Innovations and Recent Trends in Radiochemistry Research

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Introduction

The founding of Atomic Energy Establishment at Trombay (AEET) witnessed a whole gamut of research activities in basic as well as applied research in nuclear science and technology in the country. With the commissioning of India’s first nuclear research reactor, APSARA, the nuclear and radiochemistry programme received a fillip. A large number of diverse research activities related to nuclear chemistry, nuclear fission, spectroscopic investigations, development of radioanalytical techniques and other analytical methodologies for chemical quality control (CQC) of nuclear fuel materials, process chemistry of actinides, spectroscopic and X-ray studies, mass spectrometry, thermodynamic investigations, recovery of actinides from analytical waste solutions and post irradiation studies on irradiated nuclear fuel were undertaken. This diverse research field has made us scientifically very confident in making collaborations with other research institutes in different countries. In the years to come, BARC will be playing major role in Nuclear Material Safeguards related activities, when more facilities coming under IAEA safeguards.

Role of Chemistry in fuel development Program

The challenges in this program will be: (i) augmenting the existing analytical methodology base for CQC of nuclear materials, (ii) understanding thermal and thermodynamic behavior of various fission product systems and their interactions with fuel and clad, (iii) developing new analytical techniques for understanding the ageing management of nuclear reactor components (iv) carrying out post irradiation examination of new fuels for burn-up as well as fission gas release (v) augmenting the database for nuclear properties of actinides and (vi) development of special materials for strategic program of the Department.

Conventional powder-pellet fuel fabrication processes are not well suited for remote handling of Pu and $^{233}U$ based fuel materials inside the shielded facilities as they involve a large number of mechanical steps. Sol-Gel process is amenable for such fuel preparation. Studies have to be carried out in a shielded facility on the preparation of ($^{233}U$,Th)O$_2$ and (ThO$_2$-PuO$_2$) microspheres using the sol-gel process. Test fuel pins have to be fabricated for the irradiation studies to understand irradiation behavior. This program involves various experts such as, radiochemists, metallurgists, reactor physicists and fuel designers.

Future program includes the development of coated particle fuels for high temperature gas cooled reactors, SGMP process for the Th-$^{233}U$ based fuels and irradiation behavior studies of the vibro-compacted fuel pins etc.

Analytical Methodologies for Chemical Quality Control of Nuclear Materials

For optimum performance of nuclear fuel inside a nuclear reactor, the nuclear fuel material should meet stringent requirements in terms of its chemical composition, purity, stoichiometry, and many other physical and chemical properties.
Presence of a number of elements as impurities in trace amounts is detrimental to the performance of the fuel. Boron, cadmium or rare earth elements are of larger interest and their quantification in sub–ppm level is very critical. Chemical quality control of these elements in nuclear materials is determined employing a number of techniques and methodologies.

Several methods with new redox reagents have been standardized for the determination of uranium with improved precision and accuracy. Many of the methods developed are confined to the applications in safeguards laboratory. Newer methods with minimum sample size have to developed with new instrumental methods. Multielemental analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) and GD-MS will have to be developed for this purpose. The advantages of this method include the reduced time of analysis, reasonable precision and accuracy and large sample throughput.

Gaseous impurities in nuclear fuels such as H, C, N, O and S are routinely determined employing commercially available instruments. The techniques are based on thermal conductivity (CO₂), IR detection (SO₂), Inert gas fusion and Kjeldahl distillation followed by spectrophotometry for nitrogen. Halogens such as fluorine and chlorine are separated from the sample matrix by pyrohydrolysis and determined either by ion selective electrodes, spectrophotometry or by ion chromatography. Ion chromatographic technique has also been developed recently to determine nitrogen in uranium and uranium alloy samples. The advantages of this method are (i) elimination of Kjeldahl distillation (ii) reduced time of analysis (iii) requirement of small sample size (10 mg) and (iv) increased sensitivity.

A new method based on the vacuum combustion extraction-quadrupole mass spectrometry has been developed for the determination of sulfur in nuclear fuel materials. It involves the combustion of the sample in presence of oxygen supplier like UO₂ in static vacuum conditions, extraction of the gases released into a known volume and determine the composition by on-line quadrupole mass spectrometer.

An XRF method was standardised for the determination of Th in (total U+Th) sintered UO₂-ThO₂, with UO₂ varying from 1-3% in powder samples. Another method based on the same principle was developed for the determination of Ga and U present in the mixture of their solid oxides.

Chelation ion Chromatography technique was developed for the separation and determination of lanthanides in different nuclear materials.

Studies on sulphur speciation employing Ion chromatography were carried out with different mobile phase concentrations to reduce the retention time of thiosulphate without compromising the resolution between sulphite and sulphate peaks. Experiments were carried out with industrial effluents and water samples received from different locations. The sulphide content in these samples was determined by iodimetric titration for comparing with ion chromatographic values.

**Ageing management of coolant channels in PHWRs and Post Irradiation Studies**

The life of zircaloy coolant channel used in Pressurised Heavy Water Reactors depends mainly on the extent of hydride formation. Since the solubility of hydrogen in zirconium is very much limited, slight excess of hydrogen leads to the precipitation of zirconium hydride and is highly brittle. A hot vacuum-quadrupole mass spectrometry (HVE-QMS) technique has been developed for the determination of hydrogen/deuterium in samples received from zircaloy coolant channels. The entire system has been conceived, designed and fabricated indigenously at BARC.
Procedures were established for the analysis of fission gases Kr and Xe from test fuel pins of MOX fuel as a part of post irradiation examination of irradiated fuels employing quadrupole mass spectrometry (QMS). The isotopic ratios of $^{131}\text{Xe}/^{134}\text{Xe}$ and $^{132}\text{Xe}/^{134}\text{Xe}$, $^{83}\text{Kr}/^{86}\text{Kr}$ and $^{84}\text{Kr}/^{86}\text{Kr}$ were very near to those from Pu-239 fissions indicating that majority of fissions are from Pu-239.

Thermal ionization mass spectrometry has been employed to determine burn up of nuclear fuels. Triple spike isotope dilution mass spectrometry has been employed for this purpose.

**Mass spectrometry and Alpha Spectrometry**

Isotopic mass of an element determines its nuclear properties including fission and absorption cross sections. Measurement of isotopic composition of materials used in nuclear technology is therefore very important. Considerable effort and time has been spent in developing analytical methodologies for the determination of isotopic composition and concentration of different elements from Li to Cm.

Nuclear fission is one of the fundamental characteristic features in nuclear chemistry. Each fissioning nuclide breaks into two fission products (one with mass less than 100 and another mass greater than 100) and a few neutrons accompanying by large release of energy. Comprehensive data on the fission yields of stable isotopes in neutron induced fission of $^{233}\text{U}$, $^{235}\text{U}$, $^{239}\text{Pu}$, $^{241}\text{Pu}$, $^{241}\text{Am}$, $^{242}\text{Am}$, $^{242}\text{Cm}$, $^{244}\text{Cm}$) have been carried out employing TIMS and alpha spectrometry.

The expertise achieved in the field of mass spectrometry was demonstrated by the successful participation in three international experiments (IDA-72, PAFEX-I and PAFEX-II) organised by the international agencies to evaluate precision and accuracy achievable on measurements of U and Pu.

**High Temperature Thermodynamics**

Solid Oxide electrolyte galvanic cells, Knudsen effusion mass loss and Knudsen effusion cell mass-spectrometric methods were used to determine vaporization behavior of UC, (U,Ce)C, UN, stainless steel, Pd, Rh, Tellurides of U and Th and molybdates of alkali metals. The noteworthy feature of all the investigations was that all thermodynamic properties were determined by the same laboratory using a variety of techniques.

For the FBTR at Kalpakkam, a fuel, which could provide high fissile content without the use of enriched uranium, was required. $(U_{0.30}Pu_{0.70})C$ with
5-15% sesquicarbide content and very small amounts (< 1000 ppm) of O₂ and N₂ was required. However, it was observed during the fabrication that it was not possible to achieve low N+O content with out significant loss of Pu by volatilization. With proper optimization of parameters, a fuel having 5000-6000 ppm of oxygen and 500 ppm of nitrogen could be obtained. The compatibility of the fuel with SS cladding could not easily be established on the basis of available literature. Investigations carried out could establish the chemical compatibility of the fuel fabricated with SS cladding. It is heartening to note that this has borne out by actual experiment on the FBTR fuel, which has reached a burn up of 140,000 MWD/T.

For the second core of FBTR, there was a proposal at one time to use mixed nitride fuel. Theoretical calculations established that good chemical compatibility could only be achieved if the fuel has very low carbon content and a separate mixed oxide phase.

(U, Th)O₂ is a nuclear fuel proposed to be used in the advanced heavy water reactors. Hence, it is necessary to investigate the thermophysical properties of this fuel in the reactor operating conditions. In this context, the Cp values of this alloy were determined employing DSC with a predefined heating programme. The Cp values were determined for the mixed oxide containing 0%, 2%, 4%, 6%, 10% and 20% uranium. The experimental values were similar to those of thorium oxide (ThO₂).

Thermochemistry of interoxide compounds in the system M- Te-O where M is a fission product is of considerable interest to understand the internal chemistry of the oxide fuel pins in an operating nuclear reactor.

**X-ray and Solid State Chemistry**

X-ray, thermal, IR and NMR techniques have been employed to study the structural aspects of uranium and plutonium compounds to understand the nature of structure-property relation. The single crystal X-ray structure of the complex [UO₃(TTA)₂H₂O] crown shows that two of the [UO₃(TTA)₂H₂O] molecules are bridged by the crown ether ligand to give a dinuclear complex [UO₂(TTA)₂H₂O]₂(Crown). Two such dinuclear complexes are stabilized by the intermolecular hydrogen bonding to give a stable tetra nuclear cluster.

Thermogravimetry and X-ray powder diffraction procedures have been used to study the solid solubility of Pu³⁺ and Pu⁴⁺ oxides in the stabilized zirconia, a fluorite matrix, in air.

The crystal structure of Pu₅Zr₂O₇ was derived from the analysis of X-ray powder diffraction data by Rietveld analysis. The systematic absence in X-ray reflections required by the pyrochlore structure [Fd3m] were observed in the indexed pattern with cubic cell parameter of a = 10.5719 (1) Å and Z = 8. In the structure, each Zr cation has 6 oxygen anions in octahedral coordination.

**Actinide Chemistry**

The basic research programme on actinide chemistry included investigations on the interconversion of their oxidation states with a view to arriving at suitable conditions for stabilizing each of the oxidation states, studies on the complexing abilities of actinides with different inorganic and organic anions, studies on the solvent extraction behaviour of actinide ions into different types of solvent-diluents combinations and from different aqueous environments and studies related to both cation and anion exchange behavior of actinides etc. The understanding of their chemistry forms the backbone in developing methods for their estimation as well as their recovery and purification from different complex matrices.

Detailed investigations were carried out for the recovery of neptunium as a byproduct of plutonium-
uranium extraction (Purex) process. Large data generated in our laboratory on neptunium behavior in Purex Process has found a place in the standard textbook on nuclear chemical engineering by Benedict and Pigford. Extensive studies on the complexation behavior of neptunium carried out in our laboratory resulted in publishing a review article on the coordination complexes of neptunium in the journal “Coordination Chemistry Reviews” in 1978, which is a unique source material on neptunium complexes even to this day.

Studies on irradiation of Neptunium-237 targets and their processing for the recovery of $^{238}$Pu enabled in establishing methods for the making of $^{238}$Pu sources, which has many applications as an isotopic power generator.

Large scale plutonium recycling operation was carried out for meeting the Pu required for FBTR fuel fabrications. A novel method has been developed to recover gram quantities of americium, which has many applications in gamma radiography, smoke detectors etc from the waste solution. This americium could be used in measuring the uranium concentration profile in reprocessing plant streams with on-line detection.

An anion exchange studies on plutonium recovery with a large number of gel type and macroporous resins conducted in our laboratory has widened the scope of plutonium recovery from different sources yielding a pure and concentrated plutonium product.

Stability constants of the fluoride complexes of lanthanides were determined by ion selective potentiometry and the data are comparable with the estimated values obtained by interpolation from the general trend of stability constants of the lanthanide fluorides in aqueous solution. Correlation of the stability constants with their fundamental properties like ionic charge, coordination number, ionic radius and electronic configuration was studied.

Reliable thermodynamic data are of prime importance to predict radionuclide speciation in biological as well as natural environments.

**Conclusion**

A number of dedicated Radiochemists and Radioanalytical chemists are involved in this task. The expertise generated has provided enough confidence to take on fresh challenges to meet the future requirements of the Department. The Programme has a vital role to play to address many of the issues related to chemical and physico-chemical aspects of thorium based fuel technology thus fully utilizing our country’s vast resources of thorium to satiate the ever increasing energy demands to realize a self sufficient and prosperous India.