1. NUCLEAR AND ACTINIDE CHEMISTRY

INTRODUCTION

Major areas of basic research in nuclear chemistry include, nuclear fission, nuclear reactions, nuclear probes and radioanalytical techniques, such as, neutron activation analysis and ion beam analysis. Actinide chemistry research has been focused towards novel extractants in the back end of fuel cycle, actinide partitioning, separation of actinides and lanthanides and membrane separations particularly for the recovery of Cs and Sr. In the field of actinide spectroscopy, work was carried out on fluorescence studies on new phosphor materials, photoacoustic studies for speciation, EPR spectroscopy in dosimetric applications, as well as on the development of new sample preparation schemes for spectrochemical analysis. NDA equipments have been designed, fabricated and installed at the users premises for the assay of nuclear materials in the front end as well as in the back end of the Nuclear Fuel Cycle. Solid state track detector technique has been employed for the determination of sub ppb level of U/Pu in environmental/biological samples. Development of processes related to actinides preparation and purification are presented in this chapter.
1.1 NUCLEAR CHEMISTRY

Incomplete fusion reactions

Extensive studies on excitation functions and recoil range distribution of evaporation residues and gamma-ray multiplicity have been carried out during the last few years to understand the mechanism of incomplete fusion reaction, particularly at low beam energies. The gamma-ray multiplicity measurements were made to investigate the angular momentum transfer in incomplete fusion reactions involving massive transfer. The measurements revealed that the collisions between the target and projectile leading to incomplete fusion are not peripheral but deeply penetrating. With an aim to study the effect of nuclear structure of the projectile on incomplete fusion reactions, excitation functions and recoil range distribution of evaporation residues were measured in the reaction of $^{12}$C and $^{13}$C on $^{181}$Ta target. The cross section for incomplete fusion was found to be significantly higher in the case of $^{12}$C than that in the case of $^{13}$C, suggesting the role of alpha cluster structure of $^{12}$C in enhancing the incomplete fusion cross section. The following figures show the recoil range distribution of evaporation residues formed in complete and incomplete fusion reactions of $^{12}$C and $^{13}$C with $^{181}$Ta respectively.

Recoil range distribution in 82.5 Mev $^{12}$C + $^{181}$Ta

New results on the electronic structural changes at the onset of superconducting transition in MgB$_2$ have been obtained. These might be used as a benchmark for proposed mechanisms for superconductivity. Positronium behaviour in porous material has been investigated on precursors of metal dispersed silica catalysts. In diamonds, direct experimental evidence for the presence of impurity-vacancy complexes has been obtained using the 2D-Doppler facility developed in Radiochemistry Division. In addition, significant new information on the defect structure of doped ceria has been obtained that has a direct bearing on the understanding of ionic transport mechanism in the materials, which have potential applications in Solid Oxide Fuel Cells (SOFCs).

Positron Annihilation Spectroscopy and its Applications

An ion beam analysis facility was set up at Folded Tandem Ion Accelerator (FOTIA). During the last two years, the facility was used for characterisation of polymer inclusion membranes (PIM) as well as determination of oxygen in the metallic targets of rare earths and thorium. Backscattering spectrometry studies of...
Significant amount of oxygen was found in the metallic targets of holmium, thulium and thorium due to their oxidation by atmospheric oxygen. Ion beam analysis studies were also carried out using the BARC-TIFR Pelletron accelerator, wherein diffusion of cesium in borosilicate glass was studied using heavy ion Rutherford Backscattering Spectrometry. Potential applications of the ion beam facility include: Hydrogen depth profiling in solids by nuclear reaction analysis (NRA) using $^{15}$N or $^{19}$F beams, Analysis of thin film planar microelectronic devices, Diffusion in solids and surface characterisation by Rutherford backscattering Spectrometry (RBS) using low energy beams and Elemental analysis of samples by particle induced X-ray emission (PIXE) using low energy proton beam.

Electron Paramagnetic Resonance of dosimetric materials like 2-methyl alanine, ammonium tartarates and alanine was studied. It was seen that methyl alanine has 85% higher sensitivity than alanine in the dose region 10-200 Gy. However, in higher dose region viz., 0.5 kGy-50 kGy, alanine was found to be more sensitive. Also, the effect of incorporation of Pu in these dosimetric materials was seen. Use of Tm doped MgB$_2$O$_4$ phosphor was demonstrated for gamma dosimetry by thermally sensitive luminescence technique.

V. K. Manchanda <vkm@barc.gov.in>
B. S. Tomar <bstomar@barc.gov.in>
1.2 APPLICATIONS OF NUCLEAR CHEMISTRY

- Non-destructive Assay of Nuclear Fuel Materials

Non-destructive assay systems based on both gamma and neutron counting have been developed for the assay of Pu at various stages of nuclear fuel cycle. Important developments are the setting up of a Hull waste monitor at KARP, development of a 200 L waste drum scanner and development of a Neutron Well coincidence counter. A rapid method for the nondestructive assay of Fast Breeder Test Reactor (FBTR) fuel pins has been demonstrated using two step process of high resolution gamma-ray spectrometry for isotopic composition measurement in the chemical laboratory. Assuming that the ratios of $^{144}$Ce to U and that of $^{144}$Ce to Pu in the hull is the same as those in the dissolver solution, the amount of U and Pu in the hull is computed.

- Development of a Segmented Gamma Scanner

Solid alpha waste, having alpha activity $<$4000 Bq/g is recommended for shallow land burial. To screen the 200 L waste drum containing solid alpha waste, a facility based on segmented gamma scanning has been set up at Radiochemistry Division. The gamma rays from Pu and Am (hence total alpha activity) are measured using a collimated HPGe detector. Rotation of the drum is done to get the flat response. The drum is scanned in segments by moving the drum vertically across the collimated detector. Standard Pu samples were randomly distributed inside a drum containing cellulosic waste and the gamma response measured for different sample distributions inside the drum. It is seen that 100 mg of Pu can be assayed with an accuracy of ± 30-40% for a counting time of three hours per drum containing cellulosic waste. This facility is proposed to be employed for estimating the total alpha activity in the drum before storage in the interim storage facility.

During the dissolution of spent fuel by chop-leach process in reprocessing plants, small but significant amount of fuel remains as residue because of the incomplete leaching of the crimped hulls. Hence, it is necessary to estimate this material with a reasonably degree of accuracy for proper accounting of the nuclear materials. A hull monitor was set-up at Fuel Reprocessing Plant (KARP) in Kalpakkam. In this method the activity of $^{144}$Ce-$^{144}$Pr (285 days) in the hull is measured using a suitable collimator detector arrangement in the dissolver cell area. Ratio of the activity of $^{144}$Ce to U and Pu in the dissolver solution is determined followed by neutron well coincidence counting for the total plutonium content.
Development of Neutron Counting Systems for Non Destructive Assay of Plutonium

A neutron well coincidence counter based on $^3$He counters in High density polyethylene (HDPE) moderator assembly has been designed and fabricated for the non destructive assay of plutonium in FBTR fuel pins and sub assemblies. The counter has a flat radial and axial response over the active region of the fuel sub assembly. The sample is surrounded by 1.2 mm thick cadmium sleeve to prevent the entry of thermal neutrons in the sample for suppressing the multiplication of neutrons. The reflector geometry ensures that the detection efficiency for ($\alpha$, n) neutrons is reduced relative to fission neutrons to enhance the accuracy of coincidence counting. A portable neutron slab coincidence counter based on six $^3$He counters in HDPE moderator assembly has been designed and fabricated for in-situ assay of plutonium in sealed containers. The system has been installed at Radio Metallurgy Division.

Development of an Ultra Sensitive Method for the Assay of Plutonium by Fission Track Technique

Occupational radiation workers can get exposed to various radionuclides during the course of their work. Proper evaluation of the internal contamination is necessary for the assessment of internal dose to workers, following the intake of radionuclides. The new Derived Investigation Limit (DIL) for Pu compounds of Type S is 0.038 mBq and for Type M is 0.34 mBq, whereas the lowest detection limit of widely used alpha spectrometry is about 0.5 mBq. An indigenous and ultra sensitive method employing fission track analysis (FTA) has been developed which is more sensitive than the existing alpha spectrometric method. The results of the preliminary experiments carried out on actual bioassay samples shows that a Pu concentration of 0.1 mBq can be easily measured using the FTA technique. Efforts are underway to further lower the minimum detection limit for Pu using ultra pure reagents.

V. K. Manchanda <vkm@barc.gov.in>
B. S. Tomar <bstomar@barc.gov.in>

1.3 ACTINIDE CHEMISTRY

Actinide Process Chemistry

The area of research in chemistry of actinides broadly aimed at basic understanding of complexation behaviour and devising improved separation schemes relevant to reprocessing and waste management. This encompassed the chemical and radiochemical investigations on the actinides from Ac to Cf. The basic research programme on actinide chemistry included investigations on the interconversion of oxidation states of actinides with a view to arrive at suitable conditions for preferential stabilization of each of the oxidation states and studies on the complex forming abilities of actinides with different inorganic and organic anions.

The stability constants of a number of fluoride complexes of Group (III), Group (IV) and actinide elements in different oxidation states have been determined using IUPAC recommended Fluoride ion selective electrode method.
Recycle of Chemicals from Alkaline Waste Generated during Preparation of UO₃ Microspheres

Bench scale studies were carried out to recycle chemicals from alkaline waste generated during preparation of UO₃ microspheres by sol-gel process. The waste contained urea, hexamethylenetetramine (HMTA), ammonium nitrate and ammonium hydroxide. The aim of the work was to separate HMTA, urea and ammonium hydroxide and reuse them for preparation of UO₃ spheres. For removal of nitrate Dowex 1X4 anion exchange resin was used and 1.0 M NaOH was used to regenerate the resin. The column experiments showed that nitrate could be separated from the waste feed, but the resin could not be regenerated completely due to slower kinetics of elution. To overcome this problem, loading and elution cycles were modified to achieve better efficiency of separation. Nitrate free waste accumulated after the ion exchange process was further treated to recover ammonia and concentrated HMTA, urea. HMTA and urea was reused for making good quality UO₃ microspheres.

X-ray and solid state chemistry of actinides

X-ray, thermal, IR and NMR studies have been carried out on a number of uranium and plutonium compounds for structure elucidation. The reaction of [UO₂(TTA)₂.H₂O] with Benzo, 15-crown-5 ether yielded a binuclear complex in which the crown ether bridges two [UO₂(TTA)₂.H₂O] molecules by hydrogen bonding. Two of such binuclear complexes are stabilized in solid state by hydrogen bonds to give tetra- nuclear cluster. However, the reaction of dibenzo-18 crown-6 ether under similar condition yielded a dinuclear complex in which the two [UO₂(TTA)₂.H₂O] units are hydrogen bonded via the water molecules. This dinuclear unit is hydrogen bonded to the crown ether molecules via another water molecule to form a third sphere coordination compound.

<table>
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<th>Metal ion</th>
<th>log β₁</th>
<th>log β₂</th>
<th>log β₃</th>
<th>log β₄</th>
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<tr>
<td>U(VI)</td>
<td>4.56 ± 0.01</td>
<td>8.02 ± 0.02</td>
<td>10.46 ± 0.07</td>
<td>11.99 ± 0.13</td>
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<td>Np(VI)</td>
<td>3.94 ± 0.01</td>
<td>6.73 ± 0.02</td>
<td>8.29 ± 0.07</td>
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<td>Pu(VI)</td>
<td>3.80 ± 0.15</td>
<td>6.31 ± 0.15</td>
<td>8.00 ± 0.17</td>
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<tr>
<td>Np(V)</td>
<td>1.20 ± 0.10</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Th(IV)</td>
<td>7.61 ± 0.01</td>
<td>13.42 ± 0.05</td>
<td>17.65 ± 0.20</td>
<td>23.67 ± 0.11</td>
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<td>U(IV)</td>
<td>8.84 ± 0.01</td>
<td>14.66 ± 0.01</td>
<td>19.51 ± 0.03</td>
<td>23.92 ± 0.04</td>
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<tr>
<td>Np(IV)</td>
<td>8.17 ± 0.04</td>
<td>14.52 ± 0.13</td>
<td>20.05 ± 0.13</td>
<td>25.95 ± 0.18</td>
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<tr>
<td>Pu(IV)</td>
<td>7.61 ± 0.12</td>
<td>14.77 ± 0.10</td>
<td>20.11 ± 0.37</td>
<td>26.07 ± 0.16</td>
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<td>Zr(IV)</td>
<td>8.49 ± 0.11</td>
<td>15.76 ± 0.15</td>
<td>21.57 ± 0.10</td>
<td>26.68 ± 0.16</td>
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<td>Hf(IV)</td>
<td>8.22 ± 0.06</td>
<td>15.48 ± 0.15</td>
<td>21.76 ± 0.14</td>
<td>27.42 ± 0.15</td>
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<td>Ce(IV)</td>
<td>7.57 ± 0.04</td>
<td>14.50 ± 0.03</td>
<td>20.13 ± 0.37</td>
<td>24.14 ± 0.10</td>
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<td>Pu(III)</td>
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<td>6.40 ± 1.18</td>
<td>12.61 ± 0.15</td>
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<td>Am(III)</td>
<td>2.50 ± 0.08</td>
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<tr>
<td>La(III)</td>
<td>2.88 ± 0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Ce(III)</td>
<td>2.94 ± 0.02</td>
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<td>-</td>
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<td>Sm(III)</td>
<td>3.23 ± 0.05</td>
<td>5.81 ± 1.10</td>
<td>10.54 ± 0.79</td>
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<tr>
<td>Bi(III)</td>
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<td>6.13 ± 0.31</td>
<td>11.04 ± 0.14</td>
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Stability constants of Flouride Complexes, determined using ISE, of various metal ions in different oxidation states (1m ionic strength medium of NaClO₄) at 23°C
Chemical Sciences & Engineering

Nuclear and Actinide Chemistry

Structure of $[\text{UO}_2(\text{DBM})_2\text{DPPMO}]$ showing monodentate mode of bonding for DPPMO

Optimised process flow sheet for the recycle of sol-gel washing effluent generated during UO$_2$ preparation

Structure of $[\text{UO}_2(\text{TTA})_2(\mu-\text{H}_2\text{O})_2(\text{H}_2\text{O})_2(\text{DB18C6})$}
Different modes of coordination such as, monodentate, bidentate chelate and bridging bidentate for the diphenyl phosphino methane dioxide ligand have been established in the compounds [UO₂(DBM)₂DPPMO]_, [UO₂(NO₃)₂DPPMO]_ and [UO₂(DBM)DPPMO] respectively.

![Structure of UO₂(DBM)₂DPPMO showing bridging bidentate of mode of bonding for DPPMO](image)

**Dissolution and Separation Studies of Actinides**

Solid state reactions of UO₂, ThO₂, PuO₂ and their mixed oxides (U,Th)O₂ and (U,Pu)O₂ were carried out with sodium nitrate and KHSO₄, K₂S₂O₈ and K₂S₂O₇ up to 900°C, (i) to study the formation of various phases at different temperatures, which are amenable for easy dissolution and (ii) to separate the actinide elements. It was observed that only uranium oxide reacts with sodium nitrate at 450°C and could be brought in to soluble form where as ThO₂ and PuO₂ do not react with sodium nitrate up to 900°C and remain insoluble. The reactions of mixed oxides (U,Th)O₂ and (U,Pu)O₂ with NaNO₃ showed quantitative separation of U from (U,Th)O₂ and (U,Pu)O₂.

The products obtained at 400°C by heating UO₂, ThO₂ and their mixed oxides with potassium salts were identified as K₄U(SO₄)₄, K₄Th(SO₄)₄ and K₄(Uₓ,Th₁₋ₓ)(SO₄)₄, respectively, which were found to be soluble in 2 M HNO₃ or H₂SO₄. From the solution of the dissolved products of the mixed oxides, thorium was separated quantitatively by precipitating it as thorium oxalate.

K. L. Ramakumar <klram@barc.gov.in>

![Structure of UO₂(NO₃)₂DPPMO showing bidentate chelating mode of bonding for DPPMO](image)