CHARACTERISTICS OF DOLOMITE FROM SWABI, KHYBER PAKHTUNKHWA FOR ITS USE AS A RAW MATERIAL IN FERTILIZER PRODUCTION

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ABSTRACT

The potential of dolomite $CaMg(CO_3)_2$ from the Swabi district of Khyber Pakhtunkhwa as a raw material in fertilizer production was investigated in this paper. Dolomite was found as a major mineral phase when investigated via X-ray diffractometer (XRD). This was fully supported by X-ray fluorescence (XRF) results. TGA analysis indicated that the dolomite phase decomposes at about 774^{o}C when it treated with heat. Temperature usually plays a significant role in producing MgO and CaO from dolomite. The magnesium oxide produced during the decomposition process can be allowed to react with nitric acid to produce magnesium nitrite, which is a type of fertilizer that is widely used in agriculture. Because of the high content of the magnesium in local dolomite, it can be used as raw materials in fertilizer production.

Keywords: Dolomite, Fertilizer, TGA, XRD, XRF.

1. INTRODUCTION

Dolomite is a common sedimentary rock-forming mineral that can found in massive beds several hundred feet thick. It differ from calcite, $CaCO_3$, in the addition of magnesium ions to make the formula, $CaMg(CO_3)_2$. The dolomite cell parameters at room-temperature are a=b=4.8076Å, c=16.0103Å, α=β=90°, γ=120° and V=320.47 Å^3, for a rhombohedral cell in the $R\bar{3}$ space group[1].

Dolomite is relatively soft and easily crushed to a fine powder, which is used as agricultural lime ('aglime') by farmers to reduce soil acidity and also to adjust magnesium deficiencies. Dolomite is equally good as limestone in neutralizing soil acidity but magnesium is also an important element itself as a plant nutrient[2-3]. Dolomite is an inexpensive material. Its structure contains alternating planes of Ca^{2+} and Mg^{2+} cations with ideal formula $CaMg(CO_3)_2$. Occasionally one element may have a slightly greater presence than the other[4]. It is also an important industrial mineral which is used as a source of both magnesium metal and magnesia in different branches of industry. It is used as a calcium and magnesium supplement in the pharmaceutical industry. The $MgCO_3$ part of the dolomitic structure functions as a source of Mg to microorganisms and is therefore used as an additive for fertilizer. For the same reason it is also used as an additive for food and is a common ingredient in health foods[5]. Further uses are in glass, and building materials. One of the main applications is in the field of refractory materials, in order to produce fire-resistant products, used in metallurgy, chemical and ceramic industries[6-8]. Dolomite was also used as transesterification catalyst for palm kernel oil[9] and adsorbents for substances such as iodine[10], dyes[11], copper (II)[12], lead (II) and cadmium (II)[13], CO_2[14] and so on. According to the statistic division, Government of Pakistan report on Census of mining and quarrying industries, dolomite production in Pakistan was 183,952 Metric Tons in the year 2005-06. Sindh province put highest share for this year which was ~44 % (80,921 metric tons) following Khyber Pakhtunkhwa 29.73 % (54,692 metric tons) and Punjab 26.13 % (48,085 metric tons). The lowest share in this sector was from Balochistan which stood just only at 0.13 % (254 metric tons)[15].

The objective of present study is to find the suitability of local dolomite to be used as a raw material in fertilizer production. To achieve this objective, experimental techniques such as X-ray fluorescence (XRF), thermal gravimetric analysis (TGA)/differential thermal analysis (DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical microscopy were applied. Because of the high content of the magnesium in this dolomite, it can be used as raw materials in fertilizer production.

2. MATERIALS AND METHOD

For the present study, dolomite sample from district Swabi of Khyber Pakhtunkhwa province was collected (Latitude, $34^o21^/39$, Longitude, $72^o41^/81$). The original sample was rock present and has to be grinded with agate mortar and pestle until it changes to powder form. Thin sections were prepared and observed under Inverted Metallurgical Microscope (PMG-3, Olympus, Japan) with Olympus DP-12 camera connected to PC. The analysis was performed at 5-20 times magnification. Sizes of grains were determined.

Pieces of rock sample was crushed and pulverized for the chemical analysis. WD-XRF, present at Advanced Geo Sciences Research Laboratories, Geological Survey of Pakistan, Islamabad was used for chemical analysis of all the major elements in oxide form using glass heat. Loss on ignition was measured at 1000^oC. Phase analysis was done using Philips X-ray diffractometer (XRD), operating at 40 kV power and 40 mA current, with Cu kα radiations (λ = 1.54 Å) present at College of Engineering, Boise State University, Idaho, USA. The sample was scanned from $2\theta = 20^o$ to 60^o, with a count time of 1s/step and 0.02^o step angle. For XRD analysis, powdered samples were used and filled into the glass sample holders. The JCPDS database (powder diffraction file from International Center for Diffraction Data) incorporated in the search-match program suit was used for the identifications of the components.

The thermal analyses were performed in a simultaneous TG/DTA (Perkin Elmer, Diamond Series) present at Centralized Resource Laboratory (CRL), University of Peshawar. The experimental conditions were: (a) continuous heating from room temperature to 1200 ^oC at a heating rate of 10 ^oC/min; (b) N_2-gas dynamic atmosphere (20 ml/min); (c) alumina, crucible; (d) sample mass: 7 mg approximately. The thermal analysis permitted to obtain the following data: (i) reactions peak temperature and main effect (endothermic or exothermic); (ii) content of bound water, which is the weight loss in the temperature 50–500 ◦C; and (iii) content of CO_2 released during the decomposition of carbonate phases.

For scanning electron microscopy (SEM), ~4x4x4 mm^3 piece was cut with a precision low speed diamond saw and polished with a Twin Prep 3™ grinding/polishing machine in the Materials Research Laboratory (MRL), University of Peshawar. Finally, the samples were mounted onto aluminum stubs with silver paint and gold coated in order to avoid charging in the SEM. The surface morphology and micro-regions of the sample were examined using a JEOL JSM 5910 SEM at the Centralized Resource Laboratory (CRL), University of Peshawar.

3. RESULTS AND DISCUSSION

(a) Optical Microscopy

Optical microscopy was used to evaluate the average size of the dolomite grains in Swabi district dolomite sample (Fig. 1). The average dolomite grain size was found to be 1.10 x 0.75 μm^2.

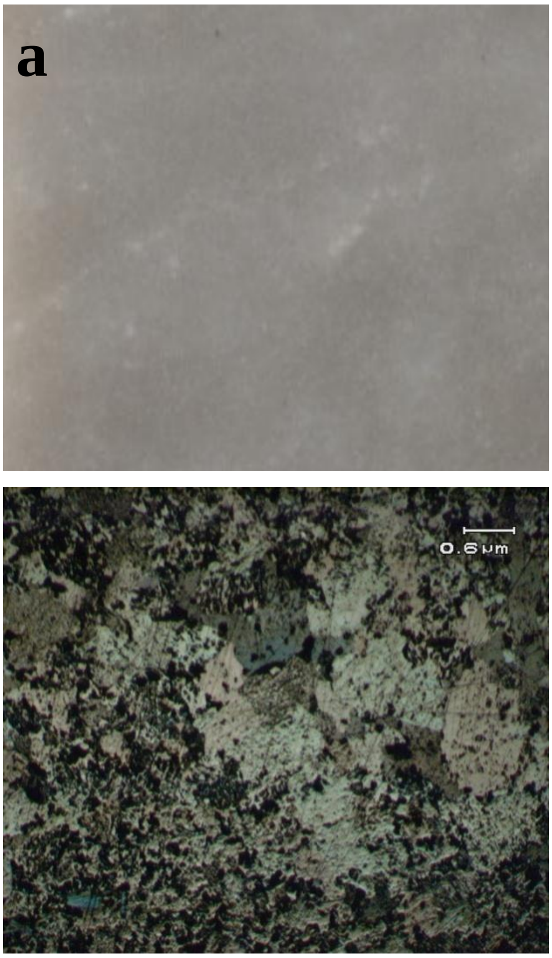

Figure 1a) Visual appearance of dolomite sample with ordinary camera and b) thin section photomicrograph of dolomite sample.

(b) X-ray Fluorescence (XRF)

A dolomite sample from Swabi district of Khyber Pakhtunkhwa was analyzed by the X-ray fluorescence spectroscopy using a Philips WD-XRF. An analysis was conducted for determining the major oxides of the powdered sample. Powders were used to make fusion bead for analyzing the following elements, Fe, Ti, Ca, K, Si, Al, Mg, Na, Mn, Ba, S, and P. Result is presented in table 1. Table 1 shows that investigated sample contains 34.500 wt% CaO, while the 17.080 wt% MgO content in the sample is connected to common dolomite. The main undesirable impurities in the sample are K_2O, TiO_2, Fe_2O_3 and MnO which occur in very small quantities. Quartz or SiO_2 is the most common mineral that contaminates the marbles. The investigated dolomite sample do not contains considerable amount of SiO_2 (2.524 wt%). Generally, the identification of CaO, Fe_2O_3, MgO, and SiO_2 is important to characterize the quality of the marble material. Iron and magnesium are admixed in the structural lattice of calcite as well as calc–silicate minerals. Generally, the theoretical composition of dolomite is 54 wt% $CaCO_3$ and 46 wt% $MgCO_3$.

(c) XRD Analysis

X-ray diffraction analysis was used to evaluate patterns considering the phase analysis and profile analysis. Figure 2 depicts the powder X-ray diffraction pattern of natural dolomite sample. The room temperature XRD pattern of the sample displays sharp diffractions that attributes to dolomite (JCPDS File card 11-78). Along with the major phase dolomite, calcite is detected as next constituent phase (JCPDS File card 5-586). The XRD pattern (Fig. 2) for untreated dolomite shows three peaks at

30θ, 41θ and 51θ. Smaller peaks were observed at 33θ, 37θ, 45θ, 50θ and 60θ. The peak at 29θ represents the existence of $CaCO_3$. Table 2 gives various Bragg reflections that are indexed using JCPDS Files card 11-78.

(d) Simultaneous Thermogravimetry and Differential Thermal Analysis (TG/DTA)

The decomposition of dolomite has been extensively studied, mainly by TGA/DTA, because of its mineralogical interest and industrial importance. The majority of above mentioned applications implies the decomposition of dolomite. Thermal processing is accompanied by structural changes within the solid product[3], causing a significant change of the crystallographic, morphological and textural properties. The correlation of the thermal data with the structural pattern should provide a broader understanding of these minerals in their natural occurrence[2]. According to the literature data[16-17], the thermal decomposition of dolomite occurs in air in two steps, as follows:

First reaction:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \quad (1)$$

Second reaction:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

The smaller size of magnesium with respect to calcium facilitates the magnesium mobility and thus the formation of CO_2 associated to MgO is kinetically favoured against the formation of CO_2 associated to CaO[17]. The decomposition of dolomite above 700 °C, corresponding to the first reaction, leads to changes in the chemical composition of the surface and in the porosity of this mineral[18]. The second reaction proceeds from 900 °C. Generally, the product of partial decomposition of dolomite (reaction (2)) consists of a rigid porous calcite and the fine powdered magnesium oxide[19]. Thermal decomposition behaviour of dolomite sample has been studied by Simultaneous Thermogravimetry and Differential Thermal Analysis (TG/DTA).

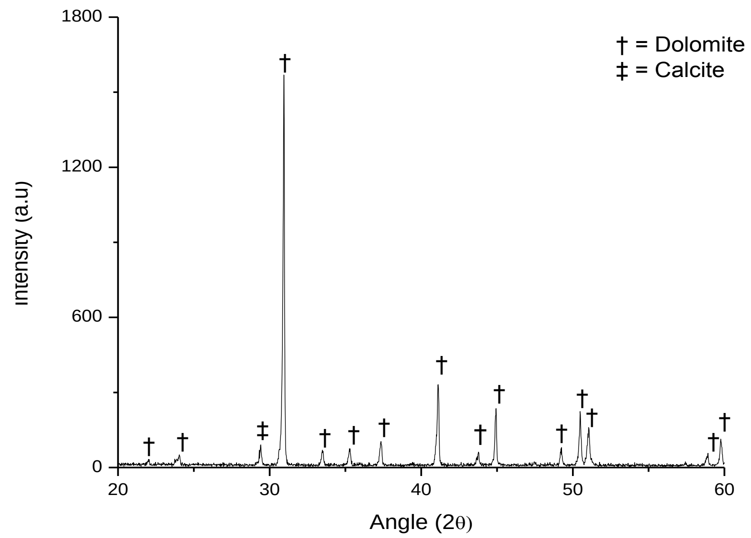

Figure 2. X-ray powder diagram of dolomite marble from Swabi, Khyber Pakhtunkhwa.

Table 1: Chemical compositions of dolomite marble sample from Swabi (KPK) (%).

Sample#	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	SrO	LOI
S-19	2.524	0.057	1.171	0.456	0.039	17.080	34.599	0.026	0.167	0.00	0.00	0.00	43.88

a. Thermogravimatric analysis

The typical TG plot (% wt. vs. temperature) for the thermal decomposition of local dolomite sample in an atmosphere of N_2 is presented in Figure 3. The observed weight loss was 0.830% below 600°C and between 600°C and 850°C; it was 43.809% while the overall weight loss remains as 45.066%. The weight loss detected in the temperature range 60–120°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. The DTG plot (derv. Wt. vs. temperature) shows endotherm at ~774^{o}C corresponding to reaction in equation 1. The small endotherm at ~1085^{o}C corresponds to reaction in equation 2. A third peak appears just before the magnesium carbonate portion of dolomite structure breaks down. This has a peak temperature of 607^{o}C. This peak is a genuine peak and also occurs as an endotherm in the DTA (differential thermal analysis) pattern (Fig. 4). This temperature is in the decomposition region for the pure magnesite. Pure magnesite has a peak decomposition temperature of 644^{o}C[5]. The difference in above temperature might indicate that this peak is due to a structural strain in the dolomite structure and not because of the spread magnesite. The endotherms below the 150^{o}C attributes to the dehydration. A small exothermic peak at ~598^{o}C shows that little crystalline behaviour take place before decomposition.

b. Differential thermal analysis

The typical DTA curve of dolomite sample is presented in Figure 4. The thermal curves representing the carbonate mineral are characterized by endothermic peaks at various temperatures caused by the evolution of carbon dioxide (figure 4). DTA curve of dolomite shows two endotherms at 607°C and 774°C. The first one begins at ~600°C, reaches a peak at 607°C and ends at ~620°C and the second one begins at ~740°C, reaches a peak at 774°C and ends at ~800°C. The higher temperature peak (774^{o}C) represents the decomposition of the dolomite structure, releasing carbon dioxide from the carbonate ion associated with magnesium part of the structure accompanied by the formation of calcite and magnesium oxide. A small peak at higher temperature of ~1085^{o}C represents the decomposition of calcite with the evolution of carbon dioxide. The high characteristic temperature indicates that the dolomite is in well-ordered crystalline structure, which is also confirmed through X-ray diffraction analysis. Smaller size of magnesium with respect to calcium facilitates the magnesium mobility and thus the formation of carbon dioxide associated to magnesium oxide is kinetically favoured against the formation of CO_2 associated to calcium oxide[17]. Presence of salt enhances the decomposition of dolomite[20]. The salts promote the formation of MgO and $CaCO_3$ during the early stage of decomposition.

c. Scanning Electron Microscopy (SEM)

Figure 5a shows the presence of discrete dolomite grains with some grains having sharp edges. The SEM indicated the presence of fine dolomite particles sticking to the dolomite crystals (fig. 5a). Fig. 5b shows the connected grains of dolomite with clear boundaries and varying size and shapes. SEM-EDS (energy dispersive spectroscopy) revealed the presence of calcium and magnesium i.e. dolomite grains with dark and bright contrast.

Table 2. Indexed XRD peaks for dolomite from Swabi (KPK).

Sr.#.	h	k	l	d(Å)obs	d(Å)cal	Diff. D(Å)	2θ (degree) obs	2θ (degree) cal	Diff. 2θ (degree)
1	1	0	1	4.026	4.03	-0.004	22.06	22.056	0.004
2	0	1	2	3.696	3.690	0.006	24.06	24.118	-0.058
3	1	0	4	3.032	3.035	-0.003	29.44	29.429	0.011
4	1	0	4	2.887	2.886	0.001	30.9503	30.986	-0.0357
5	0	0	6	2.674	2.670	0.004	33.48	33.563	-0.083
6	0	1	5	2.541	2.540	0.001	35.30	35.336	-0.036
7	1	1	0	2.405	2.405	0.000	37.3672	37.391	-0.0238
8	1	1	3	2.193	2.192	0.001	41.1361	41.181	-0.0449
9	0	2	1	2.065	2.066	-0.001	43.80	43.818	-0.018
10	2	0	2	2.015	2.015	0.000	44.9449	44.987	-0.0421
11	0	2	4	1.849	1.848	0.001	49.24	49.310	-0.070
12	0	1	8	1.805	1.804	0.001	50.5099	50.596	-0.0861
13	1	1	6	1.787	1.786	0.001	51.0751	51.143	-0.0679
14	2	1	1	1.566	1.567	-0.001	58.94	58.939	0.001
15	1	2	2	1.545	1.545	0.000	59.7932	59.863	-0.0698

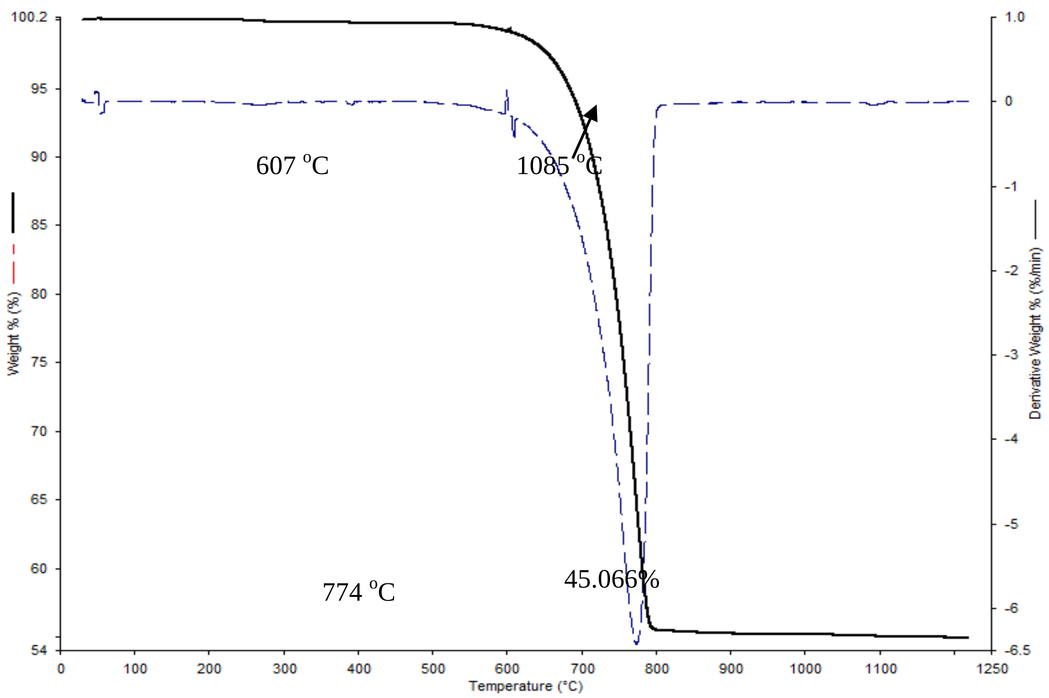

Figure 3. TG/DTG plot of dolomite sample collected a 10^{o}C/min in N_2 atmosphere (at 20 ml/min) showing its thermal decomposition temperature.

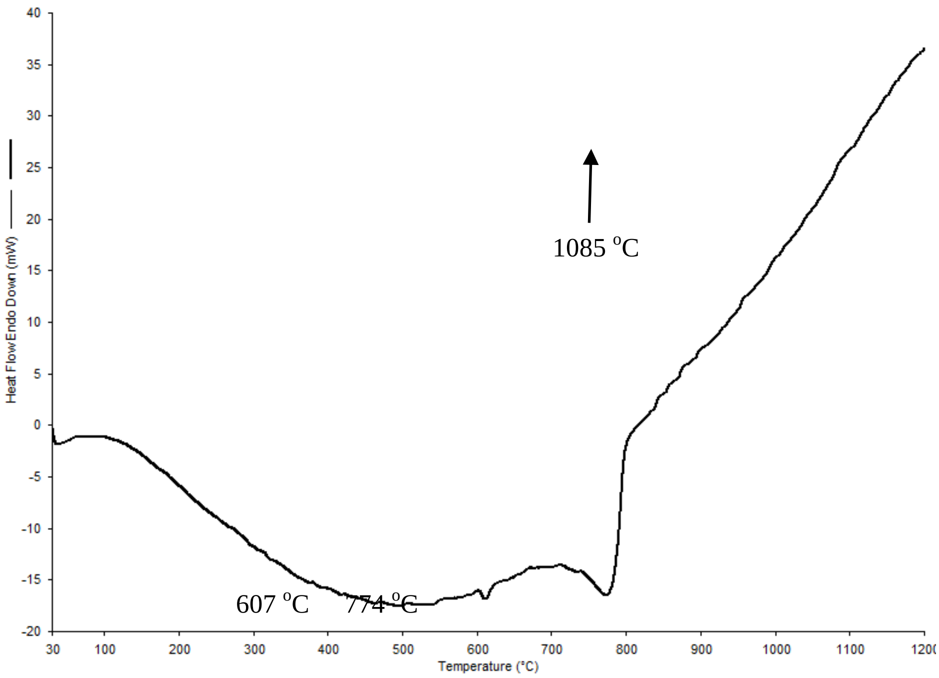

Figure 4. DTA pattern for dolomite sample, confirming the peaks observed in the DTG plot of the same sample.

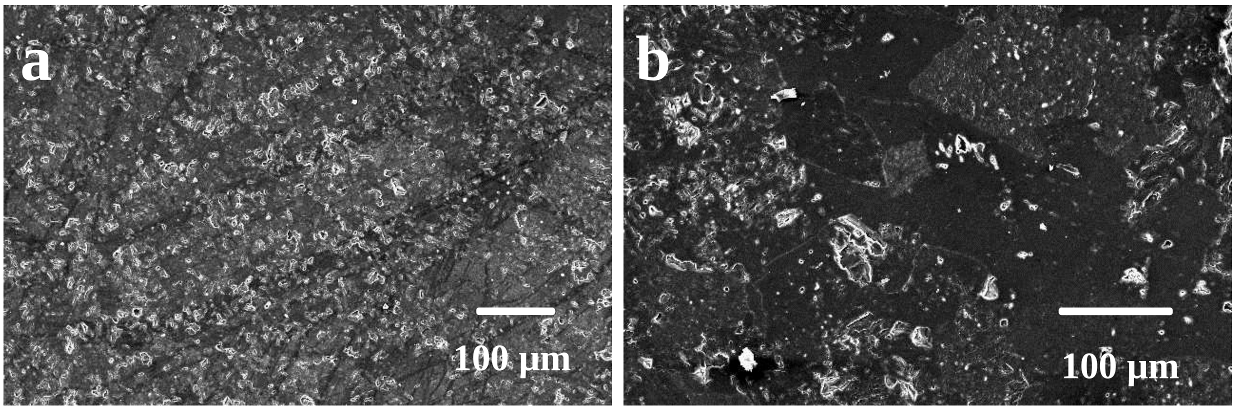

Figure 5. SEM image of dolomite from Swabi (KPK), showing variation in its microstructure.

CONCLUSION

The potential of dolomite [$CaMg(CO_3)_2$] from the Swabi district of Khyber Pakhtunkhwa as a raw material in fertilizer production was investigated. Dolomite was found as a major mineral phase, fully supported by X-ray fluorescence (XRF) results. TGA analysis indicated that the dolomite phase decomposes at about 774^oC when it treated with heat. The magnesium oxide produced during the decomposition process can be allowed to react with nitric acid to produce magnesium nitrite, which is a type of fertilizer that is widely used in agriculture. As magnesium oxide (MgO) and calcium carbonate ($CaCO_3$) were obtained as a result of heating the dolomite at ~774ºC. Further heating of dolomite can caused the formation of calcium oxide (CaO) to produced fertilizer. The resulting product of equation 1 can be mixed with water turning magnesium oxide to its hydroxide:

$$MgO_{(s)} + H_2O_{(\ell)} \rightarrow Mg(OH)_{2(\ell)} \quad (3)$$

The hydroxide of magnesium then reacts with nitrate acid (H_2NO_3).

$$Mg(OH)_{2(\ell)} + 2HNO_{3(\ell)} \rightarrow$$

$$Mg(NO_3)_{2(s)} + 2H_2O_{(\ell)} \quad (4)$$

Because of the high content of the magnesium in local dolomite, it is found to be suitable as raw materials in fertilizer production. Instead of direct using dolomite as an aglime, the dolomite can be enriched with nitrogen, which is the most important substance for most plantations.

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