POTENTIAL LONG-TERM ALTERATION OF NSF AND MINOR RADIONUCLIDES. INFORMATION FROM NNAA

by

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Evidence from laboratory experiments and natural analogue studies have indicated that the most likely solid phases to form from uraninite (UO_{2+x}) alteration under reducing conditions are secondary uraninite and coffinite ($USiO_4 \cdot nH_2O$). All the coffinitization processes observed in nature occurred at temperatures in the range 130°C to 300°C. The ages of some of the coffinitization events are not very far from the times of interest for the deep geological repository, according to the natural sites reviewed. Many evidences of the presence of minor elements in both secondary uraninite and coffinite have been found. The different coffinite compositions reported in the literature contain U, Th, Y, REE, Ca, Zr, Hf, Fe, Si, P and S.

The results of the calculation of the evolution of the composition of the fuel with time indicate that, at the moment of the canister failure (considered to happen after 10^5 years), the content in REEs, Th, Np, Pu and Zr is always lower than the content reported in secondary uraninites and coffinites, thus indicating that these secondary phases can potentially retain REEs, Th, Np, Pu and Zr released due to the fuel alteration. Elements present in the fuel as metallic inclusions will not be so prone to be retained in these solid phases, but to form individual secondary solids, mainly sulphides, as evidenced by observations in nature.

The three main conditions identified as potentially causing the formation of the secondary solid phases studied in this work are: i) the likely presence of high concentrations of Si (or silica) due to the alteration of vitrified wastes, or from the surrounding clay (bentonite) backfill material or surrounding host rocks; ii) the potential development of an alkaline plume leading to high pH values in the system due to the possible co-location of wastes and iii) the development of highly reducing conditions (or the prevention of the development of oxidising conditions) due to the anoxic corrosion of steel canisters, with subsequent hydrogen generation..