CHARLES UNIVERSITY
Faculty of science

Prague, September 8, 2018

Reviewer comments

Reviewed Ph.D. thesis of **Mgr. Filip Košek** entitled "**Application of Raman spectroscopy for detection of sulfates of self-ignited coal heaps**" deals with qualitative spectroscopic characterisation of newly-formed gas-vent minerals created by complex geochemical processes connected with burning of coal dumps.

The thesis contains almost 70 text pages, extensive references set and four appendices. The chapters 1 to 3 are devoted to a very complex introduction to the studied environment, involved geochemical processes and Raman spectroscopy application. Text and layout of this part clearly reflects very deep insight and understanding of the studied interdisciplinary topic by the author. Chapters 4 to 8 deal with the Raman spectroscopic study of synthetic anhydrous sulfates and mainly with identification of newly-formed phases in several burning coal dumps in Czech Republic and Germany. Chapters 9 and 10 contain critical discussion, concluding remarks and planned future directions concerning target topic.

The reviewed Ph.D. thesis is written in fluent English, with minimum typographic errors and with a high quality figures. One of the most remarkable results of the thesis is the critical evaluation of portable Raman spectrometers application for the characterization of studied phases with limited stability. The novelty and importance of studied topic is reflected by three included papers (appendix IV) successfully published in Journal of Raman Spectroscopy and Journal of Molecular Structure.

I must also positively highlight appendices I to III which contain list of known minerals found within gas-vents of burning coals waste dumps, Raman spectra and database of Raman bands of investigated minerals.

I have some comments, questions and suggestions concerning reviewed thesis:

1) The label "4" should be replaced by label "7" in upper part of the Figure 5.
2) The using of the term "sublimates" is very questionable (as it is discussed in chapter 2.4.2) – more appropriate expression could be "products of sublimation".
3) The localisation of the bands at 475 and 469 cm^{-1} in Figure 17 is quite problematic. Nevertheless related discussion presented on page 48 is very realistic.
4) Were the position and shape of fluorescence bands associated with 785 nm laser excitation (Figure 18) same for all samples in studied areas?
5) The expression "sublimation" should be replaced by the term "desublimation" or "deposition" in Figures 20 and 22.
6) The presence of "unknown ammonium sulfate" is mentioned in Figure 26. Anyway existence of mixed sulfate phases could also explain the presented Raman spectrum.
7) Are the expressions "anhydrous alums" and "hydrated alums" generally used?

8) The limitation of the application of PXRD method for the identification of very small prismatic crystals is mentioned on page 67. What is your opinion concerning application of single crystal XRD method?
9) There are small uncertainties in some Raman spectra and tables in Appendix II. I am also missing chemical formulae and page numbering in this very interesting part of the thesis.
10) What is your opinion concerning application of site-group analysis approach for the assignment of ν_1 and ν_3 modes of sulfate anions, which are overlapping in some presented Raman spectra?

Finally, I have to conclude that above mentioned comments and suggestions do not negatively influence overall high quality of reviewed thesis of **Mgr. Filip Košek** and I am **fully recommending** his thesis entitled "Application of Raman spectroscopy for detection of sulfates of self-ignited coal heaps" **for the Ph.D. defence**.

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