REVIEW

Of the member of the dissertation council for the dissertation of **Vladislav Vladimirovich Gurzhiy** on the topic: **"The crystal chemistry of natural and synthetic uranyl sulfates, selenites and selenates"**, submitted for the degree of doctor of geological and mineralogical sciences in a scientific speciality 1.6.4. Mineralogy, crystallography. Geochemistry, geochemical methods of mineral exploration.

General comments

The behaviour of uranium in the surficial environment is of particular importance to the health of our society, and the work done by Dr. Gurzhiy and presented here directly addresses this critically important issue. Uranium has been an important element in several aspects of human activity over the past 80 years. It was mined extensively to provide uranium for nuclear weapons and nuclear reactors, and both of these uses led to the generation of radiogenic waste, a major proportion of which is uranium oxide. Although uranium oxide (UO_2) has low solubility, U^{4+} is easily oxidized to U^{6+} when exposed to the atmosphere, and U^{6+} forms very soluble compounds. The ease with which uranyl compounds form in aqueous environments gives rise to major problems in the storage of radiogenic waste as the buildup of heat from radioactive decay tends to corrode and fracture any waste-containment vessels and can lead to the formation of extremely radioactive and toxic compounds outside the breached containment vessels, and their subsequent dissolution and dispersal *via* surficial waters and ground water, and *via* wind in arid environments. Mining of uranium causes similar problems. Mine-waste will contain small amounts of uranium, mainly as uraninite, and these will oxidize in contact with water and air, giving rise to soluble uranyl compounds that will likewise disperse *via* water and wind.

Comments on specific issues relevant to this work

Many different types of repositories for radiogenic waste have been proposed in many different countries. Because of the long half-life of radioactive uranium (and other radiogenic isotopes), such repositories must safely contain radiogenic waste for many thousands of years, and the regulations pertaining to these repositories contain minimum times of safe containment. Any leaks from such repositories must be contained as quickly as possible, and transport of leaked uranyl compounds must be stopped by chemically reacting these contaminants to form more insoluble compounds that will not be transported further.

Many different geological repositories have been proposed with different mineralogical and geochemical characteristics of the host environments in which they occur. Thus ameliorating any leakage of uranium will depend not only on uranium itself but also on the mineralogy, geochemistry and surfical drainage of the surrounding rocks. As a consequence of this, a detailed understanding of the compounds that may form from uranyl in a wide variety of geological environments is crucial to safely containing any leakage of uranium from such repositories. The same argument applies to the prevention of migration of uranyl compounds from minewaste.

The work of Dr. Gurzhiy indicates the type of work that will be needed in the future to address this crucial issue around all nuclear-waste repositories and mine-waste sites. He has synthesized 107 uranyl compounds at conditions (particularly temperature) that are directly relevant to their crystallization and behaviour in an environment typical of a breached repository. He has greatly enlarged our knowledge of the types of compounds that are likely to form if uranyl is released to an environment containing sulfur and selenium, and this in turn will allow design of a strategy for the effective fixation of uranium in such an environment.

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Comments on some specific research findings

[1] Of particular interest is the effect of initial pH on the crystallization of divalent-metal uranyl sulfates and selenates (page 391, result 9; and page 362, bottom 10 lines) where Dr. Gurzhiy states that the pH increases to 0-1.0 during crystallization. It would be interesting to know the initial and final pH values during synthesis and how these values compare to typical pH values in U-containing mine-waste dumps.

[2] Dr. Gurzhiy writes (page 391, result 10) that "Selective Se-S substitution was demonstrated, depending on the coordination state of the tetrahedral oxyanion". As far as I am aware, nobody has suggested that such a feature affects the degree to which solid solution can occur, particularly in such highly charged ions as S^{6+} and Se^{6+}.

[3] Dr. Gurzhiy mentions (page 390, result 4) the effect of heat on the linkage of polyhedra of the crystallizing uranyl phase. Again, I have not seen any systematic relation of this type suggested before for uranyl-oxysalt compounds. If this result could be expanded to other uranyl oxysalts in addition to S^{6+} and Se^{6+}, this would be an even bigger step forward in our understanding of the behaviour of uranyl compounds in general.

[4] Dr. Gurzhiy states (page 390, result 5) that " Two-connected arrangement of the S- and Se-centered tetrahedra or pyramids more likely enables easier possible rotation of these groups, which should make the structures less stable". I encourage Dr. Gurzhiy to develop this idea further, as the linkage of structural features to structure properties (such as stability) will promote a detailed analysis of possible structures for precipitation of specific uranyl oxysalts and effective fixation of the uranyl ion.

[5] It is interesting that S is such a common constituent in uranium-oxysalt minerals. Does Dr. Gurzhiy have any suggestions why this is the case?

Dissertation of Vladislav Vladimirovich Gurzhiy on the topic: "The crystal chemistry of natural and synthetic uranyl sulfates, selenites and selenates" *meets* the basic requirements established by Order No.11181/1 dd. 19.11.2021 "On the procedure for awarding academic degrees at St. Petersburg State University". The applicant Vladislav Vladimirovich Gurzhiy *deserves* to be awarded the academic degree of doctor of geological and mineralogical sciences in a scientific speciality 1.6.4. Mineralogy, crystallography. Geochemistry, geochemical methods of mineral exploration. Paragraphs 9 and 11 of the specified Order have not been violated.

Member of the Dissertation Council

Doctor of Science (Geology and Mineralogy), Professor of Mineralogy, Retired

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