Application of the Fuzzy Set Theory for the Quantitative Phase Analysis of Rocks Using Thermal Analysis Applied to the Boda Siltstone Formation, Hungary

Dedicated to the 80th Birthday of Professor György Bárdossy

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Abstract: The thick Upper Permian claystone formation in southern Hungary has been selected as a possible disposal of the high level radioactive waste. This formation has been studied by various methods in the recent years. The quantitative determination of the mineral composition by thermal analysis contains some analytical problems. The uncertainties of the analytical results have been evaluated by the methods of the fuzzy set theory.

Keywords: thermal analysis, uncertainty, fuzzy sets

1 Introduction

Geology is a complicated and diverse science. Problems the time and space relations (both past and future) are at the heart of geological thinking. Geology differs from other experimental sciences that the natural processes are uncontrolled by the investigator. The founded situation developed over a long time through more processes. Nor can observe the natural processes, most of them are finished, and the results are fixed. The most geological data are fragmentary; the geologist must make do with the data available. The data may be measurement, counting, identification and ranking. Every geologist obtain numerical data: number of specimens collected from a formation, strike and dip of a bed or fault, data of chemical, phase or other analysis. All geologists who work with numbers use statistical methods and can profit from the applied statistic.

Geological investigations are characterized by particularly high uncertainties. The uncertainty originates from the natural variability of geologic objects and process, from the error of measurements, and from the limited possibility to sample geologic objects in space and time. The mathematical methods are used to quantify uncertainty have certain limitations at the geological problems: Between the geological populations are often gradual transitions. The geological investigations are often unrepeatable [1]. For the handling of uncertainties one of the mathematical methods is the fuzzy set theory [2, 3].

In the next section the application of the fuzzy arithmetic is presented to the quantitative phase analysis of rock samples using thermoanalytical methods, applied to the Boda Siltstone Formation, Hungary [4].

2 Boda Siltstone Formation (BSF) as a Potential Disposal of High Level Radioactive Waste

The Late Permian Boda Siltstone Formation (BSF) occurring in southern Hungary. It is the candidate host formation one selected for the disposal of High Level Radioactive Waste. To protect the natural environment from exposure to radiation achieved by constructing artificial barriers, as well as by utilizing natural ones. Natural barriers comprise primarily the geological setting. The selection, characterization and confirmation of the site require increasingly detailed geological data.

BSF is belongs to the groups of the so-called argillaceous potential disposal rocks. Its currently acknowledged features are determined by its fundamentally special environment of formation, by the relatively old age (250-260 My), as well as by history. According the international literature such overconsolidated, strength aleurolites and claystones are suitable for the long-term disposal of radioactive waste. The overconsolidated rocks have a higher heatstability and better mechanical features of rock. BSF is a deep geological formation, the potential disposal located at a depth of more than 1050 m, maximal thickness of the layer between 700-900 m, the rock temperature 50 °C [5].

This formation has been studied by various methods in the recent years. It must be taken the evaluation and numerisation of the reliability (uncertainty/error) of all data of measurements [6,7].

3 Thermoanalytical Investigations

Thermal Analysis is a group of analytical techniques in which physical properties or chemical reactions of a substance are measured as a function of temperature.

The DTA (Differential Thermal Analysis) and the TG (Thermogravimetry) are the most widespread methods used in geology. Thermogravimetry is a technique in which the mass of a substance is measured as a function of temperature.

Differential thermogravimetry is suitable for the identification and for the determination of quantity of the mineral composition of rocks.

The main thermal active minerals are illite-muscovite, chlorite, calcite, dolomite and montmorillonite (in the decreasing order of the occurrence) totalling 45-65% of the rock mass. The remaining minerals are not detectable by thermoanalytical method. The typical thermoanalytical curves of the Boda claystone is illustrated on Fig. 1.

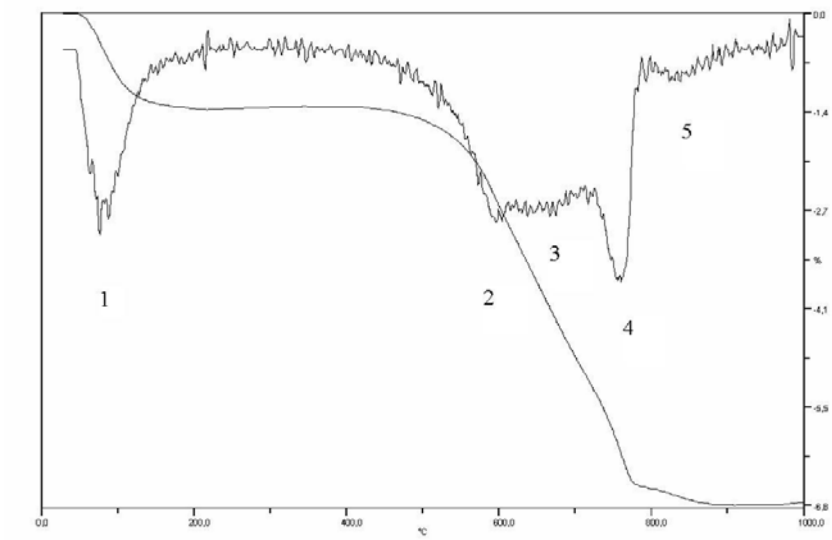

Figure 1

Typical thermogravimetric curves (TG and DTG) of a Boda Siltstone sample borehole Bat-15 18.2-18.3 m (minerals: 1. illite-muscovite, 2. illite-muscovite, 3. chlorite, 4. calcite, 5. chlorite)

The quantitative determination of these minerals calculated with stoichiometric equation of the thermal reaction based on the mass change during the heating. The uncertainty of the thermoanalytical phase analysis may be originating basically two different factors, namely the error of the mass measurement and the uncertainty of the analysis of the mineral composition.

Derivatograph-c is computer automated equipment for the simultaneous TG and DTA measurements [8]. The measuring domain is a semi-microelectronic and automatic balance. The measurement uncertainty of the balance in the case of used 100 mg sensitivity is ±0.2%, reproducibility 0.08 mg. The accuracy of the mass change is influenced by the fact that if the furnace is heated up the TG curve moves in the direction of mass increase (sample mass is constant). In the initial period of heating (up to 100-150 °C) these change is rapid, later slow and smaller. The reason is the convections stream and the changes and the density changes of the gas medium inside the furnace (buoyancy). It is evident that neglect of these changes will cause inevitable errors in the interpretation of TG data. The changes in the TG curve (base line) are not large in absolute scale (1% between 20-1000 °C) but they – especially in case of little amount of sample - are perceptible and correctable [9].

The reasons of analytical problems are different. A peak temperature of a decomposition process due to the partial pressure of the decomposed gas or vapour product depends among others on its amount. The relation between peak temperature and concentration is logarithmic. The other factor which influence the temperature of the decomposition is variability of the stoichiometry the different minerals.

The thermal reactions of illite-muscovite are influenced of the stage of diagenesis. The basic reactions of illite are dehydration and dehydroxylation (Fig. 2).

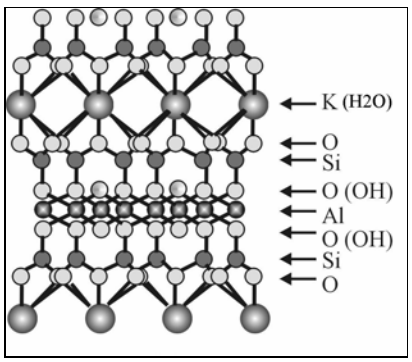

Figure 2

Water and OH in the mica structure

During the diagenesis the water content of the mineral decreasing and the temperature of the dehydroxylation shifts towards higher temperature. (Fig. 3)

The peak of the dehydroxylation temperature of illite is about 550 °C, at the BSF rocks the average is 590 °C. The amount of the adsorptive bounded water in illite is about 4%. The average value of the water content in the illite-muscovite in the BSF sample is about 1,1%.

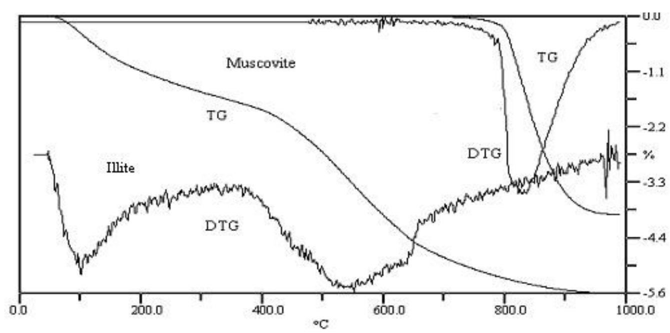

Figure 3
Difference of TG and DTG curves of illite and muscovite

The thermal reactions of chlorite theoretical dehydroxylation process in two steps. The first one is the dehydroxylation of the „brucite sheet" and the second one is the dehydroxylation of octahedral sheet (Fig. 4).

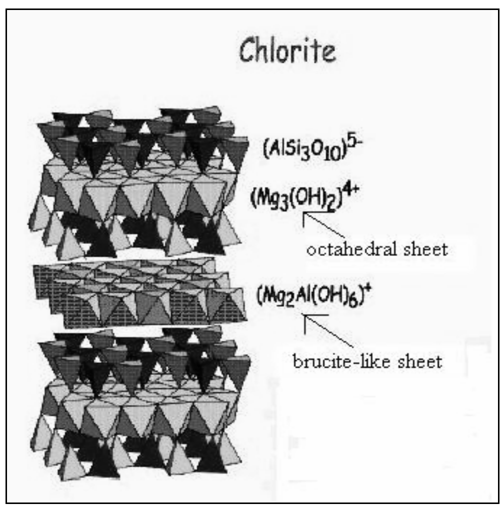

Figure 4
Structure of chlorite

The temperature of the DTG peak of the two reactions especially the second one depends on the composition of the sheets. At the primary Mg-chlorite the first reaction is at 600-650 °C and follows the second one at 150-250 °C higher. With the increasing Fe content accordingly the electronegativity of the cation the temperature of the reactions decreases, at the Fe-chlorite 520-580 °C. In the BSF sample these reactions are at the high temperature (average values are 670 °C and 850 °C).

The peak of the reaction of calcite decomposition depends on its quantity changes in the BSF samples between 740-900 °C. Dolomite has two reaction steps in the same interval.

The decomposition reactions generally take place in a broad temperature interval. The similar temperature interval of the three mineral and their different combination from sample to sample is the reason that occurs more or less overlapping situation.

Because of the above mentioned problems the uncertainties of the analytical results have been evaluated by the methods of the fuzzy set theory. Trapezoidal (sometimes triangular) fuzzy numbers have been constructed from the traditional crisp number for every mineral of each rock sample. The characteristic values of each fuzzy number, such as minimum and maximum of the phase, peak point of interval. Specific fuzzy areas were calculated which express more clearly the analytical error, and finally defuzzificated numbers are presented.

The main mineralogical and petrographical results of the studies show that the minerals of the studied rocks can be ranked according the analytical error. For the studied BAF samples the following sequences was established: montmorillonite, dolomite, calcite, chlorite and muscovite. Averages of the mineral composition, calculated separately from the traditional crisp and the fuzzy numbers showed almost perfect coincidence. The standard deviations of the crisp numbers reflect the natural variability of the mineral composition. On the other hand the standard deviations of the corresponding fuzzy numbers express the analytical uncertainty of the phase analysis. Similar results are obtained from the quantitative analysis by X-ray diffractometry [10].

Based on the different kind of investigations (thermal analysis, X-ray diffraction, geochemical and microscopic investigation etc.) [11, 12] it may be stated that the sedimentation in the Permian took place in a special alkaline lacustrine environment, under extreme climatic and geochemical conditions. During the diagenesis period these rocks were buried at a depth of 3,5-4,5 km, under temperatures between 160-200 °C (stage of illite crystallinity). Due to its thermal history the rocks have relatively low heat stability. The absence of swelling clay minerals and the presence of microcrystalline silica and high albite content have given considerably better strength properties to the BSF in comparison to other potential argillaceous host rock formations. This situation has resulted in the overconsolidated character of BSF with high heat stability. The analysis excluded an approximately 150 metres thick bottom series with uncertain properties and a weathered 30-50 metres tick outcrop area (with montmorillonite).

Conclusions

If a rock sample content more minerals, with varying compositions, with little decomposed proportion and with decomposition in similar temperature interval the evaluation of thermoanalytical curve possible only with high uncertainty. Such situation represents the sample from the Boda Siltstone Formation. This uncertainty may be numerisated by the fuzzy set methods.

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