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THE PRESENT STATE OF THERMAL INVESTIGATIONS OF CLAYS

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ABSTRACT

Recent papers on thermal analysis of clays and clay minerals are reviewed. Some trends in the applications of thermal methods in clay science have been discussed and exemplified.

INTRODUCTION

Thermal investigations of clays came into common use in the 1950's and progressed rapidly with respect to the purposes of the studies as well as to the methods applied. The first monograph concerning this topic was the magnificent work of R.C. Mackenzie of 1957 [1]. It was based on the DTA method and provided much data applicable for the interpretation of DTA curves and identification of minerals. It was followed by many publications, books and shorter papers, showing the evolution of the approaches to the problems of thermal investigations of clays. Firstly, the development of thermal instrumentation led to the enrichment of the research workshop. In the early 1960's the simultaneous methods of DTA-TG-DTG were commonly applied, primarly due to the widely used instrument - the derivatograph of F. Paulik and J. Paulik and L. Erdey [2], subsequently followed by analogous instruments manufactured by many firms, as well as new constructions of the instruments, new devices of various types and the combinations of instruments, making it possible to obtain simultaneous results from several applied methods, e.g. DTA-TG-DTG-EGA. Also calorimetric methods have been employed for the examinations of clays, sometimes

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using new constructions of calorimeters. In the majority of studies of clay minerals and rocks other techniques have also been used in combination with thermal treatments, e.g. X-ray diffraction, TEM, SEM, IR, NMR, various analytical methods for determination of the composition, etc., and therefore the contribution of thermal methods in the final results of the studies of clays ranges widely in individual papers.

RECENT TRENDS IN THERMAL STUDIES OF CLAYS

The latest thermal studies of clays have been applied to solve very many particular problems, using various techniques including calorimetry. Recently several papers delivered at the 9th ICTA Congress in Jerusalem have presented different approaches to the problems connected with clay minerals and rocks.The paper by Singer and Huang [3] may serve as a very good example of very elegant thermal studies of the clay substance showing a characteristic trend of investigations: thus the DTG analyses and isothermal heating examinations carried out on the hydroxy Al polymer/montmorillonite complexes prepared in the presence of humic acid extracted from an Orthic Black Chernozemic soil from Southwestern Saskatchewan, Canada. The results obtained suggest that some organic matter from the humic acid may have penetrated into the interlayer space of the montmorillonite, together with the aluminum, and also the presence of humic acid appears to have decreased AlOH polymer interlayering in montmorillonite. The interpretation of the temperatures of the thermal reactions of the complex studied led the authors to suggest that in the organo-clay complex there are specific sites in which the organic matter is protected from thermal reactions. These sites are probably inside the interlayers. Also the results of tracing carbon elimination from humic acid in the AlOH/montmorillonite/HA complexes have been interpreted as evidence of interlayering of a fraction of the humic acid in montmorillonite. Finally it has been concluded that (1) the presence of humic acid decreases AlOH polymer interlayering in montmorillonite, and (2) some organic material from the humic acid may have penetrated into the interlayer spaces of montmorillonite together with Al-polymer.

Similarly studies of adsorption of D_2O by sepiolite and palygorskite were carried out by Shuali, Yariv, Steinberg, Muller-Vonmoos, Kahr and Rub [4], using the thermal methods DTA, TG and

EGA, in order to identify the mechanism of adsorption and structural implications resulting from the thermal examinations. They showed that the thermal dehydroxylation of sepiolite differed from that of palygorskite. Palygorskite dehydroxylates in one stage, giving a single endothermic peak of dehydroxylation. Sepiolite, on the other hand, dehydroxylates in two stages, giving rise to two endothermic peaks, the latter is followed by a sharp exothermic peak. They demonstrated that the second stage of dehydroxylation of sepiolite is not associated with the decomposition of residual TOT units but results from the decomposition of secondary units which have been formed during the first stage of the dehydroxylation of this clay.

Thermal analysis was also applied by Yariv, Kahr and Rub [5] to identify the mode of adsorption of rhodamine 6G by smectite minerals. The mechanism of these thermal reactions of smectites was interpreted from the behaviour of the synthetic Na-hectorite, known as laponite, and from montmorillonite, both treated with the cationic dye rhodamine 6G.

Another trend of research is represented by papers dealing with the determination of thermal properties of clay minerals in relationship to their mineralogical features. Thus Minato [6] studied the dehydration stages determined by TG and DTG, and dehydration energies measured by the DSC method of 10 A halloysites of various origin (hydrothermal and weathering) and of different shape (tubular and spherical) of the crystallites. Similarly Nagasawa and Okochi [7] presented the results of X-ray studies of dehydration and rehydration of expansible clay minerals using as examples homoionic samples of three montmorillonites, beidelite and vermiculite.

Another group of papers deals with the clay-water system in different aspects of this problem, e.g. with the influence of freezing-thawing cycles on the thermal behaviour of a clay [8], or with the phenomena occurring in clay suspensions during storage, drying and/or heating [9]. In marine clays water sorption changes after cyclic freezing due to a change in the microstructure of the clay. Feldspar may be formed either at elevated temperatures or due to storage and drying.

Furthermore, a number of publications regarding the application of thermal analysis to clay studies have been issued in such journals as Thermochimica Acta, Journal of Thermal Analysis, Clays and Clay Minerals and Clay Minerals, as well as less familiar ones.

The presentation of a greater number of these papers would be beyond the limits of this short review and only some trends of thermal studies of clays and respective examples will be mentioned.

Particularly most popular in earlier papers since 1985 as well as in the recent ones are the results of thermal investigations applied as one of the methods, among other techniques, of identification and characterization of clay minerals and of determination of the composition of clay rocks. The thermal methods most commonly used for this purpose are DTA or TG (combined with DTG) and simultaneous DTA-TG-DTG [10-17]. Among them, the application of TGA for reassesment of samples of widespread occurence frequently misnamed "volkonskoite" is worthy of note [18]. It should be noted that thermal examinations of clay rocks and related materials concern not only typical clay minerals but also their non-clayey admixtures as e.g. carbonates [19] or bauxite minerals [20]. Similarly, the method of dilatometry has been employed for the identification and characterization of clays [21, 22]. In some cases the appearance of some new apparatus has provided an impetus for it testing by its use in the study and identification of clays [23, 24].

Besides the traditional applications of thermal analysis, the problems treated in the majority of papers are similar to those delivered at 9th ICTA. These include studies of adsorption as well as interaction of clays with various solids or reagents, especially those resulting in intercalation of clay minerals, which comprise thermal investigations carried out in order to identify these phenomena experimentally, and also for industrial and agricultural applications. Among these many interesting and valuable studies should be mentioned. Thus Yariv [25] studied the adsorption of organic molecules on clay minerals to identify the types of association between water molecules, exchangeable metallic cations and organic molecules or ions formed on clay surfaces. Mackenzie and Rahman [26] investigated the interaction of kaolinite with calcite on heating. Heller-Kallai, Yariv, Deutsch and Friedman [27] analysed by means of DTA the interactions between stearic acid and allophane, sepiolite, pallygorskite, pyrophyllite or talc. Hepler, Yariv and Dobrogowska [28] led the calorimetric investigation of adsorption of crystal-violet on montmorillonite. Sidheswaran, Ganguli and Bhat [29] observed thermal behaviour of intercalated kaolinite. Maza Rodriguez and co-authors [30] studied the interaction between the pesticide phenamiphos and montmorillonite.

Interesting results of the studies of intercalation of clays by means of calorimetric methods have been presented by Schmalstieg and co-authors [31] and Blumenthal and co-authors [32]; the latter investigators stated that the DCA curve of the clay-hydrazine interaction may serve for the quantitative determination of kaolinite in natural or artificial mixtures (the latter prepared for industrial purposes) and anticipate further interesting applications for intercalation chemistry. Also Bahranowski [33], Bandosz et al. [34], Fijal [35], Horte and co-workers [36, 37] reported the results of their investigations of intercalation of clays using thermal methods.

Some of the papers deal with kinetics of dehydration and dehydroxylation, the determination of enthalpy of the dehydration and other thermodynamic values [38-44]. Individual papers concern the high- temperature transformations of clay minerals [45, 46] and the application of these data for the investigations of old pottery for the reconstruction of production conditions as well as for inferring the raw materials used [47]. A scattering of some other approaches to clays with the use of thermal investigations have been presented: thermal characteristics of TiO_2-cross-linked montmorillonite obtained by Ti-introduction into montmorillonite [48], the problems of the system clay-water [49] and others.

Finally, the excellent monograph "Fuller's Earth: A History of Calcium montmorillonite" [50], which incidentally is also a masterpiece of editorial work, presents numerous thermal data on Fuller's Earths as an indispensable complement to their characterization.

FINAL REMARKS

Progress in thermal studies of clays and clay minerals, as shown by publications appearing in the last years, has been very rapid. The variety of trends of applications and the multitude of techniques permit anticipating further progress in the near future in thermal studies of clays. Most of them will probably be connected with the adsorption and intercalation of clays and have both great scientific and practical significance and very wide possibilities of further development.

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