1.8.14

Hydrothermal stability of crystalline and radiation-damaged pyrochlore

T. GEISLER[1], A. PUTNIS[1], U. GOLLA-SCHINDLER[1],
A.-M. SEYDOUX-GUILLAUME[2] AND A. JANSSEN[1]

[1] Institut für Mineralogie, University of Münster, Germany
(tgeisler@nwz.uni-muenster.de)
[2] Université Paul Sabatier, Toulouse, France

Considering the enormous amounts of high-level nuclear waste accumulated world-wide in the past decades, solutions for its safe immobilisation are urgently needed. Based on present familiarity with production technology, glasses and crystalline ceramics such as pyrochlore have been proposed as immobilization matrices for nuclear waste. However, our current knowledge about the reaction mechanism between aqueous solutions and potential nuclear waste ceramics is very limited. In particular, the complexity of the interaction of radiation-damaged materials with an aqueous solution has not yet been fully realised. Such complexity is highlighted by previous experimental work on zircon [1,2], by new experiments with crystalline and metamict pyrochlore as well as by investigations on natural analogues using x-ray diffraction analysis, electron microprobe, and transmission electron microscopy. We have performed, for example, hydrothermal experiments with a crystalline microlite and a x-ray amorphous betafite in a 1*M* HCl-$CaCl_2$ solution at 175°C. Whereas the crystalline microlite grains were partly (~ 5 µm rim) replaced by a Ca-poorer defect pyrochlore with a larger unit-cell (indicated by x-ray diffraction data), the amorphous betafite grains (up to ~ 1 mm ∅) have been transformed completely to a complex intergrowth of different crystalline phases. Interestingly, the altered betafite partly shows curved, non-equilibrium chemical banding, which resembles banding structures seen in hydrothermally treated metamict zircon [2] and also alteration structures observed in an altered betafite crystal from Betafo, Madagascar.

Our observations demonstrate that the aqueous stability of pyrochlore and the fluid-pyrochlore reaction mechanisms are dramatically influenced by structural damage created by the radioactive decay of structurally incorporated radionuclides. They also reveal that simple thermodynamic equilibrium models cannot be applied to adequately describe such systems and that natural alteration features can be reproduced under experimental laboratory conditions. What follows is that in order to develop realistic predictive models of the long-term aqueous stability of pyrochlore and other materials under consideration for waste immobilisation, more fundamental research is needed.

References

[1] Geisler T., Trachenko K., Ríos S., Dove M.T., and Salje E.K.H. (2003) *J. Phys.: Condens. Matter* **15**, L597-L605.
[2] Geisler T., Seydoux-Guillaume A.-M., Wiedenbeck M., Wirth R., Berndt J., Zhang M., Mihailova B., Putnis A., Salje E.K.H., and Schlüter J. (2004) *Am. Min.*, submitted.

1.8.15

Actinide waste forms: Rate of formation, composition, durability at underground water attack and susceptibility to radiation damages

S.V. YUDINTSEV AND T.S. IOUDINTSEVA

GEM RAS, Staromonetny 35, 119017 Moscow, Russia
(syud@igem.ru)

Development of forms for the various kinds of actinide waste immobilization is a very actual goal. Major requirements to the appropriate waste forms are: high loading in respect of actinides and the other HLW elements, chemical durability and radiation stability, feasibility for large-scale fabrication by existing methods. Crystalline host phases have advantages above glasses due to higher actinides “solubility” (isomorphic capacity) and durability under underground water attack. Up to now a number of crystalline host-phases are suggested, among which oxides with fluorite (zirconolite, pyrochlore, murataite) and garnet structure are of special interest. We have studied composition, formation rate, hydrothermal and radiation stability of a number most promising actinide host produced by cold pressing and sintering route. The results obtained showed that fluorite-type oxides and garnet-based actinide host are similar in their properties. Specific feature of the garnets is possibility for incorporation of a great number of different elements. So, these phases are more universal host relatively fluorite-type ceramics and may be applied for immobilization both of the wastes with simple composition (Pu, An-REE fraction of liquid HLW) and waste enriched in corrosion products and contaminants (Al, Fe, Si, Ga, Cr, Ni).