

## **THERMOANALYTICAL STUDY OF BARYTE DECREPITATION**

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(Received April 18, 2001; in revised form September 17, 2001)

### **Abstract**

The decrepitation results of mineral baryte BaSO<sub>4</sub> (Rudňany, Slovakia) of various quality obtained by completed Acoustic Emission (AE)-TG-DTA measurements are presented in this paper. The overall effect of decrepitation ability of major component BaSO<sub>4</sub> is not hindered by accompanying mineral siderite FeCO<sub>3</sub>. This fact confirms decrepitation study of pure minerals by the thermo-vacuum impulse method, too.

**Keywords:** acoustic emission, baryte, decrepitation, DTA, TG

### **Introduction**

According to literature [1–5], decrepitation is brought about by the action of stress that has accumulated in the lattice of minerals resulting from the presence of gas and liquid inclusions, lattice defects, cleavage of the minerals, and cracks, and last, but not least, it is function of the strength characteristics of the mineral. The data on baryte decrepitation are not published in literature and those published deal prevalingly with carbonates.

The study of mineral decrepitation is effective in three regions of research, namely

1. geology as paleothermometric research in mineral genesis [6],
2. ore dressing in relation to estimation of the decrepitation treatment of mineral [7–9],
3. materials research in relation to preparation of basic components of oxidic type for glass industry [2].

According to research specificity and applicable methods the approach to the view on decrepitation phenomenon can be different. In the first case the onset of mass

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breaking of gaseous and liquid inclusions is regarded as decrepitation temperature. In the second case it is assumed that the presence of gaseous and liquid inclusions has primary importance in decrepitation, but this phenomenon may be also due to physico-chemical transformations in crystal structure produced by thermal treatment as well as to mechanical forces resulting from thermal expansion of mineral and pressure of gases included in minute holes. Baryte, spodumene, fluorite, anglesite, gypsum, halite, mica, siderite and magnesite belong among easily decrepitating minerals [4].

The decrepitation treatment of magnesites is thoroughly studied [7–9], and also industrially realised. The theoretical basis on decrepitation treatment of carbonates and specification of strength characteristic changes of this process have been described in studies [5, 7–8]. According to [2] the decrepitation of dolomite could be eliminated by selecting the dolomite fraction with granularity index less than 20, at best in the range 0–5.

The study of mechanism of dolomite decrepitation [1–2] has revealed that the cause of decrepitation consists in the pressure of the water vapour that originates from the water included in mineral at the initial temperature of decrepitation (349–387°C, according to granularity) the value of which is related to the strength characteristics of dolomite.

There are various decrepitation techniques, which have been specified in detail in several studies [10–14], while the latest study by Lach summarizes possibilities of utilization of study results in decrepitation and thermosonimetry in a mineral research, especially phosphates, as well as ceramic and construction materials. This knowledge is broadened by the latest studies of Ozao *et al.* [15], McCauley and Johnson [1] and Dollimore *et al.* [2], who studied the decrepitation on the basis of comparative thermoanalytical study.

The unique possibilities of simultaneous measurements of acoustic emission and differential thermal analysis are published in paper [16] where applications for dehydration, phase transformation and thermal decomposition of various inorganic salts are illustrated.

In the submitted study the results on decrepitation study of baryte minerals of various quality are presented with the aim to analyse the significance of the primary factors (inclusions of liquids and gases) and the secondary factors (the quality of minerals, different cleavage of mixed minerals) on the decrepitation process.

## Materials and methods

The thermometric investigation was carried out with the baryte samples of 1–2 mm granularity the chemical composition of which is given in Table 1.

**Table 1** Chemical composition of investigated samples

Sample	BaSO <sub>4</sub> /%	Fe/%	SiO <sub>2</sub> /%	Loss of heating/%
Baryte 1	91.90	1.99	2.49	1.63
Baryte 2	46.80	16.22	9.48	12.87

The decrepitation of minerals was investigated by the thermovacuum impulse method under these experimental conditions: pressure  $10^{-4}$  torr, mass of samples 15 mg, size fraction 0.4–0.7 mm, rate of heating  $20^{\circ}\text{C min}^{-1}$ . The samples of barytes and siderite monominerals were submitted to microscopic examination.

The experimental performance is based on measuring the effect of decrepitation brought about by the explosions of liquid and gaseous inclusions which are registered as pressure changes in the system by a high ionization detector.

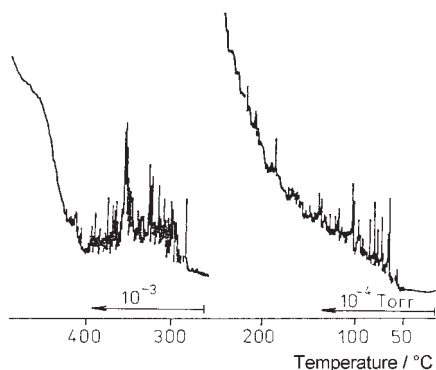
The details of AE-DTA equipment were presented in [10]. The samples of baryte are specified of Table 1, and were used without any further treatment.  $\text{Al}_2\text{O}_3$  powder is used as the reference material. The samples and reference material are put in two fused silica holders (15×15 mm) fitted with a cup. The holders are placed symmetrically in the electric furnace. A fused silica rod (8×240 mm) is attached to the bottom of the sample holder. A 140 kHz resonance frequency piezo-electric sensor is contacted at the end of the rod. The acoustic waves generated in the sample holder are transmitted through the rod to the end where they are detected and converted to electric pulses, and recorded as counts per second by an AE Tester (Electronics Instruments 9501). DTA curves are also recorded by using the chromel–alumel thermocouple. The tip is located in a 10 mm length cavity at the top of the sample cup. The mass of samples for TG-DTA study was 22.1 and 21.3 mg, respectively and for AE measurements 200 mg.

## Results and discussion

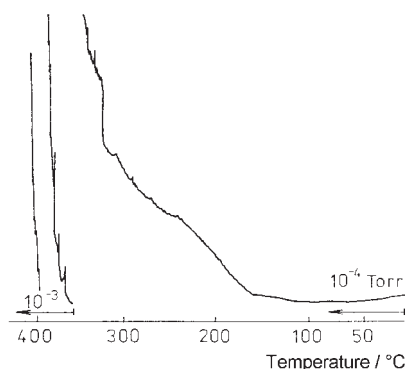
From literature [6] it is known that the decrepitation mineral explosions during the thermal heating without thermic dissociation are caused

- within the range of temperatures 60–250°C by degassing of inclusions and mass breaking of liquid-gaseous inclusions,
- at temperatures lower than 350°C by different mineral cleavage and
- at higher temperatures the increased decrepitation activity is given by the area of critical temperature of water included in a mineral (350–400°C).

Figures 1 and 2 provide information on the process of inclusions release from pure barytes and siderite minerals during thermal heating. Both decrepitolgrams confirm clearly the decrepitation ability of both minerals as a result of present liquid and gaseous inclusions in minute holes of the mineral. The decrepitation ability of barytes is already considerable from 60°C and the intensive pressure pulses within the temperature range lower than 300°C are connected with the mass breaking of mineral inclusions. In case of siderite (Fig. 2) the non-impulsive degassing can be seen at temperatures higher than 150°C. This can be explained by release of fluid inclusions with damaged sealing near the surface of studied grains. The increased decrepitation activity of siderite at the temperature of 300°C is connected with the excellent cleavage of this mineral according to rhombohedron (1011). Also in case of barytes (Fig. 1) with good cleavage according to (010) plane the character of decrepitation in the temperature area higher than 300°C is significantly impulsive with the maximum around



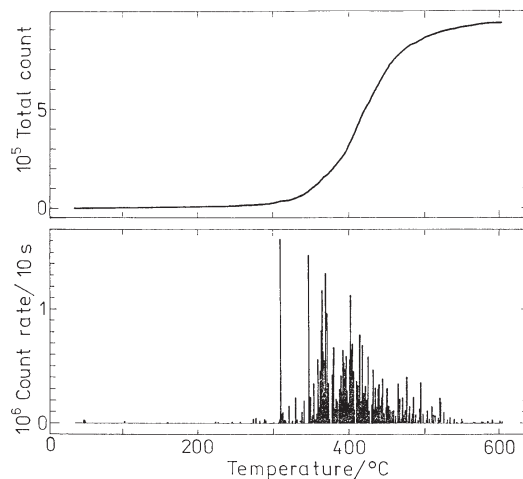
**Fig. 1** Decrepitogram of pure baryte



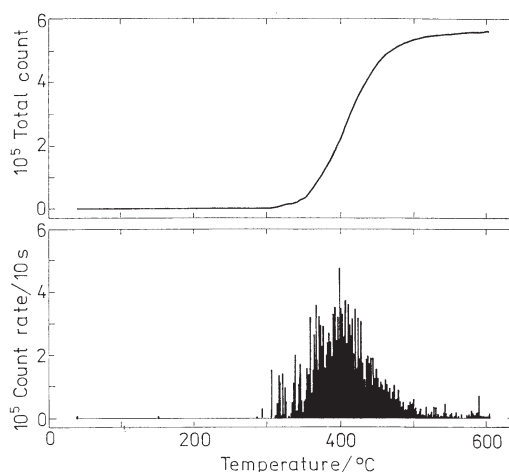
**Fig. 2** Decrepitogram of pure siderite

370°C. Within the mentioned appraisal of decrepitation diagrams of both minerals the baryte is classified as mineral with higher decrepitation ability and siderite with medium decrepitation activity. The different decrepitation activity of minerals by [6] is also very precisely indicated by thermosonimetry. It is supposed that siderite admixture, with an excellent cleavage, in barytes ore favourably influences the decrepitation activity of this sample.

Comparing records of AE-DTA curves of pure baryte (Fig. 3) and less quality baryte sample with content of siderite (Fig. 4) we can see that the values of AE-DTA curve of pure sample are an order higher ( $10^6$  count rate) than the values in Fig. 4. At the same time the course of pulses of sonimetric record of both samples is different. The pure baryte sample has numerous considerable peaks within the temperature range 320–400°C, while their intensity decreases with temperature. At moderate decrepitation of second sample (Fig. 4) the maximum intensity is recorded only at 400°C, while the course has more regular increasing and decreasing phase around maximum. From comparison of thermosonimetric records and decrepitation diagrams of both samples it is obvious that an extraordinary decrepitation ability of barytes is not



**Fig. 3** AE-DTA curve of baryte 1



**Fig. 4** AE-DTA curve of baryte 2

significantly influenced by cleavage of accompanying mineral. It follows from literature that the favourable influence of secondary factor – cleavage – may be manifested only in case of main mineral of medium or small decrepitation ability, e.g. carbonate of breuneritic type [8].

The thermoanalytical TG-DTA study of both barytes samples of different quality is shown in Figs 5 and 6. In case of pure sample (Fig. 5) an intensive one-shot 65% decrease of mass of the material at temperature  $T_1=350^\circ\text{C}$  is indicated on TG record. In case of moderate decrepitation of mixed mineral (Fig. 6) the material mass decrease runs in three phases (1.4%–3%–4.7%) within temperature range  $T_2=380\text{--}570^\circ\text{C}$ . These indicated mass changes are unambiguously caused by the material emission as a result of

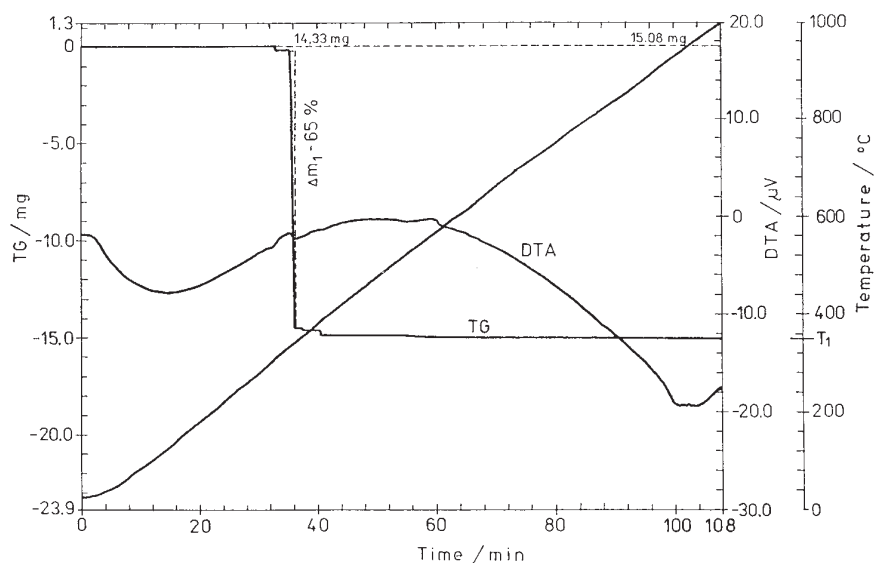


Fig. 5 TG-DTA curve of baryte 1

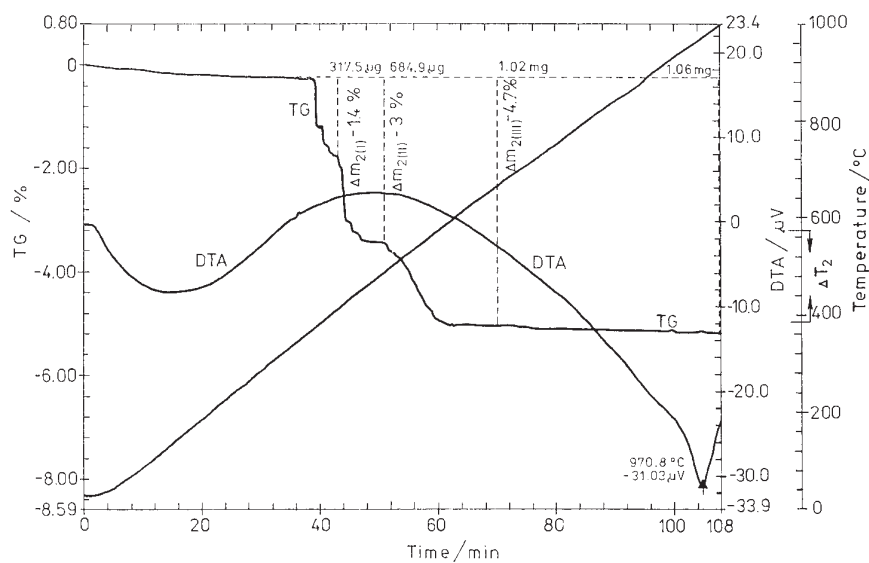


Fig. 6 TG-DTA curve of baryte 2

decrepitation without thermic dissociation of siderite. The DTA record of both samples has a similar course in the area, where the decrease in mass because of decrepitation is not recorded. The area is typical with two endothermic peaks, one of which is connected with the dehydration in the mineral and the second one is connected with the thermal decomposition of barytes. Within the temperature range of decrepitation (350–570°C) a

wide plateau of exothermic process is recorded on the DTA curve with increasing phase at starting temperatures of decrepitation indicated on TG curves. However, the character of these processes is not possible to identify unambiguously. In case of intensive decrepitation of pure mineral (Fig. 5) there are two indications of exothermic peaks on DTA record, while the first one corresponds to the decrepitation mass decrease. It is interesting that on the DTA record of the second sample with silica content of 9.48% there are no changes indicated, so the genesis of the second peak (exo-peak of silica, 574°C, Fig. 5) for intensive decrepitation is not clear.

The low decreases in mass in case of the second sample (ca 4.7 %) mean that the total emission of silica and siderite components in material did not happen. In consent with the thermosonimetry, TG-DTA study confirmed that in case of pure baryte samples the intensive explosions are achieved and they are connected with the mass reduction at temperatures that are lower than those in case of mixed mineral sample. In consent with the results of McCauley and Johnson [1] these most intensive explosions are caused by water dropped in the mineral structure, which at the temperature of decrepitation (TG curve) would produce water vapour pressure that was similar to the pressure required to break bars of mineral. This result of carbonate decrepitation [1] may be used for other minerals. However, it is necessary to note that also at temperatures lower than 350°C the process of spontaneous decrepitation desintegration of material is carried out of mass breaking of mineral inclusions, but the difference between two samples is not significant.

## Conclusions

On the basis of comparative study of decrepigrams, thermosonimetric, TG and DTA records of baryte samples of different quality it is possible to claim that

- the decrepitation activity of pure baryte is not influenced by accompanying siderite in the mineral mixture in spite of better siderite cleavage,
- the favourable influence of cleavage on decrepitation activity can be expected only with the main minerals of medium or small decrepitation ability, e.g. carbonates of breuneritic type.

In case of minerals of different decrepitation ability the maximum of decrepitation activity is achieved at lower temperatures.

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This work was supported by the Slovak Grant Agency for Science VEGA (grants 2/2108/22 and 2/2103/22).

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