Characterization of the Natural Dolomite from Thanh Liem Area, Vietnam, and Its Applications

Nguyen Thi Thanh Thao, Le Thi Duyen, and Phenglilern Sensousit

Abstract Natural dolomite is a common mineral in Thanh Liem area, Vietnam. Currently, many dolomite mines in the area have been searched, explored and put into operation, meeting raw materials for different fields of use. However, the literature evaluating the quality characteristics of limestone is limited. This paper aims to assess the quality of the natural dolomite in the study area by combining previous data and some new analytical results such as X-ray fluorescence (XRF), X-ray diffraction (XRD), the scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM–EDS), inductively coupled plasma mass spectrometry (ICP-MS) and differential thermal analysis-thermogravimetry (DTA-TG). The results show that the regional dolomite has good quality and can be used in many different fields. Dolomite ($CaMg(CO_3)_2$) was the predominant mineral in the samples, followed by calcite ($CaCO_3$) and other trace minerals (quartz,..). The main element oxide contents of CaO and MgO are 32.5–42.1%, and 12.7–19.6%, respectively. The content of other oxides such as Al_2O_3, T.Fe, SiO_2, MnO and K_2O is not significant. The mechanical and physical properties of the stone completely meet the fields of civil construction. In addition, to improve the quality of raw materials used for each field, some mineral processing charts of dolomite and their main applications are also presented in the paper. It will be useful information for planning, exploiting and using this dolomite effectively.

Keywords Dolomite · Dong Giao formation · Thanh Liem area

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1 Introduction

Dolomite is the name of a mineral with the chemical formula $CaMg(CO_3)_2$ and is also the name of a carbonate sedimentary rock. Dolomite rocks are made up mostly of the mineral dolomite. Dolomite was first described in 1791 by the French naturalist and geologist, Déodat Gratet de Dolomieu (1750–1801) [1]. The oxide composition in dolomite rock includes CaO of 30.41%, MgO of 21.86% and CO_2 of 47.73%. With the characteristics of the composition, physical and mechanical properties, as well as low cost, dolomite is selected to be used in many different fields such as road base material, a feed additive for livestock, a sintering agent and flux in metal processing, high-grade bricks, ceramics, for post-treatment of desalinated water [2–4].

In Vietnam, the potential of dolomite is quite large and they are distributed in many provinces such as Ninh Binh, Ha Nam, Yen Bai, Bac Kan, Thai Nguyen, Thanh Hoa, Nghe An, Lam Dong, Dak Lak… [2]. The origin of dolomite in Vietnam is mainly divided into two forms: primary sedimentary and metamorphic sedimentary. The carbonate sedimentary formations are mainly from Triassic to Devonian in the Dong Giao Formation (T_{2a} *dg*), the Bac Son Formation (CP *bs*), the Dai Thi Formation (D_1 *dd*), the Duong Dong Formation (D_{1-2} *dđ*)… The dolomite from metamorphic sedimentary mainly belongs to the Nui Vu Formation ($Є_1$ *nv*), the Dac Uy Formation ($Є_2$ *du*), the Cam Duong Formation ($Є_2$ *cđ*) and the Sinh Vinh Formation (O_3-S_1 *sv*)… [5]. Depending on the origin and formation conditions, characteristics of quality and physicochemical properties of dolomite are different, and therefore, the field of use for each type of dolomite is also different. Thus, it is necessary to evaluate the quality of dolomite rock in each area.

Thanh Liem area, Vietnam, is an area with great potential for dolomite materials. Although many small mines are being exploited, there are limited studies on the quality of the dolomite systematically in the area. This paper aims to assess the quality of the natural dolomite in the study area by combining previous data and some new analytical results. Some mineral processing charts of dolomite and their main applications also are presented in the paper. It will be useful information for planning, exploiting and using this dolomite effectively.

2 Geological Characteristics

In the study area, the most common are the Tan Lac, Dong Giao formations and the undivided Quaternary sediments. The Tan Lac Formation has black clay sediments that meet the criteria of being used as a cement additive. The Tan Lac Formation has a transitional relationship with the Dong Giao Formation. The sediments of the Dong Giao Formation are exposed to a strip extending from the northwest to the southeast, concentrating more in the southwest and the garbage strip in the central area of the study area. Based on the petrographic composition, the formation is divided into lower and upper strata. The lower sub-formation (T_{2a} dg_1) consists of dolomite lime

interspersed with a thin layer of clay lime. The rock is gray, light gray, medium to thickly layered structure with a thickness of 400–800 m. The upper sub-formation (T_{2a} dg_2) is limestone layered thinly to gray–green mass, interspersed with lime clay and dolomite lime with a thickness of 500–900 m. undivided Quaternary (Q) is distributed over a large area of the province. They are mainly composed of dark gray clay and sand, gray ash of marine origin, containing plant remains, and lenticular peat (Fig. 1).

3 Materials and Analytical Methods

Natural dolomite samples were taken at the typical outcrops in Thanh Liem area, Nam Ha province (Fig. 1). The samples were ground to a fine powder and homogenized using an agate mortar. A range of analytical methods, including petrographic microscopy, X-ray diffraction analysis (XRD), X-ray fluorescence (XRF), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM–EDS), inductively coupled plasma mass spectrometry (ICP-MS) and differential thermal analysis-thermogravimetry (DTA-TG), were used to assess the quality of the natural dolomite from the study area.

4 Results and Discussion

4.1 Characteristics of the Natural Dolomite from the Study Area

4.1.1 Mineral Composition

The results of the petrographic analysis show that in the studied sample, there are granular and rhombic dolomite aggregates with sizes from 0.05 to 0.8 mm (Fig. 2). Mixed with dolomite are calcite aggregates accounting for 2–20%, granular variation. The surface of dolomite is opaque and agglomerated, without polymorphic crystallization. The rock-forming components are uniformly distributed; they have a weakly oriented structure and a variable crystalline grain structure.

The results of mineral composition analysis by *X*-ray diffraction (XRD) method show that the dolomite samples in the study area have mainly dolomite minerals (79–98%) and calcite from few to 20% (Fig. 3). The XRD pattern shows that dolomite mineral (Do) is the main mineral in the sample with typical XRD peaks at 24.0°, 30.9°, 37.3°, 41.1°, 44.9°, 51.1°, 60.0° and 67.4° (Fig. 3a) [6]. The FT-IR pattern in Fig. 3b indicates that dolomite mineral (Ca, $Mg(CO_3)_2$) is the significant mineral in the sample with the presence of the bands at 3020 cm^{-1}, 2627 cm^{-1} and 728 cm^{-1} (Fig. 3b). The FT-IR bands detected at 3020 cm^{-1} and 2627 cm^{-1} are combination

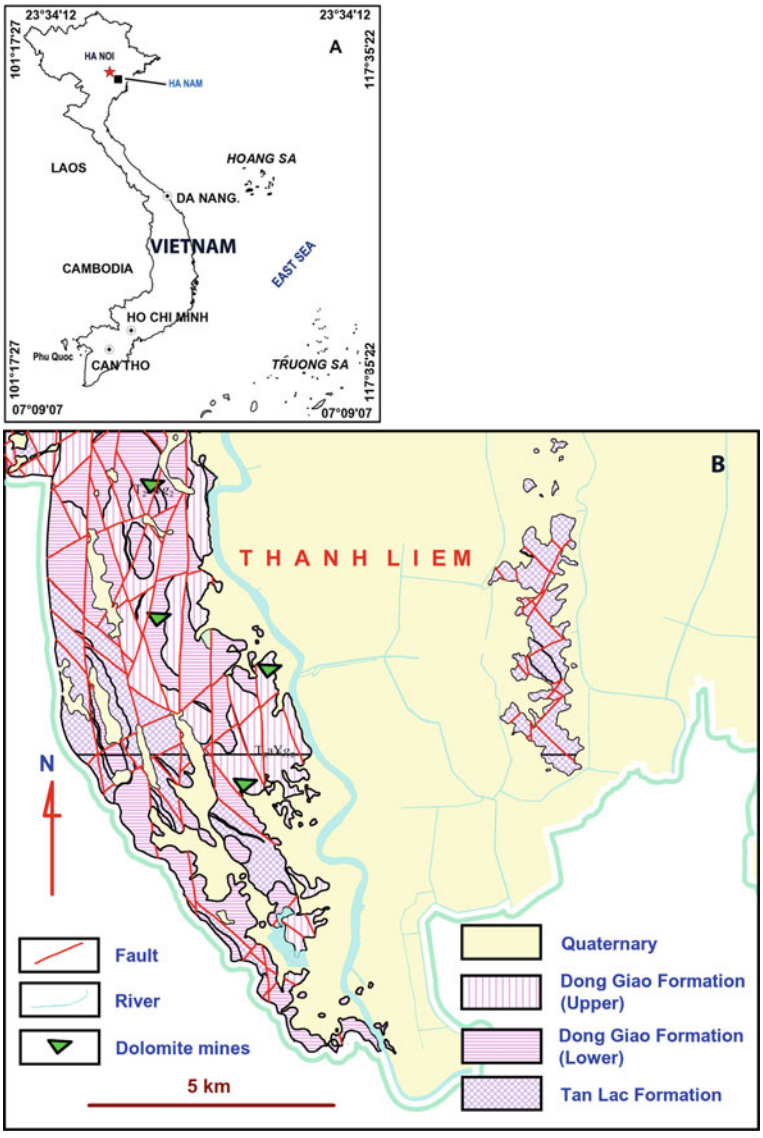

Fig. 1 Location of the study area **a** and geological map of Thanh Liem area **b**

frequencies [7], and the band at 728 cm^{-1} is assigned to the in-plane bending mode of CO_3^{2-} in the dolomite structure [8]. The appearance of both the 2627 cm^{-1} and 728 cm^{-1} absorption bands in a sample is especially useful for indicating the presence of dolomite.

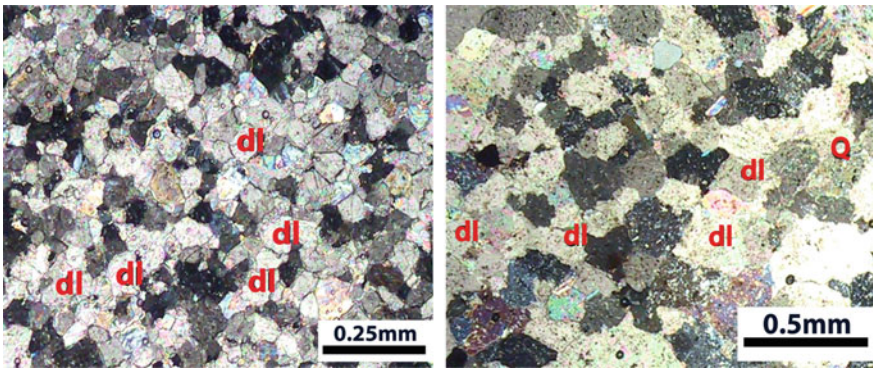

Fig. 2 Petrographic images of the natural dolomite from Thanh Liem area (*dl—Dolomite; Q–Quartz*)

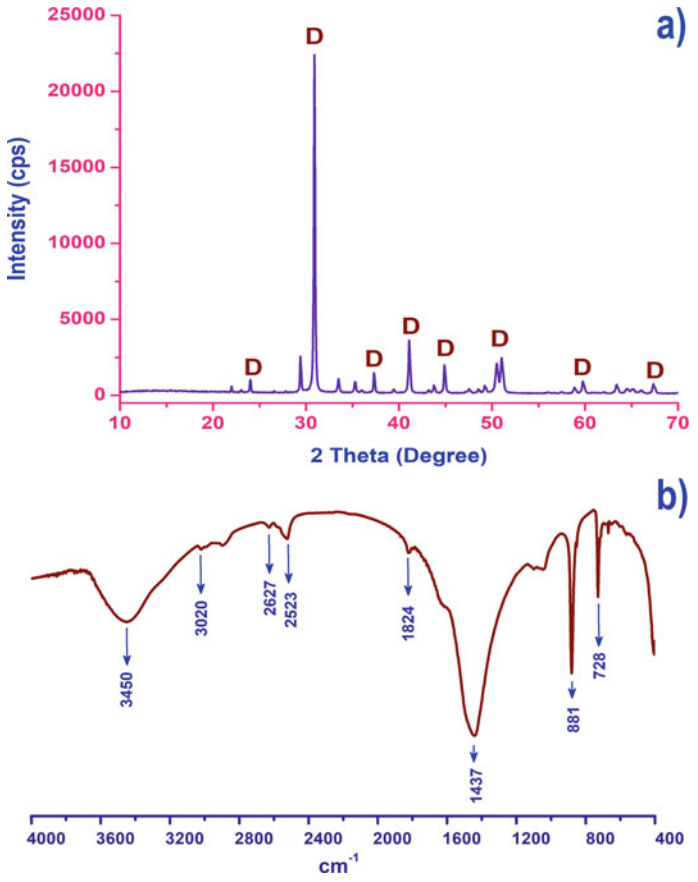

Fig. 3 XRD **a** and FT-IR **b** patterns of the natural dolomite from Thanh Liem area (*D—Dolomite*)

Table 1 Chemical composition of the natural dolomite from the study area

Chemical composition $\frac{\text{min} \div \text{max}}{\text{average}}$ (%)			
CaO	MgO	Al_2O_3	T.Fe[a]
$\frac{32.5 \div 42.1}{35.9}$	$\frac{12.7 \div 19.6}{16.6}$	$\frac{0.01 \div 0.03}{0.02}$	$\frac{0.02 \div 0.09}{0.06}$
SiO_2	MnO	K_2O	LOI[b]
$\frac{0.25 \div 0.28}{0.26}$	$\frac{0.01 \div 0.01}{0.01}$	$\frac{0.01 \div 0.02}{0.02}$	$\frac{46.7 \div 47.8}{47.2}$

Note [a]Total iron content; [b]Loss on ignition

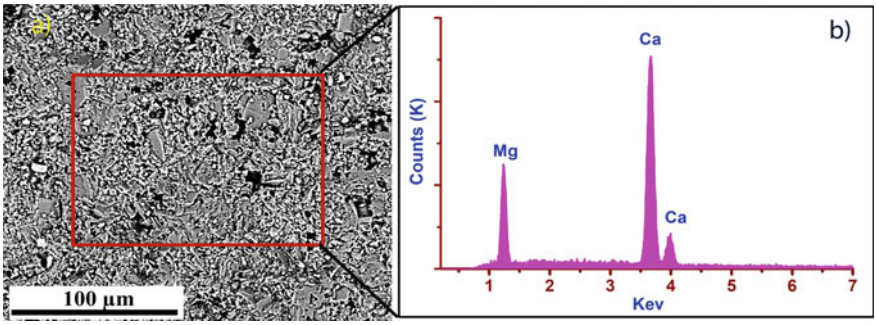

Fig. 4 SEM image: **a** and EDS result **b** of the natural dolomite from Thanh Liem area

4.1.2 Chemical Composition

Average chemical compositions of the natural dolomite from the study area are presented in Table 1. The results show that the main element oxide contents of CaO and MgO are 32.5 ÷ 42.1%, and 12.7 ÷ 19.6%, respectively. The content of other oxides such as Al_2O_3, T.Fe, SiO_2, MnO and K_2O is not significant. This result is consistent with EDS results with mainly Ca and Mg peaks, indicating the existence of quite pure dolomite (Fig. 4).

4.1.3 Trace Elements in the Natural Dolomite from the Study Area

To evaluate the composition of trace elements in dolomite, ICP-MS analytical method was used to analyze some dolomite samples in the study area. The results show that the metal elements in the rock are very small such as Cu: 5.257 ppm; Zn: 6.623 ppm. Precious and rare elements and radioactive elements with very low content (Th: 0.528 ppm; U: 0.488 ppm; …). This implies that the natural dolomite in the study area can be used for different applications (Table 2).

Table 2 Average trace elements in of the natural dolomite from the study area

Elem	(ppm)	Elem	(ppm)	Elem	(ppm)	Elem	(ppm)
Li	2.969	Cu	5.257	Nb	5.014	Ta	0.056
Be	0.113	Zn	6.622	Mo	0.152	W	9.339
P	0.062	Ga	0.153	Ag	0.046	Au	0.773
K	87.251	As	16.141	Ba	5.450	Pb	1.845
Ti	8.384	Se	5.147	La	1.581	Bi	0.093
V	9.878	Rb	0.548	Ce	2.946	Th	0.528
Co	0.867	Sr	122.108	Nd	1.468	U	0.488
Ni	2.224	Y	1.759	Hf	0.404	–	–

4.1.4 Physicomechanical Properties

The results of mechanical and physical parameters of dolomite rock samples in Thanh Liem area, Ha Nam province are shown in Table 3. The results show that dolomite has good physical and mechanical properties, meeting the fields of civil construction.

Table 3 Summary of mechanical and physical parameters of dolomite rock samples in Thanh Liem area, Ha Nam province

Parameters	Unit	Max	Min	Average
Natural humidity (W)	%	0.24	0.13	0.18
Water absorption (W_{hn})	%	0.48	0.46	0.47
Natural volumetric mass (γ_0)	g/cm^3	2.69	2.67	2.685
Saturated volumetric mass (γ_{bh})	g/cm^3	2.70	2.69	2.695
Dry volumetric weight (γ_c)	g/cm^3	2.69	2.66	2.67
Density (ρ)	g/cm^3	2.74	2.73	2.735
Porosity (n)	%	2.02	2.00	2.01
Shear strength	kG/cm^2	88	86	87
Natural compressive strength (δ_{tn})	kG/cm^2	703	400	540
Dry compressive strength (δ_k)	kG/cm^2	693	637	665
Saturated compressive strength (δ_{bh})	kG/cm^2	673	387	537
Dry tensile strength (δ_k)	kG/cm^2	69	64	66
Saturated tensile strength (δ_{bh})	kG/cm^2	64	59	61
Dry strength coefficient (f_k)	kG/cm^2	6.93	6.37	6.65
Saturated strength coefficient (f_{bh})	kG/cm^2	6.45	5.85	6.15

4.1.5 Thermal Behavior of Natural Thanh Liem Dolomite

The typical DTA-TG curve of the dolomite sample from Thanh Liem area is presented in Fig. 5. It can be seen that the observed weight loss was 46.29% between 600 °C and 850 °C. The weight loss detected in the temperature range of 100–120 °C, was followed by a weight loss attributed to the decomposition of carbonates. The weight loss in this temperature range can be attributed to the chemically bound water [9, 10].

4.2 Mineral Processing of the Natural Dolomite of the Study Area

With good quality, Thanh Liem area dolomite can be used for different applications. Depending on each application, steps in mineral processing are designed differently. Figure 6 presents two dolomite processing schemes: dolomite as raw material for ferrous metallurgy and high-quality dolomite (Fig. 6).

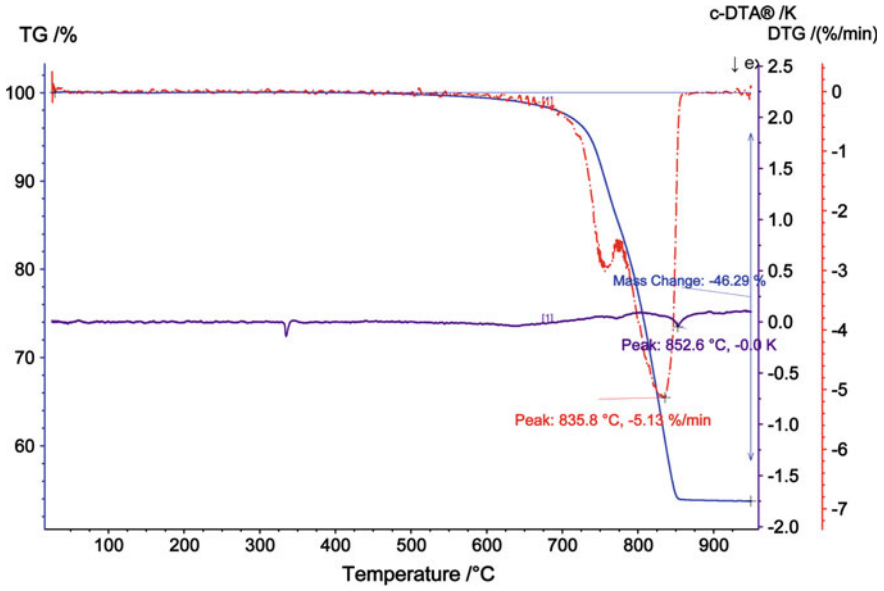

Fig. 5 DTA-TGA curves of the natural dolomite from Thanh Liem area

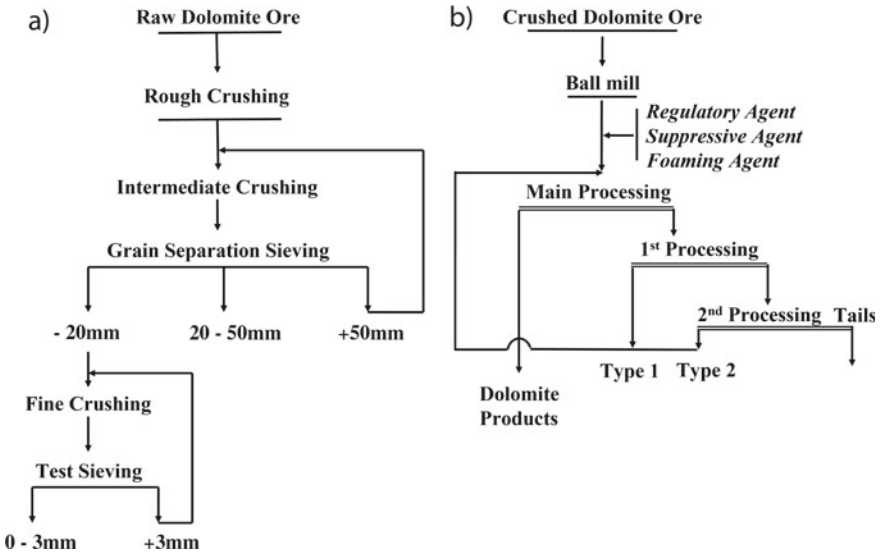

Fig. 6 Flowsheets for the natural raw dolomite processing in the study area. **a**—For ferrous metallurgy; **b**—For high-quality dolomite)

4.3 Some Applications of Dolomite Products

4.3.1 Producing Refractory Materials in Ferrous Metallurgy

Dolomite can be used as a flux or slag disintegration aid as well as in the preparation of sintering magnesium ores [11]. Dolomite used as flux in metallurgy has the following standards: MgO > 17–19%, SiO_2 < 6%, R_2O_3 + MnO < 5%, not mixed with S, P, particle size <25 mm below 8%, strength instantaneous compressive resistance >300 kg/cm^2. Therefore, dolomite used in sintering of metallurgical magnesium needs to meet the following requirements: CaO + MgO > 53%, MgO > 16%, insoluble residue < 2.5%, clay < 3%, particle size 5–75 mm accounting for 80%.

4.3.2 Producing Heat-Resistant Brick

Martensite is a self-adhesive powder made up of a mixture of magnetite and dolomite (containing 30–50% dolomite). Dolomite concrete bricks have high fire resistance, so they are used to cover electric furnaces and steel rolling furnaces [12]. Here, dolomite is required to be good at resisting fire and slag in the sintering state, that is, it does not decompose into mixtures of silicates and alumosilicates Mg, Ca, Fe and Mn which are easy to melt and easily corrode.

The oxides of Fe, Al, Ti and Mn are all beneficial because they improve the sintering stage and reduce the hydration of the sintered dolomite powder. However, if the amount of these compounds is too high, a large amount of calcium aluminate will appear, causing the sintered dolomite powder to reduce its fire resistance. The presence of free CaO will make the product more resistant to fire, but on the other hand, CaO is very sensitive to CO_2 in the air as well as reacts with Al, Fe to create fusible compounds.

4.3.3 Producing Magnesium Metal

Dolomite can be used to obtain Mg metal by the methods of silicon thermodynamics or electrolysis [13]. Dolomite material requirement for this application is MgO > 19.5%, $SiO_2 + Al_2O_3 + Fe_2O_3 + Mn_3O_4 < 2$ and > 5%, $Na_2O + K_2O < 0.2\%$, particle size 20–300 mm.

4.3.4 In the Chemical and Pharmaceutical Industry

In addition to the optimal materials such as magnesium, carnalite and saltwater, people also use dolomite to produce MgO. Since then, a series of important materials have been produced such as "white magnesium" (also known as "light magnesium" or "technical carbon magnesium" with the formula ($5MgO.4CO_2.6H_2O$), calcined magnesium (which is very light and absorbs gas). strong) used to make medicinal herbs, as heat insulators, catalysts, dye preparations, paints, aromatics, … [14].

4.3.5 In Environmental Treatment

Recently, the materials that are available, low cost and non-toxic materials are interested in many domestic scientists in the treatment of polluted water environment. Clay minerals which are often used to treat water pollution are mainly bentonite, vermiculite, kaolin and halloysite [15, 16]. However, natural clay materials have been used in many other fields with a high economic value, so their reserves are decreasing day by day. Therefore, finding alternative sources of raw materials is a necessary task, and dolomite is a potential source of raw materials for this application [17–19].

5 Conclusions

In conclusion, to assess the quality of the natural dolomite, samples were taken from the typical outcrops in Thanh Liem area. Analysis methods of XRD, XRF, SEM–EDS, ICP-MS and DTA-TG were used to characterize the dolomites. The

analytical results indicate that dolomite ($CaMg(CO_3)_2$) was the predominant mineral in the samples, followed by calcite ($CaCO_3$) and other trace minerals (quartz,..). The main element oxide contents of CaO and MgO are 32.5–42.1%, and 12.7–19.6%, respectively. The content of other oxides such as Al_2O_3, T.Fe, SiO_2, MnO and K_2O is not significant. The mechanical and physical properties of the stone completely meet the fields of civil construction. The metal elements in the rock are very small such as Cu: 5.257 ppm; Zn: 6.623 ppm. Precious and rare elements and radioactive elements with very low content (Th: 0.528 ppm; U: 0.488 ppm; …). Two flowsheets for the natural raw dolomite processing in the study area were set up with many technological solutions such as selective crushing and chemical processing to increase the quality of dolomite. In general, the quality of dolomite in the study area is of good quality, which can be used for many different application areas. It will be useful information for planning, exploiting and using this dolomite effectively.

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