

Characterization of Dolomitic Lime as the Base Reagent for Precipitation of $\text{Mg}(\text{OH})_2$ from Seawater

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The process of obtaining magnesium hydroxide from seawater involves precipitation of magnesium ions with suitable basic reagents, such as calcined dolomite. The purity of the magnesium hydroxide precipitate depends on dolomite characteristics; therefore, it is necessary to find high purity dolomite with good physical properties. The aim of this study was to characterize the specific dolomite from the location of Đipalo-Sinj (Croatia), its quality, and the favourable conditions for calcination. Certain physical and chemical characteristics were determined by pure chemical analysis, as well as by using TG/DTG-DTA, FTIR and SEM/EDS analysis. Good chemical quality of dolomitic lime (59.03 wt. % CaO, and 40.69 wt. % MgO) with low content of impurities was confirmed with the TG/DTG-DTA thermal analysis. In the atmosphere of air + CO_2 , dolomite decomposes to CaCO_3 and MgO in a temperature area between 415 and 824 °C; thereafter, another reaction begins – the decomposition reaction of calcium carbonate, completed at 897 °C. In air, the simultaneous decomposition of two carbonates occurs between 657 – 840 °C. The FTIR and EDS analyses confirmed the complete breakdown of carbonates at 950 °C. The main components (Mg, Ca, and O) confirmed the purity of the dolomite lime.

Key words:

dolomitic lime, $\text{Mg}(\text{OH})_2$, seawater, TG/DTG-DTA, FTIR, SEM/EDS

Introduction

Natural dolomite is a sedimentary rock containing more than 90 % of the mineral dolomite ($\text{CaMg}(\text{CO}_3)_2$), and it is formed near the deposition of original limestone rocks. Part of the calcium carbonate from limestone rocks can be converted to dolomite by replacement with magnesium carbonate as a secondary component (up to 46 % by weight).¹ Dolomite is commonly used as a refractory material and as raw material for the production of magnesium, in metallurgy, glass industry, cement industry, as well as a filling in the production of paper, rubber, and plastic.^{2–4} Dolomite is the best source of magnesium salts in the chemical industry, and an important raw material in the refractory industry because it contains a large amount of MgO. Calcined dolomite is dolomitic lime that can be used as a precipitation agent in obtaining magnesium hydroxide from seawater. The production of magnesium oxide from seawater is a well-known industrial process and has been studied all over the world for a number of years.^{1,5–8} The process involves the extraction of dissolved magnesium, which has a concentration of around 1.3 g dm^{-3} in

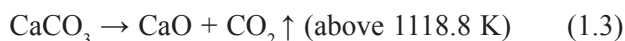
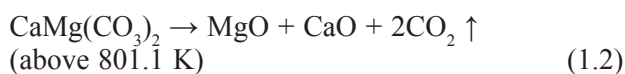
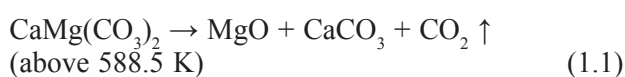
seawater, and the reaction of magnesium salts (chloride and sulphate) with lime or dolomite lime to produce a magnesium hydroxide precipitate. The use of dolomite lime holds some advantages over the use of lime, in that half the volume of seawater is required per ton of magnesia, since half of the magnesia is derived from the dolomite lime. This results in reduced size of the reaction and settling systems, and in the cost of seawater pumping and pretreatment.^{5,9} The apparently simple chemistry of the process is unfortunately complicated in practice, because seawater is not a pure solution of magnesium salts, and dolomite cannot be found free of impurities in nature.

The most common impurities in dolomite are SiO_2 , Al_2O_3 , MnO, Fe_2O_3 , sulphur, and phosphorus compounds. The quality of dolomite has a significant influence on pollution of the magnesium hydroxide precipitate as well as on the final product of MgO. Hence, it is necessary to use extremely pure dolomite (< 2.5 % of impurities and > 97.5 % MgO and CaO). According to N. Heasman⁹, the upper limit of pollution of the calcined dolomite or limestone is 0.2 wt. % SiO_2 , 0.1 wt. % Al_2O_3 , and 0.1 wt. % Fe_2O_3 .

The purity of magnesium hydroxide precipitate also depends on the calcination process of dolomite.

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The calcination process or thermal decomposition of dolomite ends with the complete breakdown of the carbonate. Insufficiently calcined or overly calcined dolomite enters in the magnesium hydroxide precipitate as pollution and shows considerably less reactivities with seawater. According to N. Heasman⁹, each 0.1 wt. % CO₂ lagged during calcination causes pollution with 0.13 wt. % CaO. Many researchers^{1,10–14} have studied the thermal decomposition of dolomite under different experimental conditions (different atmospheres, like air, nitrogen, air + CO₂, different temperatures, and other). The decomposition of dolomite depending on temperature takes place according to the following reactions.¹¹



The decomposition of dolomite depends also on the atmosphere in the course of experiment. The decomposition of dolomite occurs in a single step in air and can be described with reaction (1.2).^{10–14} According to the literature^{13–14}, under the air + CO₂ atmosphere, two stages of the process are present during decomposition of dolomite, described by reactions (1.1) and (1.3). Dolomite decomposes directly to CaCO₃ and MgO, and in next stage, calcite decomposes to CaO.

Each dolomite has a different composition, which influences the conditions of thermal decomposition and other chemical and physical properties; therefore, it is necessary to conduct an analysis of each dolomite. The aim of this study was to find dolomite with respective characteristics that could be used as a base reagent for the precipitation of magnesium hydroxide from seawater.

Experimental

Dolomite from the location of Đipalo-Sinj (Croatia) was characterized by chemical and mineralogical analysis. The dolomite sample was ground in a laboratory mill (“PULVERISETTE 0” – Fritsch, Germany) and sieved through a mesh size of 200 μm. Chemical composition was determined by chemical analysis of the individual components in the sample (wt. %). Determination of CaO, MgO, Fe₂O₃, and Al₂O₃ in the dolomite was performed by the complexometric method, while SiO₂ was determined by gravimetric method using acetic anhydride and gasification with HF. The chemical composition of the dolomite lime was converted from

the known chemical composition of dolomite and loss on ignition (950 °C/5 h).

TG/DTG-DTA was carried out for better characterization of the dolomite sample and better interpretation of the chemical analysis results. Differential thermal analysis (DTA) and thermogravimetric analysis (TG/DTG) were conducted on a Perkin Elmer simultaneous TG/DTG-DTA analyser, the Pyris Diamond model. The analysis was performed in the temperature range 30 – 1000 °C in an atmosphere of air (flow rate 100 cm³ min⁻¹) and a heating rate of 20 °C min⁻¹, and in an atmosphere of air + CO₂ at the same process conditions. Analysis of the resulting curves was performed in the software package Muse (T-Slice Analysis and the Standard Analysis).

The particle size distribution in the dolomite sample was determined by the method of sieving, using a series of sieves with a mesh size of 200 – 45 μm. The results were approximated with the LN distribution function (logarithm-normal function).^{15,16} The dolomite was heated in a muffle furnace under air atmosphere for 5 h at 950 °C in order to obtain dolomitic lime as the precipitation reagent for obtaining magnesium hydroxide from seawater.

FTIR spectra were recorded on Perkin Elmer Spectrum One FT-IR spectrometer, and the samples were analysed in KBr pastille in the range from 4000 to 400 cm⁻¹. Microstructural evaluation and elemental analysis of the sintered samples were conducted by SEM equipped with EDS analyser (a Scanning SEM/EDS Tescan VEGA Electron Microscope Oxford INCA EDS, PA, USA).

Results and discussion

The chemical composition of the dolomite used in this study is given in Table 1. Chemical analysis shows that the tested dolomite composition was: 31.07 wt. % CaO, 21.42 wt. % MgO, and loss on ignition 47.27 wt. %. The content of impurities is insignificant: Al₂O₃ = 0.0487 wt. %, Fe₂O₃ = 0.0371 wt. %, and SiO₂ = 0.057 wt. %. The same dolomite sample was subjected to TG/DTG-DTA thermal analysis, which simultaneously monitored the change in the mass and energy of the substance as a result of its thermal degradation due to heating, depending on the atmosphere (air or air + CO₂), and on the temperature program of heating (30 – 1000 °C, 20 °C min⁻¹). TG/DTG-DTA curves are shown in Figs. 1 and 2. Table 2 shows the temperature intervals and the corresponding mass loss of the dolomite. The weight loss in the temperature range 200 – 600 °C represents releasing chemically bound water, while the decomposition of carbonates occurs in a temperature range of 600 – 1000 °C.^{4,10–13} The re-

Table 1 – Chemical composition of dolomite and dolomitic lime from location Đipalo-Sinj, Croatia, in mass fraction, wt. %

Composition	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	LOI (950 °C)
Dolomite/wt. %	21.42	31.07	0.057	0.0371	0.0487	47.27
Dolomitic lime/wt. %	40.69	59.03	0.1083	0.0705	0.0925	–

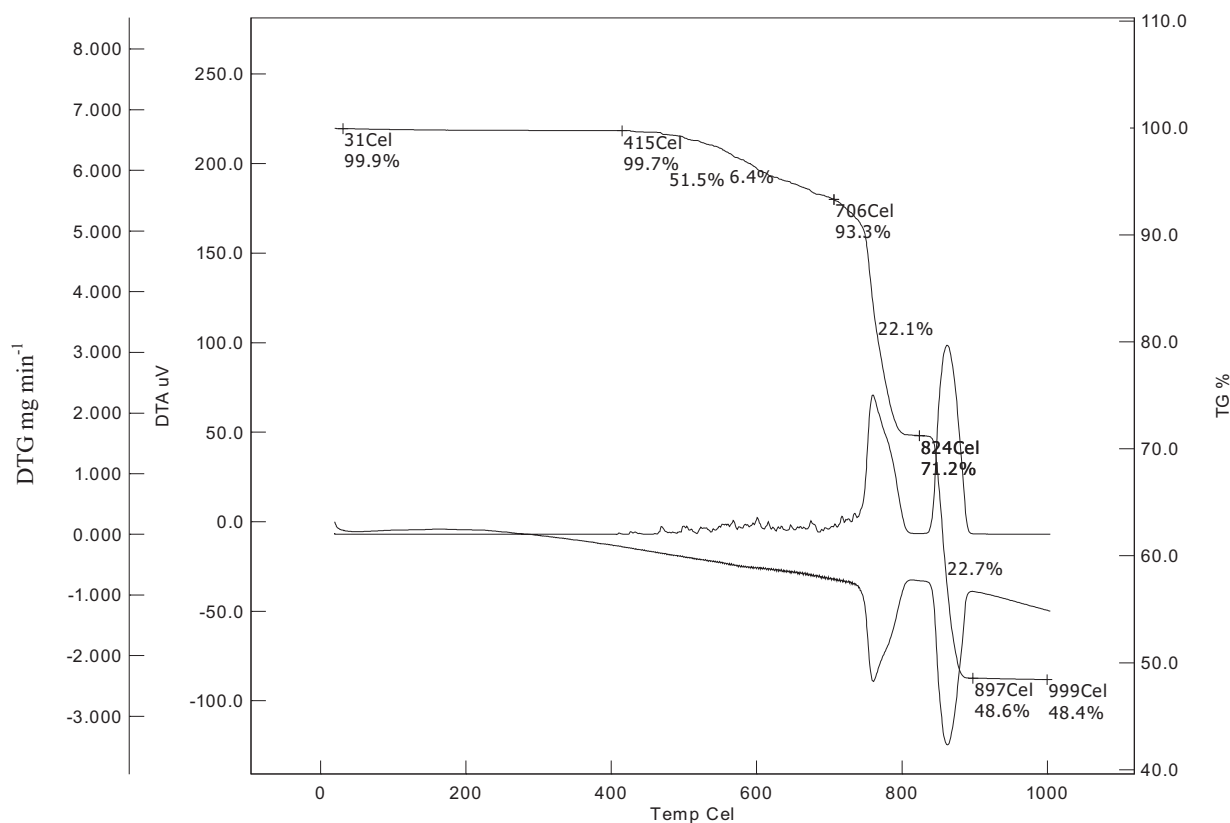
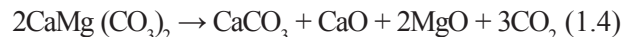
Table 2 – Results of TG/DTG-DTA analysis

DOLOMITE			
air		air + CO ₂	
temperature interval	wt. %	temperature interval	wt. %
30 – 1000	50.9	30 – 1000	51.5
421 – 657	5.3	415 – 706	6.4
657 – 840	45.5	706 – 824	22.1
		824 – 897	22.7

sults of thermogravimetric analysis (Fig. 1) show that the thermal decomposition of dolomite in the atmosphere of air + CO₂ can be defined by three temperature areas. In the first temperature interval of 415 – 706 °C, a small amount of calcium carbonate (CaCO₃) and magnesium oxide (MgO), with a

total weight loss of 6.4 % had emerged. In the second temperature interval of 706 – 824 °C, degradation of the dolomite and consequently the creation of CaCO₃ and MgO, with a weight loss of 22.1 % was observed. Although the decomposition of dolomite in this temperature area was rapid, there was still dolomite present up to about 900 °C. In the last temperature area of 824 – 897 °C, the rapid decomposition of CaCO₃ was observed in excess of the CaO. In this area, the weight loss was 22.7 %, and ends at 897 °C. These results suggested that the decomposition of dolomite took place according to reaction (1.1) in a temperature area between 415 and 824 °C; thereafter, another reaction began – (1.3), i.e., the decomposition reaction of calcium carbonate, which had completed at 824 – 897 °C.

Thermal decomposition of dolomite in air (Fig. 2) can be divided into two areas. The first temperature interval of 421 – 657 °C is characterized by slow and small weight loss (5.3 %) according to reaction (1.1). In the second temperature interval of 657 – 840 °C, rapid decomposition of dolomite occurred, and the total weight loss was 45.5 % according to reaction (1.3 and 1.4). According to the literature¹³, the thermal decomposition of dolomite results in CaO and MgO with the presence of CaCO₃ in the temperature interval of 550 – 750 °C.

Fig. 1 – TG/DTG-DTA analysis of dolomite in the atmosphere of air + CO₂

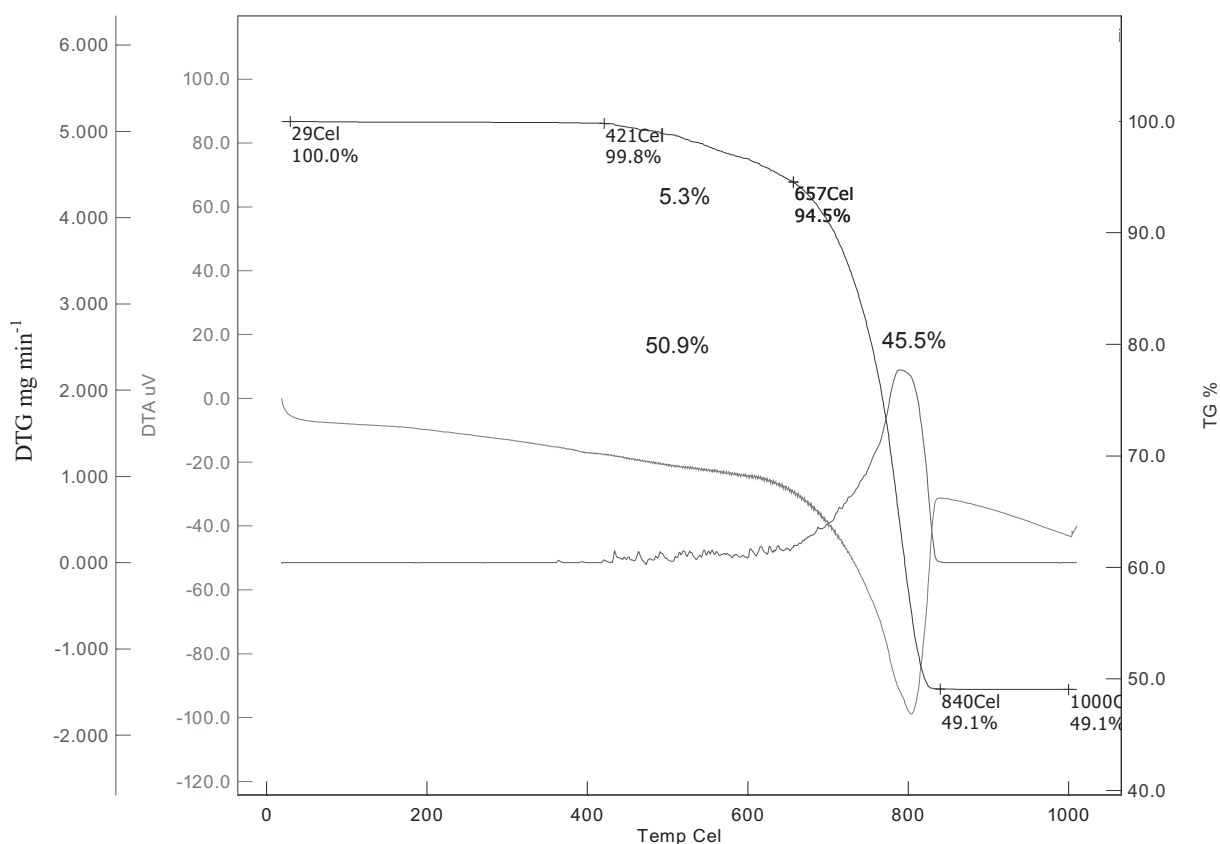


Fig. 2 – TG/DTG-DTA analysis of dolomite in the atmosphere of air

By increasing the heating temperature to 950 °C, calcium carbonate decreased in size and finally disappeared. Therefore, it can be concluded that reactions (1.3) and (1.4) of thermal decomposition of dolomite in air took place simultaneously.

From the difference in the thermal decomposition of dolomite in air and in air + CO₂ atmosphere, as well as the respective weight loss in a given temperature interval, it is possible to determine the content of CaO, MgO and loss on ignition of the dolomite from the Đipalo Sinj location. The results of the dolomite composition obtained by chemical analysis, presented in Table 3, were confirmed by TG/DTG-DTA thermal analysis. The chemical composition of dolomite lime is shown in Table 1. Good chemical quality precipitant (dolomitic lime) (59.03 wt. % CaO, and 40.69 wt. % MgO) with low content of impurities (SiO₂, Al₂O₃, and Fe₂O₃) provide

a better final product, i.e., sintered magnesia from seawater.

The results of particle size distributions of the dolomite (obtained by sieving) were processed with the LN function. By inputting the obtained data in the template of LN-function, the resulting dependence was not linear, with a deviation in the area of finer and coarser particles. This required the development of a two-parameter LN-function using a four-parameter LN-function, determined by the minimum and maximum sizes of the particles, i.e. $x_{\min} \leq x \leq x_{\max}$. The minimum particle size was 0.0225 mm, while the maximum particle size was 0.180 mm. Other granulometric properties of the dolomite are shown in Table 4. The results suggest that 50 % of the particles in the system had a size of 0.067 mm. The specific surface area (Blane) of the dolomite was about 231.52 m² kg⁻¹.

Table 3 – Contents of main constituents of dolomite obtained after the TG/DTG-DTA analysis and classical chemical analysis

		LOI (30 – 1000 °C), wt. %	CaO, wt. %	MgO, wt. %	Σ
TG/DTG-DTA analysis	atmosphere of air	50.9	29.00	20.85	100.75
TG/DTG-DTA analysis	atmosphere of air + CO ₂	51.5	28.93	20.80	101.23
	chemical analysis	47.27	31.07	21.42	99.76

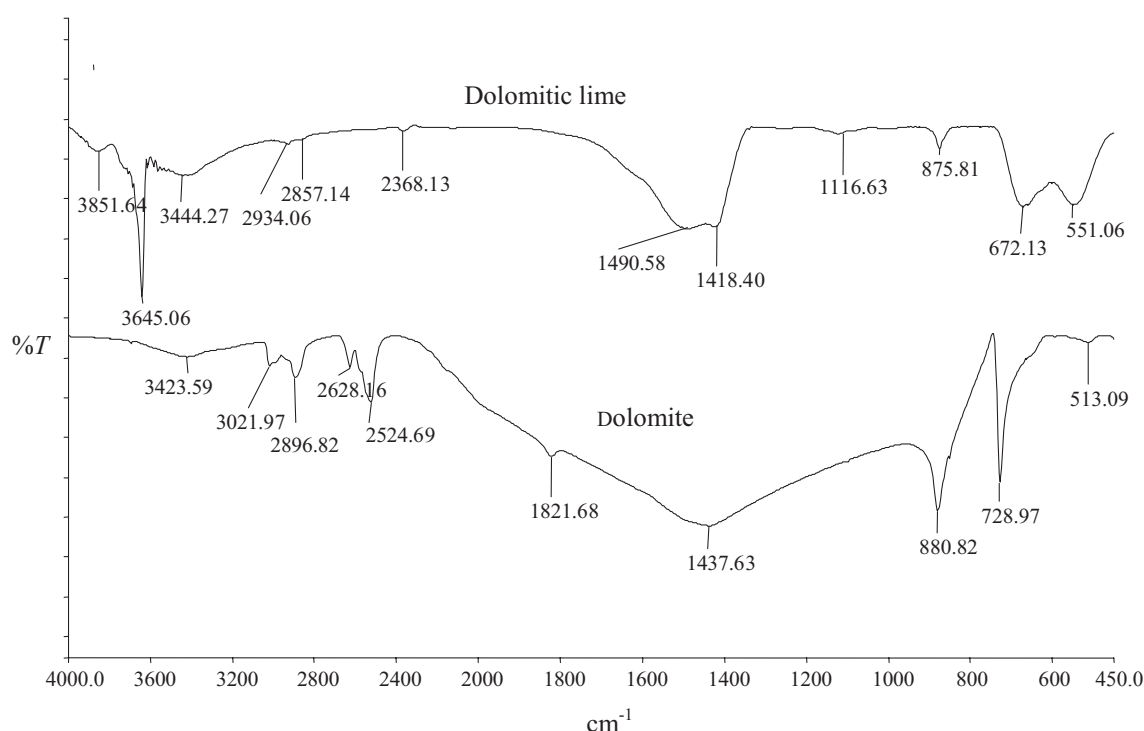


Fig. 3 – FTIR spectrum of the dolomite and dolomitic lime

The FTIR spectrum of dolomite and dolomite lime are shown in Fig. 3. According to the literature^{10,13,17}, dolomite shows custom FTIR absorption bands at 3020, 2626 and 730 cm^{-1} , and these values were used to identify the analysed dolomite samples. The FTIR bands at 1443, 882, and 728 cm^{-1} indicate the presence of CO_3^{2-} anions in the structure. From the FTIR spectra (Fig. 3), characteristic absorption bands at 2524.69, 1821.68, 880.82, and 728.97 cm^{-1} were observed, confirming the structure of dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$). The strong band at 3423.59 cm^{-1} is related to the presence of bound water in the sample. The FTIR analysis of dolomite lime ($\text{CaO} \cdot \text{MgO}$), obtained by annealing at 950 $^\circ\text{C}$, indicates structural transformation from dolomite. These changes in the FTIR spectra of the investigated samples recorded between 875.81 and 1418.40 cm^{-1} indicate a complete breakdown of CaCO_3 to CaO and CO_2 . The FTIR band at 551.06 cm^{-1} indicates the presence of MgO in the sample.

The SEM images with EDS analysis (Figs. 4 and 5) show the changes in morphology of the dolomite as a result of recrystallization at high temperatures. The EDS analysis confirmed the results of TG/DTG-DTA and FTIR analysis, i.e. the complete breakdown of carbonates at 950 $^\circ\text{C}$. The main components were Mg, Ca, and O, and no other peak for any other element could be found in the spectrum, which confirmed the purity of the dolomite lime. The presence of carbon components in dolomite, which was found in the EDS analysis, is related to the amount of the released CO_2 in the thermal analysis.

Conclusions

Based on the chemical, mineralogical, and granulometric characteristics, it can be concluded that the dolomitic lime obtained by calcination of dolomite (from location Đipalo Sinj, Croatia), may be used as base reagent in obtaining magnesium hydroxide from seawater. The TG/DTG-DTA analysis confirmed that the thermal decomposition of dolomite in air had completed at 950 $^\circ\text{C}$. A complete breakdown of CaCO_3 to CaO and CO_2 was proved by the characteristic FTIR bands between 875.81 and 1418.40 cm^{-1} . The characteristic FTIR band at 551.06 cm^{-1} indicated the presence of MgO in the sample, confirmed by SEM/EDS analysis. The EDS analysis showed that the main and only components of dolomite were Mg, Ca, and O, which confirmed the purity of the dolomite lime.

Table 4 – Granulometric characteristics of the dolomite sample obtained by LN-distribution function

Sample	$x_{g,f,50,3}^*$ /mm	σ_{\log}	x_{\min}^* /mm	x_{\max} /mm	\bar{x}_m /mm
Dolomite	0.067	0.561	0.0225	0.180	0.150

x_{\min}^* – minimum diameter of particles; x_{\max} – maximum diameter of particles;

$x_{g,f,50,3}^*$ – measure of particle range; σ_{\log} – parameter distribution; \bar{x}_m – average particle diameter by mass

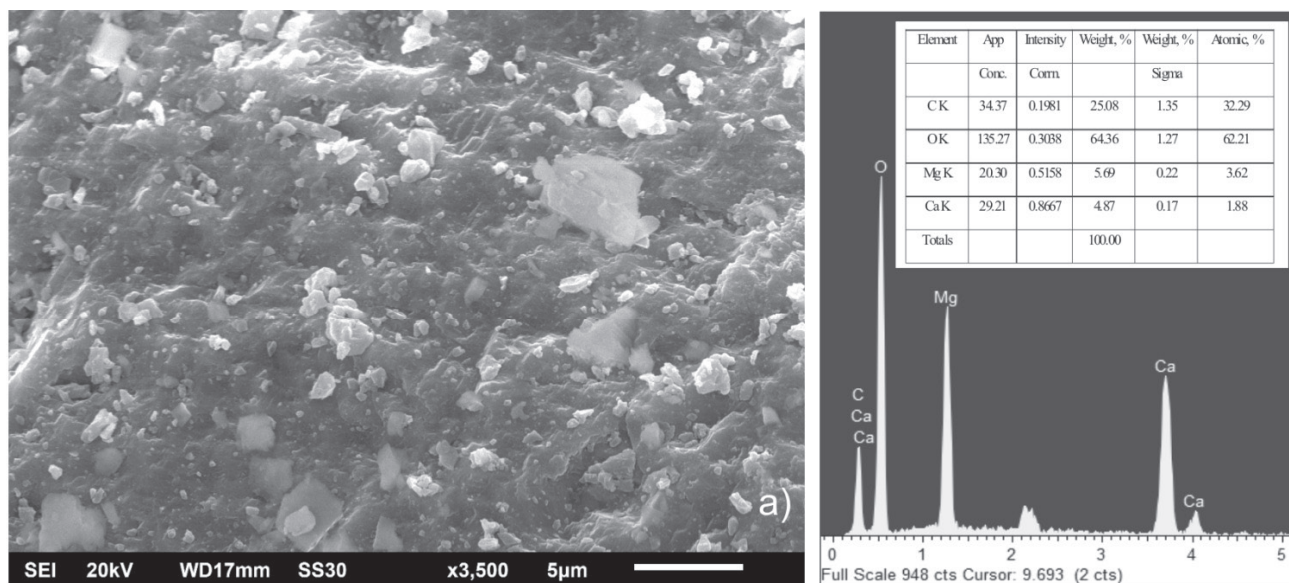


Fig. 4 – SEM image of dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) with EDS spectrum

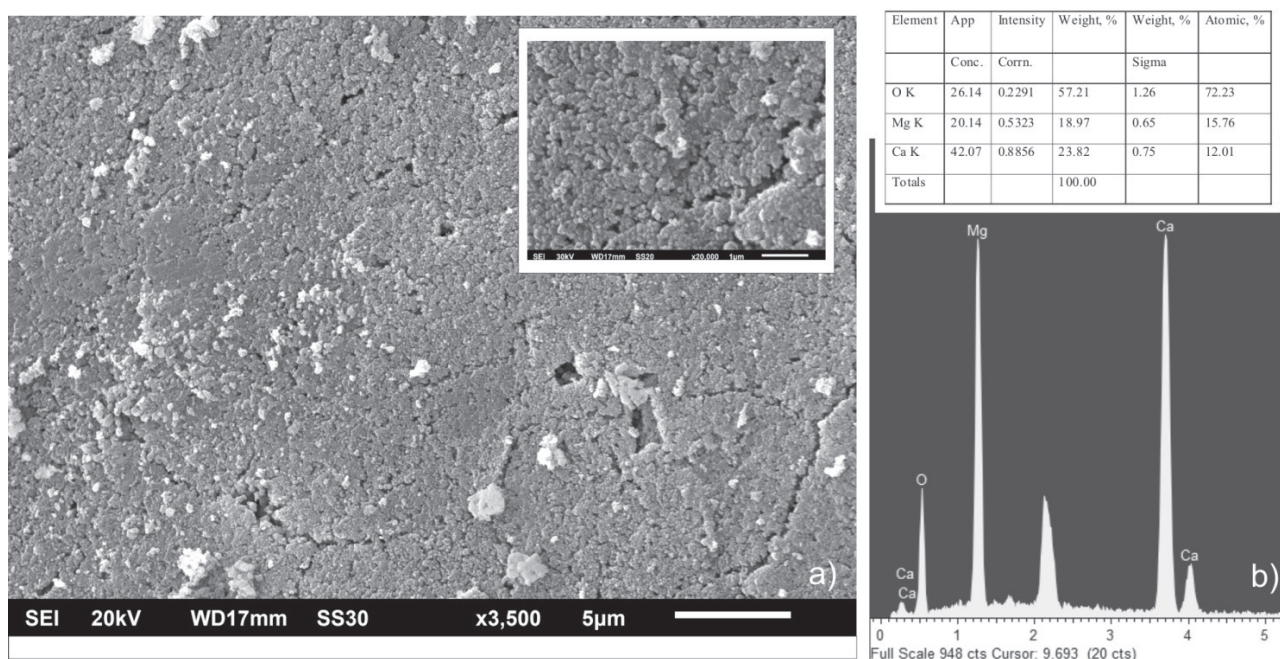


Fig. 5 – SEM image of dolomitic lime ($\text{CaO} \cdot \text{MgO}$) with EDS spectrum calcined at 950 °C/5 h in air

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