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Review of PhD thesis of Artur Kuligiewicz

PhD dissertation with title „**The refinement of adsorbed water structure in smectites using infrared spectroscopy and thermogravimetric studies"** is highly actual. Smectite, thanks to its unique properties, is long-time in the centre of the interest of various groups from clay mineralogist through mineral processing engineers or biologists to investors. The ability of smectite to adsorb and desorb water significantly affects its industrial applications as well its influence to geological processes e.g. smectite dehydration helps to migration of oil in sedimentary basins.

The thesis is written in the form of package of three peer-reviewed, published papers with short introduction and papers summary at the first part of dissertation. The short review has 33 pages, including references. The review is written equally in Polish and in English. It consists of the introduction with knowledge background about smectite, predominately relating to infrared spectroscopy, thermal analysis and layer charge measurements as tools for understanding of smectite-water interaction. The aims of the study are described at the end of the introduction. The main aim of the thesis was to refine the structure of adsorbed water in smectites. PhD student, Artur Kuligiewicz, realised three consecutive steps to reach the aim. They were transformed to the three papers, two in Clays and Clay Minerals, reputable journal of American Clay Minerals Society and one in the American Mineralogist, the flagship journal of the Mineralogical Society of America. Every paper is clearly and exactly summarised by Artur Kuligiewicz in the first part of dissertation. The second part of dissertation is composed by three full version papers as appendixes. Artur Kuligiewicz is the first author in all three articles. It has been difficult to look for shortcomings in the reviewed papers by editors, reviewers, by supervisor – Arkadiusz Derkowski, by co-authors of well-known names e.g. Katja Emmerich, Georgios Chryssikos. However, I did not find the evolution of TBW content after 12 hours of heating in Fig. 4 although the reference on it is in line 315 of the "Tighly bound water in smectites" paper. Could you show the missing curves? Then I found only a small terminological error in the introductory part. There is Boom Clay formation wrongly labelled as bentonites in the page 15. The Boom clay is a moderately swelling clay that is composed of smectite, illite, randomly interstratified illite-smectite and kaolinite-smectite and nonclay minerals. It has similar properties as bentonite but does not contain at least 50 % of smectite and this is basic definition of bentonite.

The thesis is outstanding and brings many remarkable results. I would highlight these major contributions of the dissertation:

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- ATR setup allowing smectite hydration by H_2O or D_2O at adjustable humidity
- Removing the overlap between the O-H stretching bands from H_2O and structural OH by substituting interlayer H_2O with D_2O
- A new, relatively simple spectroscopic layer charge determination method was developed base on high-energy O-D stretching band of adsorbed D_2O at range 2686-2700 cm^{-1} determined by infrared spectroscopy. The method was verified by statistically significant correlation (29 dioctahedral smectites and 13 reduced-charge montmorillonites) between νO-D and layer charge determined by common methodology (structural formula methods and alkylammonium method).
- Optimal drying protocol for smectite-bearing samples are drying at least 200°C, after prior exchange with a cation of low hydration enthalpy. It was determined by series of thermogravimetric analyses.
- Mg^{2+}-saturated nontronite was found to retain molecular water up to 550°C. It signalizes that sheet silicates with Mg^{2+} in the interlayer can be a source of water during metamorphism.
- Significant similarities were observed for tightly bound water (TBW) in smectites and in zeolites. It showed that TBW molecules are strongly bonded to interlayer cations.
- Calculation of activation energy (E_a) was realized. The dependence of E_a on the interlayer cation hydration enthalpy confirmed that TBW molecules are involved in strong interactions with the interlayer cations. The continuous changes of E_a imply a gradual transition between different reaction mechanisms and confirm overlap of dehydration and dehydroxylation.

Presented results generated many questions. They have been responsibly answered by the PhD candidate and his co-authors in the papers. I would like, however, to ask some questions to Artur Kuligiewicz:

Have you already tried to use stretching-bending combination of H_2O in smectites (band ~5230 cm^{-1}) by near-IR for layer-charged diagnostic?

The Hoffman-Klemen effect has been described for Mg^{2+} in the "Tighly bound water in smectites" paper. Could you please mention other cations relatively common in nature that could have similar behaviour as Mg^{2+} in smectites? Could this effect significantly degrade the properties of smectite in some specific application?

I would appreciate if you could show me example of entire calculation of the activation energy of dehydration with particular numbers and charts.

Do you have in mind some new series of samples in which you would like to apply your spectroscopic layer charge determination method base on high-energy O-D stretching band of adsorbed D_2O?

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Presented PhD thesis confirms that Artur Kuligiewicz is full-valued young scientist and the PhD dissertation fulfils requirements posed by Polish Act of 14 March 2003 on Academic Degrees and Titles and on Degrees and Title in Art. I recommend that the dissertation should be accepted to a public defence.

In Bratislava, April 4, 2017

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