The 14th Symposium on Analytical and Environmental Problems, Szeged, 24 September 2007

INVESTIGATION ON THE CALCINATION BEHAVIOUR OF DIFFERENT PROVENIENCES DOLOMITES

Lidia Taubert[1], Minerva Cristea[2], Smaranda Mâşu[3], Marius Costache[2]

[1] Inorganic Chemistry Department, Institute of Chemistry Timişoara of the Romanian Academy, Bd.Mihai Viteazu nr.24, RO-300223 Timişoara, Romania
e-mail: lidiat@acad-icht.tm.edu.ro
[2] Physics Department, "Politehnica" University Timişoara, Bd.V. Pârvan nr.2, Timişoara
[3] National Research and Development Institute for Industrial Ecology - Timişoara Branch, P-ţa Victoriei nr.2, Timişoara, Romania

ABSTRACT

The dolomite mineral, magnesium and calcium carbonate (54,35% $CaCO_3$ şi 45,65% $MgCO_3$), occurs in nature in some rocks, which contains it in different ratios; if the content of dolomite is of 90-100%, the name of the mineral is extended to the rock too. Romanian deposits are located in metamorphic and sedimentation formation of the Eastern and Meridional Carpathians, of the Western Mountains and of Dobrogea. The complete characterization of dolomites is determinant, regarding the establishment of a feasible direction for the processing and utilization of these resources with magnesium and calcium carbonates content. The paper presents some aspects concerning the dolomites from the Romanian deposits of Voşlobeni, Măgureni, Buru. The geographical localization and the geological description are summerized from the professional literature. The chemical composition, as well as some physical and mechanical properties were established by own contributions, both for raw dolomites and for their burning products. A comparative study including the dolomites of different proveniences was realised. The caracterization of these dolomites is determining in order to establish practical applications for each of them.

INTRODUCTION

Naturally occuring dolomite [$CaMg(CO_3)_2$] is a double salt of calcium and magnesium carbonate. Dolomite is a mineral which has received a great deal of attention in recent years, resulting in numerous papers considering its various properties [1-3].
This mineral is a major and cheap source of magnesium. This mineral can be used as a food and fodder additive in order to compensate the magnesium deficiency. Dolomite usage is increasingly important in different branches of industry, such as the food and pharmaceutical industries, production of fertilizers, glass, building materials and even the kinescopes (picture tube) for color television. Unfortunately, the dolomite is now used mainly as a building material or as filler for glass, plastics and colors, in spite of its ability to adsorb certain poisonous substances [1].
The thermal decomposition of dolomite from northwest Ohio has been widely studied, in an inert nitrogen (N_2) atmosphere, and in a vacuum [4].
The thermal decomposition of dolomite in a CO_2 atmosphere forms the basis of experimental industrial procceses, designed to utilize the Ca and Mg carbonates of dolomite as raw materials for the production of Portland cement and magnesium-based products respectively. Some samples were also calcined in air to establish the thermal decomposition characteristics of the dolomitic material, with the same chemical and mineralogical composition [5-7].

The thermal behaviour and the kinetics of decomposition were studied using the Arrhenius equation applied to solid-state reactions [4]. It was found that the dolomite supposedly decomposes via a zero order mechanism and the energy of activation for the decomposition of dolomite was 175.05 kJ/mol. The kinetic parameters and mechanism remain unaffected by a change in flow rate, heating rate and sample size.
As can be seen from the literature, the physico-chemical properties of dolomite have not been completely investigated [1].
The geologic researches had as result the identification of numerous deposits of dolomite in our country, which can integrally satisfy the requirement of our economy.
This paper is aimed at presenting the chemical composition, as well as some physical and mechanical properties, both for some raw dolomites from different locations in Romania and for their burning products.

MATERIALS and METHODS

The studied Romanian dolomites are located in formations of the Eastern and Meridional Carpathians, as well as of the Western Mountains (Table 1).

Table 1. Localization and characteristics of some Romanian dolomites

Formation - deposit geographical localization	**Characteristics**
Voşlobeni Harghita district; situated in the crystalline massive of Giurgeu (central unit of the Eastern Carpathians), parallel to Gheorghieni depression	White-grey coloured and compact dolomites, but with numerous diaclases; at upper part of the deposit: mineral pockets or even narrow layers of wollastonite and tremolite (silicates). Chemical analyses: 20.56 - 21.70% MgO; 30.56 -32.97% CaO; 0.01 - 0.08% Fe_2O_3; 0.01 - 0.06% Al_2O_3
Măgureni Maramureş district	Low mechanical resistance of rock; dolomite with the best chemical composition
Buru Cluj district, near Turda: Surduc	Big reserves; limited utilization, due to the high content of silica, included in the mass of dolomite

The raw dolomites were fashioned as cube-test specimens of 20 mm side. After their calcination, the compression resistance was measured. In order to determine the total porosity, fractionary material of 20-30 mm sizes from the quarry was calcined and then it was utilized, according to the method presented in a previous paper [3]. The evaluation of total porosity is based on the measuring of density by the pycnometer method and of apparent density by hydrostatics weighing. The chemical composition of native Voşlobeni and Măgureni type dolomites was established by complexometric and gravimetric ways. The loss on ignition, by gravimetric way, was established. Investigated dolomites were decarbonated by calcination into an laboratory electric furnace with 10˚C/min heating rate, until 900˚C, 1000˚C, 1100˚C, when the temperature was constant a time range of 60, 120 and 180 minutes respectively.

RESULTS

By own contribution, we have added new information on the chemical composition for some Romanian dolomites of different proveniences. It is mentioned the monthly medium composition of native Voşlobeni type dolomite, during 2 periods of time, summing up 4-5 years. From our experimental data, it can be noticed that the content of major components has varied in narrow limits; so, the calcium oxide content is situated in the range of 30.28 - 31.52% CaO and magnesium oxide content varied between 20.16-21.97% MgO. On the other side, the impurities content has varied in large limits, namely 0.27-3.91% SiO_2 and 0.15-2.58% R_2O_3 (iron and aluminim oxides).

The chemical composition of dolomites from Măgureni deposit depends on depth of excavation, in the following way: a) until depthes of 20-30 m, it is variable; b) on the next segment, between 30 and 180 m, it varies in narrow limits; c) over 180 m, this becomes stable in the following form: 20.10-21.95% MgO, 30.34-32.50% CaO, 0.01-0.59% SiO_2, 0.11-0.39% Fe_2O_3, 0.15-0.53% Al_2O_3.

Results on the total porosity and on the compression resistance of calcinated samples for different thermal regimes, in Figures 1 and 2, are presented.

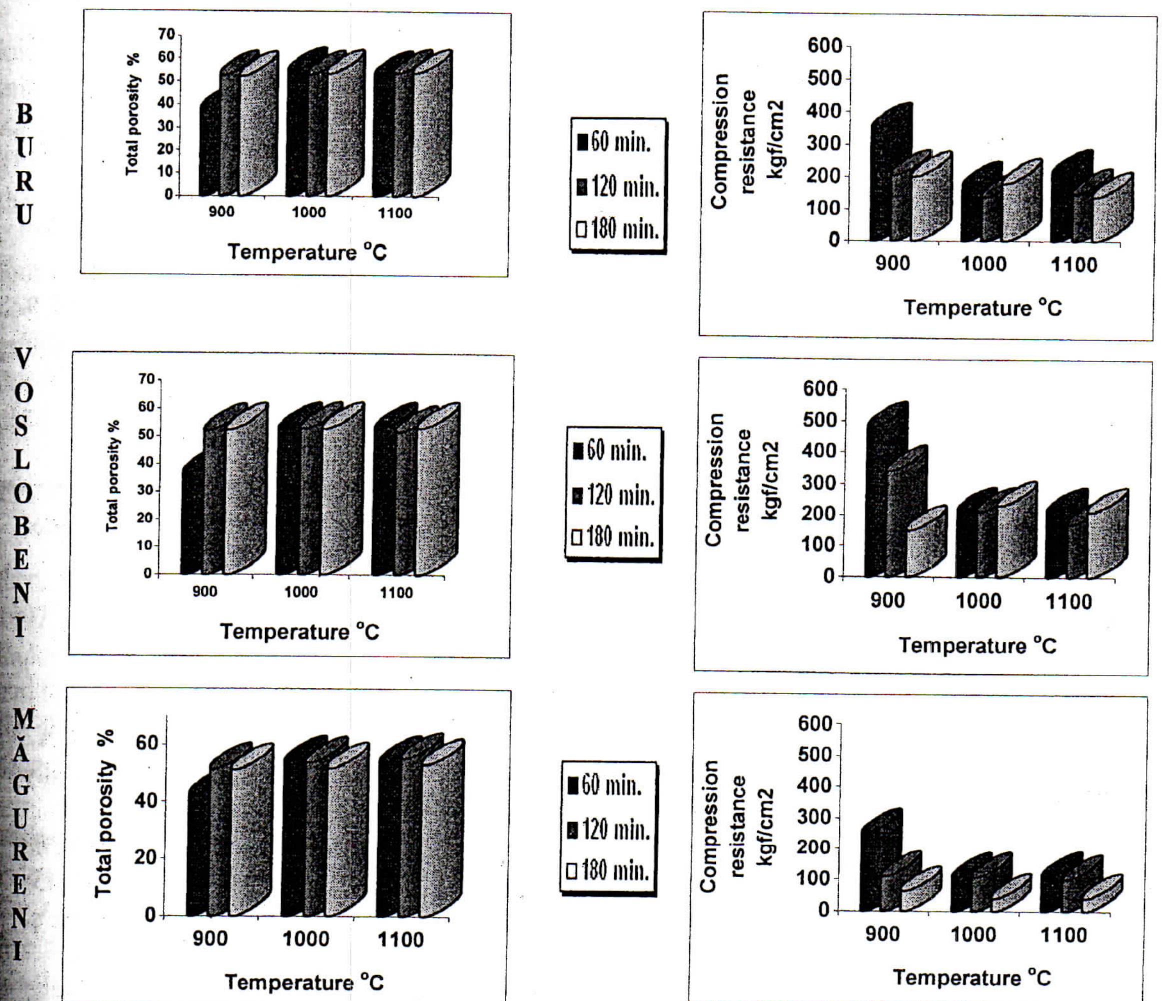

Fig. 1. Dependence of the total porosity of dolomites on calcination temperature

Fig. 2. Dependence of the compression resistance of dolomites on calcination temperature

The porosity and the compression resistance depend on the rock origin and on the burning conditions. In our case, for the burning products of the calcinated dolomites, it can be noticed, a sharp change of their values in the temperature regime which generates accentuated differences of the loss on ignition (table 2). The values of total porosity are close, being about 3% when the loss on ignition is 46%, for all calcinated dolomites, excepting the partial calcinated dolomites with 29% loss on ignition and porosity of 38% respectively.

Table 2. Properties of the calcinated dolomites at 900°C

Sample	Burning time, hours	Loss on ignition, %	Density, g/cm^3	Apparent density, g/cm^3	Apparent porosity, %	Total porosity, %	Compression resistance, kgf/cm^2
B 1	1	29.27	3.162	1.959	32.59	30.05	350
B 2	2	47.01	3.341	1.580	50.24	52.71	205
V 1	1	29.90	3.111	1.969	34.22	36.71	480
V 2	2	46.38	3.230	1.548	49.83	52.07	340
M 1	1	28.64	3.147	1.812	38.12	42.42	250
M 2	2	46.98	3.160	1.534	49.81	51.45	110

It been found that the compression resistance (R) of calcination products increases in the order $R_{Măgureni} < R_{Buru} < R_{Voşlobeni}$. The compression resistance values of the total decarbonated dolomites are substantially diminished towards to the values for partial calcinated dolomites; for the best dolomites, namely of Voşlobeni type, from 480 to 200 kgf/cm^2 (fig.2, table 2).

CONCLUSIONS

- They are summarized data concerning geographical localization of some Romanian dolomites deposits and their caracteristics, which were selected from specialty literature.
- Chemical composition of the raw dolomites was established, by own contribution, following the variation in time for native Voşlobeni type dolomite, as well as the variation of chemical composition depending on depth of excavation for Măgureni type dolomites.
- For the calcination products of the mentioned proveniences dolomites, it is presented a comparative view of the total porosity and of the compression resistance.
- The characterization of dolomites from different poin of view is determinant regarding the establishment of fesable direction for the processing and utilization of these resources containing magnesium and calcium carbonates.

LIST OF REFERENCES

[1] Staszczuk P., Stefaniak E., Biliński B., Szymański E., Dobrowolski R., Jayaweera S.A.A.. (1997). Investigation on the adsorption properties and porosity of natural and thermally treated dolomite samples. *Powder Technology*. 92, p. 253-257.

[2] Taubert L. (2002). Utilization of waste from the magnesium products industry. *The 9th Symposium on Analitical and Environmental Problems, Szeged, Hungary*. Vol, p.41-45.

[3] Craiu C., Policec S., Menessy I., Taubert L. (1979). Considerații privind calcinarea şi hidratarea unor dolomite indigene. *Revista de Chimie, Romania*. 30, no.2, p.187-188.

[4] Samtani M., Dollimore D., Alexander K. S. (2002). Comparison of dolomite decomposition kinetics with related carbonates and the effect of procedural variables on its kinetic parameters, *Thermochimica Acta*. 392-393, p.135-145.

[5] Sharp J.H., Wilburn F.W. & McIntosh R.M. (1991). The Effect of Procedural Variables on TG, DTG and DTA Curves of Magnesite and Dolomite. *Journal of Thermal Analysis*. 37, p. 2021-2029.

[6] Viswanathan V.N., Ramana Rao D.V., Kumar K. & Raina S.J. (1979). Simultaneous Production of Magnesium Carbonate and Calcium Carbonate from Dolomites and Dolomitic Limestones. *International Journal of Mineral Processing*. 6, p. 73-83.

[7] Caceres P.G., Attiogbe E.K. (1997). Thermal decomposition of dolomite and the extraction of its constituents. *Minerals Engineering*. 10, no.10, p. 1165-1176.