Abstract

The complete separation of Pu in the present nuclear fuel reprocessing (purex process) leads to diversion of plutonium for weapon purposes. The proliferation potential of the purex process can be reduced by providing some modifications to this process. The most significant modification is the dilution of plutonium with some fertile or suitable nonfertile (inert) matrices, thereby increasing the physical quantity of material to be diverted and the effort and time required for conversion. The modified process could be designated as diversion resistant reprocessing. The diversion resistant reprocessing simplifies the current process, reduces the capital cost and increases the operational safety. The process in which dilution of the Pu with some fertile materials would yield nuclear fuels that can be recycled in thermal as well as fast reactors. In contrast, for the complete utilization of plutonium in thermal reactors the Pu in the reprocessing stream has to be diluted with some nonfertile matrices and is called burn and bury option for Pu.

The main objective of the present research is to find a suitable co-processing technique to modify the purex process, such that the Pu generated is directed for civilian use as reactor fuel either recycled or once through manner. Among the various co-processing techniques, sol-gel process yields products with better homogeneity and avoids the radio-toxicity associated with the powder handling. The commonly used gelating agent for the nuclear fuel preparation is ammonia. The two ammonia gelation methods used for fuel synthesis are the external and internal gelation processes. In the external gelation process, ammonia for the gelation is supplied externally as ammonia solution or gas while in the internal gelation process ammonia is generated \textit{in situ}.

Characterization of the precursors of nuclear fuels has a vital role in optimizing the fabrication process parameters. The present study deals with a detailed investigation on the thermal decomposition behaviour of the external as well as internal gel products of a
simulated mixed oxide fuel by employing diverse characterization techniques. The formation of $U_{0.7}Ce_{0.3}O_{2+x}$ gel (simulating $U_{0.7}Pu_{0.3}O_{2+x}$) was studied through two soft chemistry routes namely external and internal gelation followed by their decomposition in Ar, vacuum and air environments. By combining thermogravimetry / differential thermal analysis (TG/DTA) with evolved gas analysis by mass spectrometry (EGA-MS) in vacuum, the formation of $UO_3$ as an intermediate product when synthesized via external gelation route was established whereas synthesis via internal gelation resulted directly in the formation of $UO_2$ type phase. The disadvantages of the conventional air calcining was discussed in the light of $UO_3$ formation and to take advantage of the microhomogeneity of the product through the internal gelation route, thermal decomposition should be performed in an inert (possibly moist Ar) atmosphere. This procedure would also facilitate sintering the mixed oxide to near theoretical density at temperatures as low as 1100°C.

The products obtained during the stepwise thermal decomposition of the external as well as internal gel products in an atmosphere of Ar laden with moisture were examined using infrared spectroscopy. In the case of externally gelated compound, the gel decomposed with the release of $H_2O$ and $NH_3$ below 500°C. A part of the $NH_3$ released was entrapped in the solid and above 500°C self-reduction occurred in which uranium in the gel was converted to $U_3O_8$. In the case of internally gelated compound, decomposition similar to the one for externally gelated compound occurred below 500°C. Above 500°C in contrast to external gelation the carbon present in the internally gelated compound reduced uranium to $UO_2$ which formed a solid solution with $CeO_2$ at around 650°C.

The oxidation behaviour of uranium in the oxidized samples with different cerium content were investigated by using oxygen-to-metal ratio (O/M), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses. The oxidized sample with a
cerium content less than 70 mol% Ce was found to be a mixture of orthorhombic and cubic phases and that with above 70 mol% was found to be a single cubic phase. The valency of uranium in the oxidized samples computed from the O/M results was compared with the uranium 4f<sub>7/2</sub> peak positions obtained from XPS.

The feasibility of the internal gelation process for the preparation of zirconia based simulated inert matrix fuel (IMF) and the thermal decomposition as well as sintering behaviour of the gel was investigated. Using the internal gelation process the simulated IMF was prepared and sintered to near theoretical density by employing microwave energy source. The thermal decomposition pattern of the dried gels of different compositions was studied by employing TG/DTA along with XRD. Pure ceria gel decomposed to crystalline ceria in a single step whereas pure zirconia and simulated IMF gel decomposed to give the respective oxides via two steps of decomposition to an amorphous oxide followed by the amorphous to crystalline transition.