bosnia and Herzegovina

Keywords: Fillers, limestone, dolomite, particle size distribution, mineralogical composition, chemical composition

ABSTRACT:
Fillers play a crucial role in enhancing product performance and reducing production costs. To be used in various industries, fillers must be readily available, affordable, pure, non-toxic, and meet specific physical and chemical standards. This study examines limestone and dolomite fillers, focusing on their chemical composition, mineralogical properties, and particle size distribution. Advanced analytical techniques were employed: laser granulometry for particle size distribution analysis, X-ray fluorescence spectroscopy for chemical analysis, and X-ray diffraction for mineralogical analysis. To assess whether harder components, such as quartz, are concentrated in the coarser fractions, all the fillers were divided into two fractions - above 45 microns and bellow 45 microns The findings indicate that the quality and composition of fillers significantly impact their industrial suitability. While limestone and dolomite fillers differ in purity and mineral content, both offer potential applications across various industries.

1. INTRODUCTION

Fillers are materials used to fill products such as plastics, concrete, composites, etc. Mixing with fillers is done to improve the properties of the final product, and also to improve economy, respectively to obtain a cheaper product. The most commonly used filling materials are calcium carbonate (ground and precipitated), kaolin, talc, and carbon black.[1]
Limestone, which main component is mineral calcite ($CaCO_3$) has a widespread utilization in various industries: production of glass, steel, certain calcium salts, production of pure alkali, production of drying and disinfection agents, natural water softener, etc. Limestone behaves as a filler if it is added to cement as a main additive.[3] Limestone has a molar mass of 100.0869 g/mol, occurs as a white powder with a chalky taste, and is odorless. It is almost insoluble in water (0.013g/L at 25℃), soluble in dilute acids, and occurs naturally in the form of a trigonal crystal structure.[4] Dolomite, or calcium magnesium carbonate, (□□□□$_3$ x □□□□$_3$) is similar to limestone, usually white in color, but can also be reddish, gray or brown due to admixtures of iron (then called ankerite) or manganese.[2]

Dolomite rocks are easily crushed; they are used in construction (dolomite aggregate) and as a raw material for obtaining magnesium. Processed dolomite serves as a refractory material for the construction of metallurgical furnaces. Due to the fact that the filler particles are of very small dimensions, they are characterized by a high degree of fineness and purity of the particles.[6]

In this study, the chemical composition, mineralogical properties, and particle size distribution of limestone and dolomite fillers were analyzed to assess their suitability for industrial applications. Advanced characterization techniques, including laser granulometry, X-ray fluorescence (XRF) spectroscopy, and X-ray diffraction (XRD), were employed to evaluate key properties. To investigate the distribution of harder components, such as quartz, within the fillers, samples were divided into two fractions: particles above 45 microns and below 45 microns. This approach provides insight into how particle size influences mineralogical composition and potential performance in various industrial processes. The findings of this study contribute to a better understanding of the quality and applicability of limestone and dolomite fillers, highlighting their advantages and limitations in different industrial contexts.

2. EXPERIMENTAL TECHNIQUES

The aim of this research is to determine the composition of the raw materials of limestone and dolomite filler, before and after the sieving process, and the possibility of using them as fillers. Raw materials used for mentioned experiment was limestone (Ribnica) and dolomite (Baumit, Kalvarija and Bijele vode).
During the research the granulometric analysis of the tested samples, mineralogical and chemical analysis were performed.
Sample preparation implied grinding the raw materials, followed by sieving on a 45 microns (μm) sieve. It was necessary to weigh 10 grams of each raw material. The sieving was performed manually. For the purposes of the research, 6 different samples were made: ground limestone (L1), ground dolomite(D1), limestone below 45 microns(L2), limestone above 45 microns(L3), dolomite below 45 microns(D2), dolomite above 45 microns (D3).
In this study, X-ray fluorescence (XRF) spectroscopy was utilized for chemical analysis, while X-ray diffraction (XRD) was employed for mineralogical analysis of limestone and dolomite fillers. Additionally, the Mastersizer 3000 laser diffraction particle size analyzer was used to determine particle size distribution.

3. RESULTS AND DISCUSION

In table 1. are presented the results of the chemical analysis of three limestone samples: ground limestone (L1), limestone below 45 microns (L2), limestone above 45 microns (L3).

Table 1. Chemical composition of prepared limestone samples

	LOI	□□□$_2$	□□$_2$□$_3$	□□$_2$□$_3$	CaO	MgO	□□$_3$	□□$_2$□	□$_2$□
	%	%	%	%	%	%	%	%	%
L1		6,89	1,25	0,57	50,36	0,16	0,06	0,07	0,09
L2	41,47	6,69	1,24	0,55	49,48	0,26	0,05	0	0,1
L3	41,43	6,79	1,37	0,55	49,32	0,19	0,04	0	0,01

From the results of the chemical analysis of the limestone, it can be concluded that the ground limestone meets all the requirements regarding the chemical composition so that it can be adequately used as a filler. At the same time, the requirements that need to be met are a satisfactory amount of □□□□$_3$, which should not be below 85%, because the amount below 85% is considered impure limestone. In the limestone sample from the analysis there is 89.87% of □□□□$_3$. If we compare the results of samples L2 and L3, i.e. limestone below and above 45 microns, it can be concluded that the differences between the two samples are insignificant, and some results are identical.

In table 2. are presented the results of the chemical analysis of three dolomite samples: ground dolomite (D1), dolomite below 45 microns (D2), dolomite above 45 microns (D3)

Table 2. Chemical composition of prepared dolomite samples

	LOI	□□□$_2$	□□$_2$□$_3$	□□$_2$□$_3$	CaO	MgO	□□$_3$	□□$_2$□	□$_2$□
	%	%	%	%	%	%	%	%	%
D1	46,22	0,63	0,44	0,1325	31,385	21,087	0,037	0,056	0,092
D2	46,71	0,56	0,28	0,12	31,34	20,98	0,04	0,058	0,06
D3	46,56	0,65	0,4	0,14	31,24	20,99	0,04	0,063	0,07

From the chemical analysis of ground dolomite, it can be noted that the highest percentage of MgO 21.08% and CaO 31.38%, as the main components. The loss on ignition is 46.22%. If we compare the results of the chemical analysis of dolomite above (D3) and below (D2) 45 microns, the largest difference will be observed in the percentage of □□$_2$□$_3$. Also, in the dolomite samples presented in the paper, there are no large deviations in the results, and some of the results are identical.

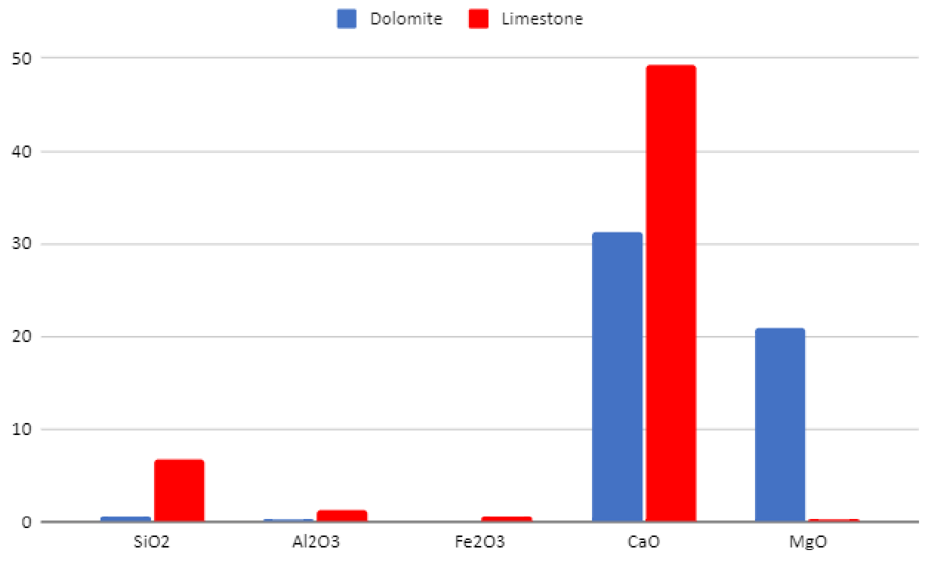

Figure 1. Comparison the results of chemical analysis limestone and dolomite

From the histogram it can be seen that limestone does not have a much higher content of certain oxides, such as silicon, aluminum, and calcium, than dolomite. On the contrary, the results differ by a smaller percentage. However, dolomite also contains a large amount of magnesium in its basic composition, and accordingly the analysis showed a significant presence of magnesium oxide in dolomite, and as such dolomite is used as a source of magnesium oxide.

Table 3. Results of mineralogical analysis of limestone and dolomite samples

Sample	Quartz(%)	Calcite(%)	Dolomite(%)	Ankerite(%)	Pyrites(%)
L1	5,59	94,41	0	0	0
L2	5,45	92,82	0,61	0	0,01
L3	5,35	94,61	0,05	0	0
D1	0,13	3,31	76,54	20,00	0,01
D2	0,12	4,17	73,02	22,69	0
D3	0,10	4,09	71,54	24,27	0

The mineralogical composition of limestone samples, according to XRD analysis, is shown in table 3. From the table it can be concluded that a smaller percentage of calcite passed through the 45 microns sieve, and that this is certainly the mineral with the highest content in limestone. Also in table 3 are presented the results of the mineralogical analysis of dolomite samples. The results showed a significant presence of dolomite, 70-77% in all three samples, which is the expected amount given that these are dolomite samples. Also, a mineral whose presence is not negligible, as much as 20-25% in all three samples is ankerite. Ankerite is very closely related to dolomite, however, it differs in that the magnesium from dolomite is replaced by certain amounts of iron or manganese.

Granulometric composition is an indicator of the mass fraction of individual fractions (part of a mixture), which include all grains of a certain diameter. A very important analysis for describing a certain material as a filler, precisely because of the correct or appropriate representation of grains of all sizes that will enable good filling of cavities during mixing with the main material.
In 2. and 3. charts represent the distribution of the limestone and dolomite particles below and above 45 microns.

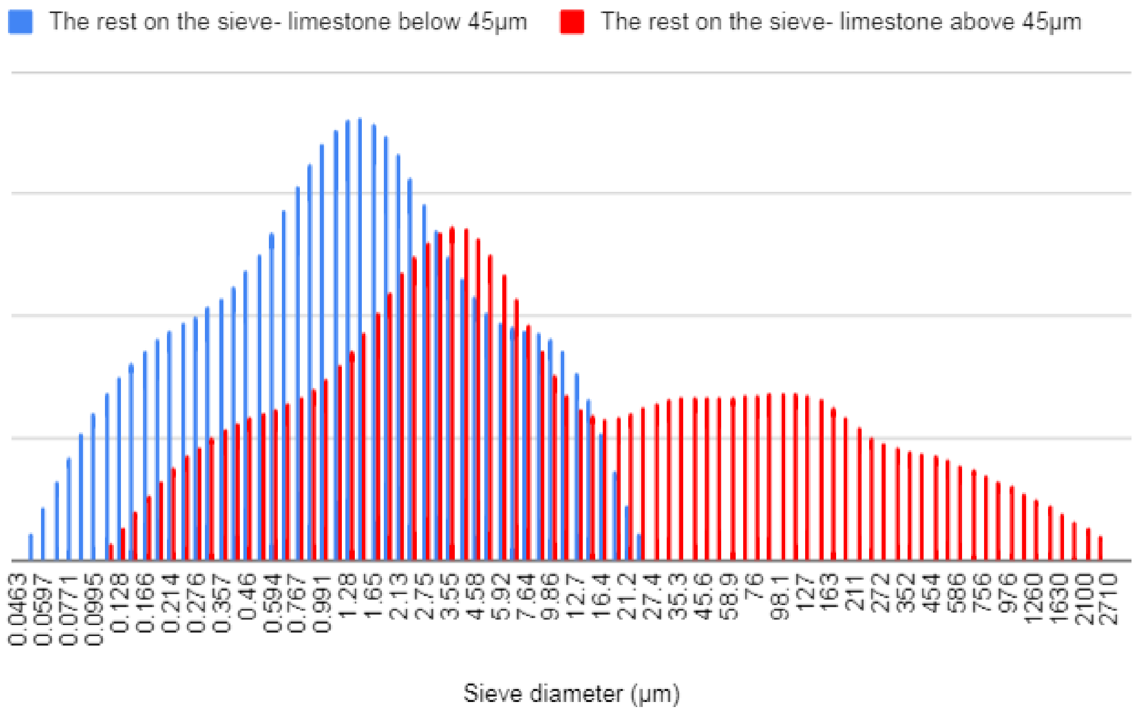

Figure 2. Particle size distribution of limestone fractions-below and above 45 microns

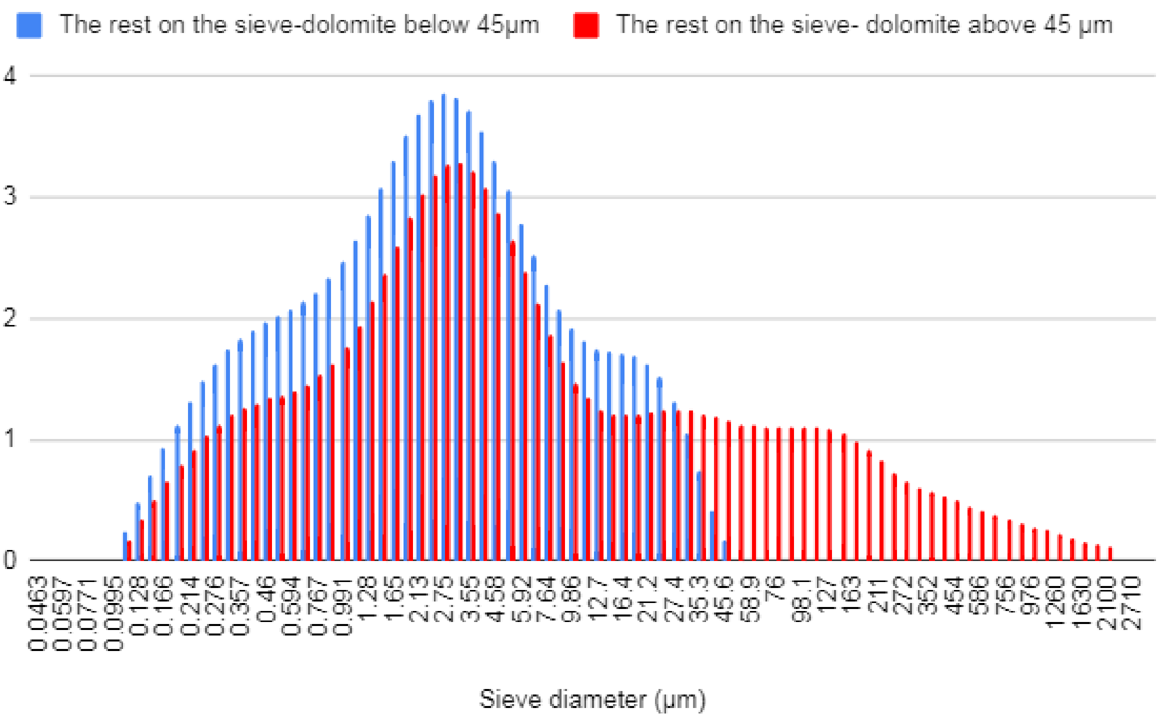

Figure 2. Particle size distribution of dolomite fractions-below and above 45 microns

The highest percentage of limestone particles above 45 microns is 2,73%, with a diameter of 3,55µm. but for limestone below 45 microns, the histogram shows the highest percentage of particles at 3.12µm, and that is 3.62%.

Dolomite above 45 microns at 3.12 µm shows the highest percentage of particles, more precisely 3.29%, but for dolomite below 45 microns, the highest presence of particles at 2.75 µm is with a percentage of 3.86%.

4. DISCUSSION

Chemical analysis of the limestone from the Ribnica query, which was used for analysis in this paper, found that it contains 89,87% $CaCO_3$. Therefore, it is concluded that this limestone sample belongs to the category of low-purity limestone, which group includes limestones containing 85-95,5% calcium carbonate.[5] According to the analysis of limestone, the requirements of the chemical industry and the sugar industry cannot be met, given that high purity of limestone (min.95%) and a small amount of SiO_2 (up to 3%) are required. Considering that calcium carbonate is used as an extender in the coatings industry (paints and varnishes) because it meets almost all industry requirements, starting from non-toxicity, through a high degree of whiteness, to the ability to adjust the fineness of the particle size distribution, it can be concluded that limestone samples can serve the coatings industry, if we consider the amounts of calcium carbonate.

The high percentage of calcite in the limestone samples from the analysis is very favourable due to its moderate hardness and mild abrasiveness, so this limestone can be used in the industry of abrasive cleaning agents, without the need for previous sieving, because there are no large deviations of the results in the mineralogical analysis. According to the distribution of particles in the granulometric curves, the most favourable for the fertilizer industry is a sample of limestone under 45 microns, considering that this industry requires particles smaller than 0.03 mm, of which the percentage in the sample is satisfactory.

The highest class of dolomite should contain a minimum of 19% MgO, a maximum of 3.5% SiO_2, max. 1% Al_2O_3,0,2% Fe_2O_3. From the chemical analysis of dolomite, it can be concluded that it is dolomite of the highest class, given that the results of all three samples of dolomite completely correspond to the parameters of the highest class, and that the results of the sieved and unsieved samples did not show deviations, so it can be concluded that sieving is not a necessary stage. Higher amounts of silica reduce refractoriness. The fact that the mean value of SiO_2 of all three dolomite samples is 0.61%, which is a very small amount, leading to the conclusion that the samples from the analysis have an acceptable degree of refractoriness.

Magnesium oxide increases the chemical stability and mechanical resistance of glass, therefore dolomite is introduced into the glass industry as the main source of MgO. From the results of the chemical analysis of dolomite, it is concluded that it is a very favourable quality of dolomite, precisely because of the significant amount of MgO, and the percentage of loss on ignition, which, according to the average value of three samples, fully corresponds to the standard of the glass industry. Dolomite samples, according to standards and parameters, represent high quality samples, which can absolutely be used in many industries according to their chemical purity, while if we talk about limestone samples, they are of lower quality, but still very usable in many industries.

5. CONCLUSION

This study evaluated the chemical composition, mineralogical properties, and particle size distribution of limestone and dolomite fillers to determine their industrial applicability. The results indicate that the limestone samples from the Ribnica quarry, classified as low-purity (89.87% $CaCO_3$), are unsuitable for industries requiring high-purity limestone, such as the chemical and sugar industries. However, they have potential to be suitable for coatings, fertilizers, and abrasive cleaning products. The fine fraction (<45 microns) meets fertilizer industry requirements, further enhancing its industrial relevance. Dolomite samples exhibited high purity, with a significant MgO content and low SiO_2 levels, meeting the standards for refractory applications, metallurgy, and the glass industry. Additionally, no significant differences were observed in the chemical and mineralogical composition between fine and coarse fractions of both fillers. Overall, while the analyzed limestone samples are of lower purity, they remain viable for multiple industries, particularly coatings, fertilizers, and abrasives. In contrast, dolomite samples are of high purity, making them highly suitable for many applications. These findings provide valuable insights for optimizing the selection and utilization of filler materials in industrial processes.

5. REFERENCE

[1] A. Mujkanović, M. Jovanović: Pigmenti i punila; Fakultet za metalurgiju i materijale, Zenica 2016.

[2] Hrvatska enciklopedija, mrežno izdanje. Leksikografski zavod Miroslav Krleža, 2013. – 2024.

[3] Bušatlić I., Bušatlić N., Merdić N., Haračić N.: Osnove hemije i tehnologije Portland cement, Fakultet za metalurgiju i materijale, Zenica 2020.

[4] I. Brizić, M. Kondža: Primjena kalcijevog karbonata u medicinske svrhe; Univerzitet u Mostaru, posebno izdanje 2018.

[5] D. J. Harrison et al.: „Procedures for rapid assesment of limestone resources“, Technical report, BGS International, Nerc, 1998

[6] T. Haramina: Utjecaj veličine čestica punila na svojstva poliuretanskih kompozita-Završni rad; Fakultet hemijskog inženjerstva i tehnologije,Zagreb 2007.