THERMAL BEHAVIOR OF CALCITE AS AN EXPANSIVE AGENT

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Abstract

In this paper, thermal behavior of calcite as raw material of CaO-based expansive agent was investigated. The products were characterized by using differential thermal analysis (DTA), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and X-ray powder diffraction (XRD). DTA curves show that calcite has endothermic peak and impurity affects the onset of reactions. The more the impurity increases, the more energy changes increase. At 800-900ºC, calcite was decomposed into solid calcium oxide (CaO) and gaseous CO_2. Lime (CaO) used as the base of expandable material is the ultimate product of heated calcite. The calcium oxide phase, in reaction to water forms portlandite, at an onset temperature of about 900ºC was also characterized by the appearance of the FT-IR mode at 867,3424 and 3644 cm^{-1}. XRD results show that quartz impurity in calcite samples at 900 ºC forms larnite phase (Ca_2SiO_4). The expansions are mainly generated from the hydrations of CaO in the CaO-type expansive agent.

Keywords: DTA/TGA, XRD, FT-IR, Katrock, Portlandite

1. Introduction

Today, mining and prevalent methods are developed and most of investigation centers related to mining try to produce non-explosive and non-environmental pollution materials. Expandable powders are suitable substitute for explosive materials in mining activities. Katrock is one of the expandable powder which is silent, non-explosive demolition agent having the capability of demolishing rock or concrete safely without causing noise, vibration, fly-rock or environmental pollution.It is a harmless, non-toxic powder which is safe, efficient, simple to use, and is very reliable under all

sorts of conditions. Katrock is used in circumstances where it is impossible to use traditional dynamite such as in close proximity to buildings, underground cables, gas, oil and water pipes.

Chemical demolition agent such as KATROCK, DEXPAN and FRACT.AG are highly expansive powder compositions for stone breaking, non toxic chemicals and environmentally friendly, safe controlled demolition agent used as an alternative for blasting. Chemical non–explosive demolition agents are mixed with clean water and poured into pre-drilled holes on rock and concrete. The holes are often prepared by pneumatic hammer. The diluted non-explosive demolition agent swells and exerts significant expansive thrust on the hole–wall. After a certain period, the pressure induced by the chemical non–explosive demolition agent fractures the wall and splits the rock across the line of the drill holes. These chemicals easily split and fracture mass rock without producing any noise, vibration, toxic gases or flying debris [1]. The rock cracker is a non-explosive rock–splitting tool that makes use of the technology of motive force. After the borehole is drilled, it is filled with water and the cracker cartridges and tee-piece are inserted. After firing mechanism, the stone is split successfully into several pieces with the rock cracker, without requiring a blasting license [2].

Shrinkage cracking occurs in constructions frequently. The cracks would be the pathway of water and harmful substances into concrete resulting in destruction of concrete. Several of measures to be developed to eliminate the shrinkage

cracking; the one of these is using expansive agents to compensate the shrinkage of concrete. Adding the expansive material to concrete, the shrinkage of concrete may be compensated by the hydration of CaO to $Ca(OH)_2$ and the hydration of MgO to $Mg(OH)_2$, so decrease deformation and fracture of concrete.

In this investigation the production of CaO–type expansive agent from calcite ($CaCO_3$) in regard of chemical components effects are considered. Studies are carried on various calcite samples in mineralogy by XRD and DTA/TGA. Particle size and chemical components play a great role in thermal behavior of minerals. Calcite ($CaCO_3$), a mineral commonly occurring in nature, finds applications in many fields of industry.

The thermal decomposition of calcium carbonate leads to the formation of lime (CaO) and the release of CO_2. Lime, which has been traditionally used for building purposes, is nowadays also employed in agriculture, food processing, disinfection and disease control, water treatment, flue-gas desulfuration, steelmaking, plastics and glass fabrication and sugar refining. The thermal decomposition of calcite also plays a role in a number of geologic processes such as high grade metamorphism, pyrometamorphism and meteorite impacts [3].

2. Experimental

The studied calcite samples collected from Dalan carbonate Formation (south Shiraz, Iran) geologically belongs to the Zagros zone. Calcite samples were grounded with agate mortar and pestle. The powdered

samples were sieved down to less than 60 μm diameter and submitted to X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and Fourier transformed infrared spectroscopy (FT-IR).

XRD analysis was performed on Philips (Xpert-pro model) instrument with Co K-Alpha (1.789010A°), monochromator on secondary optics, 40kv power and 35mA current. X-ray fluorescence analyses were used to evaluate chemical composition of the samples. DTA-TGA tests were carried out by using a "Netzsch STA 409PC instrument". The experimental conditions were: (1) Increasing the temperature from ambient to 1200 °C at a heating rate of 10 °C/min as it is known from literature [4], (2) N_2–gas dynamic atmosphere and (3) alumina, as reference material. The following data were obtained by thermal analysis: (1) reaction peak temperature, (2) 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 cm^{-1} and the band intensities were expressed in transmittance (%). Table 1 presents chemical composition of limestone samples (by XRF). 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 the least 0.11% to the most 8.18%. L.O.I (Loss on ignition) changes from 37.62% to 43.14%.

3. Results and Discussions

Thermal behavior of calcite samples were considered with DTA-TGA from the ambient temperature to 1200°C. In DTA, the differences in temperature between the sample and a reference material such as alpha Al_2O_3 is recorded while both are subjected to the same heating program. In investigation, TGA is commonly used with DTA to follow the hydration reactions. The representative DTA and TGA curves of calcite samples are shown in Fig.1 and Fig.2. Endothermic reaction was identified during the heating of calcite samples.

DTA curves of the samples show the start of the reaction, maximum peaks and the end of the reaction(using Netzsch software). Results show that in sample Ts1 the start reaction is 778 °C and the end reaction is 873.5 °C which occurs at lower temperature than other samples (Table2). Quartz percentage in sample Ts1 is more than samples Ts2 and ELG and it influences the thermal behavior of calcite. DTA curve of ELG sample shows that the onset reaction begins at 801.1°C, reaches a peak at 892.4 °C and ends at 933 °C, the sample Ts2 reaction begins at 806.6 °C, reaches a peak at 876.6 °C and ends at 891.2 °C (Fig. 1). DTA curves represent the decomposition of calcite with the evolution of carbon dioxide [4].

In TGA curves, the weight changes are determined as the sample is heated at a

Table1: Chemical analysis of selected calcite samples (Con.in %)

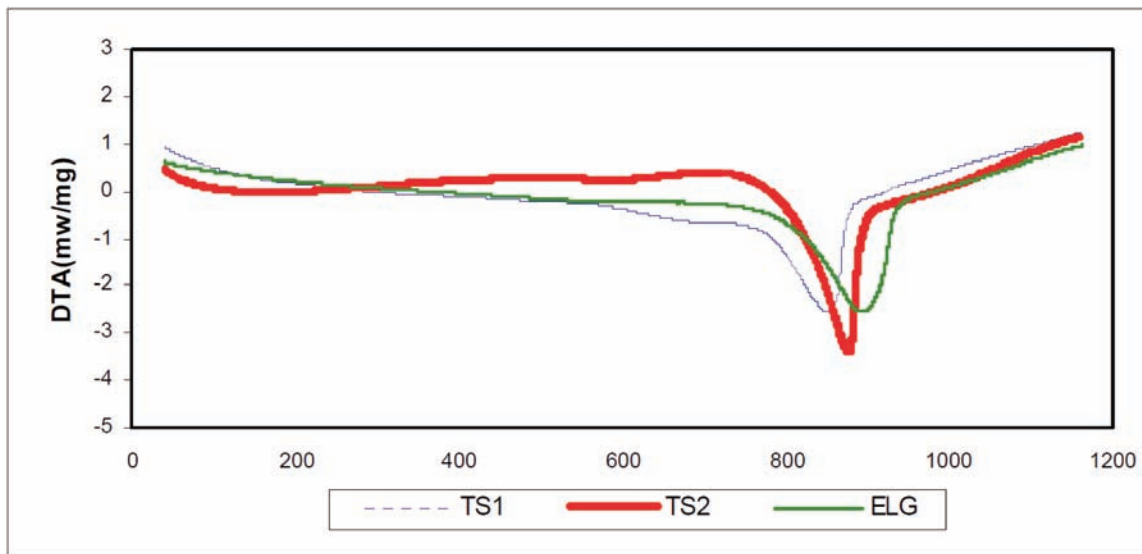| Sample	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	L.O.I
ELG	0.9	56.45	0.11	0.04	0	0	0	42.5
TS1	0.33	49.69	8.98	1.5	0.8	0.06	0.84	37.62
TS2	0.13	55.67	0.62	0.33	0	0.03	0.07	43.14

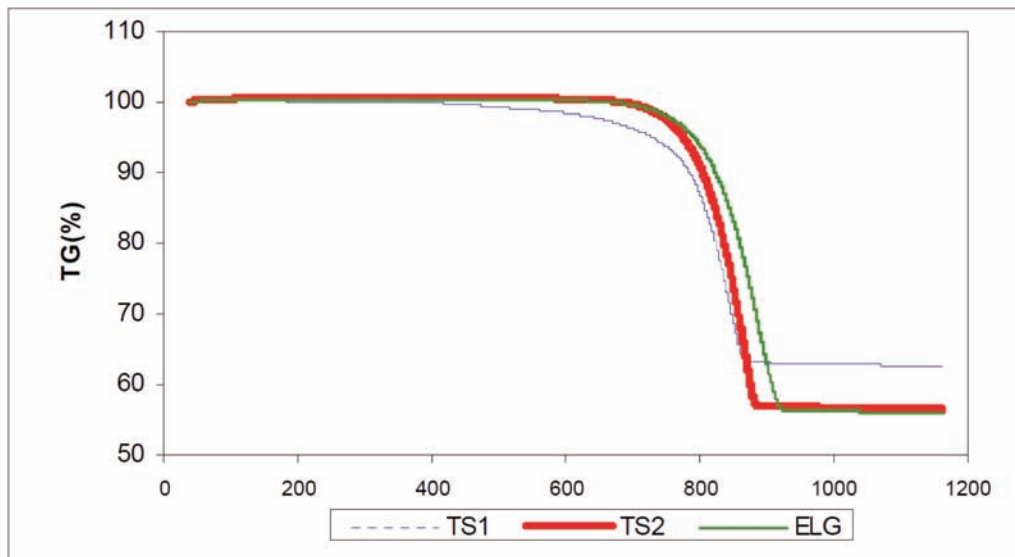*Figure 1. DTA curves showing behavior of calcite samples*

Figure 2. TGA curves showing behavior of calcite samples

uniform rate. The weight losses for sample Ts1 was 35.66% and for sample ELG and TS2 were 43.92% and 43 % correspondingly (Table2). The weight loss of calcite is attributed to the decomposition of carbonates. For pure calcite the expected mass decrease in one step (at 900 ºC) is 43.97% [5]. Values different from these, are indications for the presence of other constituents in the samples. Additionally, in case of presence of quartz in some samples, as observed in XRD and XRF results, the small peak which attributes to its endothermic transition at 573 ºC is not verified. The peak shape, the number of peaks in the heat flow diagrams and the peak

Table 2. Reaction temperature, weight loss and subsurface of peaks in calcite samples.

Sample	Start (°C)	Maximum(°C)	End(°C)	Weight loss %	Erea (j/gr)
TS2	806.6	876.6	891.2	43	-869.6
ELG	808.1	892.4	933	43.92	-1098
TS1	778	850.7	873.5	35.66	-1276

position in the DTG-TGA diagrams are also possibly connected to the presence of impurities in the host materials [6]. From the XRF measurements, it is clear that there are some very small amounts of elements which could be considered as impure or disordered minimum (Table 1).

The absolute value of level under the DTA area based on j/gr is an introducer of the energy variation of the system. In TS1 sample, due to the great amount of SiO_2 (8.98%) and the formation of new silicate phases up to 1200 °C, it has great energy changes and the amount of the level under the area is equal to 1276 j/gr (Table 2). In TS2 due to the decreases of the impurities, the energy changes is less and is equal to 869.6 j/gr. Whenever the SiO_2 of the particles become minor the energy changes will be less, whereas in ELG sample, due to the presence of MgO impurities, the energy changes increases up to 1098 j/gr.

The initial material and run products (after heating) were characterized by X- ray analytical diffraction techniques. In XRD difractogram of the samples calcite, dolomite, quartz and clay minerals are present. The results of quantitative XRD are

Table3. Quantitative XRD results of calcite samples

Samples	Calcite%	Quartz%	Dolomite%	Clay%
TS1	90.5	8	0.5	1
TS2	99	1	----	----
ELG	98.5	---	1.5	----

shown in Table 2. By XRD examination it is clear that the main constituent of samples (TS1, TS2 and ELG) is calcite. Sample TS1 has 8% quartz and small amount of clay that confirmed with XRF measurements. Fig.(3) depicts the powder X-ray diffraction pattern of sample ELG at different temperatures for an hour. The room temperature XRD pattern of sample displays sharp diffractions that can attributed to calcite (JCPDS files card 02-0623;2000) [7]. Table 4 presents various Bragg reflections that are indexed using JCPDS files card 02-0623. The X- ray diffraction results are compared with different heat treatments. The primary reflection disappeared completely and new peaks are formed at the asymmetric position of (111), (200) and (220) reflections.

Table 4. Indexed powder XRD pattern for calcite (sample ELG)

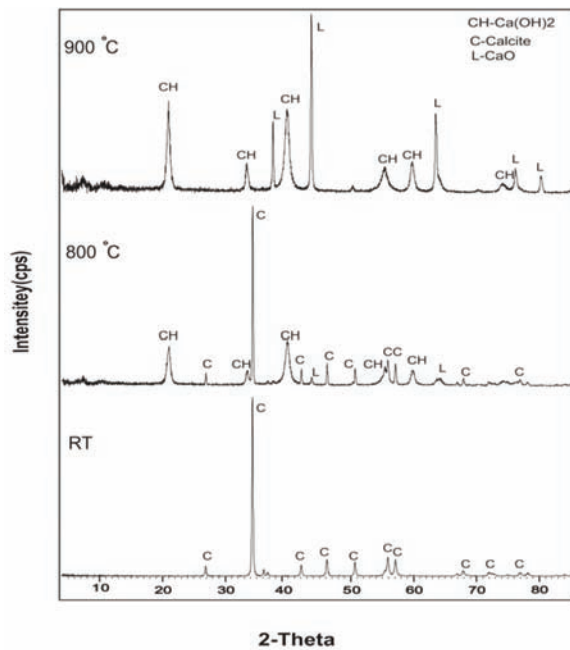| No	h	k	l	Pos. [°2Th.]	d-spacing (Å)	Rel. Int. [%]
1	1	0	4	34.341	3.03000	100.0
2	1	1	0	42.107	2.49000	40.0
3	1	1	3	46.199	2.28000	60.0
4	2	0	2	50.422	2.10000	60.0
5	0	2	4	55.535	1.92000	80.0
6	1	1	6	57.155	1.87000	70.0
7	1	2	2	67.982	1.60000	50.0
8	2	1	4	72.1	1.52000	50.0
9	3	0	0	76.805	1.44000	40.0
10	2	1	7	82.253	1.36000	10.0
11	1	2	8	86.957	1.30000	10.0

Figure 3. XRD pattern of calcite at different temperatures (sample ELG)

In table 5, the d-spacing of heated calcite (sample ELG) at 900 ºC with CaO (standard pattern) is compared which indicates that the crystal structure of calcite has been transformed completely to CaO structure during heat treatment [8].

XRD experiments show that by increasing temperature, calcite structure becomes unstable and transforms gradually to CaO (2.398 Å) [8]. In presence of dolomite, at

Table 5. Observed X-ray data for the heat treated calcite (sample ELG) at 900 ºC and reported data for lime.

(hkl)	Observed	JCPDS Card 43-1001	Intensity%
(111)	2.76698	2.77700	37
(200)	2.39813	2.40500	100
(220)	1.69791	1.70080	49
(311)	1.45003	1.45040	13
(222)	1.38518	1.38870	13

750ºC dolomite transforms to calcite and MgO, and dolomite peaks disappear. At 950ºC decomposition of dolomite is completed and calcite changed to CaO and CO_2 [9].

The unit cell parameters show an increase with temperature due to thermal expansion [10]. The hydration degree of calcite was increased by increasing the calcination temperature. X-ray diffraction analysis of heat treated samples up to 900ºC indicates that calcite transforms into CaO though Ca $(OH)_2$ was formed in reaction to atmospheric water [11, 12].

Presence of impurities such K_2O, CaO, Al_2O_3 and SiO_2, favors the formation of glassy phases. Sintering process and formation of glassy phase decrease the calcinations process. Larenite (Ca_2SiO_4) is formed due to presence of quartz in Ts1 at 900 ºC (Fig. 4).

After heat treatment, ELG samples are affected by atmospheric moisture and XRD results show the remarkable of Ca$(OH)_2$ (Fig. 4). XRD analysis is done immediately after heat treatment on sample TS1 and TS2. Atmospheric water in reaction to CaO occurs in minor content in sample TS1 and TS2 (Figs.4 and 5).
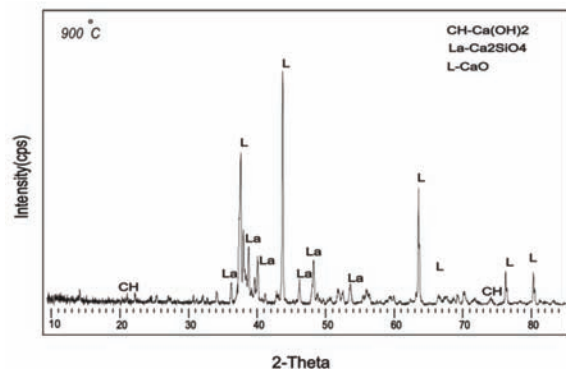

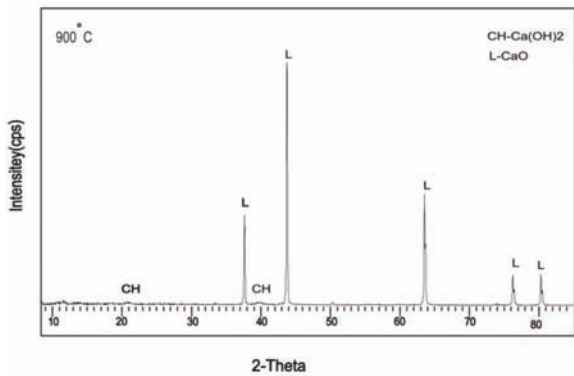*Figure 4. XRD pattern of calcite at 900 ºC (sample TS1)*

Figure 5. XRD pattern of calcite at 900 ºC (sample TS2)

Many demolition agents such as explosives, expansion gases and expansion materials have been proposed for brittle materials such as concrete, rocks and bricks etc. Among those, the explosives are a preferable demolition agent because of its strong breakage effect per unit time, but it has disadvantages that it may cause pollution such as noise, flyrock, vibration, dust and the like at an explosion time and that there may be accompanied with a danger during its operation. In order to eliminate such disadvantages, it has been proposed a method wherein a slurry of expansion material is filled into a hole drilled in a brittle material to demolish it by means of the expansive stress of the slurry. By using this method, advantages are obtained such that there is occurred no noise except a noise for drilling, no vibration and less danger. It is considered that quick lime can be used as a demolition agent because of its great expansive stress. It has, however, such a disadvantage that since it has a very high hydration speed and may expand by hydration immediately after being mixed with water, its fluidity is reduced rapidly to become difficult for pouring into the hole [1, 2]

CaO is the main component of Katrock. Based on the impurities in calcite it may contain MgO, Ca_2SiO_4 and so forth. The experiments of XRD show that the combination of water and CaO makes $Ca(OH)_2$, so the volume increase will be the consequence (Fig6). In mines and constructions, CaO is mixed with water then the mixture is poured in the holes. $Ca(OH)_2$ causes pressure in the holes and leads to breaking the stone and concrete. According to the XRD pattern (Fig. 5) the samples are heated up to 900 ºC and exposed to the less atmospheric moisture therefore $Ca(OH)_2$ formation is partial. Whereas in those samples exposed longer to the atmospheric moisture, $Ca(OH)_2$ formation is significant (Fig.6).

The typical transmittance FTIR spectra of the ELG sample at different temperatures are shown in Fig.7. In the room temperature, FTIR spectra of sample indicate $CaCO_3$ as a main component, principally in form of calcite, as identified by its main absorption bands at 1424,875 and 712 cm^{-1}. All the samples have strong bands related to the presence of bound water (around 3400 cm^{-1}). The water might be bound to hydraulic
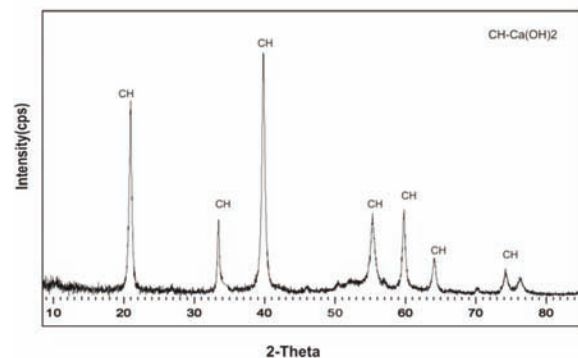

Figure 6. XRD pattern of sample ELG at 900ºC (reaction of CaO with water moisture)

compounds, like silicate and aluminate hydrates. When heat treated to 900 ºC the broad band at 1424 cm^{-1} shifted to 1417 cm^{-1} and a sharp intense band at 3644 cm^{-1} due to Ca(OH)$_2$ presence. At 900 ºC decarbonization process of calcite is completed or almost completed, but their shape is still retained. The bands at 867 and 3424 cm^{-1} indicate the formation of portlandite, due to the reaction of CaO with atmospheric moisture. An OH stretching band of Ca(OH)$_2$, formed by reaction of CaO with atmospheric water vapor appears at 3644 cm^{-1} [13].

It is well known that shrinkage is generated in the setting and hardening process of cement. Because of shrinkage microcracks in paste or cracks in concrete are often observed by scanning electron microscopy (SEM) or othe rapparatus. Cracks would be pathways of

Figure 7. FTIR spectra of calcite at different temperatures (sample ELG)

water and harmful substances into concrete that may reduce the service-ability and durability of concrete [14]. The control of cracking in concrete dams has become a problem that attracts the concerns of experts in the world. Using minerals of calcite and dolomite produce a new composite material which provides an expansive stress to decrease deformation and fracture of hydraulic concrete [15, 16]. The hard burnt CaO and MgO in cement react to water and the expansion caused by CaO and MgO hydration take place after the concrete hardened, so that the shrinkage of concrete could not be compensated effectively. The CaO in the MgO-based expansive agent reacted to water to form Ca(OH)$_2$ that caused expansion and compensated the shrinkage of concrete at early age, and the MgO reacted to water to form Mg(OH)$_2$ that caused a delayed expansion and compensated the shrinkage of concrete in later age [17, 18]. Using industrial by-products calcite and dolomite to mak CaO and MgO-type expansive agents and to compensate the shrinkage of concrete is feasible. In addition, the industrial by-products will be consumed which will reduce the environmental pollution.
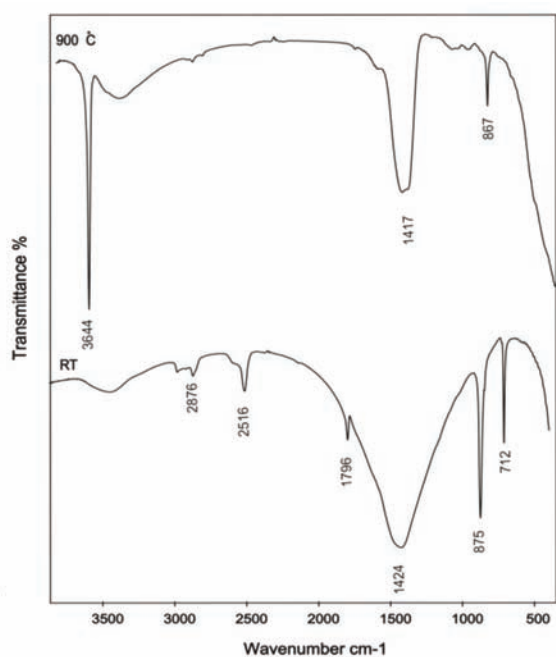
4. Conclusions

The DTA results indicate endothermic peaks at 800-900ºC which are related to decomposition of calcite into CaO and release of CO_2 with reaction (1). Comparison of various chemical components in calcites has shown that the DTA peak temperatures are varied. The peak temperatures of calcite decomposition decrease with an increase of SiO_2. CaO reacts with atmospheric water according to reaction (2) causing Ca(OH)$_2$

formation.

Reaction (1) $CaCO_3 \rightarrow CaO + CO_2$

Reaction (2) $CaO + H_2O \rightarrow Ca(OH)_2$
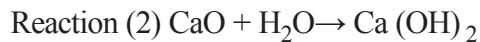
Amount of $Ca(OH)_2$ in heat treatment sample is important which is related to experimental conditions. According to the XRD pattern the samples which are heated up to 900 ºC and were exposed to the atmospheric moisture for short time, $Ca(OH)_2$ formation is partial. Whereas those samples which were exposed to the atmospheric moisture for longer, $Ca(OH)_2$ formations is significant. Presence of impurities such as K_2O, Al_2O_3 and SiO_2, favours the formation of glassy phases. Presence of quartz in samples influenced by the thermal behavior and reaction started at lower temperature and is finished earlier than pure samples. At 900 °C quartz is reacted with Ca and Ca_2SiO_4 is formed. Based on above discussion, we propose that mineral calcite and dolomite can be used as raw material to produce CaO and MgO-based expansive agents to compensate the shrinkage of cement and concrete. CaO-based expansive agent is suitable substitute for explosion materials in mining activities. Amount of CaO in rich calcite samples is more and it is preferred to be used in Katrock production. Dolomitic rocks are unsuitable for using in katrock production although they contain some amount of CaO. MgO is the impurity of katrock and presence of large amount of MgO decreases the katrok quality.

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