ON IMMOBILIZATION OF TECHNETIUM INTO CRYSTALLINE MATRICES

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^{99}Tc ($T_{1/2}$ = 213000 years) is one of the ecologically dangerous long-lived fission products, due to high solubility of the heptavalent form in water and migration as TcO_4^-. In spent nuclear fuel (SNF) Tc exists mainly alloyed with Mo and light platinoids. This phase has a low rate of leaching of Tc from SNF, especially in the negative Eh field (at reducing conditions). During SNF reprocessing the main part of Tc (up to 90%) is separated and the remaining amount is incorporated in vitreous matrices together with other radionuclides of high level waste (HLW). These matrices have a very low durability – the Tc leach rate from the glasses exceeds 10^{-2} g/m^2 • day, hundreds of times worse compared to SNF durability. In the weakly alkaline reducing waters typical for deep underground repositories of SNF (HLW) technetium will be reduced to Tc(IV), decreasing its concentration in water to ~10^{-8} M/l, corresponding to TcO_2•$2H_2O$ solubility that is an order of magnitude lower than the highest permissible amount in water for usage. Therefore, the majority of Tc leached from the glass will precipitate in the near field of the repository. A very important task is to develop ways for safe management of Tc extracted from the liquid high-level waste stream into a separate fraction. To immobilize the waste cements, alloys and crystalline materials are proposed, the best of which can accommodate high content of Tc in their crystalline structure and possess good chemical durability. These phases are prospective matrices for isolation of a few tons of ^{99}Tc annually separated from the reprocessing high-level waste. The main problem of synthesis of the waste forms is the volatility of Tc compounds and the necessity of stabilization of the Tc^{4+} ion, suitable for encapsulation in titanate-based phases due to substitution for the Ti^{4+}, which has a similar ionic radius. To achieve the oxidation state required, synthesis should be performed by hot pressing or cold pressing – sintering in reducing conditions and sealed ampoules. Such processing complicates any industrial application.

As alternate way for fabrication of matrices for Tc isolation technology via SHS (self-sustaining high-temperature synthesis) is suggested. The formation of desired phases of SHS proceeds as solid state burning for a very short time, decreasing the loss of volatile elements due to evaporation. Other ways to reduce release of Tc are achieved by introduction of Tc into the initial SHS batch not as Tc_2O_7 but in the sorbed form with TiO_2 or as TcO_2 with a higher melting point and lower tendency for vaporization. Features of promising matrices for Tc immobilization are titanates and zirconates with pyrochlore, rutile and perovskite structure are presented. Main attention was paid to study of the Mo behavior as surrogate for Tc. Possibility for incorporation of the matrices up to 40 wt.% of Mo both in the form of alloy and isomorphic admixture in structure of crystalline phases is confirmed. The optimal approach to management of Tc-rich waste is joint incorporation of Tc and rare earth-actinide fraction into pyrochlore-based forms. In this case, to stabilize the pyrochlore structure, at least part of the titanium in the initial mixture for SHS should be replaced by zirconium, because Zr^{4+} has a larger radius than Ti^{4+}. Transuranium actinide surrogates (rare earths, U) enter both pyrochlore and oxide with the fluorite structure. To confirm this approach for technetium immobilization a study of Tc-doped samples is required.

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References

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