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Subject : Review Thesis MVitkova

Dear Dr. Ettler,

As requested by your department, I have had the honour to thoroughly evaluate the PhD thesis of Martina Vitkova, entitled "Environmental characteristics of mineral waste from metallurgy – Copper-cobalt smelting in the Zambian Copperbelt", scheduled to be defended on January 31.

My assessment is that the thesis is suitable for the defence by the candidate. As motivated in detail below, I consider the thesis of a very high scientific quality, and therefore it should fully fulfil the criteria necessary for obtaining the Ph.D. degree.

Yours sincerely,

Dr. Ir. Joris J. Dijkstra
Senior Scientist, Department Environmental Assessment
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Annex: Review Thesis Martina Vitkova

Review PhD Thesis Martina Vitkova entitled "Environmental characteristics of mineral waste from metallurgy – Copper-cobalt smelting in the Zambian Copperbelt"

Joris Dijkstra, 14 January 2013

The thesis is based on six different studies of which - at the time of printing - four have already been published in high impact scientific journals and one is under review. This fact alone is a result that should be complimented; few PhD candidates have such a good publication record at the time of the defence.

The thesis is well written, in clear and correct English. The different publications in the appendix have been put in perspective in a well-readable series of chapters (chapter 1 – 6). For the reader, it is helpful that the introduction clearly provides an overview of the different waste forms that originate during pyrometallurgical processes and the severe environmental problems around these wastes in developing countries, specifically in the Zambian Copperbelt area.

The topics and goals of the thesis are clear and of scientific importance, but also have a clear applied component that are of direct relevance for the characterization of the environmental and health problems in this region and possible remediation options. Discussion on how the scientific results can be of value to practice returns a number of times in the thesis, which deserves in my opinion a lot of positive credits. A good illustration of thorough scientific study combined with an applied "outlook" is found in chapter V. Here, a detailed geochemical study has led to scientifically valuable conclusions as well as a possible remediation procedure that seems practical and workable (mixing local oxisols with contaminated soil, increasing the overall binding capacity and lowering the transport rate of contaminants).

A particularly interesting and positive feature of this thesis is that a number of very different measurement and modelling methods have been used and combined, with equal devotion and in-depth discussion of the results. Mineralogical microanalyses with spectroscopic techniques, leaching tests with variations in granulometry and contact times, geochemical modelling using different model platforms, and even health risks are assessed using leaching tests with simulated lung/gastic fluids. These widely different methods are all successfully deployed on an expert-level, and are used to characterize environmental risks from different angles: from leaching to soil to health risks by ingestion/inhalation.
An important feature of the thesis is that even though the results obtained by these different methods are very different in their scale (macro- or micro- level) and range of application, the results are referred to mutually between the different chapters, and therefore strengthen each other.One could argue that the paragraph on health risks (5.2) is – compared to the other chapters – less thoroughly developed, also due to the somewhat more empirical nature of the test methods, but still reasonable attempts are made to relate the outcome to observations done in the leaching and characterization studies elsewhere in the thesis and in literature.

A sound scientific critical attitude is demonstrated throughout the different chapters; a good example is p. 23, on the use of identified phases in mineralogical studies – of which the identification must be done with great care itself (paper no. IV) – and problems that arise when identified minerals are to be used in geochemical modeling.

My specific interest focuses on the studies on leaching, papers no. II and particularly papers III and V. The leaching studies are in my opinion all of high quality and form a valuable contribution to what is known in literature; specifically on grain sizes in relation to leaching tests (paper no. III) and characterization of processes that cause leaching (paper no. V). Sample pretreatment and in particular granulometry in leaching tests is at present a "hot" item in the present EU- wide standardization of leaching tests (CEN TC 351) and this study (paper III) is a welcome

contribution to the available data in this field. Although I agree largely with the conclusions, some criticism is possible on the observed magnitude of the effects of granulometry on leaching in paper III. The presentation of the data in Figure 2 does – for me - not obviously lead to the conclusion that granulometry is of "crucial" importance as concluded in the paper; one may deduce also different "accents" in the conclusions from the same results.

In paper V, a combination is made between micro-analyses and leaching measurements, in combination with geochemical modeling using ORCHESTRA and PHREEQC. The study is set up and carried out well, and I largely agree with the conclusions. A robust set of leaching tests is carried out with particular attention to the degree of "equilibrium", by performing tests at different pH values at different equilibration times. As the authors remark, there are not many studies on pH dependent leaching and solubility-controlling mechanisms of metallurgical fly ash, and this study (together with the others by the same candidate) is the most extensive and comprehensive.
However, criticism is possible on the way the existing model developed for soils (the Orchestra model; Dijkstra et al., 2009) has been parameterized. My main reservation is that I miss a motivation on choices that relate to the concept of "availability": the amounts of major and trace elements that are used as input in the model and are assumed to be available for leaching. The input "availability" is an important parameter in geochemical modeling that co-determines the model outcome. In the cited study of Dijkstra et al. (2009) based on Dijkstra et al. (2004), the input amounts are estimated at a very low pH 0.5, which was chosen as it can be shown that only at this low pH, contaminants are fully desorbed from reactive surfaces. In the (also cited) study of Dijkstra et al., 2008, on MSWI bottom ash, a discussion is given on availability at different pH values (pH 0.5 for soils containing organic matter, pH 2 for industrial residues). In paper V, however, it seems that concentrations at pH 5 have been used – without a clear motivation and a discussion on the possible influences of this choice on the model result. Despite this criticism, I do not think that in this particular case these choices greatly affect the overall conclusions on controlling mechanisms for Co, Cu, Pb and Zn. Also the observation that the leaching of calcium is not well described (calcite does not convincingly precipitate in the model) relates to availability: using the total amount of inorganic carbon from Table 1 (where calcium balances almost stoichiometric with carbonate, C_{tot}) would have been more consistent and would in my experience almost certainly have strongly improved the model curve for Ca, without changing the conclusions for this important major element.

I have already pointed out above that it is particularly strong that the authors of paper V use their scientific results in order to propose a possible remediation option (mixing local oxisols with contaminated soil, increasing the overall binding capacity and lowering the transport rate of contaminants).

Assessment
Overall, based on all of the above considerations, my assessment is that the thesis is of a very high scientific quality that fulfills the quality for obtaining the PhD degree, and is suitable for defense by the candidate.