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Preferential leaching of Sr from mixed (Th/Sr) oxide

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ABSTRACT

Preferential leaching of Sr from irradiated thorium may play an important role to facilitate the management of high level waste as well as provide a new route to recover valuable fission product ^{90}Sr which has potential applications as (a) compact heat source and (b) as parent radionuclide for ^{90}Y, used in therapeutic radiopharmaceuticals. In the present work, leaching of Sr from $(Th,Sr)O_2$ in nitric acid and perchloric acid medium has been investigated as a function of acidity as well as refluxation time. It was interesting to observe that quantitative leaching of Sr(II) is possible even at 0.01 M $HClO_4$ where leaching of Th is negligible (~0.01%). Leaching behavior of other metal ions, like Pd(II), Y(III), and Zr(IV), representing few major fission products was also investigated.

Keywords: Thorium; Strontium; Leaching; Perchloric acid; Fission products; ICP-OES

1. Introduction

Today about 500 nuclear power plants, with total installed capacity of 375 GW(e) are in operation worldwide generating around 16% of global electricity which are largely fueled by natural/enriched uranium oxides. Thorium is 3 to 4 times more abundant than uranium and is an easily exploitable resource in many countries. In this context, ThO_2 appears to be a strong candidate as nuclear fuel in the long run. However, unlike natural uranium, which contains ~0.7% fissile ^{235}U isotope, natural thorium does not contain any "fissile" isotope and is made up of the "fertile" ^{232}Th which can be converted to "fissile" ^{233}U, thereby enlarging the fissile material resources. Other distinct advantages of thorium based fuel cycles are: (a) higher absorption cross section for thermal neutrons of ^{232}Th (7.4 barns) compared to ^{238}U (2.7 barns); (b) favorable η (number of neutrons liberated per neutron absorbed) for ^{232}Th—^{233}U fuel cycle over a wide neutron spectrum; (c) intrinsic proliferation resistance due to the formation of ^{232}U; (d) possibility to incinerate weapon Pu or civilian Pu in once through cycle of $(Th, Pu)O_2$ fuel; (e) favorable thermo-physical properties of ThO_2 like high thermal

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conductivity and lower coefficient of thermal expansion compared to UO_2 [1]. In addition, chemical and radiation inertness of ThO_2 vis-à-vis UO_2 may facilitate the disposal of spent fuel, a great deal in the back end of once through fuel cycle. The database and experience of thorium fuels and thorium fuel cycles are, however, very limited as compared to UO_2 and $(U, Pu)O_2$ fuels and need to be augmented before large investments are made for commercial utilization of Th fuels and fuel cycles. ADSS using Thorium as energy amplifier is a promising alternative concept which has drawn the attention of nuclear scientists following Carlo Rubbia's path breaking discovery [2].

Amongst the areas of interest to radiochemists is the recovery of valuables like ^{90}Sr and ^{137}Cs from the high level waste generated after the recovery of recyclable ^{233}U from dissolver solution [3]. Recovery of these radionuclides helps a great deal in reducing the dose experienced during vitrification and subsequent storage in the interim solid state storage facility of the conditioned vitrified mass [4]. In case such selective recovery step for ^{90}Sr and ^{137}Cs precedes the reprocessing step, the reduction in dose may be immensely beneficial even to the reprocessing technologist. It is desirable, therefore, to explore the possibility of preferential leaching (recovery) of these radionuclides over Th and other fission/activation products at the dissolution stage itself rather than developing separation methods post dissolution. An attempt has been made for the first time to explore the use of $HClO_4$ for the preferential leaching of Sr over Th and over stable isotopes of some fission products from sintered ThO_2 doped with Sr/Pd/Y/Zr.

2. Materials and methods

2.1. Synthesis of mixed Th oxides

Analytical reagent grade powders of $Th(NO_3)_4 \cdot 5H_2O$ and a dopant element nitrate viz. $ZrO(NO_3)_2 \cdot 5H_2O/Sr(NO_3)_2/Y(NO_3)_3 \cdot 6H_2O/Pd(NO_3)_2$ and glycine were used as starting reagents. The appropriate amounts of metal nitrates were mixed together in demineralized water. Glycine was added as a fuel in the solution in the stoichiometric ratio. Highly viscous gels were obtained by thermal dehydration (at ≈ 80°C) of these solutions. On further heating, gels undergo auto ignition with rapid evolution of a large volume of gasses to produce voluminous powders. The main motivation for using this preparative technique was to achieve an atomistically blended precursor containing desired amounts of Sr^{2+} in ThO_2[5,6]. Hence, a better homogeneity of Sr in ThO_2 is obtained with this method. On the basis of previous experiments, it has been observed that the present procedure gives nanocrystalline material with better powder properties (such as high surface area (>50m^2), soft agglomeration, and better sinterability) [7]. In order to get rid of the excess carbonaceous materials and obtain microcrystalline doped ThO_2, the powders obtained after auto ignition were calcined at 1,273 K for 24 h. X-ray diffraction (XRD) patterns of all the powder samples were recorded on a Panalytical X'pert. The compositional characterizations of these samples were carried out using a JEOL JSM840 microscope attached with an EDS facility.

$(Th,Sr)O_2$ and other binary oxides were analyzed for minor constituents after complete dissolution of the sample by prolonged heating in a mixture of conc. HNO_3 and 0.03 M HF. Th(IV) was separated by three contacts of 30% TBP in dodecane. The raffinate was analyzed for analyte Sr by ICP-OES method and the concentration was measured as 0.23 ± .02%.

2.2. Refluxation

The present experiment was basically planned so as to yield quantitative amount of Sr from the mixed oxide. 0.23 ± .02% Sr doped thorium sample was used. Refluxation of this sample was carried out using different concentrations of HNO_3 and $HClO_4$. 50 mg sample was refluxed in a round-bottomed flask with 10–25 ml of the mentioned concentration of the acid for specified time interval varying from 5 min to 4 h using temperature controller. After the refluxation for a specific time, approximately 2 ml of sample was taken out and double centrifuged after which 500 μl of supernatant was withdrawn and diluted to 10 ml with water in volumetric flask. Subsequently, these solutions were analyzed for Sr and Th content by ICP-OES (Varian 720, ICP-OES). The residual sample was reverted to the original flask and further refluxation was carried out, wherever leaching as a function of time was studied. Calibration of ICP-OES was done by the AAS standards (1,000 ppm) which were obtained from Fluka/Fisher Scientific. Precision of ICP-OES analysis was ± 10%.

3. Results and discussion

Cumulative fission yield of ^{90}Sr during fast fission of ^{232}Th is 7.32 ± 0.36% and with 14 MeV neutrons, it is 6.2 ± 1.5%. Fission yield of ^{90}Sr during thermal fission of ^{233}U is 6.65 ± 0.07% and during fast fission is 6.39 ± 0.33% [8]. These values are distinctly larger than the cumulative yields of ^{90}Sr produced from other fissile/fissionable nuclides like ^{235}U, ^{238}U, and ^{239}Pu. It implies that in thermal as well as fast neutron spectrum, irradiated thorium is a richer source of ^{90}Sr as compared to other actinide targets (~0.25% of Sr may be present in ThO_2 at a burn up of 40,000 MWD/t). It is, therefore, pertinent to develop novel procedures for the recovery of Sr from irradiated Th. Irradiated Th like irradiated U is radiochemically a complex system comprising of large number of fission products of varying specific activity and hard gamma emitters like ^{208}Tl and ^{212}Bi (decay products of ^{232}U) necessitating elaborate shielding facilities for its handling. In addition, there are logistic difficulties like long irradiation/cooling time. The objective of the present work was to arrive at the experimental conditions for the preferential leaching of Sr over Th. As it was the first attempt made in this direction, unirradiated (but microcrystalline and calcined) ThO_2 doped with 0.23 ± .02% Sr was employed for the dissolution studies in the present work. However, it was ensured that the sample is homogeneous with respect to doped element. Homogeneity of the doped ThO_2 samples was confirmed by doping larger amount of Sr and still observing a single phase. All the experiments on dissolution were done with stable isotopes of few typical fission products viz. Zr, Y, and Pd.

3.1. Dissolution Studies

It is reported that for a given H^+ concentration and complexing ligand concentration, dissolution rate of ThO_2 follows a logarithmic relation with the complexation constant of Th^{4+} with the ligand [9,10]. Amongst the various ligands studied, the observed order was $SO_4^{2-} > NO_3^- > Cl^- > ClO_4^-$. The simplest explanation is that the ligand interacts with the surface site to form a surface complex. The formation of surface complex weakens the M–O bond, thereby enhancing the detachment of the metal and accelerating the dissolution. In the present work, initially HNO_3 (10, 5, and 1) and HCl (5 M) were employed in refluxation experiments for periods varying from 5 min to 24 h. It was interesting to observe that the mildest conditions employed (1 M HNO_3 and 5 min refluxation) were good enough as far as the quantitative leaching of Sr is concerned. There was no enhancement in the % dissolution of Sr with increase of either acidity or refluxation time confirming that complete leaching is achieved even within 5 min of refluxation at 1 M HNO_3. Activation energy required to break Th–O bond in ThO_2 is much higher than that of Sr–O bond in SrO, the latter is expected, therefore, to be dissolved at much lower H^+ and ligand concentration. On the other hand, Th dissolution was found to increase continuously with acidity as well as refluxation time as shown in Fig. 1. Larger dissolution rate of Th in the case of HCl can be explained probably due to the larger dissociation constant of HCl (log Ka ~ 4) vis-à-vis HNO_3 (log Ka ~ 1) resulting in larger concentration of Cl^- vis-à-vis NO_3^- at 5 M acidity. It is clear that both ligand concentration as well as its complexation constant play a part in the dissolution rate of Th. It was, therefore, of interest to extend these studies employing $HClO_4$ as medium.

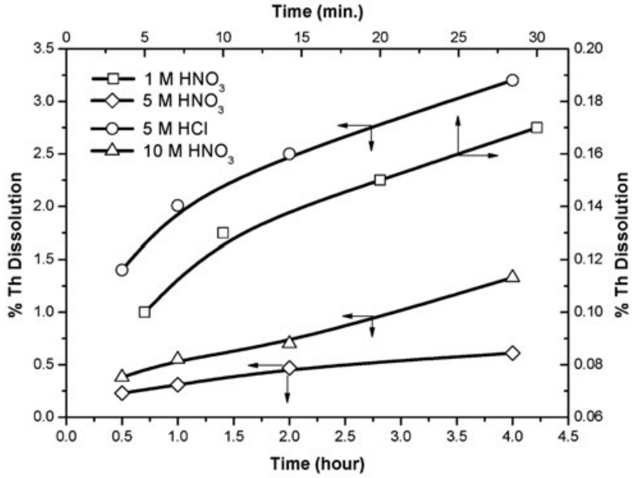

Fig. 1. % Dissolution of Th in different acid media as a function of time Sample Weight: 50 mg, acid volume: 25 ml.

Table 1 indicates that whereas 1 M $HClO_4$ dissolves quantitatively Sr, relatively lower amount of Th was dissolved vis-à-vis 1 M HNO_3 under identical experimental conditions which could be explained on the basis of its weaker complexation in spite of larger dissociation constant (log Ka = 7). Apart from Sr and Th, other fission products were also studied for their dissolution behavior from their respective doped (~0.25%) mixed Th oxides. Representative fission products were Pd(II), Y(III), and Zr(IV) (ZrO^{2+}). Similar to Th, dissolution of other fission products was significantly lower (1.6–8%) than that of Sr

Table 1
% Dissolution of constituent elements from 50 mg binary mixed (Th, Sr/Zr/Pd/Y)O_2 during refluxation experiment for 10 min., vol. = 10 mL

Acid	1 M HNO_3	1 M $HClO_4$
Sr	~100	~100
Zr	28	3.2
Pd	36	18
Y	8	1.6
Th	0.13	0.08

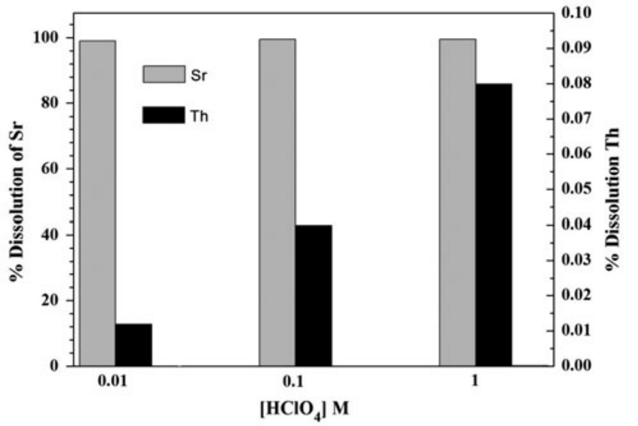

Fig. 2. % Dissolution of Sr and Th in 50 mg mixed (Th/Sr) O_2 in $HClO_4$ Medium after 10 min. of refluxation, vol.10 mL.

(∼100%). Fig. 2 shows that it is possible to further decrease the acidity of $HClO_4$ even to 0.01 M without influencing the quantitative dissolution of Sr. On the other hand, Th dissolution continuously decreased and was as low as 0.01% at 0.01 M $HClO_4$. Nevertheless, there is a possibility that high oxidation state cations present in the leached solution (like lanthanides, Y(III), Zr(IV), and Mo(VI)) as fission products may hydrolyze, thereby making the subsequent chemical treatment of leached solution cumbersome. It is desirable, therefore, to keep acidity at 1 M $HClO_4$ during leaching experiments. In spite of the fact that Sr leaching is quantitative and that of Th is only <0.1%, the leached solution will be heavily contaminated with the bulk element (Th). In addition, the contamination by other fission products will also be significant. The exact level of contamination will depend on the fission yield and % leaching of the individual fission product with respect to ^{90}Sr.

High purity of radionuclides is expected which are to be employed as radiopharmaceutical [11] or as heat source. Hence, it is desired that one should have ^{90}Sr in the possible purest form which is necessarily to be separated from Th as well as other fission products. It is, therefore, essential as a next step to develop chemical methods for the separation of Sr(II) from all the possible contaminants likely to be present in the leached Sr solution at 1 M $HClO_4$. In this context, chromatographic resin, impregnated with well-known Sr-selective extractant viz. ditertiarybutyl dicyclohexano 18 crown 6 (available commercially) is proposed to be used. This resin has been used extensively for the separation of Sr from other metal ions in nitric acid medium. However, there is no literature available for its potential in perchloric acid medium. Work is in progress in our lab to determine the distribution coefficients of Sr(II), Th(IV), and of other fission products likely to present in leached solution in 1 M $HClO_4$ medium.

4. Conclusions

(a) Interference of Th and other fission products during leaching of doped ThO_2 vary with nature and concentration of acid as well as with refluxation time. $HClO_4$ is the best candidate for preferential leaching of Sr.
(b) The quantitative recovery of Sr from $(Th,Sr)O_2$ homogeneous matrix is possible even at 0.01 M $HClO_4$ with 10 min of refluxation. However, 1 M $HClO_4$ recommended for leaching work (to avoid the hydrolysis of high oxidation state cations) will be contaminated with ∼0.1% of Th and varying amounts of Zr (3.2%), Y(1.6%), and Pd (18%).
(c) The present work describes a novel simple approach to leach preferentially Sr from sintered ThO_2. It can form a basis for the preferential recovery of fission product ^{90}Sr from irradiated ThO_2.

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