Zirconolite

Description: SYNROC is the generic name for a number of multi-phase synthetic mineral assemblages which are designed as wasteforms to immobilise HLW. The three basic phases in SYNROC are designed to include all of the chemical species in HLW by isomorphic substitution:

- zirconolite, ideally $CaZrTi_2O7$, designed to incorporate uranium, zirconium, neptunium, neptunium, and the rare earth elements;
- hollandite, ideally $Ba(Al,Ti)_6O_8$, designed to incorporate caesium, rubidium and barium;
- perovskite, ideally $CaTiO_3$, designed to incorporate strontium, neptunium, neptunium, and the rare earth elements.

Although the majority of the radionuclides in HLW do enter these phases, a number of different SYNROC formulations have been developed to take account of variations in the composition of wastes and radionuclide contents. As a consequence of the possible variations in phase proportions, SYNROC has considerable flexibility to deal with many different radioactive waste streams.

No natural equivalent of a SYNROC multi-phase rock material exists, although natural equivalents of the individual mineral phases in SYNROC can be found in some rock formations and most of the analogue studies have focussed on zirconolite (Hart et al., 1996) although some analogue studies have looked at other natural minerals as well (Lumpkin et al., 1994; Lumpkin and Mariano, 1996).

Zirconolite is a relatively rare mineral in nature, crystallising in a range of geological environments but normally associated with silica-poor rocks. To date, there are less than 100 recorded occurrences of zirconolite (Hart et al., 1997). The range of compositions of these natural zirconolites is wide and includes up to 30 elemental components with concentrations greater than 0.1 %. Natural compositions deviate substantially from the ideal structure due to extensive substitutions involving rare earth elements, actinides, niobium, iron and other elements. In terms of radionuclides, natural zirconolite can contain up to 25 % UO_2 and 18 % ThO_2. Furthermore, the abundances of substituted components in the mineral may be zoned. Despite this range of compositions, there is very little apparent variation in the stability of compositionally different zirconolites in nature, which provides good qualitative evidence for the stability of waste-loaded synthetic zirconolite in SYNROC.

The analogue studies on natural SYNROC component mineral phases, and the associated laboratory work, has indicated that these minerals are physically and chemically stable. Leaching studies suggest the remain closed systems with respect to uranium, thorium and lead isotopes for periods of up to 10^8 years, which is far longer than the time periods normally considered in performance assessment.

Relevance: Despite its appealing physical and chemical characteristics, no programmes are currently planning to use SYNROC to immobilise HLW from commercial reactor and reprocessing operations. As a result, to date, the analogue work is only of academic relevance but would be of relevance to any future programme planning to develop mineral wasteforms (perhaps for the disposal of excess weapons plutonium).

Position(s) in the matrix tables: (Near-field) Concerning waste form and demonstration of near-field processes: barrier containment (physical and chemical integrity), RN release (dissolution and leaching), RN transport (diffusion) and RN retardation.

Limitations: Natural zirconolite is a good analogue minerals for synthetic component minerals in SYNROC. However, these natural minerals are very rare and generally are acquired as detrital grains rather than from their place of formation. As a consequence, it is difficult to relate their observed stability to in situ geological conditions. Little quantitative information can be gained from the analogue studies which would be appropriate for input to performance assessment code development. Laboratory studies will probably remain the best means of investigating the stability of these mineral phases.

Quantitative information: Quantitative information is restricted to radiometric dating of the zirconolites to provide evidence to suggest they can remain stable and retain radionuclides for periods in excess of one million years certain geological conditions.

Uncertainties: Primary uncertainties relate to the conditions of formation and environmental conditions in which natural zirconolites have been preserved.

Time-scale: The time-scale of the analogue is geological, spanning up to tens of millions of years.

PA/safety case applications: There are no known applications of this analogue information in PA or safety cases because no repository programmes are planning to adopte SYNROC as a HLW wasteform.

Communication applications: There are no known applications of this analogue information in public communications.

References:
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Lumpkin GR and Mariano AN (1996) Natural occurrence and stability of pyrochlore in carbonatites, related hydrothermal systems and weathering environments. Materials Research Society Symposium Proceedings, 412, (Scientific Basis for Nuclear Waste Management, XIX), 831-838.

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Added value comments: It is unlikely that the analogue work could be improved until such time as SYNROC is planned to be used in an actual waste disposal programme, when specific compositions and environmental conditions could be addressed.

Potential follow-up work: No additional follow-on work is recommended at this time.

Keywords: SYNROC, HLW, minerals, zirconolite.

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