

THERMAL BEHAVIOR OF ZEFREH DOLOMITE MINE (CENTRAL IRAN)

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Abstract

Dolomite has a large amounts of MgO and is an important raw materials for steel, iron and refractory industries. In this paper thermal behavior of Zefreh dolomite at various temperatures was studied by differential thermal analysis (DTA), Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT - IR) and powder X-ray diffraction (XRD) techniques. The DTA curve shows two endothermic peaks at 772 and 834°C. The first peak is associated with the formation of magnesia (MgO), calcite(CaCO₃) and CO₂. The second peak represents the decomposition of calcite with formation of CaO and further CO₂ release. At 772°C quantitative XRD analysis in atmospheric condition shows small amounts of CaO (less than 2%) which form simultaneously or later than calcite. TGA curve shows total weight loss for decomposition of dolomite is 46.2%. By increasing heating time of samples in furnace, dolomite decomposes in lower temperatures. X-ray diffraction analysis of heat treated samples up to 750°C indicates that dolomite structure changes into calcite. The increases in quartz content accelerated the mechanochemical deformation and amorphization of dolomite phase. At high temperature (more than 1000°C) Ca₃Mg(SiO₄)₂ and CaSiO₄ were formed. XRD and FTIR confirm dolomite decomposition reactions.

Keywords: X- ray diffraction; DTA- TGA; FTIR; Dolomite, Zefreh mine; Iran.

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1. Introduction

Dolomite is a double carbonate of calcium and magnesium ($\text{CaCO}_3 \cdot \text{MgCO}_3$) which has a theoretical content of 45.7% MgCO_3 and 54.3% CaCO_3 [1]. Dolomite is a mineral commonly occurring in nature and with calcite are main constituents of carbonate rocks. Based on of Tucker[2] classification dolomite rock contain 90 to 100 percent of dolomite mineral[2]. Dolomite formed by dolomitisation process as by replacement of magnesium in calcite. Dolomite in small amounts formed inexist as hydrothermal deposits mainly, associated with fluorite, barite, calcite, siderite, quartz, lead minerals veins, copper and also serpentinitic.

Among different practical and industrial application, dolomite is commonly used as a refractory material as well as in the magnesium metal production. Dolomite is a fluxing agent in metallurgical, glass and ceramic industry, filling material in paper, rubber and plastic production. Large amounts of dolomite are also used in building industry and agriculture (dolomite fertilizer). In chemical industry dolomite is first of all a source of magnesium compounds. Dolomite has a large amount of MgO and is an important raw material for refractory industry [3]. As the product properties are considerably influenced by chemical composition of the raw material and operating condition, many researches have been focused on dolomite thermal behavior in recent year [4].

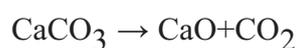
In this paper, thermal behavior of dolomite from Zefreh mine at various temperatures were studied by DTA-TGA, FTIR and powder X-ray diffraction. The

thermal decomposition of dolomite has been investigated; but the mechanism of this reaction still remains obscure. Some authors suppose the solid solutions of carbonates are formed during decomposition, others assume primary dissociation into separate carbonates or into oxides of magnesium and calcium. However, is a fact that thermal decomposition takes place in two stage; (I) and (II) which has been generally established as:

Stage (I)



Stage (II)



The studied samples were collected from the Zefreh dolomite mine, which geotectonically located in the Central Iran Zone (Fig.1) in the Permian and Triassic sequence. The oldest outcrops in the mine area are middle to late Permian rocks composed of sandstone, red quartzite with thin layer of conglomerate, limestone, dolomitic limestone and dolomite. Triassic rocks outcrop include massive yellow dolomite and limestone. Nayband formation contains shale with interlayer of limestone. Jurassic and Cretaceous rocks are mainly volcanic rocks. In Zefreh mine area dolomite is widespread including Permian and especially Triassic yellow dolomite.

2. Experimental

Several thin sections prepared and optically examined using a Zeiss polarized microscope (Axioplan2). Dolomite subsamples were grinded with agate mort and pestle down to and $-60\mu\text{m}$ diameter and

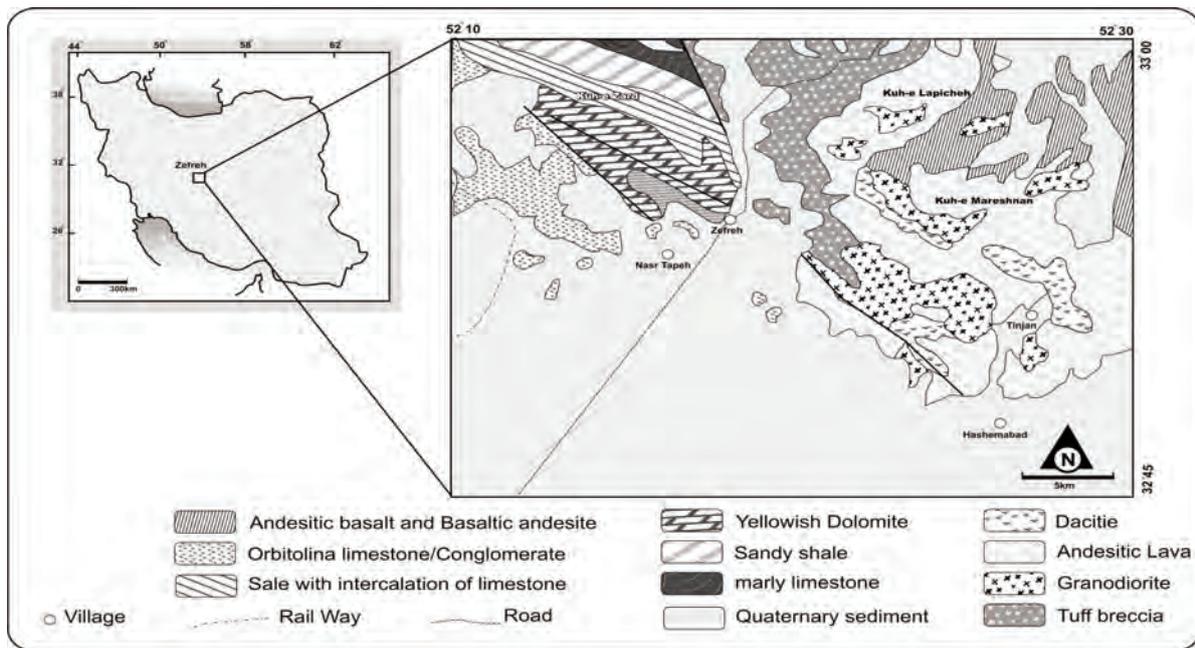


Fig.1. Geological map of Zefreh dolomite mine district.

submitted to X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR), differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

XRD analysis were performed with Philips (Xpert model) instrument with Co $K\alpha_1(1.789010\text{\AA})$, monocromator on secondary optics, 40kv power and 35mA current. Philips Magic-Pro X-ray fluorescence were employed for bulk chemical analyses in order to chemically evaluate the chemical characteristics of the samples.

DTA-TGA test were carried out using a Netzsch STA 409PC instrument.

The experimental conditions were:

(i) intinuous heating from room temperature up to 1200°C at a heating rate of 10 K/min;

(ii) N_2 – gas dynamic atmosphere and

(iii) using alumina as a reference material.

The following data was obtained by

thermal analysis:

(i) reaction peak temperature and

(ii) weight loss in the temperature ranges.

Perkin - Elmer spectrum one FT-IR spectrometer was used, and the samples were traced in range of $4000 - 400\text{ cm}^{-1}$ and the band intensities were expressed in transmittance (%).

Optical Microscopic study of dolomite samples show that dominant texture of samples is micritic. There are evidences of replacement and recrystalization in samples. The average dimension of dolomite crystals is 0.01mm. Calcite veins exist as open space filling textures with average thickness 0.02mm. Opaque mineral (iron oxide and iron hydroxide) exist as fine veinlets and disseminated in matrix. Quartz commonly fills open space and the average dimension of quartz crystals are 0.01mm.

In some thin sections there are obvious calcite and dolomite zonation. The

microscopic pictures of dolomite samples are presented in Fig.2. Table 1 presents chemical composition of selected dolomite samples. The main undesirable impurities in samples are SiO_2 , K_2O , Na_2O , Fe_2O_3 and Al_2O_3 . Amount of SiO_2 is variable and changes from minor level up to 10%.

peak at 758.2°C and 836.4°C . The first one begins at 687°C , reaches a peak at 758.2°C and ends at 781°C , the second one begins at 781°C , reaches a peak at 836.4°C and ends at 919°C . The lower temperature peak represents the decomposition of dolomite structure, releasing carbon dioxide from the

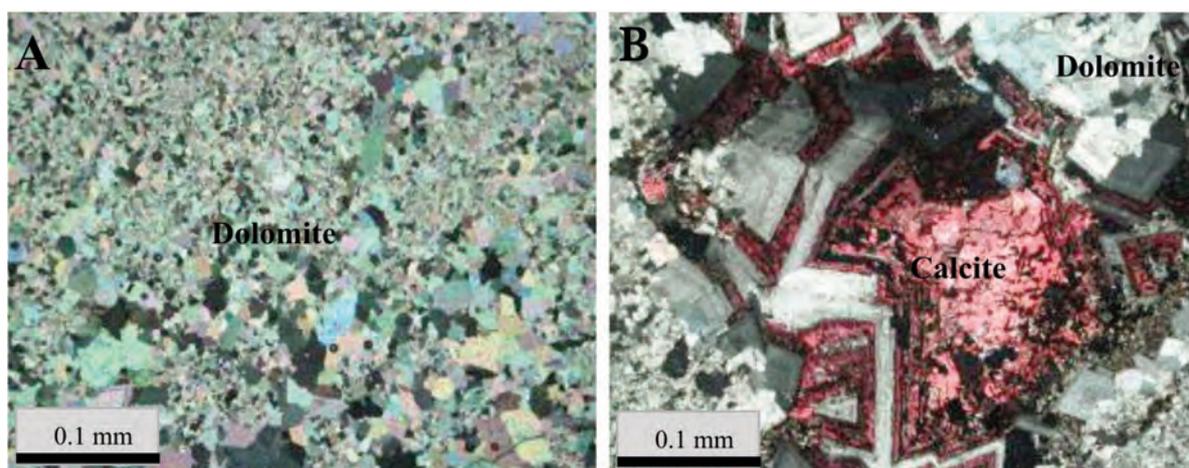


Fig. 2. Photomicrograph of dolomite samples. A, Mosaic texture with various size crystals. B- Zonation of dolomite and calcite in veins formed in micritic host.

Table1. Chemical analysis of selected samples from Zefreh Mine (Con. in %).

Sample	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	L.O.I	MgO/CaO
1	17.86	32.90	2.07	0.59	0.04	0.03	0.21	46.30	0.542
2	14.48	38.85	0.30	0.16	0.13	0.01	0.07	46.00	0.372
3	20.10	31.70	3.12	0.44	0.76	0.02	0.15	44.70	0.634
4	20.30	31.85	0.71	0.21	0.53	0.01	0.09	46.30	0.637
5	21.22	32.04	0.27	0.07	0.03	0.01	0.01	46.30	0.662
6	15.71	28.20	11.00	0.01	0.12	0.02	0.018	44.85	0.557

Thermal decomposition of dolomite was studied by DTA/TGA from room temperature to 1200°C . The typical DTA/TGA curve of dolomite sample is presented in Fig.3. The thermal curves representing the carbonate mineral are characterized by endothermic peaks caused by the evolution of carbon dioxide. DTA curve of dolomite shows two endothermic

carbonate ion associated with magnesium part of the structure accompanied by formation of calcite and magnesium oxide. The higher temperature peak represents the decomposition of calcite with the evolution of carbon dioxide [5].

The typical TGA curve of dolomite sample is presented in Fig.3. The measured weight loss was 1.33% below 600°C and

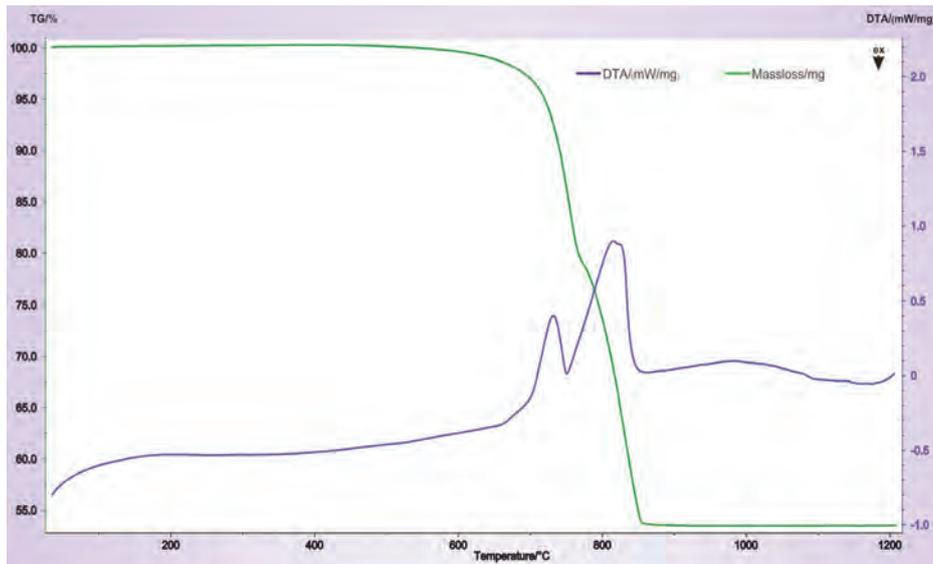


Fig. 3. DTA-TGA curves of pure dolomite (sample KD).

between 600°C and 850°C reached to 46.2%. The weight loss of dolomite attributed to the decomposition of carbonates.

The kinetics of decomposition process were analysed by means of popular methods.

Studies are shown the variation in activation energy $113.56 \text{ (KJmol}^{-1}\text{)}$ to $147.58 \text{ (KJmol}^{-1}\text{)}$ [6]. The slight variation in activation energy maybe attributed to the difference in particle size and mineral origin in the samples [7].

The mineralogical variation on primary samples were examined using quantitative X-ray diffraction analysis (Table 2). X-ray diffraction analysis shows that dolomite is

Table 2. Quantitative XRD results of dolomite samples.

Samples	Dolomite%	Calcite%	Quartz%
1	98.5	-----	1.5
2	86.3	13.7	-----
3	93.5	3.5	3
4	98	1	1
5(KD)	100	-----	-----
6(AA53)	83	7	10

the dominant mineral in samples and amount of calcite and quartz are low. Fig. 4 depicts the powder X-ray diffraction pattern of Zefreh dolomite sample at different temperatures. The room temperature XRD pattern of sample displays sharp diffractions that can attributed to dolomite (JCPDS files card 79-1342;2000) [8].

Table (3) gives various Bragg reflections that are indexed using JCPDS files card 79-1342. The X-ray diffraction results are compared for different heat treatments. The original reflection disappeared completely and new lines are developed at the asymmetric position of (104) and (202) reflections. In Table (6) the d-spacing of heated dolomite at 750°C with calcite (standard pattern) is compared which indicating that the crystal structure of dolomite has been transformed completely to calcite structure during heat treatment [9]. At 750°C dolomite transformed to calcite and MgO and dolomite peaks disappeared. At 950°C decomposition of dolomite is

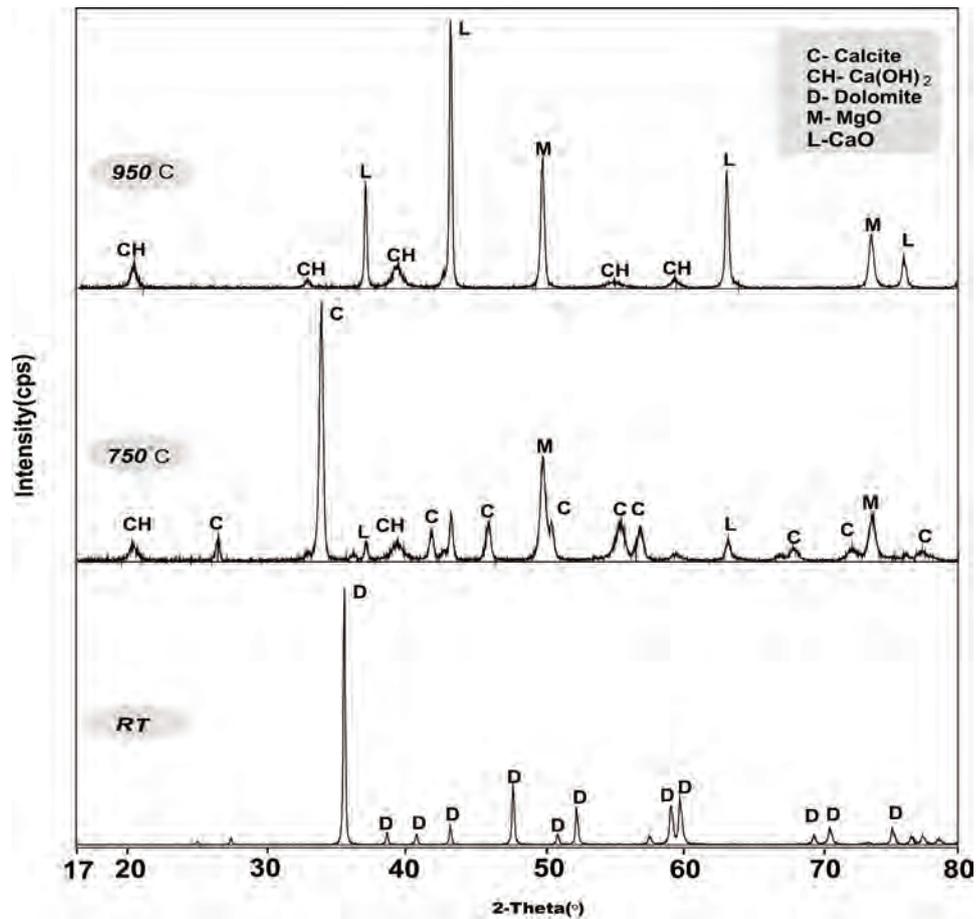


Fig. 4. XRD pattern of dolomite at different temperatures (sample kd)

Table 3. Indexed powder XRD pattern for pure dolomite (sample kd)

No	h	k	l	Pos. [$^{\circ}$ 2Th.]	FWHM [$^{\circ}$ 2Th.]	d-spacing (Å)	Rel. Int. [%]
1	0	1	2	28.0651	0.0908	3.68909	6.48
2	1	0	4	36.1502	0.0908	2.88305	100
3	0	0	6	39.2013	0.0908	2.66648	4.27
4	0	1	5	41.2981	0.0908	2.53657	4.85
5	1	1	0	43.7199	0.0908	2.40240	8.74
6	1	1	3	48.1983	0.0908	2.19071	19.87
7	2	0	2	52.7371	0.0908	2.01400	8.99
8	0	2	4	57.9544	0.0908	1.84639	2.64
9	0	1	8	59.4761	0.0908	1.80331	9.05
10	0	1	8	59.6183	0.0908	1.80331	9.07
11	1	1	6	60.1275	0.0908	1.78557	11.61
12	1	1	6	60.2716	0.0908	1.78557	11.61
13	1	2	2	70.8105	0.0908	1.54396	3.72
14	1	2	2	70.9875	0.0908	1.54397	3.69

Table 4. Observed X-ray data for the heat treated dolomite sample (750°C) and recorded data for calcite(sample kd).

(hkl)	Observed	JCPDS Card 86-2334	Intensity %
(0 1 2)	3.847	3.853	9.9
(1 0 4)	3.031	3.035	100
(0 0 6)	2.840	2.843	2.1
(1 1 0)	2.487	2.494	14.2
(1 1 3)	2.278	2.284	18
(2 0 2)	2.087	2.093	15
(0 2 4)	1.920	1.926	6.3
(0 1 8)	1.909	1.912	16
(1 1 6)	1.869	1.874	18.4

completed and calcite changed to CaO and CO₂.

The hydration degree of dolomite was increased by increasing the calcination temperature. X-ray diffraction analysis of heat treated samples up to 950°C indicates that calcite transformed into CaO which on reaction with atmospheric water Ca(OH)₂ was formed [10]. The unit cell parameters

show an increase with temperature due to thermal expansion [11]. Presence of impurities such K₂O, CaO, Al₂O₃ and SiO₂, favours the formation of glassy phases. Sintering process and formation of glassy phase decrease the calcination process [12]. Under CO₂ dolomite decomposes directly to CaCO₃ accompanied by the formation of MgO between 550°C and 765°C. No evidence was offered for the formation of either CaO or MgCO₃ [13,14,15]. Quantitative XRD analysis showed formation of CaCO₃, MgO and CaO in air condition between 550 and 750°C though CaO content is less than 2%. Dolomite samples containing SiO₂ are heated for an hour at 1100°C and 1400°C and XRD results are shown formation of Ca₃Mg(SiO₄)₂ (Merwinite) at 1400°C and Ca₂SiO₄ (Larnite) at 1100°C. At both 1100°C and 1400°C MgO exist as major and minor phase.

In order to evaluate the heating time effect

Table5. XRD results at different heating times in 600 °C for pure Zefreh dolomite (sample kd).

SiO ₂ %	CaO%	MgO%	Calcite%	Dolomite%	time/ temperature
---	---	---	---	100	Room temperature
---	---	12.4	20.9	66.8	1h/600 °C
---	0.7	18.2	29.4	51.7	3h/600 °C
---	1.6	18.6	33.5	46.3	6h/600 °C

Table 6. Quantitative XRD results at different heating times in 600 °C for impure Zefreh dolomite (sample AA53)

SiO ₂ %	CaO%	MgO%	Calcite%	Dolomite%	time/ temperature
10	---	---	7	83	Room temperature
14.6	---	12.5	21.2	51.7	1h/600 °C
15.5	0.7	17.3	26	40.5	3h/600 °C
17.1	2.7	18.1	30.5	31.5	6h/600 °C

on formed phases, the pure dolomite subsamples (KD) and subsamples from a sample with the highest impurity content from Zefreh deposit (AA53) were heated in furnace for 1, 3 and 6 hours in 600°C. The quantitative XRD analyses of formed phases are presented in Table 5 and 6, indicating that CaO is insignificant phase and major phases are MgO, calcite and dolomite, and calcite formed prior to CaO formation. By increasing residence time in furnace reactions were speed up and calcite and MgO contents were increased in 6 hours residence time test. The highest CaO content recorded in 750°C-950°C as a result of calcite decomposition.

In the room temperature FTIR spectra of samples (Fig. 5) showed dolomite and indicated main absorption bands of dolomite at 2525, 1881, 1446, 881 and 726 cm^{-1} . All the samples have strong bands (around 3400 cm^{-1}) related to the presence of bound water [16,17]. The weak bands at 1040, 799, 525 and 462 cm^{-1} indicate the presence of Si-O vibration of silicate phase [17]. The weak band due to quartz (465 cm^{-1}) is also visible. The silicate bands probably indicating the content of silicate phase in the sample, which is in agreement with the chemical analysis data. The characteristic dolomite bands are shifted to 713, 876 and 420 cm^{-1} in the FTIR spectra of 750°C heat treated dolomite

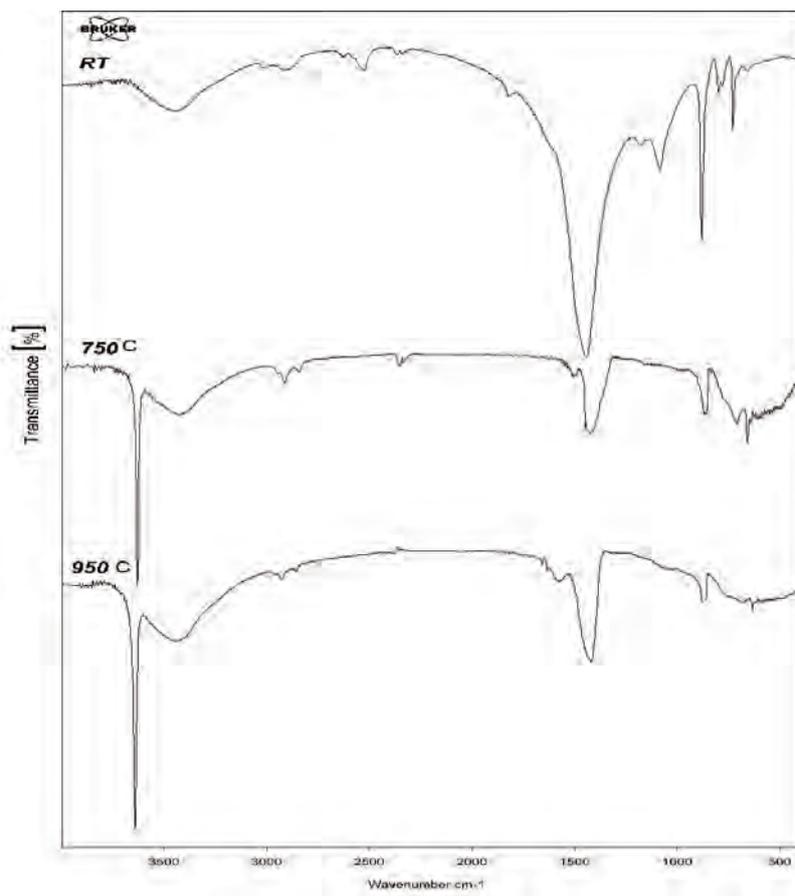


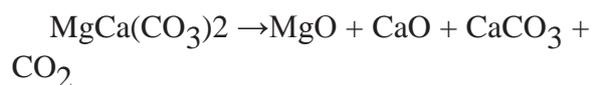
Fig. 5. FTIR spectra of dolomite at different temperatures (sample kd)

sample (Fig.5), demonstrating the structural transformation of dolomite to calcite. At this stage, a strong and broad band at 450 cm^{-1} appeared due to magnesium oxide formation. At 950°C condition, the 1420 cm^{-1} band shifted to 1413 cm^{-1} and the intensity of the band in 713 cm^{-1} were significantly decreased. Observed bands (3644 and 1410 cm^{-1}) at 750°C condition, and those of (3644 , 870 and 450 cm^{-1}) at 950°C are due to $\text{Ca}(\text{OH})_2$ formation [18]. At 950°C test, the quartz and calcite reaction probably formed wollastonite which its main bands are centered at about 550 , 890 , 1006 , 1080 cm^{-1} [19].

4. Conclusions

The DTA results indicated two endothermic peaks at 758.2°C and 836.4°C which are related to decomposition of dolomite and calcite. TGA curve shows that at 758.2°C weight loss due to dolomite decomposition is 20.77% which is indicated by formation of calcite and periclase and CO_2 releases. At 836.4°C weight loss is 25.43% and the total weight loss for decomposition of dolomite is 46.2% . The thermal decomposition of dolomite shows a peculiar characteristics depending on the experiments atmosphere. Decomposition of dolomite in air occurs in single step and can be depicted by reaction (I). Quantitative XRD showed formation of CaCO_3 , MgO and CaO in air condition between 550 and 750°C but amount of CaO is less than 2% . By increasing heating temperatures between 750 and 950°C calcite was totally decomposed to CaO and CO_2 .

Reaction (I)

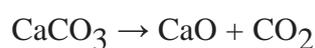


Under CO_2 atmosphere dolomite decomposes directly to CaCO_3 accompanied by the formation of MgO . No evidence was offered for formation of either CaO or $\text{MgCO}_3(\text{II})$ and in next stage calcite decomposed to $\text{CaO}(\text{III})$.

Reaction (II)



Reaction (III)



At 750°C , dolomite structure is changed to calcite which is confirmed by presence of calcite characteristic peak at 713 , 875 and 1420 cm^{-1} in FTIR spectra. The presence of characteristic reflections at 3.0334 and 2.4993 \AA for calcite and MgO , respectively also confirm the first decomposition stage of dolomite.

By increasing residence time in furnace, dolomite decomposes at lower temperature. The residence time increase compensate the higher temperature required for dolomite decomposition. The high SiO_2 content in Zefreh sample (AA53) in the temperature higher than 1000°C resulted in amorphous dolomite formation in addition to silicates ($\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, and CaSiO_4) crystallization.

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