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Report on the Thesis submitted to the Charles University in Prague by Ms. Martina Vítková

Ms. Martina Vítková has submitted a printed book to the Faculty of Sciences, Charles University in Prague, in order to be authorized to defend her Ph.D. thesis.
The subject of her studies is *"Environmental characteristics of mineral waste from metallurgy – Copper-cobalt smelting in the Zambian Copperbelt"*. It is presented in details within a 45-pages text, including Tables and Figures, and with a high technical quality; moreover, some "boxes" give specific complementary information: techniques used for solid-state studies, leaching tests, composition of physiological-like solvents.
The organization of the main text is logically presented as 4 chapters: (1) a description of the sampling sites with their industrial history; (2) a solid-state study of the various kinds of solid samples (slag, dusts and fly ashes), with a series of complementary techniques; (3) a series of standardized leaching tests applied to these metallurgical wastes, with geochemical modelling in order to discuss the results; (4) a discussion about the environmental and health issues for these solids, when dispersed in the ambient air. An up-to-date bibliography accompanies these data.

The sampling sites are 3 old copper and cobalt metallic plants in Zambia, regularly studied from an environmental point of view within the framework of Zambia/Czech Republic scientific cooperative agreements; such cooperation has soon resulted in a number of papers from the Institute of Geochemistry, Mineralogy & Mineral Resources at Charles University in Prague. Various smelting techniques were applied during more than 70 years of operation, and they have produced a huge amount of solid wastes: slag, dust from flue gas treatment, fly ash. The sampling was conducted at these 3 different smelter sites.
In order to obtain the maximum of detailed information concerning the structure and properties of these solid samples, they were characterized by the combination of a series of specific methodologies, among them: X-ray diffraction, scanning electron microscopy, electron probe microanalysis and transmission electron microscopy. The main metal-bearing phases were characterized, as also the secondary solid phases arising from weathering. Of special significance, I wish to mention the fact that Ms. Vítková was able to notice that the presence of nanophases cannot be detected with common analytical instruments, and that only

a combination of high-resolution methods can allow a complete description of such solid phases. Of course, such nanophases can have an important impact on the environmental behaviour of the solid, and this is why their detection and identification are of interest.
In order to be able to predict the environmental behaviour of these solid samples when stored or landfilled, and thus submitted to climatic events (mainly rain), it is common to proceed to leaching tests. Here the candidate has selected batch tests, either in a pH-static or a pH-free mode, with a time-dependent analysis of the main metallic contaminants (Cu, Co, Cd, Pb and Zn). In order to discuss the results, she has modelled the results with a geochemical speciation/solubility computer code, here PHREEQC combined with ORCHESTRA; this was realized within a 2-months stay at the Technical University of Denmark, Lyngby.
Because another way to enter into the environment is through particles flight and deposition, this point was studied next. The case of tropical oxisols present in the studied Copperbelt area is particularly worrying: at pH < 5, an important leaching can arise from either slag or dusts, with release of metal contaminants at high levels. However, a natural attenuation process was fortunately evidenced, thanks to metal sorption onto ferric (hydr)oxides. This is why a stabilization method was suggested under these local conditions. Health risks presented by dusts (from flue gas cleaning) are also taken into account: 2 laboratory tests were used in order to estimate the bioaccessibility of pollutants, when introduced either into the respiratory or the gastric tract. Leaching tests into artificial physiological media evidenced high level of dissolution for a number of toxic metals: the local population can thus be exposed to severe health risks when submitted to such flying dusts.
All these data confirmed that a detailed solid-state analysis of solid waste samples is a prerequisite before any impact study; the combination of a number of methodologies is necessary, especially in order to characterize nanoparticles. This should be followed by well-selected leaching tests, according to the nature of the contaminants and their chemical mineralogical form; the use of geochemical modelling is a useful complement, as is the characterization of newly-formed solid phases.

The preceding presentation of the experimental results obtained by Ms. Vítková and of their discussion is completed by the reprints of her 5 papers already published in international scientific journals (with peer review): *Mineralogical Magazine*, *Applied Geochemistry* (2), *Journal of Hazardous Materials* (2). Of course, they include a lot of information not reproduced in the first part of the book of Thesis, and their existence proves that the scientific work by Ms. Martina Vítková has already been recognized by international experts. Moreover, I want to add that the candidate has also co-authored 2 other papers about her previous studies on lead smelter fly ash (probably during her M.Sc. degree studies).

I have the pleasure to acknowledge that the candidate was not only able to conduct various experimental studies (solid phases characterization, leaching tests, modelling of solution chemistry, bioenvironmental evaluation and testing). She had also co-authored 2 important papers, both published in *Journal of Hazardous Materials*, a journal with an Impact Factor IF = 4.173, a somewhat high value in the field of Environmental Sciences. They are concerning methodological constraints in order to ascertain the best results from either solid state analysis or leaching tests, respectively. I consider that these 2 papers will have a high impact on the scientific community of researchers involved in the growing field of solid wastes microanalysis and their leaching behaviour. I have also to note that, everywhere in her studies (main text and published papers), all the experimental conditions (sample preparation, instrumentation parameters) are always given in full details: so the scientific community can easily estimate the quality of data (very high, to my opinion) and moreover know how to conduct studies with a similar degree of precision.

In summary, it is clear that the candidate combines high-level experimental skills both in solid phase analysis and in solution chemistry (including geochemical modelling). She is also able to write easily-understandable reports as her 7 published papers can demonstrate. As written before, the good quality and usefulness of her results will improve the general knowledge of the related scientific community.
This is why, as an external reviewer, I have the pleasure to inform the Department of Doctoral Studies at the Charles University in Prague, of the following:
I consider that the document presented by the candidate is of the high quality as required, and to my opinion Ms. Martina Vítková should be authorized to defend her Thesis in order to obtain the Ph.D. degree.

Limoges, 14 January 2013

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