



भाभा परमाणु अनुसंधान केंद्र BHABHA ATOMIC RESEARCH CENTRE

> स्वर्ण जयंती वर्ष GOLDEN JUBILEE YEAR 2006-2007

For further details contact:

## Dr. L. M. Gantayet

Head, Laser & Plasma Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai - 400 085, India.

E mail: headlptd@barc.gov.in

Published by :

# Dr. Vijai kumar

Associate Director, Knowledge Management Group and Head, Scientific Information Resource Division, Bhabha Atomic Research Centre, Trombay, Mumbai - 400 085, India.

E mail: vijai@barc.gov.in

#### FOREWORD

Bhabha Atomic Research Centre (BARC) is celebrating its golden jubilee year during 2006-07. On 20<sup>th</sup> January, 1956, Pandit Jawaharlal Nehru formally inaugurated the Atomic Energy Establishment Trombay (AEET), which is renamed as Bhabha Atomic Research Centre (BARC) on January 22, 1967. As a premier R&D centre of the Department of Atomic Energy (DAE), BARC has a mandate to provide R&D support to the nuclear power programme, to pursue all activities related to nuclear fuel cycle, to operate research reactors for supporting neutron beam research and supplying radioisotopes for various applications, to conduct frontline basic research in physical, chemical, biological and engineering sciences all of which leading towards improving quality of life of our people. The achievements BARC has made over the last 50 years are well known not only to the scientific community in the country but also to our people at large. Scientific achievements made by this premier research centre are well documented in various publications of DAE including a series named "BARC Highlights". During this golden jubilee year, we have made an effort to bring out some glimpses of recent research and development accomplishments in the form of 8 volumes, highlighting the following areas:

- 1. Nuclear Fuel Cycle
- 2. Physical Sciences
- 3. Chemical Science and Engineering
- 4. Materials Science and Engineering
- 5. Life Sciences
- 6. Reactor Technology and Engineering
- 7. Electronics, Instrumentation and Computers
- 8. Environmental Science and Engineering

These volumes will showcase the latest work in the aforementioned areas and will demonstrate how each of these is directed towards achieving the overall goal of using nuclear energy for the benefit of our people.

Nuclear energy programme in India has now reached a level of maturity. Today, India is self-sufficient in building nuclear power stations of 540 MWe capacities and has gained mastery over the entire fuel cycle. We are in the threshold of entering the second stage of nuclear power programme, in which a rapid growth in installed capacity is expected through the fast reactor programme. In the area of basic research in science and engineering, BARC has been maintaining a leading position both in national and international scenario. One of the strongest points of basic research in BARC lies in its capability in building sophisticated research facilities in-house. The core competence of the scientists and engineers in our centre covers a very wide range as is reflected in the 8 companion volumes getting released on the occasion of the golden jubilee year.

For our nuclear power programme, our foremost need is to develop advanced technologies to meet the demand of nuclear materials. With stress on that, novel processes and materials have been developed by BARC and implemented regularly. Research has been focused to enhance the uranium metal production and process flexibility has been achieved to handle different grades of UF4 as feed material. Significant progress has also been made in the novel indigenous process of plasma based hydrogen reduction of UF6 to UF4. Synthesis and evaluation of new organo phosphorous extractants and other solvents such as dialkyl amides, branched chain amides, and strontium selective crown ethers are the outcome of the research. The actinide chemistry research has also been extended on fluorescence studies on new phosphor materials, photo acoustic studies, EPR spectroscopy etc.

For recovery of uranium from lean sources, design capability for large capacity mixer-settler, a potential solvent extraction equipment, has been developed. New ion exchange processes for boron removal from shutdown system, selective removal of gadolinium in presence of boron, purification of moderator by electrochemical filter, and chemical decontamination before maintenance are some of the achievements in the field of power reactors.

Development of Chitosan, a natural bio-polymer for recovery of actinides in the presence of inorganic salts is significant. Indigenous technologies for recovery of Pa-231 from feed material, production of sulphur hexafluoride, tri-chloro silane, preparation of organometallic precursor and production of ultra pure arsenic, gallium etc are visible manifestations of the technological capability of our centre. Completion of the scaled up version of the industrial electrolytic cells for production of fluorine and the compact water electrolyser for defense laboratories demonstrate the capability in our electrochemical technology.

R & D in isotope separation science and technology have enabled to develop high efficiency tower internals for applications in O-18 isotope separation and B-10 enrichment by exchange distillation and to provide deuterium standards for the nuclear power reactors to maintain the quality of the moderator. The CO<sub>2</sub> laser has been used for macroscopic production of C-13 isotope.

Pulse radiolysis with high energy electrons have been used to evaluate the mechanisms of free radical reactions of antioxidant in natural sources. Application of radiation for simultaneous radiolytic formation of silver nanoparticles in the hydrogel while cross-linking the PVA chain is yet another technological advancement. Radiation polymerization of hydrogel for super adsorbent, metal extraction and other applications constitute the research and development effort in this area.

A low cost phytohormone, developed in BARC has shown improvement in silk cocoons. Similarly, the use of Para pheromones to control pest damage to the tuber crop has been patented. Role of aroma glycosides in contributing to the unique aroma of fruits (Pomegranate) and spices (Nutmeg) and monsoon coffee was demonstrated.

Development of cryogenic systems for cryo-distillation of hydrogen isotopes and the Accelerator Driven Sub-critical System (ADS) project is in progress. An indigenously designed helium based 20K cryogenic refrigerator, fabricated and tested, is testimony to this. All the critical components viz. cryogenic turbo expander, heat exchangers, bearing, bellow sealed valves, transition joints and feed troughs have been indigenously developed.

In the area of desalination technologies, BARC has set up sea water reverse osmosis (RO) plant in coastal areas, brackish water RO plant in villages for producing safe drinking water. Technologies have also been developed on Multistage Flash (MSF) evaporation plant for sea water desalination using low grade steam, Low Temperature Evaporation (LTE) plant using waste heat for sea water desalination and Waste Water Recycle and Reuse plants for the effluent.

Development of solid oxide fuel cell (SOFC) has been taken up for efficient generation of power from hydrogen, natural gas and other renewable fuels. BARC has developed mixed metal catalysts for water splitting and degradation of volatile organic compounds and also instruments for carrying out in-situ FTIR studies on catalyst surfaces. Robust noble metal catalyst, a catalyst of interest for hydrogen combination under ambient conditions, has been supplied in the form of prototype panels and strips.

In the area of 'nanophase' materials, plasma has been effectively used for bulk reactive generation of nanoparticles in addition to work on radiolytic and photolytic methods of production of nanoparticles.

This volume of BARC Highlights emphasizes the work done in BARC in the area of Chemical Science and Engineering, which has been an important part of the Indian Atomic Energy Programme.

Srikumar Banerjee Director

#### PREFACE

Bhabha Atomic Research Centre had embarked upon a comprehensive R&D in Chemistry and Chemical Engineering from its inception. The Indian atomic energy programme had to be built on the indigenous resources : the lean resources of uranium and the more abundant resource of thorium. In the last three decades the R&D programme, which addressed these issues, had also made special demands on the scientists and technologists to find innovative solutions in the face of technology control regimes. The synergy between the expanding areas of research in basic sciences and engineering sciences has yielded several novel process technologies, which have been developed indigenously and deployed to meet these challenges. The activity spanned from understanding of the chemistry of the processes, development of the process in the laboratory, pilot scale and its implementation for production. It also included development of new equipment and their utilisation. This volume on Chemical Sciences and Engineering gives a glimpse of the activities of the past three years. The chapters in the volume have been devised to focus on the mature technologies as well as the new science, at the cost of uneven distribution of pages between the chapters.

The research in chemistry has been strongly linked to the various areas of the nuclear fuel cycle, radiation application, environmental and safety aspects. Man made radioisotopes produced in the nuclear reactors and accelerators have opened up new areas of science and technology. Several contributions in this volume highlight the technology required to produce the isotopes, convert them to usable form and harness the tremendous economic and societal benefits. Radiation processing of polymers, food and waste has developed in a major way. BARC has become the premium national institute for studies in nuclear chemistry, radiation chemistry, water chemistry, analytical chemistry, environmental science and separation sciences. These disciplines in turn have given rise to more specialised branches of actinide chemistry, radiopharmaceutical chemistry, bioorganic chemistry, natural products chemistry, theoretical chemistry, etc. The demands of technology also spurred activities in study and production of ultra pure materials.

The parallel development in chemical engineering sciences took place in BARC in the diverse areas of uranium extraction, fuel reprocessing, solvent extraction, ion exchange, membrane separation, effluent water treatment and desalination, cryotechnology, electrochemical technology, mass transfer processes with and without chemical reaction, fluorination and chlorination in fluidised bed reactors etc. Isotopes and isotope separation hold a special place in the nuclear energy. Every field of science or technology is exploited for its development. Advent of new technology in any area is quickly exploited in Chemistry and Chemical Engineering. Use of lasers, accelerators and plasma in study of the reactions and in improving the efficiency of the processes are demonstrated in the reported work. Department of Atomic Energy plays a key role in the development of alternative clean and resource efficient methods of energy production. Thus, Chemical Sciences and Engineering have contributed significantly to the fuel cells and hydrogen energy.

In the several rounds of discussion with the scientists who are the real authors of the volume, it was decided that the text would have to be very brief and should highlight the activities in a manner that will be useful to a scientist from another discipline, and certainly educative to the layperson. For obtaining further information on the activities of large teams, the reader is to contact the scientist who has compiled and collected the information.

I wish to put on record the efforts of the contributors and the Heads of the respective Divisions. I am grateful to Director, BARC for entrusting and guiding us in this awesome task of compiling and editing the multidisciplinary achievements. I thank Dr. Vijai Kumar for coordinating the management and the publication in an unobtrusive but effective manner. I would also like to thank my colleagues in Laser & Plasma Technology Division for helping in the production and presentation: Shri E. Kandaswamy and Shir A. Nagaraj, and particularly the young chemist, Kum. P. Mathi, who has helped me with all the aspects of this task from the day one.

L. M. Gantayet



# CONTENTS :

#### PREFACE

#### FOREWORD

1	NUCLEAR AND ACTINIDE CHEMISTRY	1
1.1	Nuclear Chemistry	2
1.2	Applications of nuclear chemistry	4
1.3	Actinide chemistry	5
2	SOLVENT EXTRACTION CHEMISTRY AND TECHNOLOGY	9
2.1	New extractants	10
2.2	New solvent extraction equipment	13
2	MAN MADE ISOTORES	15
2 1	Braduction of new isotones in DHPUIVA	16
5.1		10
3.2	1-125	18
3.3	Applications of other man made isotopes	19
3.4	Radiopharmaceutical research	21
3.5	Isotopes for industries	25
3.6	Water resources management with radiotracers	31
4	ANALYTICAL CHEMISTRY	35
4.1	Analytical methods in fuel fabrication	36
4.2		27
4.2		57
4.3	New analytical efforts	39
4.4	Thin layer activation	40
4.5	Analytical instruments developed in BARC	40
4.6	Neutron activation analysis	41



5	RADIATION CHEMISTRY	4 2
5.1	Free radical reactions of antioxidants and radiaoprotector	43
5.2	Radiation polymerization	45
6	URANIUM TECHNOLOGY AND PROCESSES	49
6.1	Uranium recovery from low concentrate sources	50
6.2	Recovery of uranium from sea water	53
6.3	Uranium metal production	55
6.4	New plasma based processes for conversion of $\mathrm{UF}_{6}$ to $\mathrm{UF}_{4}$	57
6.5	Pollution abatement through denitration	57
7	THERMODYNAMICS OF NUCLEAR FUEL	
	FOR THORIUM FUEL CYCLE	61
7.1	Thermodynamic properties of fuel and fission products	62
7.2	Transport properties of gases and volatile fission products	65
7.3	Solid state chemistry research on nuclear materials	65
8	WATER CHEMISTRY FOR NUCLEAR FUEL CYCLE	68
8.1	Boron cleanup	69
8.2	Selective removal of gadolinium nitrate	69
8.3	Removal of Indium metal turbidity	69
8.4	Metal ion passivation studies	70
8.5	Bioremediation of Co-60	70
8.6	Bioremediation for decontamination of low level radioactive wastes	70
8.7	Nuclear effluent polishing by chitosan	71
8.8	Development and application of chemical decontamination process	71
9	HEAVY WATER TECHNOLOGY	73
9.1	Deuterium standards and labelled compounds	74
9.2	Heavy water purification	74
9.3	High efficiency tower internals	75
10	ISOTOPE SEPARATION	77
10.1	Laser isotope separation	78
10.2	<sup>10</sup> B isotope enrichment	79



11	CRYOC TECHNOLOGY	8 1
11.1	Cryogenic system development	82
11.2	Cryogenic system critical components development	83
12	FUEL CELLS AND ELECTROCHEMICAL TECHNOLOGY	8 7
12.1	Chemistry of fuel cell	88
12.2	Fuel cell technology	89
12.3	Electrochemical technology	89
13	NATURAL PRODUCT CHEMISTRY	9 1
13.1	Biological chemistry	92
13.2	Agricultural chemistry	94
13.3	Synthetic bioorganic chemistry	94
13.4	New aroma impact and bioactive compounds	95
13.5	Production of Xanthan gum	96
14	CHEMISTRY AND LASERS	9 7
14.1	Condensed phase photochemistry and chemical dynamics	98
14.2	Gas phase photochemistry and chemical dynamics	104
14.3	Development of laser dyes for dye laser	105
14.4	Time resolved laser induced Fluorescence (TRLIF) in nuclear fuel cycle	106
15	CATALYSIS AND SURFACE CHEMISTRY	108
15.1	Catalyst for hydrogen mitigation in nuclear facilities	109
15.2	Studies on uranyl anchored MCM catalysts	109
15.3	Photocatalysts	110
15.4	Dynamics of absorbate molecules in the confined interstices of porous materials	110
16	SENSORS	112
16.1	Chemical dosimeters for high dose dosimetry	113
16.2	EPR dosimetry - Investigation of new dosimetric materials	113
16.3	Chemically selective membrane optodes	114
16.4	Porous silicon based capacitive immunosensor	115



16.5	Nafion coated uranyl selective electrode	115
16.6	Diamond alpha particle detector	116
17	THEORETICAL CHEMISTRY	117
17.1	Multiscale materials modeling	118
17.2	Structure and properties of soft and condensed matter	120
17.3	Dynamics in condensed phase	121
18	MEMBRANE PROCESSES FOR WATER TREATMENT	124
18.1	Membrane desalination	125
18.2	Membrane development	127
18.3	Thermal desalination	128
18.4	Nuclear desalination	130
18.5	International collaboration	131
18.6	Consultancy	131
19	NANO MATERIALS	132
19.1	Nano materials by plasma technology	133
19.2	Nanoceramics	134
19.3	Metal nanoparticles	135
2.0	NOVEL MATERIALS PROCESSES AND TECHNOLOGIES	136
20.1	Pa - 231 extraction from natural sources	137
20.2	Sulphur bexafluoride production	138
20.3	Trichlorosilane production	138
20.4	Gadolinium nitrate production	139
20.5	Organo - metallic compounds	140
20.6	Closing the Zirconium cycle	144
20.7	Diamond like carbon and CN films	145
20.8	Structure and dynamics of organised assemblies	145
20.9	Frame work solids	146
20.10	LB films of functional materials	146
20.11	Rare earth based inorganic fluorides	147
20.12	Low temperature heat capacity measurement facility	147
20.13	Microrheology of complex fluids by light scattering	148

## 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 <sup>12</sup>C and <sup>13</sup>C on <sup>181</sup>Ta target. The cross section for incomplete fusion was found to be significantly higher in the case of <sup>12</sup>C than that in the case of <sup>13</sup>C, suggesting the role of alpha cluster structure of <sup>12</sup>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 <sup>12</sup>C and <sup>13</sup>C with <sup>181</sup>Ta respectively.





Nucl. Phys. A 739, 229 (2004)

## Positron Annihilation Spectroscopy and its Applications

New results on the electronic structural changes at the onset of superconducting transition in MgB<sub>2</sub> 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).

#### Ion Beam Analysis Studies

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 cesium loaded PIMs based on cellulose triacetate (CTA) as the bulk polymer, nitrophenyl octyl ether (NPOE) as the plasticiser, and dinonyl naphthalene sulphonate (DNNS) as the carrier with 4 MeV proton beam from FOTIA, showed uniform distribution of the carrier across the thickness of the membrane, while the Atomic Force Microscopy (AFM) spectrographs showed inhomogeneity at submicron scale.



Ion beam analysis facility at FOTIA

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 <sup>15</sup>N or <sup>19</sup>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.



Nucl. Inst. Meth. B211, 138, 200 (2005) Nucl. Inst. Meth. B227, 391 (2005) Nucl. Inst. Meth. A 533, 282 (2004)

#### Spectroscopic Studies

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<sub>4</sub>O<sub>7</sub> 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 gammaray spectrometry for isotopic composition measurement in the chemical laboratory. Assuming that the ratios of <sup>144</sup>Ce to U and that of <sup>144</sup>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  $\pm$  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.

followed by neutron well coincidence counting for the total plutonium content.

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 <sup>144</sup>Ce-<sup>144</sup>Pr (285 days) in the hull is measured using a suitable collimator detector arrangement in the dissolver cell area. Ratio of the activity of <sup>144</sup>Ce to U and Pu in the dissolver solution is determined



The segmented gamma scanner in operation

## Development of Neutron Counting Systems for Non Destructive Assay of Plutonium

A neutron well coincidence counter based on <sup>3</sup>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 <sup>3</sup>He counters in HDPE moderator assembly has been designed and fabricated for in-situ assay of plutonium



Portable neutron slab coincidence counter

in sealed containers. The system has been installed at Radio Metallurgy Division

Nucl. Inst. Meth. A 511, 437 (2003)

## 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.

Metal ion	$\log \beta_1$	$\log \beta_2$	log β <sub>3</sub>	log β <sub>4</sub>
U(VI)	4.56 ± 0.01	$\textbf{8.02} \pm \textbf{0.02}$	$\textbf{10.46} \pm \textbf{0.07}$	11.99 ± 0.13
Np(VI)	3.94 ± 0.01	$\textbf{6.73} \pm \textbf{0.02}$	$\textbf{8.29} \pm \textbf{0.07}$	-
Pu(VI)	3.80 ± 0.15	6.31 ± 0.15	8.00 ± 0.17	-
Np(V)	1.20 ± 0.10	-	-	-
Th(IV)	7.61 ± 0.01	$\textbf{13.42} \pm \textbf{0.05}$	17.65 ± 0.20	23.67 ± 0.11
U(IV)	8.84 ± 0.01	14.66 ± 0.01	19.51 ± 0.03	23.92 ± 0.04
Np(IV)	8.17 ± 0.04	$\textbf{14.52} \pm \textbf{0.13}$	$\textbf{20.05} \pm \textbf{0.13}$	25.95 ± 0.18
Pu(IV)	7.61 ± 0.12	14.77 ± 0.10	20.11 ± 0.37	26.07 ± 0.16
Zr(IV)	8.49 ± 0.11	$\textbf{15.76} \pm \textbf{0.15}$	$\textbf{21.57} \pm \textbf{0.10}$	26.68 ± 0.16
Hf(IV)	$\textbf{8.22} \pm \textbf{0.06}$	$\textbf{15.48} \pm \textbf{0.15}$	21.76 ± 0.14	27.42 ± 0.15
Ce(IV)	7.57 ± 0.04	$\textbf{14.50} \pm \textbf{0.03}$	20.13 ± 0.37	24.14 ± 0.10
Pu(III)	$\textbf{3.58} \pm \textbf{0.08}$	6.40 ± 1.18	$\textbf{12.61} \pm \textbf{0.15}$	
Am(III)	$\textbf{2.50} \pm \textbf{0.08}$	•	•	-
La(III)	2.88 ± 0.01	-	-	-
Ce(III)	$\textbf{2.94} \pm \textbf{0.02}$	-	-	-
Sm(III)	3.23 ± 0.05	5.81 ± 1.10	10.54 ± 0.79	-
Bi(III)	3.69 ± 0.01	6.13 ± 0.31	11.04 ± 0.14	-

Stability constants of Flouride Complexes, determinded using ISE, of various metal ions in different oxidation states (1m ionic strength medium of  $NaClO_4$ ) at 23°C

## Recycle of Chemicals from Alkaline Waste Generated during Preparation of UO, Microspheres

Bench scale studies were carried out to recycle chemicals from alkaline waste generated during preparation of UO<sub>3</sub> 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 UO<sub>2</sub> 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  ${\rm UO}_{\scriptscriptstyle 3}$  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  $[UO_2(TTA)_2.2H_2O]$  with Benzo, 15- crown-5 ether yielded a binuclear complex in which the crown ether bridges two  $[UO_2(TTA)_2.H_2O]$  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  $[UO_2(TTA)_2.H_2O]$  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.





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[ $UO_2(DBM)_2DPPMO$ ], [ $UO_2(NO_3)_2.DPPMO$ ] and [ $UO_2(DBM)_2DPPMO$ ], respectively.



Structure of [UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.DPPMO] showing bidentate chelating mode of bonding for DPPMO

## Dissolution and Separation Studies of Actinides

Solid state reac)tions of UO<sub>2</sub>, ThO<sub>2</sub>, PuO<sub>2</sub> and their mixed oxides (U,Th)O<sub>2</sub> and (U,Pu)O<sub>2</sub> were carried out with sodium nitrate and KHSO<sub>4</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> 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 ThO<sub>2</sub> and PuO<sub>2</sub> do not react with sodium nitrate up to 900°C and remain insoluble. The reactions of mixed oxides (U,Th)O<sub>2</sub> and (U,Pu)O<sub>2</sub> with NaNO<sub>3</sub> showed quantitative separation of U from (U,Th)O<sub>2</sub> and (U,Pu)O<sub>2</sub>.

The products obtained at 400°C by heating UO<sub>2</sub>, ThO<sub>2</sub> and their mixed oxides with potassium salts were identified as  $K_4U(SO_4)_4$ ,  $K_4Th(SO_4)_4$  and  $K_4(U_x,Th_{1-x})(SO_4)_4$ , respectively, which were found to be soluble in 2 M HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. 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>





## 2. SOLVENT EXTRACTION CHEMISTRY AND TECHNOLOGY

## INTRODUCTION

Solvent extraction is one of the most employed separation processes in the nuclear industry. Research and development in solvent extraction begins with studies on the solvent extraction behaviour of actinide ions into different types of solvents from varying aqueous environments, 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. The contributions describe the synthesis and evaluation of new solvents such as, dialkyl amides, branched chain amides, and strontium selective crown ethers. The implementation of the solvent extraction process can be made economical with the use of improved extraction equipment. Two large capacity mixer-settler class of solvent extraction equipment have been developed.

#### 2.1 NEW EXTRACTANTS

## N,N, Dialkyl Amides as Promising Alternate Extractants in the PUREX Process

Though Tri-Butyl phosphate (TBP) based PUREX process has been the workhorse of nuclear fuel reprocessing industry for the last four and a half decades yet a few drawbacks are associated with the use of TBP while treating different waste streams for their disposal to the environment. N,N dialkyl aliphatic amides have received particular attention as alternate potential extractants for the reprocessing of spent nuclear fuels in view of (i) the innocuous nature of their degradation products viz. carboxylic acids/amines and (ii) the possibility to incinerate the used solvent leading to reduced volume of secondary waste.

Work was initiated in Radiochemistry Division to design, synthesize characterize dialkyl amides and investigate the extraction behaviour of U(VI), Pu(IV), Am(III) and fission products like Cs, Sr, Eu, La, Ce, Zr and Ru from nitric acid medium employing n-dodecane as the diluent. The physical and chemical properties of these amides are influenced strongly by the nature of alkyl groups. N,N-dihexyl derivatives of hexanamide (DHDA), octanamide (DHOA) and decanamide (DHDA) in general and DHOA in particular were found to be promising amongst a large number of extractants studied.

These ligands readily dissolved in n-dodecane and did not form third phase with nitric acid (upto 7 M). Limiting organic concentration (LOC) value for 1.1 M DHOA at 3 M HNO<sub>3</sub> is ~ 100 gm/L. 5 Kg of DHOA was synthesised and characterised by elemental analysis as well as by proton magnetic resonance (PMR) spectra. Laboratory batch studies as well as mixer settler studies were performed under process conditions with DHOA and compared with those of TBP. DHOA was found to extract Pu(IV) more efficiently as compared to TBP, both at trace level concentration as well as under uranium loading conditions. Extraction of all the fission products with DHOA between 2-4 M HNO<sub>3</sub> was lower by an order of magnitude as compared to TBP. Mixer settler studies with eight stages revealed the possibility of quantitative stripping of U by 0.01 M HNO<sub>3</sub> in lesser number of stages as compared to the corresponding TBP system.





Stage analysis data of (a) the aqueous phase for extraction cycle and (b) the organic phase for stripping cycle for DHOA and TBP

## Branched Chain Amides as Promising Alternate Extractants in THOREX Process

THOREX process (used for the separation of U from irradiated bulk Th) differs from the PUREX process in view of the (i) non variable oxidation state of Th (unlike that of Pu) and (ii) poor solubility of  $Th(NO_3)_4$ . Three TBP species leading to the third phase

during the co-extraction of uranium and thorium. Lower concentration of TBP (5 %) in THOREX process as compared to PUREX process (30 %) is necessitated to improve the separation factor of U over Th.

Structural correlation of several tertiary amides with their extraction behaviour towards  $HNO_{3'}$  U(VI) and Th(IV) suggested that steric effects of the alkyl group adjacent to the carbonyl group influence the separation factor value  $(D_U/D_{Th})$  significantly. The LOC studies on Th and distribution studies in the presence of 220 g/L of Th employing TBP/tris(2-ethylhexyl) phosphate/ dihexyl hexanamide/di-2-ethylhexyl isobutyramide (D2EHIBA) showed that D2EHIBA was one of the promising reagents for the separation of U-233 from irradiated Th. Fission product extraction studies revealed that the decontamination achieved was better by an order of magnitude using 0.5 M D2EHIBA as compared to that with 5 % TBP. Degradation studies of D2EHIBA suggested that bis (2-ethylhexyl) amine (one of the degradation products) was washed out by nitric acid.

Six stage mixer settler runs were carried out for U/Th separation from THOREX feed solution using 0.5 M D2EHIBA and 5 % TBP as the extractants. These studies have clearly demonstrated that (i) thorium uptake is significantly low in the case of D2EHIBA ( $\sim 0.2$  g/L) as compared to that of 5 % TBP (6 g/L), (ii) loss of uranium to the raffinate for 0.5 M D2EHIBA and 5 % TBP are 1 % and 5 % respectively and, (iii) acid uptake is higher in the case of 0.5 M D2EHIBA (0.4 M) than that of 5 % TBP (0.2 M). Purification of uranium obtained as the stripped solution (from mixer settler) was carried out by a cation exchange method using DOWEX 50W x 4 resin. > 99 % recovery of both the metal ions was possible with a decontamination factor value of more than 10,000 for each of them.



Solvent Extraction and Ion Exchange, 20(3), (293-312) 2002,. Nuclear Technology,139, (253-262) 2002.

Extractant	[Ligand], M	Du	Dm	D <sub>U</sub> / D <sub>Th</sub>
TBP	0.18	2.4	2.3 x 10 <sup>-2</sup>	104
TEHP	0.18	6.2	3.5 x 10 <sup>-2</sup>	177
DHHA	0.18	0.4	1.7 x 10 <sup>-3</sup>	235
	0.18	1.19	4.0 x 10 <sup>-4</sup>	2975
D2EHIBA	0.5	3.95	2.4 x 10 <sup>-3</sup>	1646
	1.0	6.0	2.7 x 10 <sup>-2</sup>	222

Evaluation of extraction behaviour of linear and branched chain extractant towards U-Th seperation; [Th] = 220 G/L AT 4 M  $\rm HNO_3.$ 

## Novel Extractants for Actinide Partitioning

Development of suitable extractant for actinide partitioning from high-level waste (HLW) solution is one of the challenging areas of research in actinide chemistry. In this context, several diamides have been synthesized at Radiochemistry Division. Continuous efforts are being made to modify the diamide structure to improve the extractability of actinide ions in general and trivalent actinides in particular. A tridentate ligand, N,N,N',N'-tetraoctyl diglycolamide (TODGA) was synthesized and was tested for the extraction of actinides from wide range of acidity. The diamide was found to have much better extractability for trivalent actinides as compared to other commonly proposed extractants for actinide partitioning such as CMPO, TRPO and DMDBTDMA. The extractant was also tested for the extraction of actinides from simulated high level waste (SHLW) solution.

#### Ln(III)/Am(III) separation

The separation of long-lived trivalent minor actinides (mainly Am(III) and Cm(III)) from lanthanides is a key step in the 'Partitioning and Transmutation', a strategy being advocated for the safe management of high level waste. In Radiochemistry Division, efforts are being made to identify the right solvent for

this purpose, which can lead to reasonably high D.F. values. Out of the many solvents evaluated for the separation studies, a binary mixture of Cyanex-301 and 2,2'-bipyridyl or 1,10-phenanthroline (o-phen) in toluene has yielded a S.F. value of >40,000 which is the highest reported to date. An extraction chromatographic resin prepared at Radio Chemistry Division, effectively separated Am(III) from Eu(III) with a D.F. value of >100. Several membrane based separation methods are also being evaluated currently.

## Strontium Recovery from Simulated Radioactive Waste using a Size Selective Crown Ether

Separation of Sr-90 (T1/2 = 28.5years), from high level waste (HLW), prior to vitrification of the latter, is helpful not only to reduce the volume of disposable waste but also to reduce the risk of matrix deformation caused by the generated heat. Sr(II)-specific extraction property of di-t-butyl cyclohexano 18-crown-6 (DtBuCH18C6) is exploited for analytical applications as well as for the Sr-90 recovery from HLW. Both membrane as well as extraction chromatographic studies were carried out for the selective removal of <sup>90</sup>Sr from HLW. The transport behaviour of Sr was investigated by supported liquid membrane (SLM) technique using di-t-butyl cyclohexano 18 crown 6 (DTBCH18C6,

Feed	%Sr transported	P (cm/s)
3 M HNO3	73	1.45 x 10 <sup>-4</sup>
0.5MHN0 <sub>3</sub> + 2M AI(N0 <sub>3</sub> ) <sub>3</sub> ª	>95	2.16 x 10 <sup>-4</sup>
1 M HN0 <sub>3</sub> + synthetic nuclear waste 1 M HN0 <sub>3</sub> +	25.5	2.54x10⁵
synthetic nuclear waste + 2 M AI(N0 <sub>3</sub> ) <sub>3</sub> b	65	8. 87 x 10 <sup>-5</sup>

a: Extrapolated; b: Volume increase was observed after Al(N0<sub>3</sub>)<sub>3</sub> addition

Transport Data of 85,89 Sr under varying feed compositions. Reciever: Distilled water; Carrier: 0.05 m DTBUCH18C6 in 1-Octanol

Parameter	Total solid (T.S.)				
	1g/L	5 g/L	10 g/L	100 g/L	300 g/L
Amount loaded (as 85,89Sr, in μCi) Wash (10 ml of 3 M HN0₃)	2.42 Nil	2.46 Nil	2.98 Nil	2.98 Nil	2.98 Nil
Bute (3 ml of D.W., in μCi)	2.19	2.15	2.44	2.10	1.98
% Recovery	90.3	87.5	82	70.5	66.5

Sr (II) uptake from Simulated Wastes Containing Varying T.S.

a selective reagent for Sr(II) in 1-octanol as the carrier. The selective transport of Sr(II) from a synthetic waste solution containing a host of fission products and structural material was observed in presence of 2 M Al(NO<sub>3</sub>)<sub>3</sub> as shown in the table.

On the other hand, the extraction chromatographic studies were carried out using a resin material prepared indigenously by impregnating the crown ether onto XAD-7. The Sr-selective resin material was successfully used by 4 laboratories in BARC for the selective separation and subsequent estimation of Sr-90. The recovery of Sr(II) from simulated HLW was about 90% at a Total Solid (TS) of 1 g/L and decreased steadily with increasing TS as shown in the table. Tests are underway to recover Sr-90 from actual HLW using a column made from the resin material at Waste Management Division, BARC.

V. K. Manchanda <vkm@barc.gov.in>

B. S. Tomar <bstomar@barc.gov.in>

## Organic Chemistry in Nuclear Technology

Solvents such as CMPO and various alkyl substituted malonamides that are promising for selective extraction of the long-lived hard

 $\gamma$ -emitting actinides have been synthesized and their efficacy as nuclear extractants established. The syntheses for the above two solvents have been developed up to 2M scale and the technology for the processes have been transferred to the Heavy Water Board for their scale-up and manufacture.

S.Chattopadhyay <schatt@barc.gov.in>

#### 2.2 NEW SOLVENT EXTRACTION EQUIPMENT

## Development of Large Capacity Pump-mix Mixer-settler

Large capacity mixer-settler are required for recovery of nuclear material from lean sources. The scale-up of the mixer settler is usually based on fundamental hydrodynamic studies. Artificial Neural Network model and CFD model of head and power characteristics of pump-mixer have been developed and validated. RTD modeling of mixer settler and hydrodynamic modeling of settling phenomenon is in progress. A pilot scale plant is being installed at Chemical Engineering Division for scaleup studies and operational experience with D2EHPA - organic acid system



Bench Scale Pump-mix Mixer-settler Test Set up

S.K. Ghosh <**ghoshsk@barc.gov.in**> H.Rao <**hrao@barc.gov.in**>

#### Design of KESTRA mixer - settler

Rare Earth Development Section has designed, tested and installed a cylindrical pump mix Mixer-Settler which can process a total flow of 60 m<sup>3</sup> /hr. It is made of a special acid resistant material of construction KESTRA. It is made from special synthetic resins having excellent chemical and physical properties and chemically inert fillers such as graphite, asbestos etc. Mixer-Settler consists of a Mixer, a settler and a pump-mix impeller.

Special kind of pump mix impeller provides higher degree of dispersion and better inter-stage pumping. It operates up to 450 R.P.M.

Mixer		Settler	
Shape	Cylindrical	Shape	Cylindrical
Diameter (ID)	1310 mm	Diameter (ID)	2310 mm
Feed outlet height	1390 mm	Feed inlet height	1390 mm
Mixer height	1690 mm	Launder height	1200 mm
Total height with dish cover	2130 mm	Settler height	1700 mm
Pump well	590 mm	Total height with dish cove	er 2240 mm
Mixed Phase Outlet Dia.	250 mm	Feed well ID/Height 540	V 1250 mm
		Mixed Phase Outlet Dia.	250 mm

#### Parameters of Kestra Mixer-Settler

H. Singh <hsingh@barc.gov.in>



## 3. MAN MADE ISOTOPES

#### INTRODUCTION

Accelerators and nuclear reactors have vested man with the power of producing new isotopes, the nuclear reactors can produce them in large quantities. The radioisotopes have numerous applications in medical, environmental, industrial sectors and some of them are useful to the nuclear fuel cycle. The U-232 was produced in pure from in DHRUVA reactor by neutron transmutation of rare Pa-231, while Pu-236 was produced by proton irradiation of Np-237, both for research investigation. I-125 production by irradiation of Xenon gas for the first time in India and its use as prosta-seeds and other medical applications is a comprehensive accomplishment. BARC continues to keep its commitment to supply radioisotopes for reference sources, nuclear medicine, besides radiopharmaceutical research for site-specific diagnosis agents, new molecules for targeted therapy and therapeutic applications. The use of radiotracers in chemical industries and water resources management has been facilitated by development and deployment of sealed sources, tomographic techniques, instruments and interpretation of data for the users. This section gives a glimpse of the wide range of problems solved and R&D carried out to address them.

#### 3.1 PRODUCTION OF NEW ISOTOPES IN DHRUVA

## Production of Uranium-232 from Protactinium-231

U-232 isotope is produced in the Thorium fuel cycle along with U-233, generally in the concentration levels of a few hundred parts of U-232 per million (ppm) of U-233. U-232 is a short-lived isotope (half life  $\sim$  72 years) with hard - emitting daughter products. Study of U-232 is of interest to the U-233 fuel development.

Pure U-232 is produced by the nuclear reaction  $^{231}$ Pa (n,  $\gamma$ )  $^{232}$ Pa  $^{232}$ U.  $^{231}$ Pa was obtained as a 10 ppm concentrate in 2002 from

1g of oxides of zirconium and silica) was loaded in the Dhruva reactor for irradiation. Based on the earlier trial irradiation results, the total fluence planned for this irradiation was kept around 0.25 x 10<sup>14</sup> n/cm<sup>2</sup>. After conversion of around 5% <sup>231</sup>Pa to <sup>232</sup>U, the post irradiation chemical separation was carried out by dissolution and solvent extraction. The figure shows the  $\alpha$ -spectrometry of the separated U-232.

L. M. Gantayet <headlptd@barc.gov.in> Head, ACD <headacd@barc.gov.in>



Alpha spectrum of U-232 sample

the insoluble muck (containing 2 to 3 parts per billion Pa - 231) of the monazite processing plant.

Concentration of Protactinium-231 from 10 to 1000 ppm was carried out in the laboratory by successive elution ion chromatography in oxalic acid medium, hydrofluoric acid and hydrochloric acid media to remove the undesirable impurities. The batches were prepared for irradiation and production of U-232. The first batch of <sup>231</sup>Pa, (~7mg <sup>231</sup>Pa on a carrier of around

activity. Electrodeposited Neptunium targets (2.0 mg/cm<sup>2</sup>) were irradiated with proton beam (Ep = 23.5 MeV) at BARC-TIFR Pelletron Facility, Mumbai. After the irradiation, the stack was cooled for 15 days for allowing the complete decay of <sup>236m</sup>Np (T1/2 = 22.5 h) to <sup>236</sup>Pu. A method based on solvent extraction was standardised for effective removal of <sup>237</sup>Np. The activities of <sup>238,239,240</sup>Pu as well as <sup>237</sup>Np were below the detection limits (< 0.1 mBq). About 200 mBq of tracer grade 236Pu activity in 8M HNO<sub>3</sub> was prepared. A typical alpha spectrum of <sup>236</sup>Pu source is given .

## Synthesis of Isotopically Pure <sup>236</sup>Pu Tracer

 $^{236}$ Pu is an ideal tracer required for the assay of plutonium in biological and in environmental laboratories of nuclear installations. The p +  $^{237}$ Np reaction was used for the synthesis of trace levels of isotopically pure  $^{236}$ Pu by the recoil catcher technique. The surface decontamination of the catcher foils followed by radiochemical separation of plutonium yielded about 200 mBq of tracer grade  $^{236}$ Pu



B. S. Tomar<bstomar@barc.gov.in>

## Preparation of radioisotope endofullerenes

The discovery of fullerenes in 1985 has triggered a worldwide interest in its possible applications in various branches of science and technology and also in medical science. One of the most interesting developments in this context is the encapsulation of atoms in the fullerene cage forming endofullerenes. It may not be possible to produce endofullerenes by conventional chemical reactions.

One possibility is to put energetic atoms through the fullerene molecules. We have produced the several radioisotope endofullerenes by implanting energetic recoils obtained from heavy ion induced nuclear reactions. The high energy (80 - 140 MeV) heavy ion beams of <sup>16</sup>O, <sup>15</sup>N and <sup>20</sup>Ne from VEC machine were used to produce various recoiled isotopes from targets like Cu, As, Tb. The process involved implantation of recoils in fullerene by irradiation and then chemical extraction of endofullerenes in organic solvent by highly acidic aqueous medium. The following radioisotope endofullerenes were produced :

 $\label{eq:asymptotic} \begin{array}{ll} {}^{24}\text{Na@C}_{60}, {}^{34m}\text{Cl@C}_{60}, {}^{69}\text{Ge@C}_{60}, {}^{71}\text{As@C}_{60}, {}^{72}\text{Se@C}_{60}, {}^{75}\text{Se@C}_{60}, \\ {}^{77}\text{Br@C}_{60}, {}^{81}\text{Rb@C}_{60}, {}^{83}\text{Sr@C}_{60}, {}^{86}\text{Zr@C}_{60}. \\ \end{array}$  The yields of endofullerenes obtained was in range of

10 - 20 % for electropositive metal (<sup>24</sup>Na@C<sub>60</sub> : 15.1, <sup>81</sup>Rb@C<sub>60</sub> : 13.0, <sup>83</sup>Sr@C<sub>60</sub> : 15.0, <sup>86</sup>Zr@C60 : 20.5) and 70 - 90 % (<sup>34m</sup>Cl@C<sub>60</sub> : 71.5, <sup>69</sup>Ge@C<sub>60</sub> : 72.9, <sup>71</sup>As@C<sub>60</sub> : 73.8, <sup>72</sup>Se@C<sub>60</sub> : 82.5, <sup>75</sup>Se@C<sub>60</sub> : 76.3, <sup>77</sup>Br@C<sub>60</sub> : 79.3) for others. The yields of endofullerenes were independent of the energy of recoiled nuclides (1 - 10 MeV).

## Standardization of Dry-distillation Technique for the Recovery of Radioiodine from Irradiated Tellurium Matrix

In view of important therapeutic and diagnostic applications of different isotopes of radioiodine such as <sup>(131, 120, 123, 124)</sup>I, an attempt has been made to optimize the dry thermodistillation technique for the recovery of radioiodine in carrier-free form from irradiated tellurium matrix.

Most of the biomedically important radioiodine isotopes are produced by accelerator irradiation except <sup>131</sup>I which is produced by thermal neutron irradiation in a nuclear reactor. For standardization work, <sup>131</sup>I radioisotope, produced by thermal neutron irradiation of natural TeO<sub>2</sub> (70-90 mg) in DHRUVA reactor at BARC, Mumbai, was used. The initial experimental work on the isolation of <sup>131</sup>I from irradiated Te-matrix by thermodistillation technique produced satisfactory results. Different long-lived radioisotopes of Te (i.e., <sup>121</sup>Te, <sup>123</sup>Te and <sup>129</sup>Te), produced by (n, $\gamma$ ) nuclear reactions, were used to monitor the level of co-distilled Te in the separated <sup>131</sup>I distillate by gamma-spectrometry. The inactive Te content in different <sup>131</sup>I-distillates was found to be in the range of 1.1-4.0 ppm by radiometric analysis.

Further work is in progress to optimize different parameters in order to obtain higher yield of radioiodine with reproducible values as well as recovery of the target material.

Head, ACD <headacd@barc.gov.in>

#### 3.2 I-125 STORY

## Production of <sup>125</sup>I by neutron irradiation of Xe gas

<sup>125</sup>I is a radionuclide widely employed in the preparation of a host of radio labeled molecules used for a variety of applications in radiopharmaceuticals research and procedures. <sup>125</sup>I is widely employed in radioimmunoassay (RIA) procedures for estimating nanomolar concentrations of biomolecules such as hormones, drugs etc. in complex biological matrix.

The production of <sup>125</sup>I from natural Xe gas of the isotopic composition <sup>124</sup>Xe(0.09), <sup>126</sup>Xe(0.09), <sup>128</sup>Xe(1.92), <sup>129</sup>Xe(26.44), <sup>130</sup>Xe(4.08), <sup>131</sup>Xe(21.18), <sup>132</sup>Xe(26.89), <sup>134</sup>Xe(10.44), <sup>126</sup>Xe(8.87) is outlined schematically.

#### $^{124}$ Xe(n, $\gamma$ ) $^{125}$ Xe-(EC)-T<sub>1/2</sub>=17h $\rightarrow$ $^{125}$ I ( $\sigma$ =110b)

Parallel processes operating are <sup>124</sup>Xe undergoing double-neutron capture and electron capture to produce <sup>126</sup>I. It is also produced from <sup>125</sup>I (n,  $\gamma$ ). Since for double-neutron capture the activity produced is square of the neutron flux, <sup>126</sup>I contribution is expected to be higher for high-flux irradiation.

A carefully standardized procedure involves one-week irradiation of <sup>124</sup>Xe gas (4g at 10 atm) in a 70 ml sealed capsule. In order to minimize the extent of <sup>126</sup>I (not suitable for radioimmunoassay procedures) formation, short time irradiation at medium flux using large volumes of Xe gas is desirable. The production of <sup>125</sup>I indigenously was commenced in 2003 by neutron irradiation of natural xenon gas in a special set-up of the Dhruva reactor. The sealed capsule shown below is introduced in the tray rod for irradiation. The specific activity achievable is 15-16 mCi/µg (450-600 MBq/ $\mu$ g). Eight batches have been processed and ~130 GBq of radioactivity could be produced with the required radiochemical purity and radioactive concentration, suitable for various applications. The production of this radioisotope could greatly reduce the foreign exchange burden. The indigenous <sup>125</sup>I could be used in the radiopharmaceutical research, fabrication of <sup>125</sup>I-bachytherapy sources and in other developmental activities.



## Iodine - 125 for the management of eye and prostrate cancer

## (1) Development of "BARC <sup>125</sup>I Ocu-Prosta Seeds"

The technology for the preparation of indigenous <sup>125</sup>I-Brachytherapy sources was developed for their application in the management of eye and prostate cancers. The <sup>125</sup>I -sources were fabricated and encapsulated in titanium capsules by laser welding indigenously. Stringent quality assurance procedure was carried out in the tiny "BARC <sup>125</sup>I Ocu-Prosta Seeds" of dimension 0.8mm (OD) 4.75 mm (I), each containing ~ 93 MBq of <sup>125</sup>I.



BARC <sup>125</sup>I Ocu-Prosta Seeds were supplied to Sankara Nethralaya, Chennai for the treatment of ocular cancers The first clinical trial was carried out on 11<sup>th</sup> September-2003 and being first of its kind, the eye brachytherapy facility was dedicated to nation by Honorable President of India in a function held at Chennai on 10th October-2003 In the first phase of clinical trial five patients have been treated, including a patient hailing from Bangladesh. These sources also have the potential in prostate brachytherapy towards which the plans are being initiated to collaborate with cancer hospitals.



Position of 1251 capsule in eye



Patient Implanted with <sup>125</sup>I Plaque

## 2) Development of <sup>125</sup>I sources of higher activity for lexicoscope

 $^{125}$ I-lexiscope/ bone densitometry sources of overall dimension of ~ 3 mm (OD) 10 mm (I) find an extensive application in the diagnosis of osteoporosis and in the imaging of hidden objects at security check points. Various metallic cores have been developed for the fabrication of point sources containing ~18.5 GBq of <sup>125</sup>I.

#### (3) <sup>125</sup>I-labelled biomolecules for targeting tumour

Plumbagin (5-hydroxy-2-methyl-1,4-naphthaquinone) a naturally occurring quinone, a class of compounds documented to exhibit anticancerous propery has been labeled with <sup>125</sup>I with the aim of preparing a tumour-targeting agent. In vitro cell viability studies showed that compared to plumbagin, the radioiodinated agent exhibited higher cytotoxicity thereby warranting further evaluation.

Porphyrins, known to have for tumour affinity, were another group of molecules, chosen for radiolabeling with <sup>125</sup>I. Water soluble porphyrin derivatives with ideal chelating substituents in the periphery or the N4 donor array in the core were synthesized and labeled with <sup>125</sup>I and its bioevaluation carried out in tumour -bearing animal models.

Meera Venkatesh <**meerav@barc.gov.in**> Sharmila Banerjee <**sharmila@barc.gov.in**>

#### 3.3 APPLICATIONS OF OTHER MAN MADE ISOTOPES

## Fabrication of <sup>137</sup>Cs Sources for Brachytherapy and Industrial Applications

The growing safety concerns associated with radiotherapy has made the need for process modifications in the fabrication of tiny <sup>137</sup>Cs-brachytherapy sources [1.5 mm (OD) 5 mm (I)] a process known as "Permanent Mould Casting" a pertinent field of investigation. The process modifications in the vitrification of high amounts (~166. 5 GBq) of <sup>137</sup>Cs were carried out by removing the stable <sup>137</sup>Ba from aged <sup>137</sup>Cs solution. A novel precipitation method for the separation of stable <sup>137</sup>Ba was developed and improvements in the general texture of glass were noticed with increased specific activity. A method of providing thin coating of silver and melamine on the bare source core was also developed to reduce the leachability of radioactive sources. The rigorous quality control in accordance with the Atomic Energy Regulatory Board stipulated safety norms revealed that the sources produced by revised production protocol are safe with respect to their leachabiliy and uniformity.

The supply of <sup>137</sup>Cs brachytherapy sources has resumed from January-2004 and about six hundred <sup>137</sup>Cs brachytherapy sources each having  $\sim 1.56$  MBq of <sup>137</sup>Cs, were fabricated at the Radio Pharmaceutical Division and made available to Board of Radiation and Isotope Technology (BRIT) for their encapsulation and supply to various oncology centers. Similar vitrified <sup>137</sup>Cs sources of varying strengths of upto  $\sim 11$ GBq of <sup>137</sup>Cs were prepared for their use in industrial gauging and radiography. About twenty five sources in the form of [1.5 mm (OD) 5mm(I)] are supplied per annum to BRIT for encapsulation and supply to cater to the needs of various industrial users.

## Supply of Low-level Radiation Sources for use as Reference Sources

Every year about one thousand consignments of laboratory reference sources of different types such as those emitting beta, gamma or X-rays of various isotopes such as <sup>204</sup>Tl, <sup>137</sup>Cs, <sup>55</sup>Fe, etc., are prepared and supplied to the users in the industrial and research and development sectors in both research centres and academic institutions. Custom made electrodeposited sources of <sup>55</sup>Fe, <sup>63</sup>Ni, <sup>57</sup>Co, and <sup>147</sup>Pm were also supplied to customers as import substitutions. Some of the important ones are tabulated.

Source Type	Use	Users
Laboratory Reference Sources: (beta, gamma, conversion, X-ray & low energy gamma, positron sources of <sup>204</sup> TI, <sup>137</sup> Cs, <sup>60</sup> Co, <sup>55</sup> Fe, <sup>63</sup> Ni, <sup>147</sup> Pm Evaporated & adhesive sealed sources supplied on standard plastic holders up to ~1 MBq each)	Inst.Calibration Teaching-cum-Demo. (Educational purpose) R & D	Electronic Industries Universities & colleges, R & D units As import substitutions
Custom made Special sources: a) <sup>109</sup> Cd electrodeposited X-ray sources – 6 Nos.of ~185kBq (~5µCi) each on Silver Substrate. b) <sup>63</sup> Ni Electrodeposited beta sources i) On copper strip substrate – 40 Nos.of ~3 MBq each coated on ~10	For the calibration in Solar X-Ray spectrometer (SOXS) Thermo luminescence Dosimeter check light Sources.	Physical ResearchLaboratories, Ahmedabad- sourceloaded in theirPaγload of GSAT-2 Indian mission in 2002. Electronic industries, BARC and other DAE Units.
inmφ ii) On copper annular ring special holders supplied by users.10 Nos. of ~370 MBq (~10 mCi) each, activity coated precisely on inner curved area	lonization experiments.	Defence Research & Development Organisation, Gwalior.
c) <sup>60</sup> Co polymer film gamma point sources - prepared by using Indi- genously developed "Radioactive film Source preparation technique" - ~500 Nos. of ~37kBq (~1μCi) annually	Use in oil-well logging Operations of Industrial Applications.	Schlumberger Asia (P) Ltd. Mumbai (a French-American firm)
<b>d)</b> Special Radiochemical dispensing upto ~3.7MBq (~100 μCi) each-like <sup>64</sup> Mn, <sup>90</sup> Sr- <sup>90</sup> Y, <sup>22</sup> Na, etc.,	For calibration, tracer Studies and R & D expts.	Educational Institutions, R&D Firms
. Developmental work: Leach test (~100 μCi) on Cu was carried out an with the AERB specifications	on the electro-deposite nd these sources gave s	d <sup>63</sup> Ni sources of ~3.7 MBq satisfactory results to comply

Supply of Low-Level Radiation Sources for use as Reference Sources

## Radiochemicals - Production and Processing

The major thrust of the programme include irradiation planning, the development of radiochemical processes for isotopes, regular production, chemical processing, in house quality control and supply of radiosotopes for various applications. A wide spectrum of reactor produced radioisotopes are prepared as primary radiochemicals for applications in Nuclear Medicine (Hospitals), process monitoring and trouble-shooting (Industries) and Research and Development (Research Institutes and Universities). In the above capacity, the sectional staff process about 100-150 TBq of various isotopes in wet form, annually.

Irradiation co-ordination is also carried out for the preparation of about 1110 TBq of <sup>192</sup>Ir for radiography applications and about 740 GBq of <sup>192</sup>Ir prepared by irradiating Ir-Pt alloy for the preparation of brachytherapy sources.

Regular and uninterrupted supply of host of 70 different radiochemicals like <sup>99</sup>Mo, <sup>131</sup>I, <sup>153</sup>Sm, <sup>32</sup>P, <sup>51</sup>Cr, <sup>35</sup>S, <sup>203</sup>Hg, <sup>82</sup>Br, <sup>198</sup>Au, <sup>140</sup>La, <sup>46</sup>Sc, <sup>65</sup>Zn, <sup>133</sup>Ba, <sup>85+89</sup>Sr, <sup>141</sup>Ce etc. in the levels of TBq and in large number of consignments to various Indian and foreign customers constitute one of the major mandates of this section.

Research and Development efforts are directed towards the preparation of new radiochemicals for novel applications viz. production of high specific activity (37GBq/mL) <sup>131</sup>I from neutron irradiated TeO<sub>2</sub>, and production of new therapeutic radionuclides for application in nuclear medicine procedures.

<sup>166</sup>Ho and <sup>186/188</sup>Re were also produced for research in the preparation of radiopharmaceuticals. <sup>166</sup>Ho was also used for preparation of <sup>166</sup>Ho-hydroxyapatite, for radiation synoviorthesis and supplied to users in the country. <sup>186/188</sup>Re: The past 3 years have witnessed the production of 214 TBq radioactivity from different radionuclides in 490 batches and the supply of about 184 TBq activity in 6000 consignments. <sup>186/188</sup>Re in the form of NaReO<sub>4</sub><sup>-</sup> has been supplied to hospitals for carrying out liquid-filled balloon angioplasty in the treatment of recurrent restenosis related to coronary artery diseases.

Meera Venkatesh.<meerav@barc.gov.in> Sharmila Banerjee<sharmila@barc.gov.in>

#### 3.4 RADIOPHARMACEUTICALS RESEARCH

At the Radiopharmaceutical Division, research is focused towards development of new radiopharmaceuticals. The existing facilities which have been augmented in the past few years include most significantly an access to a host of reactor produced isotopes with varying radiochemical properties to meet the requirement of a wide range of radiopharmaceutical formulations. This facility along with a multidisciplinary support extended with respect to a synthetic organic chemistry group, expertise in radiochemical processing of the isotopes in the required chemical form and subsequent radiolabeling, a well-equipped animal house for in vivo biological evaluation, cell maintenance laboratory for in vitro evaluation and coordination with a number of clinical collaborators are paving the way of envisioning high quality research.

#### Diagnostic Radiopharmaceuticals

Molecular imaging at cellular level being currently the key word in the field of research in diagnostic radiopharmaceuticals, the major thrust in working towards the development of new agents for diagnosis with <sup>99m</sup>Tc has been shifted from conventional radiolabeling procedures to the development of new methods of radiolabeling yielding high specific activity, high stability and site-specific radiopharmaceuticals. In this respect, <sup>99m</sup>Tc tricarbonyl chemical approach is one of the recent advances in <sup>99m</sup>Tc radiopharmaceutical chemistry in which <sup>99m</sup>Tc tricarbonyl metal core is used for radiolabeling biologically active compounds. The synthesis of <sup>99m</sup>Tc[(OH<sub>3</sub>)<sub>2</sub>(CO)<sub>3</sub>]<sup>+</sup> (Tc-tricarbonyl)





(CO) - substitution stable

#### (H<sub>2</sub>O) - substitution labile

precursor has been reported earlier. A convenient procedure for in-house preparation of the radiolabeled Tc-carbonyl precursor has been standardized in the laboratory.

A number of tridentate ligands which can form tricarbonyl complexes with favourable pharmacokinetics have been identified and used for functionalization of biomolecules. Among the agents which have been labeled with the <sup>99m</sup>Tc-tricarbonyl synthon are iminodiacetate derivatives of 5-hydroxytryptamine (serotonin receptor ligand) and that of an alkaloid viz. colchicine (a tumour specific ligand). In this respect, <sup>99m</sup>Tc-TBI (tertiary butyl isonitrile) prepared through the carbonyl synthon has shown superior properties as compared to the two myocardial imaging agents which are currently available. This product has the potential to be developed as a new myocardial imaging agent.

Radiolabeling of ligands and target specific biomolecules (RGD peptide, annexin), particularly tumours using the other novel precursors viz. <sup>99m</sup>Tc-HYNIC and <sup>99m</sup>Tc-nitrido core are also initiated. Suitable ligands serving as optimum complexing agents with the <sup>99m</sup>Tc-nitrido core that have been identified are xanthates

and dithiocarbamates. In this direction, metronidazole xanthate has been prepared as a hypoxia marker. The <sup>99m</sup>Tc-nitrido complexes of tertiarybutyldithiocarbamate and methoxyisobutyldithiocarbamate exhibit considerable promise towards use as myocardial as well as brain agents. Another series of ether containing dithiocarbamates of amines such as ethoxypropyl-, methoxyethyl-, N-methyl-N-ethoxypropyl-, Nmethyl-methoxyethyl amines have been synthesized and labeled with the nitrido precursor in an attempt to prepare brain agents with optimum characteristics.



#### Therapeutic Radiopharmaceuticals

Radionuclide therapy (RNT) employing unsealed radiotherapeutic agents is fast emerging as an important modality in nuclear medicine. In order to develop effective radiopharmaceuticals for therapy, it is essential to carefully consider the choices of appropriate radionuclides as well as the carrier moiety with suitable pharmacokinetic properties that could result in good invivo localization. A variety of radionuclides including commonly used ones such as <sup>186/188</sup>Re, <sup>153</sup>Sm, <sup>90</sup>Y as well as a few less explored radioisotopes such as <sup>166</sup>Ho, <sup>177</sup>Lu, <sup>175</sup>Yb have been utilized in the above mentioned applications. The present thrust is on the development of potential therapeutic agents for a variety of situations.

#### Agents for bone pain palliation

Development of suitable pain palliating agents for cancer patients suffering from pain due to skeletal metastasis from primary carcinomas is one of the areas where considerable efforts have been given in the recent past. Keeping in mind the very high affinity of phosphonic acid ligands for bone, a variety of cyclic and acyclic polyamino phosphonic acid ligands have been synthesized. These ligands were radiolabeled with a wide variety of therapeutic radionuclides such as <sup>186</sup>Re, <sup>153</sup>Sm, <sup>177</sup>Lu, <sup>175</sup>Yb. Owing to their relatively longer half life <sup>177</sup>Lu and <sup>175</sup>Yb have logistic advantage. A comparison among all the agents studied showed that <sup>186</sup>Re labeled-1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid (CTMP), <sup>177</sup>Lu labeled-1,4,7,10tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTMP) and <sup>153</sup>Sm labeled DOTMP are most promising which can be further taken up for clinical trials. A comparative study with existing bone-pain palliatives reveal that these agents possess even greater potential towards use as radiopharmaceuticals.

#### Agents for radiation synoviorthesis

Radiation synoviorthesis is a proven modality in Europe for the treatment of joint inflammatory disorders such as rheumatoid arthritis, haemophilia etc. The availability of a wide range of emitting radionuclides and the feasibility of incorporating radionuclides into biodegradable particles and colloids, have aided in development of products such as <sup>166</sup>Ho-, <sup>188</sup>Re-, <sup>90</sup>Y-, <sup>142/</sup> <sup>143</sup>Pm- and <sup>153</sup>Sm-labeled Hydroxy apatite (HA) particles, 90Y-ferric hydroxide macroaggregate, <sup>90</sup>Y-phosphate for this purpose. Among these, <sup>166</sup>Ho-HA and <sup>153</sup>Sm-HA have been taken to human clinical evaluation after obtaining encouraging results in animal models. So far, more than 250 rheumatoid arthritis affected joints have been treated and the response has been very promising.

#### Agents for targeted radiotherapy

Radiolabeled molecules for targeted therapy of cancerous lesions is another major area of interest. A number of suitable bifunctional chelating agents (BFCA) capable of coordinating with different radionuclides have been developed for tagging radioisotopes with biomolecules such as peptides, steroids and antibodies. Lanreotide, a somatostatin analog peptide was coupled with 1,4,7,10-tetraazacyclododecane 1,4,7,10-tetraacetic acid (DOTA) and the coupled product was subsequently radiolabeled with <sup>90</sup>Y and <sup>177</sup>Lu. Tyrosine-3-octreotate (TATE) conjugated with DOTA is yet another somatostatin analogue which has been labeled with <sup>177</sup>Lu to target somatostatin receptors overexpressed on tumours of neuroendocrine origin. Recently, the feasibility of developing receptor-specific agents with therapeutic potentials is being studied. A modified estradiol derivative (6 -aminoestradiol) had been successfully coupled with p-NCS-benzyl-DOTA and subsequently radiolabeled with <sup>177</sup>Lu. In similar lines,

testosterone a steroidal molecule has been conjugated with a BFCA for radiolabeling with <sup>177</sup>Lu with the aim of obtaining an androgen receptor-targeting agent.

#### Agents for hypoxic tumours

Several tumour-specific radiolabeled agents have been designed and synthesized to target both for diagnosis and for therapy of tumour hypoxia which is prevalent in many large tumours. Towards this, nitroimidazoles viz. metronidazole and sanazole as molecules which have affinity for hypoxic tissues were conjugated with DOTA or suitably functionalized DOTA for complexation with <sup>177</sup>Lu and these compounds exhibited favourable characteristics.

#### Agents for treatment of superficial cancers

To avoid the inconveniences faced with the gamma sources used in teletherapy, particularly in case of superficial cancerous lesions, radioactive skin bandage patches incorporating high energy beta emitters were developed. Immobilized <sup>90</sup>Y labeled ferric hydroxymacroaggregates (FHMA), <sup>188</sup>Re-tin-colloid and <sup>32</sup>P-chromic phosphate have been prepared and tested for mould brachytherapy. Fractionated dose treatment using such patches has resulted in nearly complete regression of fibrosarcoma and melanoma tumours in animal models. Efforts to develop it further for human clinical applications are underway.



Bioevaluation of <sup>90</sup>Y-Ferric Hydroxide Macroaggregates skin-patch in Swiss mice bearing fibrosarcoma

Meera Venkatesh <meerav@barc.gov.in> Sharmila Banerjee <sharmila@barc.gov.in>

## Radioisotope guided surgical gamma probe

Radioisotope Guided (RIG) surgical gamma probe is a gamma detecting device developed to assist the surgeon in sentinel lymph node dissection, to locate radioactive sentinel lymph node intra-operatively in patients having breast cancer in its early stage. It finds application not only in sentinel node biopsy but also in radio-guided occult lesion localization and radio-guided surgery.

This  $\gamma$ -probe was clinically evaluated for its performance at the Rajiv Gandhi Cancer Institute and Research Centre, New Delhi and found useful in accurately locating the radioactive sentinel node during biopsy.



Surgical Gamma Probe unit

#### 3.5 ISOTOPES FOR INDUSTRIES

## Radiotracer Investigations

Radioisotopes as sealed sources and as tracers were used for a number of investigations for troubleshooting, process optimizations and design modifications in different industries. These include leakage and blockage location in underground pipelines, measurement of various process parameters and investigation of fluid flow behaviour in industrial process systems including residence time distribution study in a fluidized catalytic cracking unit (FCCU) at M/s Engineers India Ltd. (EIL), Gurgaon, leak location in heat exchangers for M/s Indian Oil corporation, Panipat Refinery and M/s Oil and Natural Gas corporation for effective management of oil fields. A few radiotracer investigations were carried out at Kandla Port, Gujarat and Hoogly Estuary, Kolkata Port Trust etc for examining suitability of dumping sites for spoil generated during maintenance dredging operation at the respective approach channels. About 100 Ci



and %0 Ci of Tritium(Tritiated water) were injected into two oil well i.e. WI-2-2Z and WI-3-2Z respectively in North Mumbai High Oil Fields of M/s ONGCL.

Kadiotracer Investigations	Problem/ Objective	Tracer Used for tracing of	Kesults) Findings	Benefits) Remarks
2. Mixing Time Measurements				
Jet mixer at UICT, Mumbai	Mixing time measurements and validation of CFD simulations	Br-82	Mixing times measured and CFD models validated	Helped in designing industrial scale mixers.
3. Leak Detection				
High pressure heat exchangers at M/s India Oil Corporation, Panipat Refinery, Panipat (Investigation carried out twice)	Product contaminated due to leakage in the heat exchangers	Br-82	Leaking heat exchanger identified	The down time was reduced by about 6-7 days
Heat exchanger at M's Tamilnadu Petro- chemicals, Limited, Chennai	Pressure in the inlet bellow did not hold leading to suspicion of leakage	Br-82	No leakage found	Other causes of problem were looked into
In a 3.2 km long buried pipeline at M/s Gas Authority of India Ltd., Visakhara tnam	Pressure in the pipeline did not hold indicating leakage in the line	Br-82	Two leakage detected	Helped in repairing and putting the line back to operation
Chilled water line in BARC premises, Mumbai	Pressure in the pipeline did not hold indicating leakage in the line	Br-82	Leak detected	Leakysection was replaced and chilled water supplyrestored
4. Sediment Transport		C K	<b>D</b>	** * * *
Kolkat Fort Trust, Kolkata	Assessment of suitability of the proposed dumping site	Sc-46	found not suitable	Helped in selecting alternative site
Tata Electric Company, Mumbai harbour, Mumbai	Validation of numerical models	Sc-46 and Au-198	Model validated	Helped in understanding the dynamics of suspended and bed load in the harbour
Kandla Port Trust Kandla (Two studies)	Assessment of suitability of the proposed dumping site	Sc-46	Dumping site found suitable	Helped in optimizing dredgeing operations.
5. Tracer in Oil fields		1000		1000 C
Tracer injection in North Mumbai High Fields of M/s ONGCL, Mumbai	To establish interconnection between injection and oil production wells	Tritiated water (HTO)	Interconnection established	Helped in proper management of oil fields

#### Gamma Scanning

Gamma scanning is used as an indispensable non-destructive tool for solving online problems in industrial process columns. A number of investigations including for M/s Reliance Industries Ltd, Hazira, for a quench oil tower were carried out for trouble shooting and process optimisation.

#### Gamma scanner for inspection of process column

The development work for a fast-automated gamma scanning system for a specific in house requirement has been completed. The system comprises of a two-axis computer controlled mechanical scanning assembly, an in-house designed nucleonic data acquisition system and a customized integrated software for machine control, data acquisition and analysis. The system is designed for a maximum activity of 40 mCi of Ir-192 or 25 mCi of Cs-137 source. The system is being evaluated for its performance with various process-materials having different densities.

#### Automated column scanning system

Automated Gamma Scanning System has been designed to obtain on-line information in the industrial process columns as shown in the figure. This system contains a collimated source and a radiation detector for diagnosis of industrial process columns. It can be used as a temporary or permanent installation on any existing process column for which gamma scanning is to be performed. A radioactive source and the detector is suspended from top of the column using wire ropes of the automated




Real-Time Gamma Radiometry System for In-House Use (CTD Scanner)



Software Component for CTD Scanner

winch arrangement. Source and the detector move along the desired height of the column at the same elevation. The transmitted radiation from the source through the column at the detector is recorded at each desired location to see the internals of the column and thus to diagnose the possible damages/malfunction.

The system consists of a nuclear signal processing unit and a PLC based source-detector motion control unit. The system is

integrated with Lap-top PC to program and control the complete sequential-scanning in Auto and Manual modes for the required time of counting of the incoming detector pulses and to store, display and plot the counts obtained in specified counting period at specified locations.



#### Gamma ray tomography

# Industrial computed tomographic (ICT) imaging system

Research and development work has been carried out on X-ray based ICT systems for non-destructive testing (NDT) applications. In the earlier years, an experimental prototype tomography system using constant potential X-ray unit (160kV) and linear array detectors have been developed. Different computer codes for machine control, data acquisition, 2D and 3D image reconstruction and analysis have been developed. The specific area where extensive studies were carried out are: Studies of the suitability of low-energy Linear Detector Array (LDA) for tomographic imaging, manifestation of artefacts in CT images due to positionally-invariant abnormal pixel behaviour and studies on the effect of varying kV and mA on reconstructed attenuation values in tomographic imaging. A dedicated facility for 420 kV X-ray based digital radiography and tomography experiments for industrial imaging applications is being set-up at HIRUP, BARC.



Experimental 160kV X-Ray ICT System



Experimental 420kV X-Ray ICT System (Insight HPMS)

# Industrial tomographic imaging with non-uniform data collection regime

In the regime of non-uniform data collection modes, a different class of reconstruction algorithm is employed and the associated complexities relating to specific hardware requires a coordinated approach. A complete set of reconstruction codes based on iterative methods has been developed. These codes have been validated with simulated data.







A PC based prototype 10-channel nucleonic data acquisition system has been designed and developed for data acquisition purpose in Process CT. It can also be used in Tracer Technology Application, Gamma Scanning etc. It consists of a PCI based PC add-on card and GUI software developed to acquire, plot and store the data in real time. The software is developed under windows environment using Visual Basic. The system has been successfully lab tested using a NaI(TI) detector and a standard source of Cs-137.



Prototype 10 Channel Nucleonic Data Acquisition System Software Interface

#### Radiometry

# Radiometry and radiography testing of central shield structure

Isotope Applications Division carries out Radiometry and Radiography Testing for various shield structures and transport casks. M/s. Larsen & Toubro Ltd, Powai, has fabricated Central Shield structure, consisting of lead, steel and concrete for Reactor Projects Group, BARC. The shielding integrity test of the structure having varying thickness and configuration, was carried out using Cobalt - 60 sources.



#### Radiometry testing of antimony pin cask

Radiometry testing of Shielding Cask was carried out. The cask has a capacity to hold 16 antimony pins and weighs about 5 ton. Each antimony pin has a maximum activity of 1,500 curies for Sb-124 and 8,000 curies for <sup>122</sup>Sb. Radiography camera Amertest 676 with 138 Ci, Co-60 source was used for this work.

#### Radiometry testing of shielding flask for NPCIL

The design capacity of each of the shielding flasks of NPCIL is for 300 kCi of Co -60 source. The 711 mm diameter and 2830 mm long cask weighs approximately 12,500 Kg. The radiometry was carried out using Amertest 676.



Radiometry Testing Set-up for Central Shield Structure



Radiometry Testing of Shielding Flask

G.Singh <gsingh@barc.gov.in> S.V.Navada <svnavada@barc.gov.in> H.J.Pant <hjpant@barc.gov.in>

## 3.6 WATER RESOURCES MANAGEMENT WITH RADIOTRACERS

Radiotracers play a vital role in the management of water resources in India. They also help in identifying the leakages in large reserves.

## Investigation of the recharge zone of springs in the mountainous Himalayan region, Gaucher Area, Uttaranchal

In the mountainous region of Uttaranchal, springs are the only available source of water for domestic and agricultural use. Insufficient spring water due to low discharge causes a lot of hardship to the people in summer. At the request of Himalayan Environmental Studies and Conservation Organisation (HESCO), Uttaranchal, environmental isotope investigation was carried out, along with hydrogeology and hydrochemistry, to identify the recharge zone of the springs in the mountainous Himalayan region.

Stable isotope (<sup>2</sup>H & <sup>18</sup>O) data of springs collected from 3 different valleys indicated that the springs located in valley 1 and 2 could be getting recharge from the same area while the springs located in the valley 3 could be getting recharge from different area. Local precipitation is the main source of recharge. Hydro-chemical results indicated that the quality of spring waters is fresh and contain Mg-Ca-HCO3.



View of Gaucher Valley, Dehradun, Uttaranchal

The investigation for identification of the recharge zone of the drying springs in Gaucher Area, Uttaranchal has been completed. Based on these studies artificial recharge structures are being planned by HESCO.

## Evaluation of artificial recharge measures in augmentation of the coastal sedimentary aquifers of Tiruvadanai, Tamil Nadu

For sustainability of the coastal aquifers of Tiruvadanai in Ramanathapuram district of Tamil Nadu, in terms of both quality and quantity, Tamil Nadu Water Supply and Drainage Board (TWAD) has planned a number of artificial recharge methods for replenishing the groundwater resources of Tiruvadanai. At the request of TWAD authorities, environmental isotopes (<sup>2</sup>H, <sup>18</sup>O, <sup>3</sup>H & <sup>14</sup>C) investigation was carried out, in conjunction with hydrogeology and in-situ physico-chemical parameters, to evaluate the effectiveness of artificial recharge measures being adopted on a pilot scale by TWAD at the recharge area of aquifer.

From the investigation it was concluded that the modern recharge to the aquifer, through natural, incidental and artificial means, appears to be very low or slow and the suitable river for planning (large-scale) artificial recharge measures could be the one lying on the north-east boundary of the aquifer, namely the Manimutharu River, rather than the south-west bounded river (Sarugani).



C-14 sampling at one of the deep tubewell (>300 m)



type. The south-east located and west flowing perennial river, namely Kallada is not in hydraulic communication with the lake.



A Recharge Borewell in Sarugani River in the project area

## Environmental isotope studies on the largest freshwater lake in Kerala

Hydrological investigation on Sasthamkotta lake and it's catchment was carried out in collaboration with the Center for Water Resources Development and Management, Kozhikode using environmental isotopes (D, <sup>18</sup>O, <sup>3</sup>H, <sup>137</sup>Cs).

From the isotope study, it appears that the recent sedimentation rate in the lake ranges from ~0.18 to 1.81cm/year, with higher values very close to an existing earthen bund, constructed at southeast of the lake and the predicted future life of the lake is estimated to be about ~1400 years (assuming the lake's average depth as ~7 m). The  $\delta D$  - <sup>18</sup>O data and groundwater contours suggest that the lake-groundwater system is a flow through

Therefore, there is a need for effective management of the lakes environment for sustenance of some of dug wells located in the N and NE part of the lake.

Hydrodynamics of fresh water-saline water interface in coastal aquifers of southern parts of Chennai metropolitan area, Tamil Nadu: An isotope hydrological investigation was carried out in collaboration with Central Ground Water Board and Dr. M. S. Swaminathan Research Foundation, Chennai to assess the ground water quality, source of recharge, interconnection between aquifers in the multi-aquifer system and ground water salinity in Tiruvanmayur aquifer. From the investigation, it was



Sampling of water for isotope analysis

concluded that the precipitation is the main source of recharge to the aquifer and the water quality is mostly fresh, except at Mettukuppam, Nilangarai and Shilanagar.

Stable isotopes (D & <sup>18</sup>O) data indicated that the salinity and brackishness of ground water is not due to present day seawater intrusion but it is due to dissolution of evaporites of marine origin at Mettukuppam. The brackishness found in Nilangarai, Taramani, and Shilanagar deep zones could be due leaching of salts (non-marine) from formation as indicated by D, <sup>18</sup>O and <sup>14</sup>C data. [The saline and brackish groundwaters measured a <sup>14</sup>C age of ~7000 and ~11, 000 a B.P, respectively].

Also from the investigation, it was found that the aquifer system in the study area could be considered as two-aquifer system, viz., top sandy aquifer, and weathered, fractured aquifer (basement). The groundwater occurs under unconfined condition in top sandy aquifer and under semi-confined condition in the underlying basement. Interconnection has been ascertained at Mettukuppam, Ekkatur, Sholinganallur and Uthandi. The investigation would help the end user to effectively manage the groundwater resources in this coastal area.

## Investigation of source of salinity in coastal aquifers of Sirkhazhi area, Nagapattinam district, Tamil Nadu

To investigate source of groundwater salinity, dating of saline groundwater and possibility of seawater-fresh water interface in the coastal aquifer of Nagapattinam district, Tamil Nadu, an isotope hydrological investigation was initiated in March 2004. A number of water samples were collected from existing hand pumps and tube wells in and around the study area for the analysis of environmental isotopes (<sup>2</sup>H, <sup>18</sup>O, <sup>3</sup>H, <sup>14</sup>C & <sup>34</sup>S), hydrochemistry (major & minor ions) and in-situ physical parameters (pH, T, EC etc). The results of the <sup>14</sup>C analysis of post monsoon samples indicated that the saline ground waters are old waters (8000 - 10000 a B.P).

## Investigating environment and water resources in Tatapani Geothermal area, Surguja Chhattisgarh

This study is being carried out in collaboration with Geological Survey of India (GSI) (Central Region), Nagpur. 31 water samples

from various water bodies in and around the geothermal area have been collected for chemical and isotopic analyses. Chemical analysis of the water samples will be carried out at GSI, Nagpur. The <sup>18</sup>O analyses of the samples are completed. D analyses will be taken up shortly. <sup>3</sup>H values of the samples indicate that the hot thermal waters (~1 TU) are older compare to cold thermal waters of the area.

## Leakage Problem of Nagewadi Dam, Maharashtra

At the request of dam authorities, isotope hydrological investigation on leakage problem of the minor irrigation dam, Maharashtra was carried out using environmental isotopes (D & <sup>18</sup>O) and dye tracer (Rhodamine-WT) to know the source of tail channel leakage and identify entry levels for d/s face leakages. From the investigation, it was concluded that the source of tail channel leakage is from the reservoir and not from the local groundwater and the entry levels for d/s face leakages do not lie near the head regulator. Thus it was suggested to the dam authorities that the earlier planned remedial measures near the head regulator is not essential.



Upstream view of Nagewadi Minor Irrigation Dam, Sathara, Maharashtra

## Confirmation on the location of a hydraulic pi ezometer of Ranjit Sagar Dam Project in Punjab

Environmental isotopes (<sup>18</sup>O, D & <sup>3</sup>H) investigation was carried out to confirm the location of hydraulic piezometer (no. 13 indicated in the figure) embedded in the foundation gallery of the multi-purpose and inter-state project. It was concluded that the piezometer as per the design records is not located at the d/s of core of main dam instead it is wrongly placed at the u/s of core of main dam. This finding corroborated the dye tracer experiments carried out by the resident geologist of dam project. Thus it was suggested to the dam authorities that higher pore potential readings of the piezometer, which was a deep concern from safety point of the dam, might be either ignored or taken as the u/s pore potential readings.

G.Singh <gsingh@barc.gov.in> S.V.Navada <svnavada@barc.gov.in> H.J.Pant <hjpant@barc.gov.in>



Schematic layout of Ranjit Sagar Dam with interpreted geology (Comprising of alternate sandstone and clay stone bands)



## 4. ANALYTICAL CHEMISTRY

## INTRODUCTION

Analytical chemistry in BARC has been in the vanguard in developing various analytical methods, some of them for the first time, for quality control, diagnostic studies and in providing standards. The methods devised by the analytical chemist in BARC, have at times sown the seed for development of processes for preparatory and large-scale production. Post irradiation analysis of occluded gases provided feed back data to the fuel designer and the nuclear reactor operator. Thin layer activation by accelerator has added a new analysis tool. Besides extending the limits of the various sophisticated analytical instruments to analyze some difficult samples, the analytical group has contributed in developing new instruments and facilities. The reliability and the strength of the analytical laboratories in the Department of Atomic Energy have increased manifold through the Inter Laboratory Comparison exercises.

#### 4.1 ANALYTICAL METHODS IN FUEL FABRICATION

#### Total Gas Content in Pu Bearing Fuel Materials

During the fabrication of sintered fuel pellets, some permanent gases are occluded in the interstices.. These gases, under the operating conditions of the reactor, get released and affect the performance of the fuel and clad. The occluded gas content and its composition is determined by employing hot vacuum extraction technique followed by quadrupole mass spectrometric analysis. The pellet is heated to 1000 °C and 1650° C for mixed carbide (MC) and mixed oxide (MOX) respectively. These temperatures have been arrived at based on the central line temperature of the pellets during the operation of the reactor. It can be seen from the figures that within 20 and 10 min of heating all the gases were released from MC and MOX pellets. The main constituent of the gas is hydrogen (>90%). In MC pellets above 1000° C, the gas content goes on increasing exponentially and it was mainly carbon monoxide. It is a reaction product i.e.,  $[MO]_{MC}$  + 4 <  $MC_{1.5}$  > 5  $[MC]_{MO}$  + (CO) and not occluded gas.







The total gas content of MC pellets in the initial stages of fabrication was > 0.3 cc/g. A vacuum degassing step after sintering, was therefore suggested. Incorporation of this step reduced it to < 0.03 cc/g and < 0.08 cc/g respectively in high and low density pellets. In MOX fuel pellets, the gas content is > 0.5 cc/g. The clad in fast breeder reactors is stainless steel. It is known that hydrogen diffuses out of stainless steel at elevated temperatures. Hence, there may not be any detrimental effect on the fuel pin. Based on these observations, the specifications for total gas content was revised as the occluded gas content excluding hydrogen.

#### Hydrogen/Deuterium Determination

Zircaloy coolant channels of pressurized heavy water reactors (PHWRs), over a period of continuous usage in the reactors can become brittle due to the formation of hydride/deuteride thus severely limiting the life of these channels. Thus the ageing management of zircaloy channels needs to be addressed from the point of view of hydrogen / deuterium determination. An accurate method for hydrogen determination in zircaloy needed to be established. Two new techniques were developed and standardised at the Fuel Chemistry Division. Both made use of mass spectrometry.

In the first, a two-level exposure technique was developed to determine hydrogen in zircaloy employing spark source mass spectrometry (SSMS). Until this method was established, SSMS though a multi elemental analysis technique has been reported to be not amenable for hydrogen determination because of its "pre-dispersion" in the mass analyzer itself. For the first time, using the two-level exposure technique, it was demonstrated that even hydrogen could be determined employing SSMS also.

The second method developed is based on hot vacuum extractionquadrupole mass spectrometry (HVE-QMS). Necessary vacuum extraction system had been indigenously fabricated to suit the unique requirements of hydrogen determination.. As little as 10 mg of zircaloy sliver samples are adequate for determining both concentration and isotopic ratios of hydrogen. The schematic of HVE-QMS system is given below.



Schematic of HVE-QMS Set up for hydrogen/deuterium determination

V: All Metal Valve; Lv: Micro Leak Valve; Mc: Mcleod Gauge; Ig: Ionisaion Gauge; Dp: Mercury Diffusion Pump; Ep: Ejector Pump; Tmp: Turbomolecular Pump; Rp: Rotary Pump; F: Furnace; R: Quartz Reaction Tube;S: Sample; PC: Personal Computer; Qms: Quadrupole Mass Spectrometer

Hundreds of sliver samples received from different PHWRs in the country have been analyzed by this technique. Detailed investigations were carried out for optimizing the analysis conditions in such a way that at the monitoring pressures, formation of molecular ions such as  $H_3^+$  and  $D_3^+$  is negligible so that H / D values could be measured without resorting to any corrections. Figure shows typical intensity of  $D_3^+$  peak as a function of pressure. The isotopic data has been quite useful not



only in validating the theoretical computational codes but also in assessing the annual deuterium pick-up rate. This exercise has demonstrated the symbiosis between research and its immediate direct application.

#### Thermal Ionisation Mass spectrometry

#### Methods for isotopic analysis

Analytical methodologies were established for the determination of isotopic ratios of various elements across the periodic table starting from Li to Cm. Detailed theoretical computations were also carried out to elucidate the requirement of choice of the molecular ion ratios for error-free mass spectrometric measurements in the case of Li and B. It should also be mentioned that the mass spectrometric analysis of boron by monitoring  $Cs_2BO_2^+$  ion had been the first ever publication of this type in the literature.

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

#### 4.2 INTERLABORATORY COMPARISON EXERCISES

## Spectrochemical Analysis: DAE Inter Laboratory Comparison Experiment (ILCE) for trace metal assay of uranium

An Inter Laboratory Comparison Experiment (ILCE) for trace metal assay of uranium was planned and co-ordinated by Radiochemistry Division. In the first phase of ILCE, nine DAE laboratories which routinely analyse uranium samples participated. The aim of the experiment was to have a uniform methodology for U analysis throughout the DAE family to gain more confidence in providing the results and also to have DAE certified standard reference materials (CRMs). Two samples were prepared by adding 14 analyte elements at specified concentrations to high purity uranyl nitrate solution for the first sample and by dry grinding and mixing with high purity  $U_3O_8$  for the second sample. All labs were required to analyse the samples using a "Nodal" method wherein U was chemically separated from analytes using solvent extraction giving three contacts with TBP/CCl<sub>4</sub>/4MHNO<sub>3</sub> system followed by one contact with TOPO / CCl<sub>4</sub> / 4MHNO<sub>3</sub> system and analysing the raffinate by using ICP-AES. In addition

Element	CRM-1 (ppm)	CRM-2 (ppm)	CRM-3 (ppm)	CRM-4 (ppm)	CRM-5 (ppm)
Ag	1.1	2.2	0.05	0.56	<0.05
Al	28	53	1.1	56	210
В	1.0	1.6	0.22	1.1	0.77
Ca	63	96	4.7	100	510
Cđ	1.6	2.1	<0.05	0.1	0.06
Cr	28	66	0.17	32	5.6
Cu	26	51	0.1	9.2	0.94
Dy	1.1	2.0	<0.01	0.15	0.3
Eu	1.1	2.1	<0.01	0.31	0.06
Gd	1.2	2.1	<0.02	0.2	0.32
Mg	32	61	1.7	64	2400
Mn	31	56	0.13	15	16
Ni	25	58	0.11	17	7.3
Sm	1.3	2.3	<0.05	0.26	0.32

Concentration of different elements in CRMS

#### The participating laboratories:

- (i) Process Development Division, Mumbai (ii) Advances Fuel Fabrication Facility, Tarapur
- (iii) Atomic Minerals Division, Hyderabad
- (iv) Nuclear Fuel Complex, Hyderabad
- (v) Spectroscopy Division, Trombay
- (vi) Uranium Extraction Division, Trombay
- (vii) Rare Materials project, Mysore
- (viii) Analytical Chemistry Division, Trombay (ix) Radiochemistry Division, Trombay
- (ix) Radiochemistry Division, Trombay(x) Fuel Chemistry Division, Trombay
- (xi) National Centre for Compositional
- Characterisation of Materials, Hyderabad
- (xii) Materials Chemistry Division, BARC

to this, some participating labs also used other extractants such as cyanex-923, TEHP, KSM-17 etc., as well as other instrumental methods such as d.c. arc carrier distillation in AES, ICP-MS, AAS, etc.

The experimental data obtained from the participating laboratories was treated as a randomized block for statistical the normal solution techniques involve sample dissolution, the use treatment using the analysis of variance technique. The results showed very good agreement between the data obtained from various labs. The overall precision of determinations was better than 30% for both the samples.

The whole exercise resulted in the declaration of these two samples as certified reference materials. Following this, three more samples prepared in 10 kg lots were similarly analysed, resulting in three more CRMs, in the second phase of ILCE.The percentage RSD was better that 30% for all the 5 CRMs.

V. K. Manchanda <vkm@barc.gov.in>

B. S. Tomar <bstomar@barc.gov.in>

#### Biological Certified Reference Materials

Estimation of trace elements in leafy agricultural samples (Spinach leaf, Koigura leaf and stem) and variation of their concentration with respect to sample mesh size was carried out. Agricultural samples, namely, Palak leaves of 50, 75, 100 and 200 mesh size and koigura leaf and stem of 50 and 100 mesh size samples were analysed for 11 trace elements (As, Se, Te, Sb, Cu, Co, Cr, Ni, Mn, Pb, Mo). It was observed that the concentration of the elements increased with the mesh size for most of the elements. The concentration of As, Se, Te, Sb were < 0.5 mg/g. All samples solutions were prepared by microwave digestion technique.

## Neutron Activation Analysis for Biological Reference Materials

Characterisation of food materials is extremely important in view of the role of toxic and essential metal ions in them on human and animal metabolism and in connection with health and safety of people. The analysis of biological materials is prone to error due to the complex matrix, large number of constituents and large organic matter content that affect their direct analysis. The use of sample digestion procedures and separation techniques may result in loss of constituents or increased blank due to contamination from reagents and water. The use of certified reference materials helps in recognizing these effects and also validating the analytical methodology. However, in the absence of commercially available reference materials it is necessary to prepare or to characterize secondary reference materials. Since of non-destructive methods or techniques with freedom from blank are valuable. Nuclear analytical techniques are valuable in this task in view of their high sensitivity, specificity and relative freedom from blank, especially in the case of instrumental neutron activation analysis. In this connection, the division participated in the characterization of a candidate reference material of milk powder prepared by National Physical Laboratory, New Delhi jointly with Central Food Technology Research Institute, Mysore. Milk powder was analysed by INAA to identify and quantify various elements like Na, K, Ca, Rb, Zn and Br. The studies were extended to the food sample standards prepared by CFTRI, Mysore.

As part of this programme, the milk powder samples and a reference material of fish homogenate prepared by RRL, Trivandrum were also analysed by GFAAS and electrochemical techniques. The contribution from blank was sought to be minimized in these measurements by adopting microwave digestion procedure.

#### 4.3 NEW ANALYTICAL EFFORTS

Interference from matrix elements, low levels of analytes present (in the case high purity metals), complexity and lack of information on the nature of matrix, necessitate development of rigorous special analytical procedures. Techniques, like Inductively Coupled Plasma - Mass Spectrometry (ICPMS), Graphite Furnace Atomic Absorption (GFAAS), Differential Pulse Squarewave Voltametry (DPP), Atomic Absorption Spectrophotometry (AAS), Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICPAES), Neutron Activation Analysis (NAA), Energy Dispersive X-ray Fluorescence (EDXRF) analysis, Inert Gas Fusion (IGF) technique, thermal analysis (TG-DTA-EGA), etc. had to be specially adapted for such measurements by taking care to reduce blank contributions. Some of the samples received from users, for which special technique had to be developed are presented in the table.

Head, ACD <headacd@barc.gov.in> P. V. Ravindran <ravipv@barc.gov.in>

Matrix	Source	Specific requirement	Analyte	Range	Technique
Process samples	IGCAR	Determination of enrichment factor	<sup>10</sup> B, <sup>11</sup> B	Isotopic composition	ICPMS
Blood		Determination of Se toxicity levels	Se	ррь	GFAAS, ICPMS
U-Mo alloys	AFD	Analysis for Mo	Mo	%	DPP
Black powder of unknown composition	HWD	Identification in the context of narcotic trafficking	Pd, Al, Si	%	EDXRF, DPP, ICPAES
Titanium, nickel, silicon, gadolinium, copper	LPTD, HWD, Hindustan Copper Ltd.	Trace impurity analysis	H, O, N. S, Zn. Fe, Bi, Cr, Ni, Mn. Pb. Sb, Ag	ppm	ICPAES, NAA, EDXRF, IGF
Special alloys like nimonic 75 alloy, Zr-1% Nb tube	LWRD	Check on specification prior to purchase	H, O, N, Co, Nb and a number of trace elements	ppm - %	AAS, NAA, IGF
FCC flash catalyst	Hindustan Petroleum	To help selection of appropriate catalyst	Rare earths	%	NAA
NPK fertilizer ( Suphala')	Rashtriya Chemicals and Fertilizers Ltd.	Identification of features affecting flowability of the product	Elemental composition, nature of deliquescent phases	%	AAS. TG-DTA-EGA
Serpentine ore	RPD	Determination of amount of constitutional water, moisture, release of toxic gases, contaminants	S, release of CO, SO <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> S, H <sub>5</sub> O at high temperatures, AI, K, Na, CI, alkalinity	ppm to %	AAS, Spectro- photometry TG-DTA-EGA, Ga chromato-graphy

New Analytical Efforts

#### 4.4 THIN LAYER ACTIVATION

## Study of Electric Erosion by TLA Technique using Heavy Ion Induced Reactions

Thin layer activation technique (TLA) using charged particles from an accelerator, has become a sensitive nuclear technique for the determination of surface loss of materials in various engineering components in the micron level. TLA technique has been applied to study the surface erosion in brass electrodes used in safety circuit of radio frequency (RF) system of VEC machine due to discharge spark under high voltage electric field.

A stacked foil irradiation was carried out with thin Cu foils (1 - 4 m) using 110 MeV <sup>16</sup>O heavy ion beam from VEC machine to determine the excitation functions of many nuclear reaction channels from Cu target and <sup>16</sup>O projectile as shown in figure. It has been found from the measured cross sections of the above reaction channels that <sup>75</sup>Se, <sup>72</sup>Se and <sup>65</sup>Zn are the most suitable isotopes for TLA work. The same stacked foil irradiation was used



Excitation functions of nuclear reactions: O  ${}^{63}Cu({}^{16}O, 3pn){}^{75}Se,$   ${}^{63}Cu({}^{16}O, \alpha p2n){}^{72}Se$  $\Delta {}^{63}Cu({}^{16}O, 3\alpha pn){}^{65}Zn$ 



to generate the yield curves of isotopes, <sup>75</sup>Se, <sup>72</sup>Se and <sup>65</sup>Zn as presented in figure The calibration curves have been obtained from yield curves for the measurement of surface erosion in brass electrodes. The brass electrodes (15 mm length, 12 mm dia.) were irradiated using 110 MeV <sup>16</sup>O with 50 nA beam current for 24 hours. The surface erosion experiment of irradiated brass electrodes with a gap of  $\sim$  3 mm was carried out under high voltage (10 - 30 kV) using a power supply that produced a continuous electric spark discharge causing the erosion of materials from electrode surface. The activity loss was measured after each spark experiment by -spectrometry and compared with calibration curves to determine the thickness of eroded material. The rate of surface erosion was 300 nm per hour in air. The maximum and minimum erosion measured was 22 m and 100 nm, respectively, and the sensitivity of TLA technique was found to be 50 nm.

## 4.5 ANALYTICAL INSTRUMENTS DEVELOPED IN BARC

#### PC-based Home-built Carbon Analyser

Determination of carbon in uranium is routinely being done in Analytical Chemistry Division by a low pressure technique involving combustion of the sample followed by trapping of the evolved moisture and carbon dioxide and determination of volume of carbon dioxide through manometric measurements under expansion into standard volumes. Though enabling precise measurements, this is a cumbersome procedure not easily amenable to automation. In the Analytical Chemistry Division, a thermal conductivity based system has, therefore, been designed indigenously and adapted for automatic data acquisition and display by interfacing with a Windows based software developed in-house for the purpose. The measurements are based on combustion of the sample, trapping of moisture and carbon dioxide in successive traps of magnesium perchlorate and Molecular Sieve 5A, release of trapped carbon dioxide by heating the molecular sieve (MS) trap and detecting and quantifying the same by sweeping it to a thermal conductivity detector (TCD) using helium as the carrier gas. The necessary gas-flow-line switching arrangement employing three solenoid valves, the bridge circuit for thermal conductivity measurement and the microcontroller based analogue to digital converter card, with RS232C based serial port connectivity to PC, were fabricated from locally available components. The new setup has eliminated the requirement of liquid nitrogen for preparation of the traps, and helped doubling of sample throughput. The setup could be used conveniently for the measurement of carbon content in a large number of uranium samples from Atomic Fuels Division.

Head, ACD <headacd@barc.gov.in> P. V. Ravindran <ravipv@barc.gov.in>

#### 4.6 **NEUTRON ACTIVATION ANALYSIS**

A k0-based internal mono standard instrumental neutron activation analysis (IM-INAA) method has been developed for the analysis of samples of non-standard geometry and larger size. The method utilizes an in-situ relative efficiency using gamma rays from the activation products to take into account the  $\gamma$ -ray attenuation in the sample. The method was standardized using large size synthetic solid and liquid samples and was applied to reference materials, high purity metals like aluminium and alloys like Zirclaoy and stainless steel (SS) cladding materials. This standard-less analysis is a significant contribution to the analytical field. This approach of standard-less analysis is being applied to other alloys, metals and reference materials for compositional analysis. To compliment the conventional neutron

activation analysis, the Prompt Gamma Neutron Activation Analysis (PGNAA) method has been standardized at a temporary facility set up in Dhruva research reactor using reflected neutron beam. An internal mono-standard method was developed to determine the relative concentration of different elements in the matrix. This method is useful for impurity determination in the samples with respect to the major constituent. The relative concentrations can be converted to absolute concentrations in the cases where all the elements in the matrix are amenable to PGNAA. The method has been used to analyse real life samples of various shapes and sizes. The methodology to correct for the self-shielding effects and analyze the samples containing large amounts of self-shielding elements was also standardized.

Head, ACD <headacd@barc.gov.in> P. V. Ravindran <ravipv@barc.gov.in>



## 5. RADIATION CHEMISTRY

## INTRODUCTION

Studies on the effects of radiation, such as  $\gamma$ -rays and electrons, on aqueous and non-aqueous solutions are important to understand fundamental aspects of the interactions, the primary and secondary processes occurring as well as their applications. The linear electron beam accelerator is extensively used to study free radical reactions, redox chemistry, kinetic and spectroscopic properties of a number of molecules important in biology and material science. The gamma radiation source has long been used for production scale polymerization. It continues to be an attractive method for preparing new functional polymers. Pulse radiolysis with short pulses of high energy electrons was used to evaluate the mechanisms of free radical reactions of antioxidant in natural sources, such as, turmeric, spices, carrots and herbal extracts. Use of radiation for simultaneous radiolytic formation of silver nanoparticles in the hydrogel, while cross-linking the PVA chain is a technological advancement. Radiation polymerization of hydrogel for superadsorbent, metal extraction and other applications constitute the research and development effort in this area.

## 5.1 FREE RADICAL REACTIONS OF ANTIOXIDANTS AND RADIOPROTECTORS

Aerobic organisms produce a number of reactive free radicals continuously in living cells during respiration, metabolism, etc., which can induce multiple chemical changes in cellular organelles, like membrane lipids, DNA and proteins, eventually leading to cell death. The excessive production of free radicals, termed as "oxidative stress", has been implicated in many ailments, like heart disease, cancer and other diseases related to ageing. Antioxidants are substances which, when present in small quantities, prevent oxidation of the bulk induced by excessive free radicals.

Under normal healthy conditions, a balance is maintained between oxidative stress and antioxidant requirements. However, under pathological conditions, during stress, smoking, or radiation injury, the balance is lost, and additional supplementation of antioxidants is necessary. In this context, the search for new, effective and appropriate antioxidants aimed at minimizing the



oxidative stress, and providing defence against free radical induced stress in diverse clinical and pathological conditions has gained a lot of importance. A number of herbal formulations used in traditional Indian medicine are also some of the potent antioxidants which need to be explored.

Exposure of cells to ionizing radiation also causes similar effect, as oxidative stress. Interaction of ionizing radiation is nonselective, and in cells, water being the major constituent, undergoes radiolysis, producing hydroxyl radicals, which can react with cellular organelles, similar to those produced by oxidative stress. Due to this similarity, an antioxidant can, in principle, also act as a radioprotector.

In order to manipulate the phytochemicals for therapeutic gains, it is necessary to understand the antioxidant action at molecular level. Direct monitoring of free radical reactions of antioxidants is necessary for the understanding of such processes.

As most of the free radicals are highly reactive, fast techniques are required to follow their reactions. Pulse radiolysis, a technique using short pulses of high-energy electrons, is a versatile technique for studying reactions of these free radicals. It is possible to generate selectively and quantitatively most of the reactive oxygen and nitrogen free radicals. The reaction kinetics, radical lifetimes, diffusion length and one-electron redox



potentials establish the likely and unlikely reactions as well as competitive reactions of antioxidant substances under suitable biological conditions.

It was possible to evaluate the molecular mechanisms involved in free radical reactions of antioxidants belonging to the classes of curcuminoids from turmeric, flavonoids from natural herbs, methoxy phenols from spices, carotenoids from carrots, etc. Having understood the mechanism of action at molecular level, it is necessary to correlate these results with antioxidant potency in cellular systems.

Curcumin, a pigment from turmeric, shows remarkable antioxidant activity, and has been found to be an excellent free radical scavenger. It is lipid soluble, and is a chain breaking antioxidant. Its in vitro antioxidant ability has been found to be as high as that of vitamin E. It has two sites for free radical attack, o-methoxy-phenolic moiety and the methylenic moiety.



Based on pulse radiolysis studies, DFT calculations and in vitro biochemical studies of curcumin and its dimethoxy derivative, it was concluded that the methoxy phenolic OH group is essential for the antioxidant activity. Such studies helped in derivatising curcumin to new synthetic models through the methylenic moiety with desired therapeutic potential, without disturbing its original antioxidant potential. Thus, a copper complex of curcumin was found to show promising superoxide dismutase (SOD) activity, with comparable free radical scavenging ability and an improved antioxidant efficacy. The chemistry of the antioxidant action of a meroterpene, bakuchiol, was also established. The protective activity of bakuchiol against oxidative damages to lipids and proteins was investigated, and rationalized on the basis of scavenging activity against various oxidizing radicals. The results from this study showed importance of the terpenoid moiety of bakuchiol in controlling its antioxidant action via radical scavenging.

The interaction between a-lipoic acid radical and folic acid was studied as synergic relation between antioxidants. This is an important chemical and biological aspect in evaluating the antioxidant potential of a compound. Exogenous free lipoic acid (LA) may be effective as a thiol substitute. Until recently, the antioxidant perspective of folic acid has not been considered, although its role in the pathogenesis of cardiovascular disease and cancer prevention was known. The first report on the free radical scavenging efficacy and possible role of folic acid as an antioxidant was determined in Radiation and Photochemistry Division. The methylene group present in folic acid actually scavenges hydroxyl radicals. It has also been proven that folic acid can modulate the fenton chemistry, thereby reducing iron overload. The presence of phenolic group, on top of a  $\alpha$ - $\beta$ unsaturated functionality, in these molecules makes them efficient antioxidants.

It is commonly believed that the beneficial effects of phyllanthus emblica (Amla) are due to ascorbic acid. Correlating the physicochemical properties with in vitro antioxidant studies, it was confirmed conclusively that ascorbic acid alone cannot account for its activity, and polyphenols, such as ellagic acid, gallic acid, etc., contribute significantly. The plant extracts and formulations with good antioxidant efficacy can be promising radioprotectors of the future. Such mechanistic studies with different classes of antioxidants have opened a new strategy of derivatising natural antioxidants to new synthetic models with desired therapeutic potential, without disturbing their original activities.

## Radiation Induced Redox Chemistry in Aqueous-Acid

Although aqueous solution had been a medium of choice for generation of free radicals. Its use gets restricted when highly acidic species are involved, as fast water assisted deprotonation, prior to any other reaction, reveals only the undesired, deprotonated-radical chemistry. Thus, for routine and convenient generation of highly acidic free radicals (cationic and transient), and gaining insight into their chemical reactivity, an alternative solvent systems is required. Detailed studies suggest the suitability of the mixed solvent system of water and sulfuric acid as the reaction medium. With appropriate physico-chemical pre-characterization, the medium was subsequently employed to measure the acidity of a variety of radical cations (RH·<sup>+</sup>), compare and complement their chemistry with that of the related deprotonated radicals (R·).

(Aqueous-acid medium)  $RH^{+} = H^{+} + R^{-}$  (Aqueous medium)

#### Characterization of Aqueous-sulfuric Acid

Interestingly, for over a century, the solubility parameter of  $O_2$  has remained ambiguous, and incorrectly answered. Recently, based on in-situ measurements of selected free radical- $O_2$ 



reactivity, the required  $O_2$  solubility values, are shown in the figure. The results suggest a steady decrease in the dissolved  $O_2$  concentration with increase in the acid fraction, that finally reaches  $\sim 25\%$  of the aqueous medium value. Such data also have direct use in atmospheric chemistry studies, involving sulfuric acid liquid hydrometeors and aerosols, in hydrometallurgy and related industries.

#### Phenol Degradation via Cationic Route

Phenolic chemistry is synonymous with chemical reactions dealing with auto- and anti-oxidation, in biochemical synthesis, in dye, pesticide and drug industry, as stabilizers in polymers and plastics, in atmospheric and water pollution control, etc. To complement the existing knowledge of phenolic reactions, and its degradation under such conditions following the neutral, phenoxyl radical route, radiation chemical studies were carried out in aqueous-H<sub>2</sub>SO<sub>4</sub> medium. The results from parent phenol oxidative studies presented in the figure suggest completely new cationic reaction



route, which involves successive reactions of the parent (vis-à-vis the known phenoxyl radical dimerization route not involving the parent phenol), thus resulting in faster parent degradation and possible formation of polymeric product.

## 5.2 RADIATION POLYMERIZATION

Ionizing radiation can be used for understanding mechanism of polymerization reaction as well as for initiation of the polymerization process. Some of the advantages of the radiation initiated polymerization over the conventional methods are: (i) absence of foreign matter, like initiator, catalyst, etc., (ii) polymerization at low temperature, or in solid state, (iii) rate of the initiation step can easily be controlled by varying dose rate and (iv) the initiating radicals can be produced uniformly by  $\gamma$ -irradiation. The kinetics of polymerization of a variety of monomers was studied extensively which led to better understanding of the mechanism of polymerization reactions. Using the technique of pulse radiolysis, the rate constants of the various initial steps, initiation and a few propagation steps, were evaluated, and correlated with the structures of the transients formed by initiation with H, OH, and  $e_{aq}$  species. The different intermediates in the polymerization reactions were also characterized by absorption spectra, pK<sub>a</sub>, redox behaviour, their decay and formation kinetics, etc., which further helped in understanding the polymerization process.

#### Radiation Synthesis of Polyaniline

Polyaniline (PAni) is an important conducting polymer, with wide range of applications. PAni was synthesized, for the first time, by



TEM picture of poiyaniline

radiation polymerization method. It was characterized by optical absorption, TEM and light scattering techniques. The light scattering study indicated formation of PAni particles of average sizes 160 and 200 nm, with low polydispersity, in aqueous medium, without any stabilizer. TEM picture showed presence of spherical particles of about 100 nm size, along with long fibers of similar diameter, in the dry sample.

### Metal Nanoparticles in Hydrogel Matrix

Metal nanoparticles in hydrogels have many advantages over the conventional sols, e.g., smaller size, higher stability, easy accessibility and separation from reaction mixtures, etc. During the formation process, the aggregation of nanoparticles is very



Silver nanoparticles in dry PVA gel



Silver nanoparticles in hydrogel (Low concentration)



Silver nanoparticles in hydrogel (High concentration)

much restricted, and once formed, these do not coagulate or settle down in a hydrogel matrix. Thus, nanoparticles of nonnoble metals, like Cu and Cd, could also be stabilized in hydrogel matrix for a few hours, which otherwise are stable only for a few seconds in aqueous medium in presence of air. Most of the reactants/products can diffuse easily in a hydrogel network, thus having easy access to well separated nanoparticles for any catalytic application. Separation of nanoparticles of a catalyst from reaction mixtures generally requires tedious ultrafiltration or centrifugation processes, whereas nanoparticles in the hydrogel matrix can easily be separated from the reaction mixture, after completion of the reaction.

PVA is a major component of hydrogel wound dressings and an efficient stabilizer for Ag nanoparticles (prevents aggregation). Silver is a well known disinfectant. Thus, PVA hydrogel wound dressings containing Ag nanoparticles, will be highly desirable for treatment of infected wounds. Ag clusters have been radiolytically produced in the PVA hydrogel matrix, using AgNO<sub>3</sub> and AgCl. Viscosity, absorption spectra and swelling studies indicated that on radiolysis, Ag<sup>+</sup> ion reduction is followed by crosslinking of PVA chains in the presence of AgNO<sub>3</sub>.

While restricted availability of Ag<sup>+</sup> ions, in case of AgCl, helps in simultaneous radiolytic formation of Ag nanoparticle, along with crosslinking of PVA chains. Ag clusters of sizes smaller than the pore size of the hydrogel matrix (~ 2 to 20 nm) have been

produced. The swollen hydrogel containing two different concentrations of silver nanoparticles is shown in figure.

## Hydrogel Resins for Removal of Toxic Metals from Aqueous Waste

Organic pollutants can be decomposed/oxidized by various methods, but metal ions have to be removed from waste water, otherwise they accumulate, enter into food chain, and never get destroyed by natural processes. Study on the development of a



Hydrogel resin with Cu2+



Hydrogel resin with Co<sup>2+</sup>

hydrogel based resin to remove metal ions from the polluted water was carried out. A hydrogel resin containing about 80 % water, with capacity greater than 220 mg/g for cobalt adsorption, has been synthesized by radiation-induced method.

It has shown efficient extraction of Co<sup>2+</sup> and Cu<sup>2+</sup> ions from aqueous solutions and could be recycled without any loss of capacity.

#### Superabsorbents

Superabsorbents are materials which can absorb about 100 gm or more of solvent per gram. These are extensively used in medical, chemical and agriculture industries. An acrylic acid–carrageenan based superabsorbent hydrogel, with high equilibrium degree of swelling (EDS) of about 800 g/g, was prepared by  $\gamma$ -irradiation method. It was found to be sensitive to pH and ionic strength of the medium and can have applications in concentrating many natural extracts and drug formulations by absorption/removal of water.

#### Solid/Liquid Phase Extraction of Radionuclei

The solid/liquid phase extraction of U(VI), Pu(IV), Am(III) and some fission products from aqueous nitrate solutions, using extractant immobilized PVA/acryl amide copolymer gel, was carried out in collaboration with FRD. More than 90 % extraction, under the optimized conditions, of U(VI), Pu(IV) and Am(III) was obtained, while extraction of Cs and Sr was negligible. Radiation modification of polymeric films and fibers to attach suitable extractant groups was also carried out. The loading capacity, extraction and elution efficiency were evaluated for both the systems, and were found to remain nearly the same, even after three to four cycles of extraction and elution. These modified polymers could selectively extract ~ 90% U/Th from nitric acid medium, in presence of Cs, Bi, Ph, Tl, etc.

S. K. Sarkar <sarkarsk@barc.gov.in>



## 6. URANIUM TECHNOLOGY AND PROCESSES

#### INTRODUCTION

Uranium technology is vital to the nuclear energy programme. Given the lean sources of uranium in India, BARC has been concerned with the development of processes for recovery of uranium from secondary sources and dilute waste streams. The sea water has the lowest concentration uranium source, but holds enormous quantities of uranium. BARC has taken the first few significant steps in the long journey towards establishing a economically feasible process for recovery of uranium from sea water. The uranium metal production process is continually improved to enhance recovery and to handle different grades of feed material, such as, crude  $UF_4$  from monazite. Abatement of pollution of nitrates has been taken up on a mission mode, while modifications to the process have ensured minimisation of waste. Progress in the novel indigenous process of plasma based hydrogen reduction of  $UF_6$  to  $UF_4$  is also described in this chapter.

## 6.1 URANIUM RECOVERY FROM LOW CONCENTRATE SOURCES

 Application of Liquid Membrane System for Recovery / Concentration of Uranium from Dilute Solution



Emulsion based liquid membrane (ELM) system has been studied for recovery and concentration of uranium from dilute nitrate solution. An emulsion type liquid membrane system composed of D2EHPA, SPAN80, kerosene and nitric acid has been developed.

Using this system a synthetic solution of dilute ( $\sim$ 0.5g/l) Uranyl nitrate was polished to below 50 PPM of uranium content. The concentrated pure solution contained around 5 g/l of uranium in nitrate form. The effort now is to improve the performance of the LEM process with respect to emulsion stability and efficient de-emulsification.

S.K.Ghosh <ghoshsk@barc.gov.in> H.Rao <hrao@barc.gov.in>

## Development of D2EHPA - TBP Process for Uranium Recovery from Weak Phosphoric Acid

An innovative dual cycle extraction process has been developed at laboratory and pilot plant scale for extraction of hexavalent uranium from 4-6 M phosphoric acid. The process incorporates

> selective scrubbing of co-extracted rare earths in second cycle, followed by two stage precipitation to yield high purity yellow cake. The process patent was filed in the US (Patent ApplicationNo. 09/947,349 dt 7/9/2001)) The figure (on following page), gives the main steps of the process.

H. Singh <hsingh@barc.gov.in>

## Technology Demonstration, based on Alkaline Leaching Process, at UCIL Jaduguda for Recovery of Uranium from Tummalapalle Ore

A joint developmental activity has been undertaken by the Chemical Engineering and Technology Group, Materials Group, BARC, Atomic Minerals Directorate and Uranium

Corporation of India Limited, for recovery of uranium from Tummalapalle ore. The objective is to set up a pilot plant (Capacitybatch mode-250kg ore/batch; continuous mode-50 kg/hour) based on alkaline leach process. The pilot plant will incorporate complete process integration. The operation of the plant will confirm the laboratory results and generate experimental data to establish the techno-economic feasibility of the process for recovery of uranium from Tummalapalle ore. Further, engineering data, required for the design of production scale plant, will be collected. Detail engineering work has been completed and the pilot plant is being installed When commissioned, it will establish an efficient process for recovery of uranium.





## Process Development for the Production of Nuclear Grade Uranium from Secondary Source (Crude UF<sub>a</sub>)

Crude  $UF_4$  is generated as a byproduct during thorium nitrate production from monazite. This crude  $UF_4$  is treated with NaOH.

The resultant  $UO_2$  is dissolved in HCl. Crude uranium thus generated is purified using Alanin 336 and Tri-Butyl Phosphate. This has led to better management of resources with high recovery.

S. B. Roy <mrsued@barc.gov.in>



#### 6.2 RECOVERY OF URANIUM FROM SEA WATER

The effluent rejected from the desalination plant contains a number of materials and is a source for many chemicals. Some of the elements are very scarce and expensive. There is thus a strong motivation in recovering these elements from the reject brine of a desalination plant. This also adds value to a desalination plant apart from making it more environment friendly. Recovery of uranium (U), germanium (Ge) cesium (Cs), indium (In) and other high technology materials from the reject brine of desalination plant appears promising. The recovery of these materials is desirable not only for meeting the demand but also for reducing the cost of desalinated water.

R&D work on 'Recovery of Uranium from Sea Water pilot programme (RUSWapp)' has been taken up. Chemical synthesis

route and lonising radiation route were pursued. Ionizing Radiation route using Electron Beam Irradiation was further pursued to provide irradiation grafting of ACN on a non-woven PP Fibre substrate availing the expertise of RTDS. About 130% grafting was achieved. Conversion of ACN to PAO up to 50-60% of the substrate weight was achieved.

Experimental data were collected for immersion depth, alkalination optimisation, bio and dirt fouling, tidal wave velocity

A total of about 800  $\mu$ g of U was collected in 5 campaigns from CIRUS Jettyhead, about 1.8 mg from TAPS seawater intake and outfall canals and around 200  $\mu$ g from Andaman & Nicobar Islands. The specific collection was found to be from 60 to 160  $\mu$ g/g of PAO in 12 to 24 days. This can be compared to adsorptionequilibrium of 1000  $\mu$ g /g of PAO in 52 days at 25°C in laboratory condition results as reported by Japanese researchers. It was observed that vanadium is also getting collected on the adsorbent.



Plant Facility (under construction) for Uranium Recovery from Seawater

and uranium pick up efficacy, at:

CIRUS Jetty head. Kalapakkam, near seawater intake tunnel. Tarapur 1&2 Seawater intake and outfall canals. Andaman & Nicobar Islands. A 100 grams per year U pilot plant facility RUSWapp100 is under installation as shown in the Figure.

P.K.Tewari < pktewari@barc.gov.in >

#### 6.3 URANIUM METAL PRODUCTION

 Production of 450 Kg Uranium Metal Ingots in India

> In India, for fabrication of research reactor fuel, production of uranium metal ingot was started in Uranium Metal Plant, BARC with the production of a 44 kg uranium ingot by calciothermic reduction of uranium tetra fluoride. Thereafter, in the intervening years, there has been a substantial scale up of production and extensive investigation of the metal and its compound. Recently in Uranium



Magnesiothermic reduction (MTR) reactor. Extraction Division, an augmented uranium metal production facility (AUMP) for safe and secure production of 450 kg U ingot has been successfully commissioned by magnesiothermic reduction of uranium tetra fluoride.



Magnesiothermic reduction (MTR) reactor with mould.



Magnesiothermic reduction (MTR) reactor with lining.



### Pelletized Charge Magnesiothermic Reduction (MTR) for Production of U metal

Charge pellet was prepared under controlled atmosphere using hydraulic press. In a  $MgF_2$  lined reactor of 5 Kg capacity, pelletized

charge was randomly stacked and fired for completion of reaction.

Pellets for handling could be prepared without compromising purity of product and recovery. This facility is to be scaled up to the required plant size

## Recovery of Uranium from Scrap U-Cu Cluster Generated during Fuel Fabrication

With the objective of maximising overall recovery in the fuel production cycle, a process has been developed to selectively remove copper from U-Cu clusters, and thereby making available the uranium for fuel fabrication without reprocessing. It involves preferential leaching of Cu with  $HNO_3$  under controlled conditions. Uranium in the leach liquor (0.6 %) is recovered as ammonium diuranate by ammonia precipitation. High recovery of 99.4 % is achieved during solid-liquid separation. Typical batch size is ~100 Kg.

#### Production of Uranium Powder

A process has been developed for production of a specified grade uranium powder. It involves metallothermic reduction of UO<sub>2</sub>. The product uranium powder is recovered by selective

leaching of the slag mass at controlled condition. This has led to production of high purity metal powder of reproducible quality.

## Study of Uranium Peroxide Precipitation for Reduction in Nitrate Waste

Studies were carried out with the objective of developing a process for UO<sub>3</sub> without generating nitrogenous liquid waste and obtaining UO<sub>3</sub> of required chemical purity and physical characteristics, suitable for uranium metal ingot production. Uranium compound (oxide or diuranate) is dissolved in sulphuric acid. Uranium is precipitated as UO<sub>4</sub> by maintaining stringent parameters and filtered to get UO<sub>4</sub> cake. The product UO<sub>4</sub> is chemically nuclear grade. The effluent generated in this process is disposable as per MPCB guidelines. Physical characteristics of the UO<sub>4</sub> and the UO<sub>3</sub> obtained after calcination are to be of suitable grade for further conversion to metal ingot.

#### S. B. Roy <mrsued@barc.gov.in>



## 6.4 NEW PLASMA BASED PROCESS FOR CONVERSION FROM UF<sub>6</sub> TO UF<sub>4</sub>

UF<sub>6</sub> is the only known compound of Uranium which is highly volatile at ordinary temperature. UF<sub>6</sub> is used as a feed material in enrichment processes like gas diffusion, gas centrifuge etc. The enriched UF<sub>6</sub> as well as tails of the enrichment plant can not be stored in cylinder for a longer duration of time because of their toxic and corrosive nature. Hence they should be converted to more stable compounds like UF<sub>4</sub>/U<sub>3</sub>O<sub>8</sub> for storage. Conventionally UF<sub>6</sub> is reduced to UF<sub>4</sub> by hydrogen at about 600°C. Thermal plasma process offers a clear, faster and advanced technology for processing waste UF<sub>6</sub> without needing any additional chemical and hence significantly reducing the waste generated.

## 

A plasma chemical process is currently being developed for efficient conversion of  $UF_6$  to  $UF_4$ . A special constricted arc plasma generator has been designed and fabricated at Laser and Plasma Technology Division to produce argon hydrogen plasma that exits through a nozzle into a plasma reactor. Additional hydrogen and  $UF_6$  gas will be input in the reactor that has been designed in three sections namely the inlet and mixing zone, reaction zone and collection zone.



The segmented arc Plasma Torch



Provision for measurement of gas temperature at various sections has been done. A 2D axisymmetric simulation for temperature and velocity mapping has been carried out.

L.M. Gantayet <headlptd@barc.gov.in> A. K. Das <akdas@barc.gov.in>

## 6.5 POLLUTION ABATEMENT THROUGH DENITRATION

## Recovery of Nitrate Values from Raffinate Stream, as Concentrated Metal Nitrate and Nitric Acid by Evaporation and Distillation

Based on the studies conducted on lab scale earlier in Chemical Engineering Division, a facility has been set up capable of processing 40-60 litre/hr of dilute nitrate waste stream. The process consists of filtration, organic removal (TBP) by diluent wash / ion-exchange, and vapor feed rectification for recovery of 6-8 M nitric acid. This facility when, operated with raffinate stream of uranium refining plant, will generate engineering data and establish the process on pilot scale. This will also provide a concentrated nitrate solution suitable for thermal denitration plant.

S. K. Ghosh <ghoshsk@barc.gov.in> H. Rao <hrao@barc.gov.in>

## Development of Fluidized Bed Thermal Denitration Technology.

The thermal denitration programme is targeted for processing both product and waste nitrate streams of nuclear fuel cycle. Using fluidized bed thermal denitration, streams with high concentration of nitrate values (> 200 gm/lit) will be denitrated. The nitrate values will be recovered as nitric acid (for reuse) while the metal values as oxide for storage or further usage. A bench scale plant of 5 litres per hour capacity has been commissioned. The process flow sheet is represented below.

The various sub-systems in the plant are solid handling system, feed spray system, heat input system, off-gas treatment system. The plant is under operation for comprehensive development of the fluidized bed thermal denitration technology.

#### Chemical Denitration

A uranium recovery from Uranyl nitrate raffinate cake (UNRC) and silica cake cum denitration process of aqueous waste containing nitrates, has been developed. Bench scale trial on 1 kg batch of UNRC and silica cake has been carried out. UNRC and silica cake generally contains 2-5% uranium and 2-10% nitrate. The process involves leaching of UNRC and silica cake with dilute sulfuric acid and reduction of nitrate to nitrogen gas with metallic reductant.



Control room



Fluidized bed reactor



Uranium values are recovered as carbonate. This process has been tailored to process UNRC and silica cake from the Uranium refining plant and will help in the disposal of these wastes.

S. K. Ghosh <ghoshsk@barc.gov.in>

H. Rao <hrao@barc.gov.in>

physical characteristics, suitable for uranium metal production. The crude diuranate cake is dissolved in sulphuric acid and ADU is precipitated in presence of selective complexing agents namely CDTA to obtain nuclear grade ADU. This results in almost total recovery of uranium and it does not generate any nitrate waste.



aqueous nitrate waste by Chemical Method

## Nitrogeneous effluent management at Uranium Metal Plants

## Purification of Crude Diuranate Cake Without Generating Nitrate Waste

A process has been developed for purification of crude diuranate cake without generating nitrate waste. This should obtain ammoniun diuranate (ADU) of required chemical purity and

### Lab Scale Studies on Biodegradation of Nitrogenous Waste

Removal of nitrogen from nitrogenous effluent generated during uranium metal production process by biodegradation is an attractive option for treatment of nitrogeneous waste. Bench scale set up consisting of nitrification and denitrification reactors has been designed and rigged up for feasibility and efficiency studies. The process schematic is shown in the figure. In nitrification reactor more than 90% reduction efficiency has been consistently achieved with ammoniacal nitrogen feed concentration up to 450 mg/L. In the denitrification reactor more than 99% reduction efficiency has been consistently achieved with nitrate nitrogen feed concentration up to 1450 mg/L. Cascading of two reactors and scale up of the reactors will be tried.

Acclimatization of bacteria for higher concentration nitrogenous effluents more specifically for ammoniacal effluent is a challenge to be met.

## Development of Process for Decontamination of Byproduct Hydrofluoric Acid

A process was developed in Uranium Extraction Division with the objective of obtaining zero fluoride effluent discharge and thereby by reusing / recycling the treated effluent. Concentrated aqueous HF was treated to remove radioactivity. After clarification it was suitable for industrial utilization. Dilute aqueous HF solution was treated to fix the fluoride as insoluble salt and recycle the filtrate for process requirement. These processes reduce the load on effluent management to a considerable extent.



S. B. Roy <mrsued@barc.gov.in>

#### **Raffinate Recycle**

Recycle of raffinate will utilise the nitric acid for plant recycle. This will also result in reduction of nitrogen bearing effluent. Laboratory scale trials have been conducted under a controlled temperature with conditioned feed. Nitric acid concentration was increased from about 1.5 N to 6 N which is suitable for plant recycle. The proces is being scaled up.

## 7. THERMODYNAMICS OF NUCLEAR FUEL FOR THORIUM FUEL CYCLE

### INTRODUCTION

Studies of chemical thermodynamics and phase equilibria of the systems involving nuclear materials are of great importance in predicting changes in chemical constitution of the fuel during operation as well as accident condition of the nuclear reactor. As thoria based fuels are going to play an important role during the third stage of the Indian Nuclear Power Generation program, the behaviour of the thoria based fuels needs to be understood and a comprehensive database built. Changes in the chemical constitution of the irradiated fuel can influence the physical properties of the fuel, the rate of diffusion of fission product elements within the lattice of the fuel and their release to the fuel – clad gap during the normal operation or during operational transient ingresses of energy. The presence of fission products in the fuel – clad gap of a fuel element may cause corrosion of the cladding material and thus limit the life time of a fuel element. For understanding and predicting the scenario in such circumstances, thermodynamic data and physicochemical data on a large number of chemical species (solid, liquid or gaseous) are required. One of the noteworthy aspects in the investigations is that they have been carried out using in – house built apparatus.

## 7.1 THERMODYNAMIC PROPERTY OF FUEL AND FISSION PRODUCTS

Identification and thermodynamic characterization of reaction products of different fission products with thoria based fuels, and clad have been made. The investigation has successfully worked out the chemical states of alkali and alkaline earth fission products in the fuel matrix. Accurate thermodynamic data of the solid oxide phases such as cesium zirconate, cesium, rubidium, barium, and strontium thorates, nickel tellurate, intermetallics like rhodium/ruthenium telluride, and vapor phase like Ba(OH)<sub>2</sub>(g), polymeric vapor species of cesium and its oxides have been generated. Phase diagrams of ternaries of Mo-O-(Cd/Sb/Te), Sr-Te-O and Te-rich binary Te-Ru have been established.



Ru - Te Phase diagram study using indigeneously developed DTA setup Inset : Vacuum sealed quartz sample holders mounted on DTA probe stand

Evaluation is made on the essential difference in the fission products chemistry in the thoria based AHWR fuel arising from its inferior buffer capacity for the fission generated oxygen and its poorer oxygen transport property as compared to that in



Mo-Te-O ternary at 1073 K , TG-DTA & XRD

urania fuel. The fuel-clad compatibility aspect is now being examined using the generated information. Parallely, the data acquisition of highly oxidized phases important in the analysis of the fission products states in thoria fuel is pursued. Independent verification is also being made for the already acquired data of some of the fission product phases that have large bearing in the compatibility analysis. The thermodynamic investigations completed on the fission product states and their significance are presented in the Table.

#### Apparatus for thermodynamic studies

The above mentioned high temperature studies have been carried out using indigenously built in-house equipments. The apparatus for Knudsen vaporization study (also, with mass spectrometer attachment), gas/vapor transpiration study, galvanometric study, calorimetry, etc. were designed and fabricated in-house, and reliable

thermo-physical and thermodynamic data has been generated on scores of compounds, alloys and intermetallics of interest in nuclear reactors and other industrial applications. Two such equipments are shown in the following Figures.



Knudsen Effusion Apparatus



Transpiration Apparatus
	Method	Reaction studied	Thermodynamic property	Significance
Cs2ThO3 (8)	Knudsen effusion	Cs2ThO3(s)=Cs2O(g) +ThO2(s),1100 ≤T≤ 1250 K	$\Delta_t G^0(Cs_2 \text{ThO}_3(s)) = -$ 1780+0.44T (±20 kJ mol <sup>-1</sup> )	Evaluation of Cs redistribution, & I generation by ThO <sub>2</sub> + 0.5O <sub>2</sub> + 2CsI=2I(g) + Cs <sub>2</sub> ThO <sub>3</sub> .
Cs2ZrO3(s)	-do	$Cs_2ZrO_3(s){=}Cs_2O(g){+}ZrO_2(s){,}1140{\leq}T{\leq}1275{\rm ~K}$	$\Delta_{f}G^{0}(Cs_{2}ZrO_{3}(s)) = -$ 1672+0.44T (±18 kJ mol <sup>-1</sup> )	-do- (Additionally, Zr+3/2O2+2CsI =2l(g)+ Cs2ThO3)
Rb2ThO3 (s)	-do	Rb2ThO3(s)=1/2O2(g) + 2Rb(g)+ThO2(s) 1058 ≤T≤1232 K	$\Delta f G^0 (Rb_2 ThO_3(s)) = -1822+$ .45T (± 8kJ mol <sup>-1</sup> )	cf. Cs2ThO3 case
	-do	BaThO <sub>3</sub> (s)=BaO(g) +ThO <sub>2</sub> (s) 1770 ≤T≤ 2140 K	$\Delta_f G^0$ (BaThO <sub>3</sub> (s)) = - 1802+0.28T (±15 kJ mol <sup>-1</sup> )	Evaluation of bulkier perovskite formation in addition to the zireonate perovskite,
BaThO3 (s)	Transpira- tion	BaThO3(s)+H2O(g) = Ba(OH)2(g)+ThO2(s), 1548 ≤T≤1683 K	Δ <sub>f</sub> G <sup>θ</sup> (BaThO <sub>3</sub> (s)) = - 1791.8+.27T, (±10 kJ mol <sup>-1</sup> )	and Ba release evaluation in accidental situation
SrThO3 (s)	Knudsen effusion	5SrThO <sub>3</sub> (s)+W(s)=3Sr(g)+Sr <sub>2</sub> WO <sub>5</sub> (s)+5ThO <sub>2</sub> (s), 1670 ≤T≤ 2040K 4SrThO <sub>3</sub> (s)+W(s)= 3Sr (g) +SrWO <sub>4</sub> (I)+4ThO <sub>2</sub> (s), 2135 ≤T≤2420 K	$\begin{split} \Delta_f G^0 & (SrThO_3(s)) = * \\ 1954 + 0.37T, & (\pm 10 \text{ kJ mol}^{-1}). \\ \Delta_f G^0 & (SrThO_3(s)) = * \\ 1960 + 0.37T \\ & (\pm 15 \text{ kJ mol}^{-1}) \end{split}$	-do-, and Sr release evaluation in accidental situation
RuTe2(s)	-do	RuTe <sub>2</sub> (s)=Ru(s)+Te <sub>2</sub> (g), 831 ≤T≤ 1148 K	∆fG <sup>0</sup> (RuTe <sub>2</sub> (s)) = -161.7 +0.10 T, (± 7 kJmol <sup>-1</sup> )	Te redistribution in alloy, and in gaseous species
Rh3Te2(s)	-do	Rh3Te2(s)=3Rh(s)+Te2(g). 1151≤T≤1234 K	$\Delta_{f}G^{0}(Rh_{3}Te_{2}(s)) = -176.9+$ 0.039T, (± 7 kJmol <sup>-1</sup> )	-do-
RhTeg,9 (s)	-do	3RhTe <sub>0.9</sub> (s)= Rh <sub>3</sub> Te <sub>2</sub> (s)+0.35Te <sub>2</sub> (g). 1151≤T≤1234 K	Δf <sup>G0</sup> (RhTe <sub>0.9</sub> (s))= • 4.7+0.015T , (± 3 kJ mol•1)	-do-
Ba(OH)2(g)	Transpiration	BaO(s)+H2O(g)−Ba(OH)2(g), 1346≤T≤1451 K	$\Delta_f G^{(j)} \circ (Ba(OH)_{2,g} = -667.3 + 0.12T (\pm 5 \text{ kJ mol}^{-1})$	Ba release in accidental situation

Thermodynamic investigations of fission products states in thoria based fuels

The following reaction equilibria has been studied by Knudsen effusion technique:

- (a)  $5SrThO_3(s) + W(s) = Sr_2WO_5(s) + 3Sr(g) + 5ThO_2(s),$  $1670 \le T \le 2040 \text{ K}$
- (b)  $4SrThO_3(s)+W(s)=SrWO_4(l)+3Sr(g)+4ThO_2(s),$ 2135  $\leq T \leq 2420 \text{ K}$

The following reaction equilibrium was studied by Transpiration technique

 $BaO(s) + H_2O(g) = Ba(OH)_2(g)$ 

## 7.2 TRANSPORT PROPERTIES OF GASES AND VOLATILE FISSION PRODUCTS AND OF THE FISSION GENERATED OXYGEN INSIDE FUEL

High temperature transport properties of the gas/volatile fission products, xenon, iodine and tellurium, and the fission-generated oxygen have been investigated after developing the required experimental facilities. The generated transport data of Xe, I, and Te show that their release rates are significantly less in thoria based AHWR fuels as compared to those in urania. The chemical diffusion study of oxygen in thoria fuel made so far shows that oxygen transport coefficient in the thoria based fuel is several



orders of magnitude lower than that in urania. Presently, the measurement of the chemical diffusion of oxygen in the thoria rich fuel is being extended to higher temperature (> 900 K) and under low oxygen pressure. The diffusion study of Xe, I, and Te in simulated thoria-urania fuels is also being carried out.



Post irradiation annealing apparatus

# 7.3 SOLID STATE CHEMISTRY RESEARCH ON NUCLEAR MATERIALS

## Phase relations and thermal expansion behaviour of thoria based systems

Since Thorium itself is not a fissile material in the thermal region of neutrons, in the Advanced Heavy Water Reactor, it is proposed to use about 2 to 6 % of fissile uranium and plutonium dioxides in the  $ThO_2$  matrix. Thermal expansion directly affects the performance of a fuel. As part of the programme identified by the Task Force on Thoria based Fuels, a number of systems were investigated for their phase relations and thermal expansion behavior. They are:

(i).  $ThO_2 - UO_2$ (ii).  $ThO_2 - CeO_2$ (iii).  $ThO_2$ :  $Mn + (M = Y^{3+}, Sr^{2+}, Ba^{2+})$ (iv).  $ThO_2 - M_2O_3$  ( $M = Nd^{3+}, Eu^{3+}, Gd^{3+} and Dy^{3+})$ (v).  $MThO_3(M = Sr, Ba)$ 

Lattice thermal expansion behaviour of  $ThO_2$ -2,4,6 wt %  $UO_2$  was investigated from room temperature to 1350°C by HT-XRD to reveal an increase in the average thermal expansion coefficient, which is more or less commensurate with the amount of  $UO_2$ . Thermal expansion behaviour of plutonia based composition was simulated using ceria as a surrogate material. It was found that the thermal expansion coefficient of  $ThO_2$  increases on substituting with CeO<sub>2</sub>. The linear thermal expansion coefficients

of  $BaThO_3$  and  $SrThO_3$  are higher than that of pure  $ThO_2$  by about 21.9 and 15.3 %, respectively. The nano-crystalline thoria powder, prepared by gel combustion technique, could be utilized for producing high bulk density thoria pellets relatively at lower temperatures (93 % at 1300°C). It was observed from these investigations that the thermal expansion behavior of thoria based mixed oxides depends on nature and concentration of the dopant species. Another observation was the role of lattice defects on thermal expansion behaviour. For these investigations, a thermodilatometer was indigenously designed and fabricated

# Phase Relations and Thermal Expansion Behavior of Inert Matrix Fuels

The development of uranium free inert matrix fuel (IMF) is of worldwide interest as this concept promotes faster annihilation of large stock of plutonium. In addition, this concept is also being contemplated to prepare targets for transmutation of minor actinides transmutation. In these fuels, an inert matrix serves as a support for the actinide phases, as does the non-

superior

fissile  $^{238}$ UO<sub>2</sub> matrix for PuO<sub>2</sub> in a typical fast breeder MOX fuel. The inert matrix, as the name suggests, does not lead to the formation of

any fissile material, after the

irradiation. A material to act as an

inert matrix has to satisfy a number of stringent conditions

e.g., a good neutron economy,

properties, compatibility with the cladding material, stability against

radiation, good mechanical

properties and insignificant leachability. A number of host

lattices are being considered to act as an inert matrix, for diluting plutonium, viz., multi-phase ceramic-ceramic composites (MCC) and ROX (rock-like oxides). India is having large deposits of thorium,

which is envisaged to be used for

thermophysical



Dilatometer for thermal expansion studies

nuclear power production. Thoria being a very stable oxide (chemically inert), could also be considered as a potential host

for diluting and burning plutonia. The inclusion of thoria is likely to improve the reactivity control of the inert matrix based fuel. In view of this, research program has been initiated on the IMF. Several ternary phase relations, as mentioned below, have been established after slowly cooling the samples from 1400°C.

 (i).
 CeO2-ThO2-ZrO2

 (ii).
 CeO2-Dy2O3-ZrO2

 (iii).
 CeO2-Gd2O3-ZrO2

 (iv).
 ThO2-Gd2O3-CeO2

 (v).
 YSZ-ThO2-CeO2

Ceria has been used as a surrogate material in place of plutonia for these studies.  $Gd_2O_3$  and  $Dy_2O_3$  are potential burnable poisons. Different phase fields could be identified by refining powder XRD data. A wide cubic phase field was observed in these phase relations. A few silicates having zircon type structure were also investigated. The thermal expansion behaviour of a few single phasic compositions, investigated by dilatometry and HT-XRD, has also been studied. A large number of single phasic compositions prepared during the course of this work are likely to be potential new nuclear materials.

D. Das <dasd@barc.gov.in>

S. Bharadwaj <htschem@barc.gov.in>

## 8. WATER CHEMISTRY FOR NUCLEAR FUEL CYCLE

#### INTRODUCTION

The power reactors based on water as coolant and moderator benefit from continual development of new water chemistry processes, which helps them to handle their immediate problems. These result in reduction in man rem burden and income in the bottom line. New ion exchange processes for boron removal from shutdown system, selective removal of gadolinium in presence of boron, purification of moderator by electrochemical filter, and chemical decontamination before maintenance are described in the contributions in this chapter.

Management of aqueous effluent of fuel cycle plants by biochemical processes appears attractive. Bioremediation is currently being investigated as an economically viable alternative to remove toxic metals and radionuclides in the waste materials. It also aims to recover the metal ions with commercial value like strategic metals, nuclear fuel materials and other radioactive elements. Chitosan, a natural bio-polymer, shows promise of recovery of actinides in the presence of inorganic salts.

#### 8.1 BORON CLEANUP

Recovery of D<sub>2</sub>O from the solution of lithium pentaborate solution (used in secondary shutdown system) has been evaluated with the mixed bed of strong acid cation exchanger and strong base anion exchanger with the capacity ratio of 1:1 as well as with strong base anion exchanger at various concentrations of lithium pentaborate. Boron removal capacity increased with the increasing concentration of lithium Pentaborate due to formation of polymeric species of boron at higher concentrations and the boron removal capacity of upto six times of the theoretical capacity could be obtained elaborating the presence of polymeric species containing even hexaboron at higher concentrations. The mixed bed configuration had shown faster kinetics of boron removal as indicated by the sharp breakthrough curve obtained as compared to that obtained with only anion exchanger. The ion exchange method is advantageous over the currently used energy intensive evaporative condensation method of D<sub>2</sub>O recovery.

#### D. Das <dasd@barc.gov.in>

## 8.2 DEVELOPMENTAL WORK ON SELECTIVE REMOVAL OF GADOLINIUM NITRATE- FOR TARAPUR ATOMIC POWER PROJECT # 3 AND 4

A scheme for selective removal of gadolinium nitrate in the presence of boron from moderator system of 540 MWe PHWRs was developed, employing mixed bed ion exchange resin with gel type strong acid cation resin in H+ form and macroporous weak base anion resin (topped with strong acid cation resin). The scheme was successfully employed in Tarapur Atomic Power Project # 4 during its first approach to criticality. A spectrophotometric method for monitoring gadolinium in moderator at 10 ppb level was optimized and employed at Tarapur Atomic Power Project # 4. The optimised method has improved the lower limit of detection from 20 ppb to 10 ppb.

H. Bose <hbose@barc.gov.in>

## 8.3 REMOVAL OF INDIUM METAL TURBIDITY FROM MODERATOR WATER IN NUCLEAR POWER REACTORS

A problem due to indium turbidity arose in Rajasthan Atomic Power Station (RAPS) -1 moderator system which originated from the indium sealant of the Over Pressure Relief Device of the Calendria Vessel. Two alternative procedures for removal of indium turbidity from RAPS-1 moderator system were developed and employed on experimental basis. One of the procedures involved the use of a Mg(OH)<sub>2</sub> precipitated weak acid cation exchanger and the other was an electrochemical filter constituting graphite felt as cathode and anode. Mg(OH)<sub>2</sub> precipitated cation exchanger has shown 97% indium turbidity removal while 85 to 90% removal efficiency could be achieved using electrochemical filter. Based on the results obtained, a large scale electrochemical filter has been designed. This has been fabricated at the Centre for Design and Manufacture, BARC, and will be tested for its efficiency for turbidity removal at RAPS.



Electrochemical Filter

#### 8.4 METAL ION PASSIVATION STUDIES

Though chemical decontamination is the ultimate cure for the reduction of radiation field, research work on how to slow down the radiation field buildup has been taken up. Metal ion passivation studies carried out on different austenitic stainless steels and martensitic stainless steel in presence of injected Zn2<sup>+</sup> and Mg2<sup>+</sup> have shown that the Zn additive not only inhibits cobalt pickup but also restructures the existing oxide. It was shown that Zn addition resulted in a higher reduction in the radiation field buildup than magnesium addition.

D. Das <dasd@barc.gov.in>

# 8.5 BIO-REMEDIATION OF Co-60 FROM DECONTAMINATION EFFLUENT

Bio remediation of Co-60 from the simulated spent decontamination formulation has been evaluated using various varieties of fungi and bacterium. Microorganisms generally take up the metal ions by two different mechanisms (a) biosorption and (b) bioaccumulation. A number of fungi both natural and mutant types have been tested for their sensitivity to cobalt pickup in presence of a large background concentration of iron, chromium and nickel under various experimental conditions.

Co-60 removal was successfully carried out in lab scale. In a typical experiment, from solution containing ~2 ppb level of Co (in excess of Fe ~3 x10<sup>5</sup>) in a few microgram (~1-2 µg) quantity, the former could be removed using 1g of the bacteria within first 3 hrs during the course of 48 hrs experiment. The bacteria were alive even at the end of the 48 hrs period.

Presence of high affinity Co transporter genes was found to be the main mechanism of Co removal. The Co pickup capacities exhibited by the fungi depended on the initial concentration of Co in the solution. Bioremediation of Co-60 using different bacterium possessing high affinity cobalt transporters, vitamin B12 and non-corrin cobalt containing enzymes has also been evaluated under various experimental conditions. The capacity for Co removal was of the order of  $\mu$ g/g for some bacterium while it was of the order of ng/g for some of the fungi.

D. Das <dasd@barc.gov.in>

## 8.6 BIOREMEDIATION FOR DECONTAMINATING THE LOW LEVEL RADIOACTIVE WASTES (LLW), DERIVED FROM PUREX AND TRUEX PROCESSES

An efficient bioremediation protocol for decontaminating the low level radioactive wastes (LLW), derived from PUREX and TRUEX processes has been developed. On the basis of extensive screening, the biomass from Rhizopus arrhizus NCIM 997 was found to be best suited for decontamination of radioactive wastes. Besides showing excellent capacity to remove Am-241 with good kinetics, it showed a pH-dependent differential selectivity for the actinides. For example, while it could sequester the trivalent actinides at pH 2, U and Pu ions were selectively adsorped at pH 6-7. Subsequently, a novel cross-linked biomass prepared from the microorganism showed good mechanical strength while retaining the metal ion trapping characteristics of the native biomass. This has been subsequently used for the treatment of LLW, delay tank solution, TRUEX wastes and even HLW after dilution. Its sorptive capacities for different metal ions were 9.93 and 807.6 g per g of the dry immobilized preparation respectively for Am-241 and Pu-239 at pH 2.0-6.0, and the stripping of the metal ions from the columns could be carried out easily with 1.0 M HNO<sub>3</sub>, leading to a considerable confinement of the waste volumes. The process has been developed successfully using 10 L LLW. The biomass is being currently explored by the Nuclear Recycle Group for its application in managing the LLW streams.



Native biomass







Column experiments with cross-linked biomass

S. Chattopadhyay <schatt@barc.gov.in>

#### 8.7 NUCLEAR EFFLUENT POLISHING BY CHITOSAN

In line with the Research and Development work on bioremediation, experiments have been carried out to explore the feasibility of using Chitosan for treatment of low level radioactive waste streams. Chitosan is a natural bio-polymer derived from chitin, which is a major component of crustacean shells.

In this context, systematic studies have been carried out to find the absorption characteristics of the actinides like Thorium, Uranium, Americium and Plutonium on chitosan in detail. The sorption of the metal ions by chitosan may be due to complexation of metal ion by the amino group, ion exchange by hydroxyl group, or simply micro-precipitation of metal ion on the chitosan matrix or by physical adsorption. Recovery of the material from loaded chitosan could be done easily with 1M Nitric acid. The study shows that chitosan can be used for treatment of low level effluents to further reduce the amount of radioactivity discharged into the sea and to recover the valuable elements even in presence of high concentration of inorganic salts.

	Initial concentration	Final concentration at various pH					
Radionuclides		3 PH	4 PH	5pH	6pH	8 PH	
Pu (μg/L)	2.00						
U (μg/L)	6.80	0.1 4	-	-	-	0.6 4	
Am (µg/L)	0.42						
Gross beta (µCi/L)	5.43	4.4 8	4.73	4.68	4.39	5.1 0	
Th (mg/L)	70	25	0.5	0.5	-	-	
U-233 (mg/L)	8	-	-	-	-		

Recovery of Actinides from simulated samples at various PH



#### D. N. Sharma <dnsharma@barc.gov.in>

## 8.8 DEVELOPMENT AND APPLICATION OF CHEMICAL DECONTAMINATION PROCESS

Chemical decontamination of the primary heat transport system of nuclear reactors used to reduce the radiation field near system components and piping prior to major refurbishment work during shutdown in order to decrease on man-Sv load. In PHWRs in India and abroad full system chemical decontamination has been carried out instead of component decontamination, as removal of radioactive deposit from the surfaces of feeders and headers is best done by full system chemical decontamination only. Such full system decontamination will be carried out with fuel present in the core. Hence the quality assurance for the performance of the chemical formulation has to be quite stringent.

Water and Steam Chemistry Division has carried out extensive

	MAPS #1	MAPS #2	MAPS #1	MAPS #2	MAPS#2	RAPS #1
Date of Campaign	Dec-93	Apr-95	Nov-97	Feb-99	Jan-02	May-02
Duration (h)	19.00	21.50	22.75	20.50	18.5	22
Formulation	EAC	EAC	EAC	EAC	NAC	NAC
IX Rad.waste (m²)	4.5	5.2	5.0	6.5	7.0	7.0
Fe removed (kg)	233	203	163	254	222	232
60-Co(Ci)	346	121	155	46	12.9	40.3
Total activity (Ci)		138			35.8	50.8
DF on Pumps	7- 30	2 - 6	1.3 - 2.7	1.2 - 5	1.3 - 6.0	3 - 5.4
DF on Boiler cabinets	1-4	7 • 2	1.3 - 10	1.8 - 8.0	2 – 12.5	1.3 - 2.4
DF on Feeder cabinets	7 - 30	10-17	3.3 - 20	4.5 - 15	2 - 7	4 - 5
Dose Averted (MANREM)	400	490	300	~300	50% for EMCCR	80% for ISI

Dilute chemical dicontamination if Indian PHWRS: A performance statistics research and development and optimized on a mixture of ethylene diamino tetra acetic acid (EDTA), ascorbic acid, citric acid. At a total concentration level of 1 g/lit, this formulation was used in a dilute decontamination campaign (DCD) of a few Indian reactors where good DF was achieved on carbon steel surfaces as given in the table. In an advanced formulation the pick up of EDTA by cation exchanger during the decontamination was reduced considerably by substitution of nitrititriacetic acid.. There was no considerable change in the performance of the DCD formulation or its efficacy.

This will permit decontamination of Incoloy 800 tubes also along with carbon steel in a single run. It is necessary to alter the conditions of chemical decontamination. The base metal susceptibility to corrosive attack and the rate of dissolution of oxide deposited over carbon steel and Incoloy differ considerably in the decontaminating

formulation at 80-90°C. By employing a formulation at 150°C, simple acid aided dissolution of the Cr containing oxide occurred.

S. V. Narasimhan <svn@igcar.gov.in>



# 9. HEAVY WATER TECHNOLOGY

## INTRODUCTION

Heavy water production technology in India has reached a mature stage. The technologies and products developed in the process have numerous spin-off, applications in other industries. Deuterium standards provided by BARC help the nuclear the nuclear power reactor operators maintain the quality of the moderator. The research community's demands for deuterium labeled compounds are met. The R&D efforts are directed towards processes involving removal of tritium impurity , and efficient contactors for the isotope separation. The high efficiency tower internals are a proprietary product, which have new applications in O-18 isotope separation and B-10 enrichment by distillation.

# 9.1 DEUTERIUM STANDARDS AND LABELLED COMPOUNDS

#### Heavy Water Standards

Certified heavy water standards are essential for quality assurance in the PHWR power stations. High isotopic purity heavy water standards were prepared for use at Tarapur Atomic Power Project (TAPP 3 & 4) and for Rajasthan Atomic Power Project (RAPP 3 & 4) for analysis of isotopic purity of high grade/ concentrations heavy water samples. Six heavy water standards of different isotopic purity were prepared during the last 2 years and were sent to TAPP 3 & 4 and RAPP 3 & 4.

In all, about fifteen such heavy water standards of different isotopic purity values have been prepared and sent to different power stations in India. A picture of two such drums is shown below.



Heavy water standards of high accuracy were prepared and supplied to Heavy Water Board for exports

## Synthesis, Preparation and Application of High Purity Deuterated Compounds.

Deuterated Chloroform (CDCl<sub>3</sub>) was prepared for its use in NMR studies. Various deuterated organic compounds were synthesized and supplied to different universities and R&D institutes to study reaction kinetics and mechanism.

Deuterated compounds were synthesized for preparation of high sensitive radiation detectors.

The distribution pattern of nutritional values between the mother and infant were studied in collaboration with Rajasthan Agricultural University by analysing the deuterium content in milk and saliva samples.

H. Bose <hbose@barc.gov.in>

#### 9.2 HEAVY WATER PURIFICATION

# Design & Development of Combined Electrolysis and Catalytic Exchange Technology

The moderator inventory in the PHWR needs to be cleanned up continually of tritium to maintain the activity levels prescribed by Atomic Energy Regulatory Board. A Combined Electrolytic and Catalytic Exchange (CECE) process was developed earlier in Heavy water division. The design of a pilot plant based on CECE has been completed. The plant which is being set up will help in detritiation of heavy water at room temperature resulting in reduction of the cryogenic load substantially.

The CECE Pilot Plant facility will be used to study the process parameters and develop the necessary design information for



setting up a full-scale plant for detritiation of Heavy Water for 220 MWe PHWR. The present Pilot Plant is designed to handle maximum liquid  $D_2O$  feed rate of 2 - 4 LPH with a tritium level of approximately 5 Ci/lit.

The CECE process employs electrolytic cell to provide bottom reflux in the form of  $D_2 / DT$  gas. D2 / DT gas is allowed to pass through a de-oxo bed to remove any Oxygen ( $O_2$ ) present as impurity and then through catalytic exchange column counter current to the tritiated  $D_2O$  liquid (see figure). The  $D_2 / DT$  gas depleted with respect to tritium comes out from the top of the Catalytic Exchange Column and enters a burner condenser where it is recombined and condensed to provide top reflux to the Catalytic Exchange Column. The feed to this pilot plant is tritiated heavy water and enriched tritiated gas from the electrolyser is fed to cryogenic distillation system where it gets detritiated.

V. K. Tangri <vktangri@barc.gov.in>

S. K. Das <skdas@barc.gov.in>

#### Off-line Heavy Water Purification Unit

In order to purify oil contaminated impure heavy water accumulated since the initial years of reactor operation, a sorption/ion-exchange scheme was developed and the design for a purification unit was worked out. Subsequently with the collaboration of Reactor Operation Division, an off-line assembly was fabricated and installed at Dhruva. About eight tons of waste heavy water has been successfully purified to date. The purification scheme was a variant of a method employed earlier



in Cirus to purify three tons of heavy water during the refurbishing outage.

H. Bose <hbose@barc.gov.in>

## 9.3 DEVELOPMENT OF HIGH EFFICIENCY TOWER INTERNALS

Heavy Water Division is actively involved in the development of a variety of high efficiency tower internals, for vapor-liquid & gasliquid separation. The main objective is to achieve minimum plant volume for desired separation in addition to energy saving. The internals have been tested and now used for the following applications.

## Phosphor Bronze corrugated wire mesh structured packing

Phosphor bronze packing are being fabricated for commercial upgradation and final enrichment of heavy water. Nine final enrichment towers and fourteen upgrading towers have been



Fabrication facility of highly efficient distillation packing

supplied to Heavy Water Board & NPCIL respectively. The state of the art Instrumentation and controls has been provided for Heavy Water-Upgrading Plant for improved performance.

## Packing for O-18 distillation

Small sized tower packing has been recently developed and incorporated in Oxygen- 18 enrichment pilot plant & Cryogenic application.



Packing modules for Cryogenic Application



Test Facility for Performance Evaluation of commercial size packing



Control Room of Upgrading Plant at Heavy Water Division

- V. K. Tangri <vktangri@barc.gov.in>
- S. K. Das <skdas@barc.gov.in>



## **10. ISOTOPE SEPARATION**

# INTRODUCTION

Isotope separation science and technology have grown mainly due to the demands made by nuclear industry. Being one of the most difficult processes, the scientists have kept on innovating to find more efficient processes. The processes developed for isotope production for nuclear fuel cycle are also useful for producing medical isotopes. Lasers with the narrow bandwidth, high intensity, low divergence, pulse duration control are a boon to photochemical separation of isotopes. The CO<sub>2</sub> laser has been used for macroscopic production of C-13 isotope. Two processes for B-10 enrichment namely, distillation and Ion exchange chromatography, have been developed to a mature level and deployed at the users' site.

#### 10.1 MOLECULAR LASER ISOTOPE SEPARATION

Laser separation of light and middle-mass isotopes like carbon-13, sulphur-33 and oxygen-18 by selective photochemical methods is of interest to the medical community. The major activities involved in the development areas of these processes are :

- a) Laser selective photophysics and photochemistry of various polyatomic molecules
- b) Dynamics of infrared multiple photon dissociation (IRMPD) processes probed with elegant time-resolved techniques like infrared fluorescence (IRF), optoacoustic ( OA ) and uv - visible kinetic spectrometry.
- c) Development of required infrared lasers
- d) Production of Carbon isotopes

Laser and Plasma Technology Division has developed the process for laser separation of carbon isotopes, and now in the process of developing it for macroscopic production.

Natural carbon consists of two stable isotopes, viz. C-13 (1.11%) and C-12 (98.99%). Carbon-13 is an important isotope as a tracer in chemistry, life science, medicine, and biochemical synthesis. An optimistic projection of hundred-fold increase in the demand is anticipated in view of rapid development of routine medical applications such as breath tests and whole body NMR.There are immediate uses of such isotopes in DAE activities like high resolution spectroscopy, catalyst development, isotopically labelled gas lasers, tracer in biology and making `super' diamonds. In view of the growing demand, Laser & Plasma Technology Division is actively engaged in developing MLIS processes.

The process is based on  $CO_2$  laser induced Infrared Multiple Photon Dissociation (IRMPD) of  $CF_2HCI$  molecule. Excitation and dissociation selectivities are extremely high for this system so that  $CF_2HCI$  MPD is possible even at fairly moderate pressure (133 mbar) at room temperature yielding  $C_2F_4$  with 50 % 13-C: The prototype facility with the major components is shown in the figure. (1) Laser and accessories include various optical elements like windows, gratings, mirrors, lenses etc, detectors



of energy and temporal profile, oscilloscopes and control electronics

- (2) Photochemical reactor (PCR) incorporates a Herriott multipass refocusing (MPRF) optics in flow configuration with circulatory pump / blower, mass flow meter, metering valves, pressure transducer etc.
- (3) Product separator / collector consists of (i) cryogenic distillation unit and (ii) preparative gas chromatograph
- (4) Diagnostics includes FTIR spectrometer, gas chromatograph and quadrupole mass spectrometer
- (5) Feed gas handling system with purifier etc. form an integral part of the facility.

Presently, in a production run of 8 hr, the unit provides about 100 mg of Carbon ( 40% C-13 ) with 10 Hz CO<sub>2</sub> laser (ca. 20 gm / yr ). Overall, this facility has generated database, operating experience and trained manpower in the general area of laser processing of high value and strategic materials. Based on this expertise and infra structure developed, the processes for Laser Separation of Oxygen-18, and Sulphur-33 isotopes are being developed.



L. M. Gantayet <headlptd@barc.gov.in>

A prototype facility for laser separation of carbon isotopes in L&PTD, BARC

#### **10.2** <sup>10</sup>B ISOTOPE ENRICHMENT

## Exchange Distillation Plant

Enriched <sup>10</sup>B is essential to Fast Reactor programme. It is also useful for nuclear instruments. The technology of isotopic enrichment of <sup>10</sup>B has reached a mature stage. The plant based on the exchange distillation had been set up by Chemical Engineering Division, operated and  $\sim 90\%$   $^{10}B$  in the form ethyl ether complex was produced

The material was supplied to Nuclear Physics Division, Electronics Division and Electronics Corporation of India for use in neutron counters. Subsequently, the plant was relocated at Heavy Water Project (HWP), Talcher, where it has been made operational. Chemical Engineering Division provided the conversion kit



Product Reflux (Reboiler)

(  $BF_3$  ethyl ether complex to  $BF_3CaF_2$  complex), isotopic analysis support and trained the HWP plant personnel in operation of the plant and associated works.

#### Ion Exchange Plant

Another process of <sup>10</sup>B enrichment was developed by Chemical Engineering Division based on ion exchange process, namely displacement chromatography. The plant was set up and operated for over a year and ~ 50% B<sup>10</sup> in the form of boric acid was produced. This material was supplied to Electronics Division. Some material of ~ 30% B<sup>10</sup> was supplied to IGCAR, Kalpakkam for their use. This Division provided consultancy to IGCAR and shared the operating experience with their engineers build a bigger plant based on displacement ion chromatography.

S.K.Ghosh <skghosh@barc.gov.in> H. Rao <hrao@barc.gov.in>





# **11. CRYOTECHNOLOGY**

### INTRODUCTION

Cryogenic refrigeration technology in the temperature range of 20 K to 2 K, is an essential input for other advanced technologies. BARC has set out a road map for acquiring core competence in this important area. Development of cryogenic systems concerns with technology generation for the cryogenic needs of DAE with a special reference to cryo-distillation of hydrogen isotopes and the Accelerator Driven Sub-critical System (ADS) project.

In a significant development effort, a fully indigenously designed helium based 20 K cryogenic refrigerator has been fabricated and tested. All the critical components, cryogenic turbo expander, heat exchangers, bearing, bellow sealed valves, transition joints, feed throughs also have been indigenously developed. The chapter shows the capability of BARC in mastering this advanced technology.

## 11.1 CRYOGENIC SYSTEM DEVELOPMENT

## Helium Gas based Cryogenic Refrigerator (1kW at 20 K).

Cryogenic Technology Division has developed a cryogenic refrigerator for 1kW of refrigeration at 20 K with helium gas as the refrigerant and installed at Engineering Hall no. 8, BARC, Trombay. This refrigerator can be used for cryo-distillation of hydrogen isotopes and has undergone operational tests The plant is based on reversed Brayton cycle with two stage turbine based expansion. The system, in effect, consists of a cold box housing components such as turboexpanders, brazed plate and fin heat

exchangers, gas purifiers and piping with cryogenic extended stem valves together with temperature sensors, pressure transducers and vibration monitoring instrumentation for the turboexpanders.



The prototype 1kW at 20K Cryogenic Refrigeration system developed and installed at BARC.



A close-up of the prototype refrigeration system showing turboexpanders, extended stem valves, and external piping mounted on the top cover of the cold box

The operational tests revolve around measuring cool down time, lowest temperature reached, turbine speeds, vibration, and overall system reliability. Preliminary tests conducted have enabled us to reach a lowest temperature of 14.9 K without any refrigeration load. The cryogenic system has been tested with a refrigeration load of 200 W at 16.5 K. The turboexpanders reached an operational efficiency of about 60% during loading.

#### Test Set-up

A test set-up has been built to test the efficiency and vibration levels of turboexpanders, efficacy of vacuum system, cryogenic insulation, indigenous temperature sensors and overall system performance and reliability. These apart, air screw compressors modified for helium service are being used to provide first hand data regarding the viability of using such compressors in larger plants in future. Currently, the test set-up can accommodate a single turboexpander and a temperature of about 170 K is achieved. A second cold-box when incorporated with the facility would allow to simulate plant conditions in laboratory with a full two staged expansion.



Laboratory test set-up built to test the performance of turboexpanders, efficacy of vacuum system, cryogenic insulation, indigenous temperature sensors and overall system performance and reliability



Air compressors modified for helium service are being used for laboratory test set-up



Turboexpander mounted on the test bench

## 11.2 DEVELOPMENT OF CRITICAL COMPONENTS FOR CRYOGENIC SYSTEMS:

#### **Cryogenic Turboexpanders**

Turboexpanders, being the active cooling component of modern plants are considered the heart of the system. The mixed-flow turbines rotate extracting energy from the high pressure process stream thereby inducing the cooling. Cryogenic conditions necessitate the use of smaller gas passages in the turbines that translate into small size and correspondingly high speed for high operational efficiency. For our process, turbines of two different sizes (16 mm and 26 mm diameter) are planned to be employed. The smaller of the two designed to achieve a speed of around 2,40,000 r/min, have already been developed and tested in existing plants with satisfactory performance.



Miniature turbomachinery: expansion turbine and brake wheel

The turboexpander rotor consists of a vertical shaft with a turbine and a brake compressor wheel mounted at the two ends. The shaft consists of a collar, which together with flexibly supported spiral grooved plates, forms the axial/thrust bearing system. The cantilever arrangement of the grooved top thrust plate ensures higher flexibility at the outside diameter of the bearing to conform to the shaft collar shape during conical whirl. To prevent wear during occasional touches at high speeds, the bearing surfaces are provided with a hard coating. Precision photo-etching techniques required for fabrication of the grooves have been developed and standardised. The high speeds required for high



Turboexpander rotor with turbine (R) and brake (L) wheels mounted at the ends



Brake wheel





Expansion turbine wheel





Turboexpander rotor with tilting pad bearing housing



Balancing machine developed in conjunction with Shenck Avery for vertical in-situ balancing of rotors

operational efficiency of the system presents typical problems of radial bearing instability. Tilting pad journal bearings consisting of three pads per bearing and possessing excellent stability characteristics constitute the journal bearing system. The entire bearing system is designed to provide enough damping to cross over critical speeds easily. The balancing problem of the high speed rotor was addressed with a specially developed vertical in-situ balancing machine as well as a small (capacity less than 2 kg) rigid bearing precision horizontal balancing machine.

## ■ Heat Exchangers for Cryogenic Service.

High effectiveness (in excess of 0.95) brazed plate and fin heat exchangers are a necessity for modern high performance cryogenic plants. As the technology for these exchangers (fins, large brazing furnaces, transition joints, etc) is not available in India, Cryogenic Technology Division has undertaken development of these components. In a transition joint between aluminium and SS 304 pipes using diffusion bonding techniques have been fabricated at the Centre for Design and Manufacture, BARC. The joint withstood a full vacuum (Leak tight to 10<sup>-10</sup> mbar.l/s) and pressure holding of 30 bar. As a step towards the future development, high effectiveness (0.97 or higher) matrix type heat exchangers, which are used in small cryo coolers, have been designed.



Transition joint between aluminium and stainless steel pipes

#### Accessories for Cryogenic Systems.

Most valves used in cryogenic processes need extended stem with thin wall to serve the following primary purposes:

- a) The valve handle is maintained at ambient temperature to protect the operator (whether operated manually, pneumatically, or by solenoid),
- b) The valve stem may be sealed at ambient temperatures instead of cryogenic temperatures, thereby eliminating a severe sealing problem and improving the reliability of the valve, and
- c) In order to prevent a loss of cold from process to environment. Special long stem bellow seal cryogenic valves have been developed for use in the proposed helium liquefier. Ceramic feed-through for wire connections (temperature sensors) inside the high-vacuum cold box, have also been developed indigenously.



Indigenously developed extended stem bellow seal cryogenic valve



Indigenously developed 5-pin ceramic feed-throughs

Trilok Singh <tsingh@barc.gov.in>



# 12. FUEL CELLS AND ELECTROCHEMICAL TECHNOLOGY

### INTRODUCTION:

The generation of energy by clean, efficient and environmental-friendly means is now one of the major challenges for engineers and scientists. One such technology is the solid oxide fuel cell (SOFC), which is one of the most efficient and environmental-friendly technologies available for generating power from hydrogen, natural gas, and other renewable fuels. New low temp ceria based ionic conductors, instead of the high temperature yttria stabilized zirconia and also new low temperature cathode materials are being studied. The completion of the scaled up version of the industrial electrolytic cells for production of fluorine, and the compact water electrolyser for defense laboratories demonstrate the capability in electrochemical technology. This experience has been used in designing the 5 KW solid oxide fuel cell.

#### **12.1 CHEMISTRY OF FUEL CELLS**

## Development of Newer Electrolytes for IT-SOFC and Testing their Performance

The state-of-the-art electrolyte for the current generation SOFC is yttria stabilized zirconia (YSZ), which has high ionic conductivity only at high temperature and therefore the operating temperature is about 1000°C. The high operating temperature results in severe compatibility problems with the other components of the SOFC such as the cathode material. Moreover expensive alloys have to be used in the fabrication of the cell, if the operating temperatures of SOFC are brought down, it would bring both technical as well as economical benefits. Therefore, newer electrolytes that have high ionic conductivity at lower temperature should be developed to be used in Intermediate Temperature Solid Oxide Fuel Cells (ITSOFC).



Test facility for wafer size SOFC

Ceria based oxide ion conductors are of potential interest because doped ceria exhibit a significantly higher ionic conductivity at intermediate temperatures. . Rare earth doped ceria have been prepared and characterized as a low temperature electrolyte. A



Closer view of the test facility

test bed has been designed and fabricated which will be used to test the performance of wafer sized single cell using the newer electrolyte materials along with other newer cathode and anode materials.

## Physicochemical Studies on Cathode Materials for ITSOFC

Lowering the operating temperature of SOFC brings in other problems such as kinetics of electrode processes. Cobaltites, nickelates and ferrites are known to enhance the electro-catalytic activity of the cathodic reaction and therefore can be used as cathode materials at lower temperatures.

In this context, Co, Ni and Fe substituted Lanthanum Strontium Manganite (LSM) were investigated for their suitability as cathode materials. The effect of Co, Ni and Fe substitution (in place of Mn in LSM) on the thermal expansion, conductivity and microstructure of the compound were studied in detail. The chemical as well as mechanical compatibility of materials like  $La_{0.95}MnO_3$ , LSM and  $(La_{0.8}Sr_{0.2})_{0.95}Mn_{1-x}M'_xO_3$  (M' = Fe, Co and Ni) with electrolyte materials viz., Sm or Gd doped Ceria and YSZ was carried out at both operating (900°C) and fabricating temperature(1400°C).

D. Das <dasd@barc.gov.in>

S. Bharadwaj <htschem@barc.gov.in>

#### **12.2 FUEL CELL TECHNOLOGY**

Heavy Water Division is developing the fuel cell developmental activity to demonstrate the technology for 5 kW Solid Oxide Fuel Cell (SOFC) and 1kW Proton Exchange Membrane Fuel Cell (PEMFC). A roadmap has been envisaged for the development of the prototype fuel cell system, in which a centarlised fuel cell fabrication and test facility will be set up.



Pursuing the goal of self sufficiency in critical technologies, Chemical Engineering and Technology Group, BARC is carrying out sustained R&D work on Fluorine Process Technology. With an objective of improving technoeconomic parameters, an industrial scale fluorine cell has been developed, commissioned successfully and integrated with fluorination plant. Development of the fluorine electrolyser involves thorough understanding of nanoscale/ microscale phenomena at electrode-electrolyte interface and their influence on production scale performance of the unit. Specific energy consumption and service life of

The conceptual SOFC fuel cell system consisting of various sub systems such as fuel reformer, SOFC cell stack, waste heat recovery and DC/AC inverter is given in the SOFC schematic. The sulphur-free CNG is reformed to generate hydrogen rich fuel for the SOFC stack. The fuel and the air (oxidant) are fed into the fuel cell (working at 1000°C) which electrochemically produce DC electricity that is transformed into AC by the DC/AC inverter. The hot product gases of SOFC stack are used to heat the CNG feed / air. The hot unreacted fuel and residual air are catalytically burnt in the catalytic recombiner and the heat generated is recovered by preheating of the incoming feed water to the reformer.



V.K.Tangri <vktangri@barc.gov.in>

S. K. Das <skdas@barc.gov.in>

#### 12.3 ELECTROCHEMICAL TECHNOLOGY

# Commissioning of high Capacity Fluorine Electrolytic Cell

electrodes are being improved. This unit will not only meet the increased in house requirement of fluorine but will also pave way for indigenous development of fluorine based non-nuclear applications such as production of SF6 and other useful fluorine compounds.

Prasad <csrprasad@barc.gov.in>

#### Advanced Compact Electrolyser

An advanced high current density compact electrolyser meeting the stringent technical and environmental requirements of DMDE, Hyderabad has been designed, installed and demonstrated satisfactorily.

This Prototype electrolyser plant is a very compact oxygen generator with an oxygen production rate of 4.35Nm<sup>3</sup>/hr at temperature 55°C and pressure 1.6Kg/cm<sup>2</sup> (abs). The electrolyser used a 40 cell module (weighing about 1 ton) incorporating porous Nickel electrodes, which can operate at a high current density of 4500 amps per sq. meter.

The feed to this pilot plant is tritiated heavy water and enriched tritiated gas from the electrolyser is fed to cryogenic distillation system where it gets detritiated.



Advanced Compact Electrolyser

V.K.Tangri <vktangri@barc.gov.in> S. K. Das <skdas@barc.gov.in>



# 13. NATURAL PRODUCT CHEMISTRY

## INTRODUCTION

Recent advances in biological and material sciences have led to the demand of target specific specialty chemicals. These are essential not only in the high-tech atomic energy programmes, but also for societal benefits. Use of natural reserve and development of new green synthetic technology are the focus of R&D in the biological chemistry. A low cost phytohormone, developed in BARC has demonstrated improvement in silk cocoons. Similarly, the use of para pheronmones to control pest damage to the tuber crop has been patented. Aroma gylcosides are bound aroma compounds are known to be precursors of aroma compounds in food. Release of free aroma compounds from their glycosidic precursors results in enhanced aroma of foods during processing and storage. Role of aroma glycosides in contributing to the unique aroma of fruits (Pomegranate) and spices (Nutmeg) and monsoon coffee was demonstrated.

A process for production of Xanthan gum, an additive with special rheological property, was demonstrated on an industrial bench scale. The chapter also describes bioactive compounds prepared by biosynthesis route.

#### **13.1 BIOLOGICAL CHEMISTRY**

Considering the great bio-diversity of Indian flora, phytochemical research is anticipated to provide potent radiomodifiers and anticancer agents as well as formulations for eco-friendly agriculture and sericulture. To this end, a new polysaccharide obtained from the Indian medicinal plant, Tinospora cordifolia has been found to possess impressive immunomodulatory (Indian Patent 183805) and radioprotective properties. The tissue culture technique has been evoked for its optimized generation.



Silkworm feeding on mulberry + phytohormone



Aromatic plants for high-value chemicals

A cheap moulting phyto-hormone (MH) preparation that provides better quality of silk in a short time has been developed from an indigenous natural source. The MH formulation was prepared by a continuous extraction technique using an indigenous plant that is widely growing in the costal region of India. Application of the formulation at a very low concentration (20 ppm) assists in faster and uniform spinning of the silkworms leading to better silk productivity with minimum loss of silk. The MH technology has been developed up to a scale of 5 kg of the plant. The product is given to Central Sericulture Research & Training Institute, Mysore for free distribution to silk farmers.



Improved silk cocoons after phytohormone

#### Application of phyto-hormone for sericulture

In the area of chemical biology, the radioprotective and ironmodulatory activities of folic acid has been established, and the involvement of a C-centred over a N-centred radical in its oxidative cleavage has been proven using fast techniques. In related efforts, various new concepts such as the positive roles of 1,3-diketone function and unsaturated terpenoid side chain (via allylic proton abstraction) in preventing free radical induced biological damages have been introduced.



Coralyne-induced photo-damage of A431 cell line mitochondria. 1. control cells, 2. with coralyne, 3. with UV-light, 4. with coralyne & UV-light

Two novel hydroxystilbenes with equivalent radioprotecting and anticancer properties as that of resveratrol has been developed via rational drug design. The resveratrol analogues induce copper (II)-mediated DNA damage as revealed by comet assay, explaining their bioactivity. The photo-nuclease activity of the plant-derived alkaloid, coralyne and its possible use against skin cancer cell lines have been established. The process involves primarily mitochondria damage of the used cancer cells (A431) without affecting the lysosome.

S. Chattopadhyay <schatt@barc.gov.in>



Coralyne-induced photo-damage of A431 cell line lysosome. 1. control cells, 2. with coralyne, 3. with UV-light, 4. with coralyne & UV-light







#### **13.2 AGRICULTURAL CHEMISTRY**

Insect pheromones, the communication chemicals for insects, are of great importance as they can provide viable, eco-friendly solutions in modern Integrated Pest Management (IPM) programmes. An IPM package using pheromone technology has been developed to control the sweet potato weevil (SPW) induced damage to the tuber crop, thereby increasing its marketable yield. Several parapheromones (Indian Patent 190568) for the cotton pests have been devised and synthesized from renewable natural sources. Field application of the parapheromones improved the productivity of cotton, the most important Indian cash crop. The pheromone and parapheromone technologies have been established for the field application stage. The SPW pheromone is used for the All India Coordinated Field Trials being conducted by the Centre of Tuber Crop Research Institute, Thiruvanthapuram.



A pheromone-baited trap

#### **13.3 SYNTHETIC BIO-ORGANIC CHEMISTRY**

#### Asymmetric Synthesis

This challenging area of organic research plays a crucial role in the synthesis of high-value products required in medicinal and



Insect catch in a pheromone Application of pheromone technology for the control of sweet potato weevil

high-tech areas. Several efficient asymmetric methodologies have been devised using biocatalysts, designing novel chiral aminol and hydroxythiol auxiliaries as well as employing chiral pool materials (sugars, amino acids). Especially using solvent engineering, biocatalysts have been used to carry out diastereoselective transformations, tune selectivity of the enzymatic reactions and separate olefinic isomers. The methodologies were subsequently used for the syntheses of various cytotoxic compounds (duryne), enzyme inhibitors (SPIKET-P), anti-tumour compounds etc.



#### Organometallics

The low valent titanium (LVT) reagents that can carry out various single electron transfer (SET) reactions exist as intermetallic highly coordinated species. Using external additives such as solvents, n - and - donor ligands, redox agents and ionic salts, a series of LVT reagents (Patent No. BOM/56) with modulated SET potential has been prepared via rational design. These reagents have been

used in chemo- and stereoselective fashion to synthesize antioxidant stilbenoids, and other bioactive oxygen heterocycles as well as supramolecular cyclophane assemblies. Various new chemistry have been developed using organo silicon and selenium compounds, which have been used for the synthesis of peptides (used in nuclear medicine and as food additive) as well as medicinal heterocyclic compounds.

S. Chattopadhyay <schatt@barc.gov.in>

## 13.4 IDENTIFICATION OF NEW AROMA IMPACT AND BIOACTIVE COMPOUNDS

(1) Monsooned coffee: Monsooned coffee is a specialty coffee of India valued for its unique flavour. Major compounds responsible for its characteristic aroma were identified as iso-eugenol and 4-vinyl guaiacol.



These compounds were released from their glycosidic precursors during the monsooning process. Mechanism of monsooning process was elucidated for the first time. Radiation processing was found to enhance the monsooning process and could be utilized to considerably reduce the processing time for this speciality coffee.



(2) Pomegranate: The delicate aroma compounds of the pomegranate fruit were characterized by GC/MS and GC-Olfactometry as hexanol, cis-3-hexenol and (Z)-3-octenyl acetate with the acetate imparting a strong characteristic fruity aroma. This is the first report on the identification of aroma impact compounds of pomegranate.

(3) Turmeric: Novel natural phenolic compounds with significant antioxidant activity were isolated and identified for the first time in turmeric. These include yet to be named compounds I, II & III of chemical structures.

(4) Nutmeg: A novel fluorescent napthaquinone derivative, the content of which increased with radiation dose, was identified in nutmeg based on its mass fragmentation and NMR data.





Excitation and emission wave lengths of this compound were found to be 277 and 565 nm, respectively.

- A. K. Sharma <ksarun@barc.gov.in>
- P. S. Variyar <pvariyar@barc.gov.in>

### **13.5 PRODUCTION OF XANTHAN GUM**

Xanthan gum is a high molecular weight anionic polysaccharide produced by the fermentation of a carbohydrate source with *Xanthomonas campestris*. This polymer exhibits three desirable



properties: (1) high viscosity at low concentrations; (2) pseudoplasticity; and (3) insensitivity to a wide range of temperature, pH and electrolyte variations. Because of its special rheological properties, xanthan is used in food, cosmetics, pharmaceuticals, paper, paint, textiles, adhesives and oil and gas industry. The flow characteristics of xanthan, coupled with its stability to salts and extremes of pH, gives it a technical advantage over the most polymers used in drilling. The greatest potential for xanthan gum appears to lie in the enhanced oil recovery operations.

A process for producing xanthan gum using Xanthomonas campestris pv glycines was developed using a 30 L fermenter. The process parameters have been optimized for a 20L batch to achieve increased yields of xanthan gum. This yield was obtained by using a modified production medium.

A. K. Sharma <**ksarun@barc.gov.in**> P. S. Variyar <**pvariyar@barc.gov.in**>





# 14. CHEMISTRY AND LASERS

#### INTRODUCTION:

Since the invention of the laser, chemists have been interested in using its radiation as a reagent to drive chemical reactions, with the hope that lasers could be used to inject energy selectively into a specific chemical bond, thereby causing the particular bond to break. Although the final goal is to achieve active control of chemical reactions, the first step towards this endeavour is to understand the microscopic details of chemical reactions. In the course of photo and radiation chemical processes, reactants are converted into products with the possibility of various transition states and transient intermediates on the reaction pathway. Lifetimes of these intermediates vary from a few tens of a femtosecond to seconds. Femtosecond time resolution is the ultimate achievement for studies of fundamental dynamics of the chemical reactions. With femtosecond lasers, it is now possible to record the snapshots of chemical reactions with sub-angstrom resolution. A chemical reaction can be reduced to a number of elementary reactions – breaking and forming of chemical bonds, energy transfer within and between molecules, electron transfer, proton or hydrogen atom transfer, etc. Understanding a chemical reaction at atomic or molecular level not only requires a description of the reactants and products, but also the interaction with the medium or surroundings, in which the reaction takes place. The contributions in this chapter describe the study of the molecules of interest to dye sensitized solar cell, solvent relaxation dynamics in micellar media. The use of time resolved laser induced fluorescence (TRLIF) for estimation of low concentration of actinides in the nuclear fuel cycle is yet another application of lasers. Indigenous development of new laser host materials by polymer chemistry is a contribution of chemistry to laser technology.

## 14.1 CONDENSED PHASE PHOTOCHEMISTRY AND CHEMICAL DYNAMICS

#### Photoinduced Electron Transfer

Electron transfer (ET) reactions are ubiquitous in chemistry and biology. All redox reactions in chemistry involve ET in some way or the other. Understanding the mechanisms and dynamics of ET processes in different media is an important research area of Radiation and Photochemistry Division. ET under diffusive (donoracceptor in noninteracting solvent) and nondiffusive conditions (electron donor as the solvent) are mechanistically different, and cannot be treated on the same footing to correlate their dynamics. Under diffusive condition, due to the intervention of solvent molecules between the reacting donor-acceptor pairs, the ET process becomes much slower than in nondiffusive conditions.

Inversion in the ET rates at higher exergonicities is an important prediction of Marcus ET theory, for which experimental demonstration was lacking for a long time. Typical Marcus inversion behavior for intermolecular ET reaction remained illusive, due to the limitation imposed by the diffusional rates on the observed reaction rates. Carrying out intermolecular ET reactions judiciously in heterogeneous media, like micelles, the above limitation of the diffusional process was removed effectively and Marcus inversion was convincingly demonstrated for the first time.

Though amines are normally considered as the efficient electron donors, it is observed that for the same exergonicity, aliphatic amines are substantially weaker in their electron donating abilities than aromatic amines. Lower electron donating abilities of aliphatic amines is related to the localized shape of the highestoccupied molecular orbitals (MO) of these donors as compared to the highly delocalized MOs of the aromatic amines.

Solvent relaxation dynamics are of direct relevance to ET processes and was extensively studied in different micellar media using the time dependent emission spectral shift. Results indicate that micellar size, structure and hydration play significant roles in determining solvation dynamics in these heterogeneous media. Following temperature effect on solvation dynamics in TX-100 micelle, an unique behaviour on the solvation rate with temperature was observed for first time. This clearly indicated that not only the water inside the micellar phase, but also those



just outside the micelle contribute to the solvation dynamics, particularly when the micellar size becomes comparable to the probe used

For useful light harvesting, for example, in solar cells, artificial photo-systems, photogalvanic cells, etc., it is essential to reduce the energy wasting back electron transfer (BET) process. Dissociative electron transfer (DET) reactions are among the several possible approaches to beat BET, where one of the reactants dissociates following electron transfer. For the first time, it was demonstrated that, by changing the driving force of the reaction, it is possible to change the DET reaction mechanism,





from stepwise to concerted routes, and consequently, the reaction efficiency can be controlled.

- J. Chem. Phys. 117, 10744, 2002,.;
- J. Chem. Phys. 116, 2002, 8006.
- Photochem. Photobiol. 79, 2004, 1; J. Chem. Phys. 116, 2002, 1658.
- J. Phys. Chem. B. 108, 2004, 19246.;
- J. Phys. Chem. B. 109, 2005, 18528.

# Excited State Relaxation Dynamics of Inorganic Dyes: Time Resolved Emission Studies

Relaxation dynamics of transition metal complexes, with many accessible d-d charge transfer electronic states and several available oxidation states, is of considerable interest in understanding elementary processes in inorganic photochemistry. This is important for development of many technological applications, and to formulate mechanistic pathways to execute controlled chemical reactions. Two prototype Ruthenium based compounds, tris(2,2'-bipyridine)ruthenium(II), [Ru-(bpy)<sub>3</sub>]<sup>2+</sup> and

Ru-(dcbpy)<sub>2</sub>(NCS)<sub>2</sub> (where dcbpy is 4,4'-dicarboxy 2,2'-bipyridine, RuN<sub>3</sub> dye) were employed to explore the early time events in the excited state relaxation pathway. Since the fluorescence emission from these compounds was extremely low, detection of the emissive S1 state remained a challenging task in the case of these molecules. Using fluorescence upconversion measurements, some of its extremely fast intramolecular relaxation pathways were evaluated. For the first time, it was shown that the intersystem crossing from the higher excited state of [Ru-(bpy)<sub>3</sub>]<sup>2+</sup> complexes takes place in about 40 fs. It also revealed fast vibrational relaxation in the hot triplet states, with a fast decay time of 600 fs to1 ps. A cascade relaxation in 40±15 to 213±60 fs along the S<sub>1</sub> state, which are strongly coupled to the triplet energy levels, was observed in RuN<sub>3</sub> system.

#### Rotational Relaxation

In the recent past, efforts were directed toward understanding molecular rotation in homogeneous liquids as well as in microheterogeneous media. Primarily, the studies in liquids were carried out to address the role of specific solute-solvent interactions on molecular rotation, as these interactions significantly alter the physicochemical properties of liquids and solutions. For this purpose, rotational relaxation of a pair of
closely related medium sized nondipolar solutes was examined in a set of appropriately chosen solvents. Role of solvent size, both in the absence and presence of specific interactions was examined and it was observed that size of the solvent has a bearing on solute rotation. With strong solute-solvent hydrogen bonds the rotation of the solute molecule was impeded. In such a scenario, hydrogen bond dynamics and rotational dynamics occur on comparable time scales. This aspect was substantiated by measuring reorientation times of the chosen solutes in solvents, such as ethanol and trifluoroethanol, which have distinct hydrogen bond donating and accepting abilities, and correlating them with solute-solvent interaction strengths.



Optimized structure of a typical solute-solvent complex formed due to hydrogen bonding interactions between two carbonyl and secondary amino groups of an organic solute with two ethanol molecules.

Similar studies were carried out in micro-heterogeneous media, such as nonionic micelles and reverse micelles to comprehend the microenvironment of these systems, which governs the rates of bimolecular reactions in confined systems. These investigations revealed that solute molecules undergo two kinds of rotational motion, lateral diffusion inside the spherical surface of the micelle, and wobbling motion, which are coupled to the overall rotation of the micelle. These studies have demonstrated that parameters, like temperature and water content in these micelles, significantly influence the location and mobility of the solutes solubilized in them. By judiciously selecting the solute molecules, the microviscosity of the micelles could be obtained. Further studies carried out in aqueous triblock copolymer solutions indicate that critical micelle temperature (cmt) has a significant influence on the rotational diffusion of the probe molecules. It was observed that below cmt, the diffusion of the probes is similar to that observed in homogeneous media, whereas above cmt, their rotational behaviour is akin to that in micelles.

Chem Phys Chem 6, 413, 2005; J. Phys. Chem. B 109, 4923 2005

# Femtochemistry: Exploring the Dynamics of Ultrafast Photochemical Processes

Femtochemisry in concerned with the observation a of the very act of the molecular motion that brings about chemistry. Now it is possible to characterize the 'transition state', which determines the course of a reaction. Over the years, the RPCD Division has developed fast and ultrafast transient absorption spectrometers, with time resolution ranging from microsecond to femtosecond. These spectrometers have been proved to be the work-horses for conducting research in the advanced areas of chemical reaction dynamics in condensed phase. Various unique facilities like (i) the pico and nanosecond laser flash photolysis equipment based on picosecond Nd:YAG laser (ii) the colliding pulse modelocked dye laser and five-stage dye amplifier based sub-picosecond transient absorption spectrometer and (iii) the Ti:sapphire oscillator and multi-pass chirped pulse amplifier based femtosecond transient absorption spectrometer have been created at BARC, and till date these are only of their kind in India. The progress made in the study of ultrafast dynamics in the condensed phase is described below.

Recently large size organic molecules are being routinely used in photonics and molecular electronics, optical sensors and optical





A view of the femtosecond transient absorption spectrometer

switches as well as in devices for solar energy conversion. Although, the working principle of these devices show that one of the three fundamental photo-induced intramolecular processes, namely, charge or electron transfer, proton transfer or energy transfer, is responsible for the desired action of a particular device, unfortunately, more than one of the other processes, always accompany the primary process and reduce the efficiency of the device. Hence it is important to have a full understanding of the excited state dynamics of the molecular system before it is used in any molecular device.

Studies on the ultrafast intramolecular charge and twisting dynamics in the excited states of amino-substituted benzophenones, in which the electron donor and acceptor moieties have provided important information regarding the intimate coupling of the intramolecular charge transfer processes with the conformational changes via the twisting motion of the phenyl groups as well as the surrounding solvent molecules. However, in LDS-821 molecule, in which the donor and acceptor moieties are linked with a spacer group consisting of  $\pi$ -conjugated hexane chain, the charge transfer and twisting dynamics are mainly controlled by intramolecular modes rather than solvent motions. Figure shows the twisting dynamics in the excited state of LDS-821 dye and the various states involved and their time scales .

Investigations of photoinduced intermolecular electron transfer from the excited singlet (S1) state of perylene (Pe) to an electron-accepting cationic surfactant molecule, N-cetylpyridinium chloride in aqueous micellar solutions have been carried out. Following the excited states of both the donor and the cation radical formed, a distance-dependent light-induced ultrafast ET dynamics have been demonstrated for the first time,. Since charge recombination or 'back electron transfer' (BET) reactions reduce the efficiency of a device working on the principle of electron transfer reaction, efforts have been made to investigate the BET dynamics and to search for suitable chemical systems in which BET reactions are minimized or eliminated. It was shown that ET reaction between the excited state of phenothiazine derivatives and carbon tetrachloride, the concerted photodissociative electron transfer reaction gave the ET reaction yield of near unity while stepwise reaction reduced the yield due to the presence of BET reaction. It was also shown the switching over the reaction mechanism from concerted to stepwise could be achieved either by changing the substrate or the solvent.

Since Ru-complexes have only 10% efficiency as sensitizing agents for solar energy conversion process, new bichromophoric



ligands, based on indolyl pyridyl moiety attached to different energy antenna, such as anthracene and pyrene, linked through different kinds of spacer group were synthesized. The investigations have shown that the change over of the relaxation processes from ultrafast energy transfer to the electron transfer or loss of the bichromophoric character of the ligands is sensitive to structure of the spacer group as well as the energy antenna. Hydrogen bonding is a fundamental element of chemical structure and reactivity. It is the key to understanding the structure and properties of water, proteins and DNA, the building blocks of life. Intermolecular hydrogen bonding represents an important type of local interaction in which a hydrogen atom is linked to donor and acceptor groups on different molecules. Femtosecond visible and IR absorption spectroscopic technique



bichromophoric molecule is sensitive to the nature of the donor, acceptor and spacer groups

have been used to investigate the dynamics of hydrogen-bond in different kinds of hydrogen-bonded systems . It was observed that following photoexcitation of the hydrogen-bonded complex, the hydrogen-bond breaks within 100 fs and then the dangling hydrogen-bond undergoes geminate recombination, which is mainly controlled by the biphasic solvent motion.

J. Phys. Chem. A	108,2583,	2004
------------------	-----------	------

- J. Phys. Chem A. 109,6836,2005;
- J. Phys. Chem. B 109, 4014, 2005
- J. Phys. Chem. A 109,12798,2005
- J. Phys. Chem. A 108, 7843 2004
- J. Phys. Chem. A 107, 10798, 2003;

### Interfacial Electron Transfer Reaction in Dye-Sensitized Solar Cell

Solar energy conversion through design and development of dye-sensitized  $TiO_2$  semiconductor solar cell has been a subject of intense research in recent years. A highly efficient solar cell requires a fast electron injection rate from the sensitizer to the semiconductor, and a much slower back electron transfer rate to the sensitizer. The most efficient cells of this type, based on  $Ru(dcbpy)_2(NCS)_2$  (dcbpy) (4,4'-dicarboxy-2,2'-bipyridine)] (or Ru N<sub>3</sub>) sensitized nanocrystalline  $TiO_2$  thin films, can achieve a solar to electric power conversion efficiency of about 10%. However, such expensive inorganic dye materials can be substituted with low-cost organic dyes. Using fast and ultrafast transient absorption techniques dye-sensitized semiconductor nanoparticles systems were investigated in an effort to increase the conversion efficiency.

Electronic coupling plays an important role in dye-senstized ET reaction dynamics. Strong coupling in dye-nanoparticles systems can facilitate fast electron injection, but this will also facilitate charge recombination, an energy wasting process. This phenomenon has never been verfied experimentally. This knowledge could be of immense help for design and development of efficient dye sensitized solar cell (DSSC). For this purpose, we had chosen two structurally similar tri-phenyl



methane (TMP) dyes, prrogallol red (PGR) and aurin-tricarboxylic acid (ATC), for sensitization of  $TiO_2$ nanoparticles, using fast and ultrafast spectroscopic techniques. PGR couples with  $TiO_2$  nanoparticles through catecholate binding, with the formation of a five membered ring. On the other hand, ATC couples with  $TiO_2$  nanoparticles through phthalate binding, with the formation of a six-membered ring. The five membered ring offers stronger coupling to  $TiO_2$ surface as compared to the six-membered ring. Transient measurements on these dye-nanoparticles systems showed that



charge recombination is much faster in PGR/TiO<sub>2</sub> system. Our studies suggest that strong coupling of the sensitizing dye molecule with nanoparticle should be avoidable, because it facilitates energy wasting process in solar cell.

Interfacial ET reaction were also carried out in dye-nanoparticle

chosen for sensitization. It is observed that quantum yield for electron injection (inj) is 1.6 times higher in C-343/TiO<sub>2</sub> system as compared to that in D-1421/TiO<sub>2</sub> system. Steady-state and time-resolved fluorescence measurements confirm that the excited D-1421 molecule predominantly exists as a twisted intramolecular charge transfer (TICT) state, after photo-excitation, whereas the excited C-343 exists as a intramolecular charge transfer (ICT) state. As TICT state is a higher charge separated state compared to ICT state, charge separation, within the molecule, takes place very efficiently in TICT state. Consequently, electron injection is more efficient from TICT state than that from ICT state. This is an important observation for optimization of molecular structure of the sensitizing dye molecules to design an efficient solar cell.

It is expected that defect states, widely known as surface states, can bring down the efficiency of the DSSC. Therefore, it was planned to study interfacial ET dynamics, after modifying the surface states of the nanoparticles. TiO, nanoparticles capped with sodium dodecyl benzene sulphonate (DBS) were synthesized through phase transfer mechanism. These surface modified (SM) particles can be dispersed in many polar and non-polar solvents. The optical and photochemical behaviour of the SM particles was different as compared to that of the bare particles. Interfacial ET reaction of these SM particles was investigated by sensitizing through di-bromo fluorescein (DBF) and alizarin (Alz), and the results were compared with those of the bare particles. It was found that there is no effect of surface modification on electron injection kinetics. However, charge recombination dynamics is much slower on the modified surface as compared to that on the bare surface. On surface modification, the Fermi level of the modified nanoparticles shifts towards more negative value, increasing the overall free energy of reaction (- G0) for BET reaction. High exoergic BET reaction in dye-sensitized TiO,





nanoparticles surfaces fall in the Marcus inverted regime, and hence BET rate decreases on the modified surface.





- J. Phys. Chem. B. 109, 15445. (2005). J. Phys. Chem. B. 108, 12489. (2004).
- J. Phys. Chem. B. 108, 1701 (2004).

### 14.2 GAS PHASE PHOTOCHEMISTRY AND CHEMICAL DYNAMICS

#### Photodissociation Dynamics

Radiation and Photochemistry Division is engaged in investigations on photodissociation dynamics of polyatomic molecules to understand the correlation between the potential energy surface and state resolved product channel. In addition, the reactivity of radical species with polyatomic molecules are also studied.

For the investigation, a highly sensitive laser induced fluorescence set-up, with detection sensitivity less than part per trillion has been developed. Photodissociation dynamics of simple polyatomic molecules was studied under collisionless conditions, using a pump-probe technique, laser photolysis-laser induced fluorescence (LP-LIF), shown in the figures. Various carboxylic acids, such as acetic, acrylic and propiolic acids, were investigated by detecting OH radical, a primary product. Nascent state distribution of the products was measured, and the energy partitioning into the various degrees of freedom of products was interpreted with the help of various models, namely, statistical, impulsive and hybrid models. Partitioning of the available energy was mapped by probing the intensities and Doppler profiles of ro-vibronic lines. Although decarboxylation is the major channel from the ground electronic state of carboxylic acids, in the present studies on electronically excited carboxylic acids, OH formation has been found to be the predominant channel. This result, in combination with the high translational energy in the photoproduct, indicate that intersystem crossing (ISC) from the initially prepared excited state to the ground state is very slow, and the excited molecule dissociates, either from the initially prepared excited state, or another lower energy excited state. Going from the saturated acid, acetic, to the highly unsaturated acid, propiolic, the amount of energy partitioned into the internal states of the OH photofragment increases, implying that an unsaturated bond facilitates the randomisation of the available energy. This is further substantiated by the strong visible fluorescence observed on photoexcitation of acrylic and propiolic acids at 193 nm, which is absent in the case of acetic acid. Similarly, dissociation dynamics of several alcohols and enones was studied, and compared with that of carboxylic acids. Also, a direct evidence of a radical channel in photodissociation of 1,4-cyclohexadiene at 193 nm was obtained.



Laser photolysis-laser induced fluorescence (LP-LIF) set-up: Pump laser, flow system, probe laser, along with detection system



Supersonic molecular beam system

Recently, photodissociation dynamics of strained cyclic compounds, and the consequent effects on opening up of high energy channels, and partitioning of the available energy into the photoproducts were also investigated. Tetrahydrofuran, on excitation at 193 nm, undergoes intersystem crossing to the ground electronic state, and dissociates therefrom, giving OH radical. It has been established that formation of OH, a high-energy reaction channel, involves C-O bond cleavage of the ring, H atom migration to the O atom, and C-OH bond scission.

J Chem Phys 117,10097,2002. J Phys Chem A106,11847,2002. J Chem Phys 12,124309,2005.

#### Free Radical Reactions

The lower atmosphere (troposphere), below about 15 km altitude, contains an enormous range of inorganic and organic trace substances. It is well known that reactions of OH radical and oxygen atom ( $O_3P$ ) with organic compounds are the most important processes for both atmospheric and combustion chemistry. Reaction with OH radical is the main loss process in the troposphere for both hydrogen containing saturated and unsaturated organic molecules. A significant amount of work was done on accurate measurements of the rate constants for reactions of OH radical and oxygen atom  $O(^3P)$  with atmospherically important molecules, an area of current research in chemical kinetics. A discharge flow chemiluminescent system was developed to study reactions of  $O(^3P)$  with organic molecules.



Unlike the closed static system, a flow system is an open system, where the reactants continuously enter, and the products leave the observation zone.

Reactions of oxygen O(<sup>3</sup>P) atom with atmospherically important organic sulphur, cyano and cholro compounds were studied, and new chemiluminescent channels were observed. Reactions of OH radical with unsaturated (allyl and propargyl derivatives) compounds were studied, using LP-LIF set-up. The rate co-efficient and mechanism for oxidation for the above systems have been studied

S.K.Sarkar <sarkarsk@barc.gov.in> P.N. Bajaj <pnbajaj @barc.gov.in>

# 14.3 DEVELOPMENT OF LASER DYES FOR DYE LASER

Dye lasers are the most versatile class of lasers with diverse applications in basic and applied sciences. We have carried out systematic investigations on the synthesis & performance testing of high purity laser dyes. In view of the increasing demand of laser dyes in DAE units, the uncertainty in availability of good quality dyes, and also because of invention of new classes of laser dyes with higher efficiency or better photo-stability, L&PTD in collaboration with MUICT, Mumbai, has initiated a programme for bulk synthesis and testing of high purity laser dyes. Detailed tests comparing the purity, absorption and emission spectra, quantum yield of fluorescence, excited state lifetime, laser performance, and rate of photo-degradation confirmed that most frequently used Rhodamine dyes synthesized indigenously



in bulk quantities, compared very well with the imported dyes in all respect. Having established this capability, synthesis of superior laser dyes of Pyromethene & Perylene class and new derivatives that are expected to perform better in our application programmes, has been started.

An efficient synthesis of the pyrromethene laser dyes has been developed. The laser dye would be useful import substitute. Further, various laser dyes-doped polymeric materials have been developed and their optical properties studied by the L&PTD. Successful formulation of these materials would be very useful in developing compact solid state dye lasers for high end and medical applications. The following figure shows a comparison of the performance of Pyromethene 567 dye with an imported commercial sample, studied in a narrowband dye laser oscillator pumped by the second harmonic of a Nd:YAG laser.



Some Dye-doped Polymers



New Laser Dye-doped Polymers

L. M. Gantayet <headlptd@barc.gov.in>

S. Chattopadhyay <schatt@barc.gov.in>

#### 14.4 TIME RESOLVED LASER INDUCED FLUORESCENCE (TRLIF) IN NUCLEAR **FUEL CYCLE**

Fast and matrix independent methods are required for ultra trace determination of Actinides & Lanthanides in the nuclear fuel cycle. A laser spectroscopic technique for such estimation would be extremely useful in PUREX and THOREX processes. We have taken up the development of Time Resolved Laser Induced Fluorescence (TRLIF) technique for this purpose in collaboration with NRG. Its attractive features are (i) fast and matrix independent (ii) excellent detection sensitivity (iii) highly element selective and (iv) potential for on-line remote monitoring. Additionally, it can provide information on complex formation, speciation and sorption of actinides, which are needed as input for predicting radionuclide migration in the environment.

The principle of TRLIF consists of pulsed laser excitation followed by temporal resolution of the fluorescence signal, which eliminates unwanted short lifetime fluorescence, The fluorescence is detected by a polychromator and ICCD. For radioactive samples, measurement would be carried out by setting up lasers and related signal processing instruments in a non-active laboratory and use fibre optic cable to transport the laser beam and collect the fluorescence from samples kept inside a glove box.

Presently, a working apparatus has been developed while the major components of the actual set-up are being procured. The investigations carried out so far established (i) Effects of nitrate in the concentration range of 0.5 - 5M on the excitation and emission spectra of uranyl ion quantified (ii) Lifetime of uranyl ion in nitrate medium measured to understand the effect of quenching on the excited state lifetime (typically 2 - 3 s)

(iii) Linear absorption and emission occur over a range of nitric acid and uranium concentration (50 g to gm/ lit ) implying a large dynamic range of the technique.

L. M. Gantayet <headlptd@barc.gov.in>





# **15. CATALYSIS AND SURFACE CHEMISTRY**

# INTRODUCTION

The areas of heterogeneous catalysis, surface chemistry and nanomaterials with the broad objective of developing certain dedicated catalysts are of interest to various units in DAE. Along with development of catalysts, fundamental research in these frontier areas of chemical sciences are also pursued. A catalyst of interest, robust noble metal catalyst for hydrogen combination under ambient conditions has been supplied in the form of prototype panels and strips. Mixed metal catalysts for water splitting and degradation of volatile organic compounds are described in this chapter. BARC has also developed instruments for carrying out insitu FTIR studies on catalyst surfaces.



Catalytic panels

# 15.1 A CATALYST FOR H<sub>2</sub> MITIGATION IN NUCLEAR REACTORS

Accidentally released hydrogen during the postulated severe accident conditions in nuclear power stations requires to be removed immediately from the containment volume in order to prevent any explosion. One such method is catalytic reaction of hydrogen with atmospheric oxygen. Catalysts were developed for this purpose, which consist of noble metals dispersed over strips of stainless steel screens and show high activity for  $H_2 + O_2$  reaction under ambient conditions. These catalytic panels were found to be resistant to poisoning by contaminants such as  $CH_4$ ,  $CO_2$  and moisture. A novel prototype device using these catalytic strips was developed in the Applied Chemistry Division that helps in the mitigation of hydrogen under ambient conditions S. K. Kulshrestha <kulshres@barc.gov.in>D. Das <dasd@barc.gov.in>

# 15.2 STUDIES ON URANYL ANCHORED MCM CATALYSTS

The objective of this study was to exploit the absorption characteristics of uranyl ions in UV-Vis region and also the multiple oxidation states and high thermal stability of uranium to prepare highly efficient photocatalysts for the photodegradation/ oxidation of volatile organic compounds in heterogeneous mode. For this purpose, uranyl groups and nano-size uranium oxides crystallites were anchored within the mesopores of MCM-41 and MCM-48 silicates using different synthesis routes. These materials were found to be efficient photocatalysts for the photocatalytic oxidation/degradation of alkanes ( $C_1$ - $C_4$ ), alkenes (ethylene and propene), alcohols ( $C_1$ - $C_3$ ) and  $C_6$  - ring

hydrocarbons under exposure to sunlight and ambient atmospheric conditions.

#### **15.3 PHOTOCATALYSTS**

# Studies on nanocrystalline TiO<sub>2</sub> photo catalysts

In order to develop efficient titania photocatalysts for photocatalytic oxidation reactions, uniform-size nanocrystallites (~2 to 10 nm) of titania were dispersed within the mesopores of MCM-41 matrix via wet-impregnation route and by varying the titania content (5-21 wt%). The catalysts have been found to be highly active for UV-assisted photo catalytic oxidation of various organic molecules at room temperature. In situ Fourier Transform Infrared and thermal desorption spectroscopy techniques were employed to investigate the mode of adsorption and nature of surface transient species formed during the adsorption/oxidation reaction. The reaction mechanisms involved in the photocatalytic reactions are delineated on the basis of these studies.

# Novel mixed metal oxides of tailored photo-catalytic and catalytic properties

Novel materials based on substituted oxide systems are being contemplated as potential catalyst for VOC abatement and water splitting. The strategy of the present study was to synthesize certain substituted mixed metal oxide systems to develop new visible light driven photocatalysts. Various titania and vanadia based samples, i.e.  $InVO_4$ , and  $ATiO_3$  (A=Ca,Ba,Sr,Zn,Cd) with multiple substitutions at A and B sites were synthesized via solid state route and their absorption behavior and band gap (Eg) values were estimated by DR-UV Visible spectroscopic and AC impedance measurements, respectively. Substitution resulted in lowering of Eg values particularly on Ti-substituted indium orthovanadate samples and this was responsible for appearance of an additional band in the UV-Vis spectra in 400 – 500 nm regions. These materials are being explored further for photocatalytic decomposition of water to generate H<sub>2</sub>.

Studies were also undertaken on substituted mixed metal oxide catalysts based on pervoskites (ABO<sub>4</sub>), and Scheelite (ABO<sub>4</sub>)

structures and lanthanum substituted thorium pyrovanadate (ThV<sub>2</sub>O<sub>2</sub>) with a view to exploit the non-stoichiometry generated during substitution in the lattice for enhancement of catalytic activity. In a typical synthesis, Fe substitution at B site in La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-</sub>d (LSM) has resulted in considerable reduction of the particle size (15-20 nm) with higher surface area as compared to LSM (~30 nm). Substitutions dependent changes in the structure and phase compositions were correlated with their redox behaviour, thermal stability, reaction start-up temperature and the conversion attainable for a given reaction. The enhancement in catalytic activity was attributed to synergy of mixed phases and also to the distortion in crystal lattices of independent phases present in such systems. About 100% conversion of CO to CO, was achieved at  $\sim$  300°C by  $La_{0.8}Sr_{0.2}Mn_{0.4}Fe_{0.6}O_{3.}d$  (substituted Lanthanum based pervoskite) catalyst

# 15.4 THE DYNAMICS OF ADSORBATE MOLECULES IN THE CONFINED MEDIUM OF POROUS MATERIALS

Adsorption/diffusion behaviour of adsorbate molecules in a porous host is governed by the pore characteristics of the host matrix, which in turn has a direct relationship with their shape selective catalytic properties. This phenomenon is of both fundamental as well as of practical importance in the chemical industry where zeolites are widely used as catalysts. In situ Fourier Transform Infrared (FTIR) Spectroscopy and Quasi-elastic neutron scattering (QENS) studies were undertaken in our laboratories to get an insight about the dynamics and the conformational properties of the occluded guest molecules in a porous host matrix under the moderate temperature and pressure conditions. These studies were carried out on various micro (X, Y, ZSM-5 zeolites) and mesoporous (MCM-41, MCM-48) materials using methanol, benzene and cyclohexane etc as probe molecules. It has been demonstrated that the molecules mentioned above existed in a clustered state when occluded at room temperature and the physical state of these entrapped molecules depended not only on the structural characteristics of the host matrix but also on the chemical properties such as, dipole moment of the guest molecules.

Applied Chemistry Division has developed an indigenous cell system, made completely of stainless steel, for in situ



high-pressure high-temperature infrared spectroscopy studies on catalyst surfaces. The cell enables a required pre-treatment and subsequent exposure of catalyst surface to reacting gases at temperatures up to 400 °C and in a wide range of pressure from  $10^{-4}$  torr to  $\sim 10$  bar. The transient species formed during the process can be recorded simultaneously to give vital information about the transformations in chemical bondings, occurring at the catalyst surface as a function of time and other reaction parameters. The changes occurring in the catalyst framework, particularly in case of microporous and mesoporous alumino-silicate materials, as a result of lattice substitutions and on incorporation of guest moieties in their host matrix are also amenable to investigation using this cell. A stainless steel cell for in-situ Fourier-transform infrared spectroscopy studies of catalytic processes under the high-temperature and high-pressure reaction conditions

An IR cell of this kind, fabricated in final form at the Center for Design and Manufacture (CDM), BARC, has been supplied to R & D Centre, Indian Oil Corporation, Faridabad, along with peripheral accessories at a total cost of Rs. 18 lakhs.

- D. Das <dasd@barc.gov.in>
- S. Bharadwaj <htschem@barc.gov.in>



# 16. SENSORS

#### INTRODUCTION

Sensors have been identified as a key area of science and technology in India. The radiation detectors for radiation field and dosimetry are of particular interest to Department of Atomic Energy. A number of commonly used substances have been characterized for EPR dosimetry. These are useful for retrospective dosimetry, that is determining the dose following an incident. Work on porous silicon based immuno-sensor, uranyl selective electrode and diamond alpha detector underline the multi disciplinary environment required for sensor development.

# 16.1 CHEMICAL DOSIMETERS FOR HIGH DOSE DOSIMETRY

# Spectrophotometric Readout Method for Free Radical Dosimeters

Formation of stable free radicals in irradiated amino acids and their estimation by Electro Paramagnetic Resonance spectrometry is an established technique in high dose dosimetry. Spectrophotometric read-out method for amino acid dosimeters alanine and glutamine was developed at Radiation Safety Systems Division as an inexpensive alternative technique for EPR spectrometry. It involves indirect oxidation of ferrous ions to ferric ions when irradiated amino acid is dissolved in aqueous acidic solution of ferrous sulphate and xylenol orange. The ferric – XO complex is measured spectrophotometrically. The accuracy of this technique was established by dose inter-comparison with international standard laboratories.

Glutamine (spectrophotometric read-out) dosimeter was used for plant commissioning dosimetry and quality dose audit in Gamma Radiation Processing Plant – Spice (GRPS), BRIT, Vashi, as per Control of Irradiation of Food Rules for AERB. dose range 0.015 to 4 kGy was investigated where only a few dosimeters are available. Reproducibility of dose measurement was within  $\pm$  2%.

#### (2) 'Sugar Free' Aspartame tablet system:

Commercially available 'Sugar Free' sweetener aspartame tablets were investigated spectrophotometrically for their use as routine dosimeter in Gamma Radiation Processing Plant. This dosimeter has a reproducibility of  $\pm$  4% in the useful dose range of 1 to 10 kGy. These tablets are commonly used as sweetener they have a potential for retrospective dosimetry in case of radiation accident.

D. N. Sharma <dnsharma@barc.gov.in>

# 16.2 EPR DOSIMETRY: INVESTIGATION OF NEW DOSIMETRIC MATERIALS

Electron Paramagnetic Resonance (EPR), a method of magnetic resonance, is useful to detect the unpaired electrons / radicals by their magnetic moment, under suitable microwave stimulation.

formulate

radiation.

For paramagnetic radical concentration 10<sup>9</sup> spin/cc, the intensity of EPR spectra due to radical has found wide applications in the field of radiation dosimetry. The advantages are: It's ability to

equivalent to mammalian tissues, water and products processed by irradiation and for dosimetry of high-level

dosimeters

S. No.	Dosimetric system	Dose range, kGy	Applications
1	Glycine	0.015 – 4	<ol> <li>Food Processing Dosimetry</li> <li>Calibration and dose mapping of irradiation facilities such as Food Package Irradiator, PANBIT, Gamma Chamber, etc</li> </ol>
2	'Sugar Free' Aspartame	1 – 10	<ol> <li>Routine dosimetry in food processing</li> <li>Retrospective dosimetry</li> </ol>
3	Glutamine	0.1 – 50	1.Plant commissioning dosimetry 2. Quality dose audit in Gamma Radiation Processing Plant – Spice (GRPS), BRIT, Vashi for AERB.

Applications of the chemical dosimetry systems developed at RSSD

### New Amino Acid for High Dose Dosimetry

#### (1) Glycine system:

Dosimetric characteristics were established by spectrophotometric read-out method and its use in food irradiation dosimetry in the

Accelerator Dosimetry:

In an organic amino acid material, Alanine [CH<sub>3</sub>CH(NH<sub>2</sub>)COOH], the radical generated by ionizing radiation [CH<sub>3</sub>CHCOO-], has EPR gamma dosimetric applications; It is found useful in dose calibration at Industrial Electron Beam Accelerator ILU – 6, for accelerated beam energy 1 - 2 MeV, for wide dose range.

# Retrospective Dosimetry with Inorganic Materials

During high intensity radiation incidences, the commonly available material in the vicinity of accident site register the radiation signatures, could serve as potential source of free radicals, thereby useful as materials in retrospective dosimetry.

Detergent Powder: Commonly used commercial detergent powder

(Surf) used as a decontamination agent, was examined for the radiation induced radicals by EPR technique and was evaluated for its suitability as dosimetric / dating material. The detergent powder samples, constituents of the detergent powder and the mixture of the same, on gamma irradiation exhibited EPR dosimetric response due to radiation induced signals at g = 2.0123, 2.0030 and 2.0006. On post irradiation storage for about 100 days, it was found that the paramagnetic radical concentration got reduced by  $\sim 25$  %.

**Inorganic chemicals:** Li<sub>2</sub>CO<sub>3</sub> was found to have dosimetric application for high range dosimetry, had radiation induced signals at g = 2.0036 and 2.0006, with linear dose response. The radiation induced CO<sub>2</sub>- with high radical stability, is useful for retrospective dosimetry. TL phosphor CaSO<sub>4</sub>:Dy has TL response saturation at ~10 Gy. The pieces of TLD disc (130 mg) on gamma irradiation showed signal at g = 2.0030 and g = 2.0139. The dose dependence of signals SO<sub>3</sub>-(2.0030) and SO<sub>4</sub>- (2.0139) was found linear in kGy range. The radiation induced signals in the same phosphor matrix was found useful for EPR dosimetry, for higher range dosimetry. Thus, the two techniques EPR & TL supplement the dose evaluation in mGy – kGy range.

**Neutron dosimetry:** In case of neutron dosimetry the problem of the choice of dosimetric material becomes complex. The physical mixture, 2:1  $\text{Li}_2\text{SO}_4$ :CaSO<sub>4</sub>, was found to have linear gamma dose response. An inter comparison for gamma dose response of the mixture using EPR technique vis-à-vis Ceric – Cerrous system was carried out; It showed that doses



due to either of the systems agreed within  $\pm 3$  %. The yield of radical SO<sub>3</sub><sup>-</sup> (g = 2.0030) for neutron irradiation was found to be 15 times more as compared to gamma irradiation. Another mixture, 2:1 Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>:Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, exhibited response for EPR dosimetry, with CO<sub>2</sub><sup>-</sup> (g = 2.0045), gamma dose response linear in 6 Gy – 11 kGy, while for neutron in 40 – 1500 kGy.

D. N. Sharma <dnsharma@barc.gov.in>

# 16.3 CHEMICALLY SELECTIVE MEMBRANE OPTODES

Membranes having desired diffusion properties and selective uptake of metal ions in the membranes are being developed and studied using radiotracers. In this context, it has been observed that the hydrophobicity of the membrane plays an important role in its selectivity towards anions. Using this concept, a hydrophobic anion-exchange membrane (polymer inclusion membrane) has been designed for selective uptake of Cr(VI) from aqueous medium, which has been converted to membrane optode by immobilizing a Cr(VI) selective colour indicator 1,5-diphenylcarbazide (DPC) into the matrix of membrane. The proportionality in intensity of the magenta colour on the optodes loaded with varying amounts of Cr(VI) suggests its potential applications for estimation of Cr(VI) in aqueous samples by visual colorimetry.



Another kind of optode, viz., scintillating polymer inclusion membrane, has also been developed for preconcentration and detection of a-emitting radionuclides. This membrane produces scintillation pulses proportional to the amount ofa-emitting radionuclides sorbed in the matrix of membrane. This membrane has been made a-radiation selective over beta radiations by pulse height discrimination and by controlling the thickness of the membrane.

V.K. Manchanda <vkm@barc.gov.in>

B. S. Tomar <bstomar@barc.gov.in>

# 16.4 POROUS SILICON BASED CAPACITIVE IMMUNOSENSOR

This work involves the design, prototyping and characterization of a novel capacitive immunosensor based on porous silicon. The capacitive immunosensors were fabricated by silanization of the oxidized porous silicon followed by covalent immobilization of the antibody (mouse IgG). For the porous silicon immunosensor more than five times increase in sensitivity compared to polished



silicon sensor was observed when antibody-analyte (goat anti-mouse IgG) interaction takes place. Impedance modeling of the electrochemical cell incorporating the electrolyteinsulator-porous silicon (EIS) structure has been carried out and the model has been used to optimize the porous structure for porous silicon capacitive biosensors.



S. K. Kulshrestha <kulshres@barc.gov.in> Hassan <hassan@barc.gov.in>

# 16.5 NAFION COATED URANYL SELECTIVE ELECTRODE BASED ON CALIXARENE AND TRI-N-OCTYL PHOSPHINE OXIDE

Uranyl ion selective electrode based on 5,11,17,23,29, 35-hexa-tert-butyl-37,38,39,40,41,42-hexahydroxy calixarene and tri-n-octyl phosphine oxide (TOPO) incorporated into a poly(vinyl chloride) (PVC) membrane has been developed. The PVC membrane containing the active ingredients was cast on the surface of a graphite electrode. The electrode showed a near Nernstian response to uranyl ion in the concentration range of  $10^{-1}$  to  $10^{-5}$  M with an average slope of 27 mv / decade. The best performance of the electrode could be obtained by using a sensor mixture of calixarene and TOPO in the weight ratio of 1:100. The optimum pH range was between 3.2 and 4.6. Alkali and alkaline earth metal ions did not interfere with the determination of uranyl ion. There was nominal interference from Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Al<sup>3+</sup>, while Fe<sup>3+</sup>, Th(IV), EDTA and F-interfered seriously. The interferences from these ions



could be eliminated by coating the membrane surface with Nafion. The nafion coating eliminated also the anionic interference while the interference from transition metal ions and thorium, could be minimized by converting them to their anionic complexes with EDTA or F-. The response of the electrode has been validated with standard procedure of determination for uranyl ion and used successfully for the analysis of a few samples.

Head, ACD <headacd@barc.gov.in>

#### **16.6 DIAMOND ALPHA PARTICLE DETECTOR**

Diamond has extreme, unique and diverse properties such as very high mechanical hardness, dielectric strength, energy band gap, thermal conductivity, radiation resistance, and corrosive resistance and very low electrical resistivity, thermal coefficient of expansion, etc. made this material endowed with large application potential. Diamond is crystalline form of carbon and it occurs in nature. The availability of natural diamond is limited and the purity of such diamond is not controllable, demands the efforts to synthesis it in the laboratory. There are several methods reported in the literature for its synthesis.

Because of its extreme properties, diamond can be used for developing many electronic devices for application in very

stringent conditions. One of such applications is for the in-situ monitoring of alpha particle activity in the reprocessing plants where active spent fuel is dissolved in concentrated acids. The range of alpha particle in such solution is few micrometers, necessitating the device to be immersed in the highly corrosive and active solution. A device based on diamond can fulfill this requirement.

Diamond films were prepared under various conditions, using the Hot Filament Chemical Vapor Deposition (HFCVD) method. These films were characterized by SEM, XRD, Raman spectrometer and Positron annihilation coincidence Doppler broadening spectroscopy. The films were annealed, chemically cleaned and metal ohmic contacts were deposited for developing device for the alpha particle detection in air and vacuum atmospheres. The I-V behavior measurement showed that the resistance of the film prepared vary from  $10^8$  to  $10^{14} \Omega$  cm. Samples having resistance above  $10^{12} \Omega$  cm were used for further studies. The metal- insulator- semiconductor (MIS) structures of these films were made by using gold vapor deposition and their I-V and C-V characteristics were measured before using these films for alpha particle detection experiments. Few of the samples showed alpha signal in certain locations.

S. K. Kulshrestha <kulshres@barc.gov.in>

C. G. S. Pillai <cgspil@barc.gov.in>



# **17. THEORETICAL CHEMISTRY**

#### INTRODUCTION

The research in theoretical chemistry aims at the understanding and rationalization of the observed chemical phenomena as well as prediction of new phenomena by developing concepts or performing computations. Formulation of new and more powerful theoretical tools, modeling strategies and simulation techniques have thus formed an integral part of research activities in theoretical chemistry. Proposing new experiments, guided by theoretical insight, also constitutes a valuable component of research in theoretical chemistry. The field of theoretical chemistry is now fairly interdisciplinary having close interconnections with other areas such as theoretical physics and biology, condensed matter physics, computational material science and chemical engineering.

The theoretical chemistry research carried out in BARC consists of investigation of the (i) structure and properties of materials at microscopic, mesoscopic and macroscopic length scales, and (ii) dynamics of physicochemical phenomena at ultrafast, fast and slow time scales.

#### **17.1 MULTISCALE MATERIALS MODELING**

# Quantum Chemical Investigation of Molecules, Clusters and their Assemblies:

Ab-initio electronic structure calculations for the ground as well as excited states are carried out using the post-Hartree-Fock and density functional methods in order to gain insight into the structure, properties and bonding in various molecular and supramolecular systems.

# Water Clusters: Structure, Properties and Dynamics

Ab initio calculations have been performed to obtain the structure of water clusters  $(H_2O)_n$  upto n = 20 and their anions. For the negatively charged water clusters, excited state calculations are also performed using the configuration interaction method to obtain the absorption maximum corresponding to the lowest electronic transition, thus providing insight into the spectra of solvated electrons.

this dependence is found to be quite general irrespective of the nature of the basis set used in the calculation and the inclusion of correlation effect etc.



J. Chem. Phys. 118, 8547 (2003)



# Polarizability of Water Clusters

Through *ab initio* calculations of the polarizability of water clusters  $(H_2O)_n$  upto n = 20, a simple linear relation involving the aggregation number is shown to fit the polarizability results extremely well (with correlation coefficient >0.999) indicating a near additive nature of this quantity for weakly bonded molecular clusters. Calculated dynamic polarizabilities are also shown to follow the same trend. The linear dependence of the polarizabilities on n is shown to be surprisingly accurate and in fact can easily be used to calculate the polarizabilities of larger water clusters. Also

 Proton Transfer in Water Dimer on Ionization

In view of the importance of the minimum energy structure (proton - transferred vs hemibonded) of the water dimer on ionization, we have performed advanced theoretical calculations to obtain very accurate relative

energies of different structures and predicted the proton transferred structure to be the most stable ones. The variations of hardness, polarizability, chemical potential, and energy for the proton-transfer process in this weakly interacting system (ionized water dimer species) are shown to provide insight into the proton transfer process. It is observed that the transition state corresponding to the proton-transfer process is associated with maximum polarizability at different O-O distances for the water dimer cation.



Variations of Total Energy (E),Polarizability (a), Chemical Potential ( $\mu$ ),Hardness ( $\eta$ ), and scaled Hardness along the reaction coordinate corresponding to proton transfer in water dimer on ionization at oxygen-oxygen distance of 2.988 A

J. Phys. Chem. A 106, 4200 (2002)

#### Solvation of Uranyl Ion (UO, <sup>2+</sup>) in Water

The solvation of the uranyl cation  $UO_2^{2+}$  in water has been studied through *ab-initio* density functional and complete active space self consistent field calculations with fragment potential approximation for the water molecules. The arrangement of the water molecules around the ion as a function of their number as well as the corresponding solvation energies and the absorption maxima ( $\lambda_{max}$ ) of the solvated  $UO_2^{2+}$  ion are obtained.



# Structure of Hydrogen-Bonded Supramolecular Systems

Ab initio and density functional theoretical calculations have been performed to quantify the hydrogen-bonding interactions for selected supermolecular systems. An analysis and rationalization of the nature of pairwise interactions in different hydrogen bonds involved in the ternary supermolecular systems is presented using the frameworks of Morokuma energy decomposition as well as Bader's topological theory of atoms in molecules involving the electron density, its Laplacian, and also other related quantities at the bond critical points. The pKa values of the aromatic acids, which have been used earlier to rationalize the specific intermolecular interactions between aromatic acids (hydrogenbond donor) and isonicotinamide (hydrogen-bond acceptor as well as donor), are, however, found not to show any regular trend with the calculated binary interaction energy values or the electron density-based bonding parameters using experimental geometries. The calculated quantities corresponding to the computationally optimized geometries of the molecular species, however, do show some regular trends with the corresponding pKa parameters.



Structure of three ternary organic supermolecu

J. Phys. Chem. A 107, 7062 (2003)

#### Cluster-Assembled Materials

Two doped gold clusters are shown to clearly qualify as magic clusters from consideration of their individual stability and properties in the context of cluster-assembled materials. Although they deviate from the conventional magic nature with dimerization energies as large as 5-7 eV, which is rather unusual, the gross geometrical features of the individual clusters are retained in the dimer. This work suggests that the conventional ideas of magic clusters may have to be reframed to judge their suitability as building blocks for cluster assembled materials and the requirement of a weak intercluster interaction may be relaxed if the condition of retention of identity in the assembled materials is satisfied. This would have important implications in the design of novel cluster-based nanomaterials for various nanoscale applications.



Interaction of two doped gold clusters to form a cluster dimer

J. Chem. Phys. 120, 11363 (2004)

# One-Electron Oxidation of Selenourea in Aqueous Solution

One-electron oxidation of selenourea in aqueous solution has been studied through theoretical calculations as well as pulse radiolysis and cyclic voltammetry experiments. The theoretical result confirms that the transient optical absorption band at 410 nm is due to the dimer radical cation of selenourea. The calculation also illustrates the formation of an *intermolecular*  *two-center, three-electron* (2c-3e) bond between two Se atoms with a binding energy of 21.1 kcal/mol.

J. Phys. chem, A 108, 1552, (2004)

# 17.2 STRUCTURE AND PROPERTIES OF SOFT CONDENSED MATTER (MESOSCOPIC LENGTH SCALE)

# Density Functional Theory for Structure of Polymers at Interfaces

The density behavior of polymers has been investigated near interfaces through a new density functional approach. The density distribution of a system of freely jointed hard sphere chains confined between hard walls at various packing fractions provides insight into the oscillatory behavior of the density profile arising from competition between packing and configurational entropic



fraction ( $\eta$ ): theoretical prediction (lines); Monte Carlo simulation (symols)

effects. Monte Carlo simulations are also utilized to predict the

A 1.862 1.003 1.003

Geometry of selenourea dimer radial cation and plot highest doubly occupied molecular orbital

configurational properties of the system. The chains are observed to stay as flattened structure as well as reoriented near the wall as evident from the parallel and perpendicular components of the mean-square radius of gyration profiles for different packing fractions.

J. Chem. Phys., 121, 4865, (2004)



Parallel (open symbols) and perpendicular (filled symbols) components of mean-square radius of gyration profiles for n=0.1 ( $_D$ ) and 0.4( )



# Modeling Fluid Behaviour in Porous Materials

Probing the adsorption behaviour of nonpolar fluids and their mixtures in porous materials has fundamental as well as technological importance because of its relevance to separation and storage of natural gases. The conventional Kelvin equation cannot be used for adsorption in micropores and mesopores because of the simplified assumptions on which this theory is based. We have used density functional theory, which is based on statistical mechanics and deals with atomic description of the fluid, to investigate the fluid behaviour in porous materials. The most interesting behaviour observed is that at suitable intermediate pressure, the absorption is maximum. From the calculated microscopic density distribution, we are able to predict optimum conditions for maximum adsorption of fluids in the porous materials. Various fundamental aspects such as wetting and capillary condensation have also been studied.

# Vapour-Liquid Phase Diagram of Nonpolar Fluids.

In order to characterize the behaviour of fluids in porous materials, prior knowledge of its bulk vapour-liquid phase diagram is essential. Using a simplified description of the manybody interactions in terms of a bridge function in the integral equation theory, we have calculated the liquid-vapour phase diagram of nonpolar fluids over the entire range of temperatures and pressures.



vapour-liquid phase diagram of a model honpolar flu

J. Chem. Phys. 116, 8517 (2002)

#### **17.3 DYNAMICS IN CONDENSED PHASE**

# New Universal Scaling Laws of Diffusion in Simple Liquids

A new universal scaling law relating the self-diffusivities of the components of a binary fluid mixture to their excess entropies is derived based on mode coupling theory. These scaling laws yield numerical results, for Lennard-Jones, hard sphere fluid as well as liquid metals, in excellent agreement with simulation results even at low density region, where the existing empirical scaling laws fail completely. The present scaling law provides a route to obtain diffusivity even for an unknown interaction potential from the experimentally measured radial distribution function.



for a binary Lennard-Jones fluid mixture.

# Structure Stability Correlation of End-Linked Polymer Gel

The mechanical stability of end-linked polymer network (gel) at large deformation has been studied with the aid of a simplified model which consists of a fractal network of end-linked Hookean springs, each representing an ideal polymer chain. The structurestability relation in presence of an external strain is explored using repetitions of three consecutive steps: incremental compressive displacement of the boundary chains, potential energy minimization and force calculation at the boundary for the equilibriated structure. It was observed, that the load versus displacement graph is linear; while all the networks studied here can withstand up to a certain maximum load, beyond which at a single incremental displacement (strain) step the load generated at the boundary suddenly drops by two to three orders of magnitude. The latter is a manifestation of the fact that the given structure is collapsed in the sense that one has achieved the maximum load-carrying capacity,  $F_m$  of the fractal network. The results from this model calculation corroborate with the non-monotonous structure-stability relationship, as observed in radiation induced cross-linked polymer networks. The maximum load carrying capacity of the networks as a function of their fractal dimension at various values of the spring constants of the polymer chains shows interesting behaviour.





# Diffusion Assisted End-to-end Relaxation of a Flexible Rouse Polymer Chain: Fluorescence Quenching Through a Model Energy Transfer

The diffusion-influenced end-to-end conformational relaxation of a flexible polymer chain molecule (within the Rouse model) is





Phys. Rev. Lett. 92, 145901 (2004)



and with the initial end-to-end distribution of the Gaussian chain assumed to be peaked at x=25. The numbers in the figure refer to times at which the intermediate distributions are drawn. For clarity the peak values of the distributions are scaled to unity.

investigated theoretically in the Markovian limit utilizing a generalized diffusion equation for the probability distribution of the end-to-end distance. The resulting diffusion equation with a sink term representing this energy transfer through a suitably modified Forster rate expression is solved numerically for equilibrium close/open conformations, and end-to-end irreversible ring opening or closure of the chain. It is found that a nonmonotonic distribution of reaction times is a confirmative signature for a cyclization transition. The knowledge of the distribution of energy-transfer distances is utilized to help delineate the features associated with the reaction time distribution during the end-to-end relaxation.

S. K. Ghosh <skghosh@barc.gov.in>



# 18. MEMBRANE PROCESSES FOR WATER TREATMENT AND DESALINATION

# INTRODUCTION

As a part of the national programme to improve the quality of life in our society, Bhabha Atomic Research Centre (BARC) has been engaged in research and development (R&D) activities on desalination since last several years. BARC has been responsible for the deployment of seawater and brackish water of desalination and water purification technologies, for a wide range of water related applications in India. It includes sea water reverse osmosis (RO) plant in coastal areas, brackish water RO plant in villages for producing safe drinking water, multistage flash (MSF) plant for sea water recycle and reuse plants for the effluent, RO technology and domestic water purifier technology transferred to various agencies in different parts of the country. BARC also provides guidance and consultancy to several agencies in these technologies.

#### **18.1 MEMBRANE DESALINATION**

Reverse Osmosis (RO), which is a pressure driven membrane process using semi-permeable membrane, is the most popular method for desalination. Ultra filtration is a membrane based pre-treatment system to improve the reliability of the RO plants.

#### Rural Sector

BARC has recently set up a 30,000 litres/day brackish water desalination plant at Satlana Village, Rajasthan in December 2002 as a societal need which has been providing drinking water to the 1000 population of villagers till date. The reverse osmosis plant is not only capable of desalinating the brackish water to potable levels but are also capable of removing contaminants such as fluoride, arsenic nitrate etc.

A project report has already been submitted to union territory of Lakshadweep for 6,00,000 litres/day seawater desalination plant at Kawaratti island. The design of the plant has been carried out keeping in mind the inherent limitations of the island as compared to mainland.

In a bid to provide potable quality water in water scarcity coastal areas, work on building a barge mounted desalination plant for providing 50,000 litres drinking water from seawater has been designed. The plant could be useful to the people on shore, in areas like Rann of Kutch, small islands like Lakshadweep and Andaman & Nicobar. The plant uses state of the art reverse osmosis (RO) technology with membrane based ultrafiltration



A view of the reverse Osmosis plant put up at Satlana Village, Rajasthan (Feed salinity : 6000 ppm, Capacity : 30,000 litres / day, Operating pressure : 14 bar, Product quality : Drinking water)

(UF) pretreatment system along with built-in back wash provision and remineralisation, and is designed to withstand frequent relocation from site to site. Space limitation, variable feed water quality and proper positioning of plant equipment & machineries in line with desired strength, stability and floatability of barge are the key design features. Detailed system design is carried out in consultation with Indian Register of Shipping.

NTU & SDI are the two input feed quality requirements for RO plant. While NTU is a measure of the feed quality in terms of turbidity, SDI is an empirical parameter and assess the fouling



designed in consultation with Indian registrar of shipping.

potential of the feed water. UF system is rather insensitive to the reasonable changes in the quality of the feed water. For a reasonable variation of feed NTU, the filtrate from UF system is fairly constant at less than or equal to 0.1 NTU and Silt Density Index (SDI) less than 3, which is the precondition as the quality of the feed water to RO elements. The economics of the UF system as the precursor to RO, is being established in our pilot plant studies under progress.



Ultrafiltration (UF) based feed pretreatment system at SWRO plant, Trombay

Feed flow rate	15.0 m³/hr.
Average recovery	80 %
Product flow rate	12.0 m³/hr.
Operating Pressure	2-3 Kg/cm <sup>2</sup>
Reject flow rate	3.0 m <sup>3</sup> /hr.
Mode of operation	Auto/Manual
Membrane Type	Polysulphone
Membrane configuration	Hollow-fibre
Membrane Area	50.5 m <sup>2</sup> /element

#### Decontamination by Membrane Process

The membrane technology has also been demonstrated for the decontamination of radioactive effluents and separation of radio-contaminants from inactive constituents such as ammonium nitrate. Reverse osmosis has been used for the decontamination of low level radioactive effluents of Effluent

Treatment Plant (ETP). At an initial activity of about 0.001 to 0.0001 microcurie/ml, a decontamination factor of 10 at a volume reduction factor of 10 could be demonstrated. Using cellulose acetate membranes the ammonium diuranate effluents of uranium metal plant could be separated into two streams with all radiocontaminants retained in the reject (DF>20) at volume reduction Factor of 20. The decontaminated stream contained nearly 90% of the ammonium nitrate which was originally present in the feed.

#### Disaster Management

BARC has installed a RO based desalination plant (5000 litres/ day capacity to provide drinking water to 2500 people) in the Tsunami



5,000 litres / day RO Plant in Tsunami Affected Area (Nagapattinum General Hospital) for providing Safe Drinking Water to Victims



5,000 litres / day RO Plant in Tsunami Affected Area (Chandrapadi village Nagapattinum) for providing Safe Drinking Water to Victims



5,000 litres / day Trailor mounted RO Plant in Tsunami Affected Area (Kalpakkam) for providing Safe Drinking Water to Victims

affected area of Tamil Nadu. Soon after the Tsunami, the turbidity and salinity of bore well water had increased manifold. The desalination plant has been installed by BARC at General Hospital in Nagapattinum disaster as shown in the figure. Two more plants of the same capacity have been supplied for Tsunami affected villages of Nagapattinum (Chandrapadi village) and near Kalpakkam for providing drinking water to the victims.

### **18.2 MEMBRANE DEVELOPMENT**

### Water Desalination

BARC is engaged in indigenous development of membranes for brackish water and seawater desalination, waste water recovery,

fuel cells and indigenous development of membrane manufacturing technology. Efforts are directed towards development of state of art thin film composite polyamide (TFCP) membranes. They are three layered membranes, prepared in two stages. The fabric supported macro-porous poly-sulfone membrane is prepared by the conventional phase separation technique while the interfacial polymerization of the mixed aliphatic-aromatic reactive systems gives an ultra-thin separation barrier deposited over it.

The technique of poly-sulfone support membrane preparation involves dissolution of the polymer in a suitable solvent and spreading it uniformly over the fabric using a knife-edge under controlled environment of humidity and temperature. The subsequent gelation is carried out in filtered demineralised water to produce macroporous poly-sulfone membrane. The ultra thin barrier is coated insitu by interfacial poly-condensation of aqueous amine and the organic solution based acid chloride and subsequently stabilized by curing at higher temperature. The laboratory machine used for making 30 cm width membrane is shown in figure. The membranes thus prepared were rolled in spiral configuration using the technology developed in-house.

During the development of desalination membranes, a few membranes could be prepared which have different applications. The support poly-sulfone membrane prepared as precursor to TFCP making has been found to be good for the clarification of fuel pond water as indicated by the preliminary results based on the trials conducted at PREFRE, Tarapur.



A view of TFC Membrane Preparation System & Spiral Elements using In-house Technology

#### Domestic Water Purification

A spin-off idea in coating of the Poly-sulfone dope on a porous cartridge resulted in the development of an affordable 'point of use' domestic water purifier, which physically eliminates biocontaminants. Unlike other devices available in the market which only deactivates the micro-organisms, this device altogether eliminates them. It is very effective as it removes bacteria to the extent of > 99.99% (4 log scale) and removes complete turbidity and produces crystal clear water. This device does not need electricity or addition of any chemical.The know-how of the technology has been transferred to various parties and six of them already are doing a good business in the market covering different parts of India.

#### **18.3 THERMAL DESALINATION**

Thermal desalination gives desalinated water that is almost of distilled purity good for industrial use. It has a distinct edge where high purity water is required.

R&D efforts in thermal desalination have led to master the Multi Stage Flash (MSF) evaporation and Low Temperature Evaporation (LTE) related technologies. Utilization of low grade heat and waste heat for desalination in nuclear and non-nuclear industries has been the main mandate in the last 3-4 years. Efforts are continued to reduce the desalination cost through R&D including innovative improvements in technologies such as MSF, LTE and Multi Effect Desalination (MED) utilizing Horizontal Tube Thin Film Evaporation coupled to Thermo Vapor Compressors (TVC) and Mechanical Vapor Compressors (MVC).







LTE Desalination Plant at Kawaratti, Lakshadweep using Waste Heat of Diesel Generator



HTTF Desalination Unit (MED)

Multi-Stage Flash

The experience gained from the 425 m<sup>3</sup>/d MSF desalination plant at Trombay was useful in designing the 4500 m<sup>3</sup>/d MSF plant as a part of 6300 m<sup>3</sup>/d Nuclear Desalination Demonstration Project (NDDP) at Kalpakkam.

# Low Temperature Evaporation

A 10,000 litres/day LTE desalination plant using the waste heat of diesel generator was installed and commissioned at Lakshadweep under consultancy and guidance from BARC for producing desalinated water from seawater. Such plants would be ideal for industries where

waste heat is available in the form of process heat. These plants can also produce high purity distilled quality water from high salinity or seawater for the rural areas where waste heat from DG sets/solar energy is available.

In order to provide desalted water to water scarce areas an innovative modification to this technology has been made and the development of Two-Effect LTE Desalination plant with Cooling Tower has been undertaken. In this plant total raw water requirement has been drastically brought down (by 30 times), this plant will utilize low grade waste heat.



#### Multi Effect Distillation (MED)

A 1000 litres/ day HTTF desalination unit has been developed and is being operated for basic studies on boiling heat transfer and hydrodynamics by varying the operating parameters to generate data over a wide range of temperatures for design of large scale MED desalination plant. The special features of this type of plant are the Horizontal Tube thin Film (HTTF) evaporators having high heat transfer efficiency, less pumping power requirement and lower raw water consumption. MED-MVC requires only electrical power for sea water desalination. MED-TVC will be employed







Nuclear Desalination Demonstration Project, Kalpakkam

where high-pressure steam is available. This plant also uses an innovative Spray Enhancing Demisters (SED) to produce ultra high pure water (conductivity < 0.5 iS/cm).

### **18.4 NUCLEAR DESALINATION**

#### Hybrid Desalination Technology

The hybrid technology which is a combination of RO and MSF has several advantages. It has provision for redundancy, utilization of streams from one to another and production of two qualities of water for best utilization. RO operates with the help of electricity whereas MSF uses low grade steam. Two types of desalinated water are produced. The desalinated water produced from MSF is very pure which is good for industrial use. The desalinated water produced from RO is potable quality. The two can be blended for either human or industrial consumption. The quality is close to rain or river water as opposed to well water.

BARC is engaged in setting up a Nuclear Desalination Demonstration Project (NDDP) at Kalpakkam based on hybrid technology. It consists of a hybrid MSF-RO desalination plant of 6.3 million litres per day (MLD) capacity (4.5 MLD MSF and 1.8 MLD RO) coupled to Madras Atomic Power Station (MAPS), Kalpakkam. The requirements of seawater, steam and electrical power for the desalination plant are met from MAPS. The RO plant is already commissioned and it has been operating as per design intent producing potable water from seawater. The plant incorporates necessary pretreatment and an energy recovery system. It operates at relatively lower pressure (48-52 bar) and employs lesser pretreatment chemicals because of relatively clean feed seawater from MAPS outfall. The potable water produced is supplied to nearby areas. The MSF plant (4.5 MLD capacity) is under construction. As many of the water scarce urban areas are lying in the coastal regions, there is great potential for seawater desalination. These areas are also witnessing rapid industrialization requiring very pure water. The requirement of desalinated water in such urban areas is estimated to be in the range of 100-200 MLD where high purity water is required by the industries and potable water is required by the local population for domestic use. The hybrid technology is very promising in urban areas of coastal regions.



#### Waste Heat Utilization

A 30 m<sup>3</sup>/d LTE desalination plant using waste heat for sea water desalination was coupled to the CIRUS reactor for utilizing about 1 MW<sub>th</sub> of waste heat from the Primary Coolant Water (PCW) system and produce desalted water from seawater to meet the make-up water requirements of the reactor. The plant has been commissioned in April 2004 and is being regularly operated and product water is being taken to dump tank for use in the reactor as make up water. It is operating as per design intent on regular basis with production rate of approximately 20 lpm and conductivity in the range of 12-15 mS/cm. Operational data is being analysed for performance evaluation and further

improvisation in the system for future plants.

This type of plant is envisaged to be coupled to AHWR utilising waste heat of MHT purification system and produce 500 m<sup>3</sup>/d of desalted water to meet the DM water make up requirements of the reactor.

#### **18.5 INTERNATIONAL COLLABORATION**

BARC is a member of International Nuclear desalination advisory Group (INDAG) of International atomic Energy Agency (IAEA) for providing advice and guidance for IAEA activities on nuclear desalination and has participated in Coordinated Research Projects (CRPs) of IAEA and sharing the expertise with other Member States in different aspects of nuclear desalination. Recently, BARC has organized a Technical Meeting (TM) on 'Integrated Nuclear Desalination Systems' at Chennai including a technical visit to Nuclear Desalination Demonstration Project (NDDP) at Kalpakkam in which members from IAEA, Argentina, China, Egypt, France, India, Indonesia, Israel, Russian Federation, Saudi Arabia and UAE participated.

#### **18.6 CONSULTANCY**

Based on the expertise available, consultancy services have been offered for feasibility studies, design, operation and trouble shooting for state governments and organizations such as BPCL, GPPIL etc. Consultancy is being provided to National Institute of Ocean Technology (NIOT), Chennai under a MOU for setting up

> a 100 m<sup>3</sup>/d desalination plant utilizing Ocean Thermal Energy Gradient (OTEG) at Kavaratti, Lakshadweep islands. Collaboration with Karunya Institute of Technology (KITS), Coimbattore under BRNS project for studies of Low Temperature Flash Evaporation desalination has been initiated.

P. K. Tewari <pktewari@barc.gov.in>
S. Prabhakar <sprabha@barc.gov.in>



# **19. NANOMATERIALS**

#### INTRODUCTION

Recent years have witnessed a considerable growth in the research activity in the area of 'nanophase' materials. Since the sizes of crystallites exist over nanoscale dimensions, these materials exhibit novel variation of inter-atomic potentials, leading to enhanced physical and chemical properties that are not observed in their bulk (coarser grain) counterparts. One-dimensional nanostructures such as nanowires and nanotubes have also been developed rapidly over the last decade. This chapter describes some of the efforts in this area in BARC. Plasma has been effectively used for bulk reactive generation of nanoparticles. The nano-ceramics (size less than 100 nm) are potential materials for a variety of technological applications. The characteristics of a sintered body fabricated through the powder metallurgy route are highly dependent on the starting powder characteristics. Radiolytic and photolytic methods of production of nano particles are also investigated

#### **19.1 NANOMATERIALS BY PLASMA TECHNOLOGY**

Plasmas provide a high temperature and catalytic media for carrying out a variety of activated as well as endothermic chemical reactions for generation of advanced materials. The yield is improved due to the presence of reactive species, electromagnetic fields and large enthalpy flux. Some of the areas where attempts are being made for specific uses are in reactive generation of nanoparticles.

Synthesis of Nano particles of Iron Oxide and Aluminum Nitride through Arc Evaporation – in-flight formation technique (work done by Laser and Plasma Technology Division in collaboration with Department of Physics, University of Pune and Centre of Plasma Physics, Guwahati, facilitated by board of Research in Nuclear Sciences, Department of Atomic Energy).

AlN is a piezoelectric ceramic possessing a high thermal conductivity, high hardness and low electrical conductivity. Iron oxide is known to be magnetic in nature. Bulk iron oxide exists in the a-phase and has spinel structure. However, nanophase material exhibits  $\gamma$ - phase which is difficult to be produced by normal chemical routes.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is ferromagnetic in nature and exhibits high saturation magnetization with a low coercive field. This material is a precursor in forming the ferrites

A transferred arc DC plasma torch capable of providing a maximum power of 45 kW was employed with argon as the plasma gas, generating a plasma column; impinging over the anode in the form of Iron or aluminium block. The metal vapors

react with oxygen or nitrogen fed into the chamber enabling the reaction to occur inside the reactor chamber. The base pressure was controlled at  $10^{-2}$  Torr and the reaction pressure was varied from 760 Torr to 300 Torr.

### Al-N System

$$\begin{split} \mathsf{Al}(s) \,+\, 1/2 \mathsf{N}_2(g) \,&=\, \mathsf{AlN}(g) \,\,(\text{-318 kJ/mol},\, \Delta \mathsf{H}^0_{\,\,\mathsf{f}}) \\ \mathsf{2Al}(g) \,+\, \mathsf{2O}(g) \,\,=\,\, \mathsf{Al}_2\mathsf{O}_2(g) \\ \mathsf{Al}(g) \,+\, \mathsf{O}(g) \,\,=\,\, \mathsf{AlO}(g) \\ \mathsf{Al}^{3+}(g) \,+\, \mathsf{N}^{3+}(g) \,=\,\, \mathsf{AlN}(s) \,\,(\text{-9506.8 kJ/mol},\, \mathsf{lattice\, energy}) \end{split}$$

Presence of trace amounts of oxygen can give rise to sub oxides of Al-O. However the powder was analysed using X-ray diffraction, transmission electron micrographs etc. It was found



TEM of Al-N system showing Size  $\sim$  20 nm rods



The Plasma System

The Plasma Fireball

The Plasma Torch and the collection dome

that AI-O was absent and the product consisted of nanowire and nanoparticles.



An alternate method is to inject AlCl<sub>3</sub> Vapor and NH<sub>3</sub> gas in an argon plasma jet expanding through a nozzle in to a vacuum chamber. The cooling triggers homogeneous nucleation of AlN on a substrate placed perpendicular to the jet. The chemical reaction AlCl<sub>3</sub> (gas) + NH<sub>3</sub> (gas)  $\rightarrow$  AlN (solid) + HCl (gas) is carried out in the plasma. The adjoining figure shows the system and the SEM micrograph of products. This work was done in collaboration with Centre of Plasma Physics at Guwahati.

#### Fe-O System

The reactions inside the plasma chamber which can occur at the temperatures >2300K are as follows

$$\begin{split} Fe(s) &+ O(g) = FeO\\ 2Fe(s) &+ 3O(g) = \gamma \text{-} Fe_2O_3(-823 \text{kJ/mol})\\ 3Fe(s) &+ 4O(g) = Fe_3O_4 \quad (1120 \text{kJ/mol}) \end{split}$$



TEM of Fe – O system showing, size  $\sim$  10 nm Particles of  $\mathrm{Fe_2O_3}$ 

 $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was found to form exclusively and remains stable even at room temperature. The high heating and cooling rates available with thermal plasma resulted in nano particle of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> mixed with Fe<sub>3</sub>O<sub>4</sub>. The photographs depict the system and the Nano materials formed. This collaborative work was done at Pune University and part of the Host lab experiments.

L. M. Gantaytet <headlptd@barc.gov.in> A. K. Das <akdas@barc.gov.in>

#### **19.2 NANOCERAMICS**

#### Research on Nano-ceramics

The methods of producing the starting powder for nano ceramics can be broadly categorized into solid state and wet chemical processes. Among the available solution chemistry routes of powder production, the combustion technique is capable of producing the nanocrystalline powders of the oxide ceramics at lower calcination temperature in a short time. The powder obtained by this technique generally has the highest degree of phase purity coupled with the improved powder characteristics like narrow particle size distribution, higher surface area and better sinterability. The very high exothermicity generated during combustion manifests in the form of flame, and the process is termed as auto-ignition. In our studies, citric acid, glycine, hydrazine, etc. were used as a fuels whereas metal nitrates were used as oxidants. The nano-materials prepared by this route can be classified into two broad categories.

#### (i). Nuclear Materials:

 $ThO_2$ , yttria-doped-thoria (YDT),  $MThO_3$  (M = Ba, Sr),  $CeO_2$ , ZrO<sub>2</sub> etc.

#### (ii). Functional materials:

$$\begin{split} &Y_{2}O_{3}, \ Ce_{_{0.55}}Y_{_{0.45}}O_{_{1.775}}, \ Zr_{_{0.80}}Ce_{_{0.20}}O_{_{2.0}}, \ BaTi_{4}O_{9}, \\ &Ba_{_{2}}Ti_{_{9}}O_{_{20}}, \ SrCeO_{_{3}}, \ Sr_{_{2}}CeO_{_{4,}} \ Rare-earth \ ortho-ferrites \ (REFeO_{_{3}}), \\ &SOFC \ materials \ etc. \end{split}$$

The powder properties like surface area, particle size etc. could be controlled by varying the oxidant-to-fuel ratio. It may be noted that most of the above mentioned materials need prolong heating at higher temperatures, if prepared by conventional



solid state method. The combustion process could be efficiently used to prepare a number of thermo-dynamically not so favorable materials e.g.,  $GdFeO_3$  and  $Sr_2CeO_4$ , which often suffer from the presence of thermodynamically more stable phase  $Gd_3Fe_5O_{12}$  and  $SrCeO_3$ .

- S. K. Kulshrestha <kulshres@barc.gov.in>
- D. Das <dasd@barc.gov.in>

#### **19.3 METAL NANOPARTICLES**

# Preparation, Characterization and Applications of Metal Nanoparticles

Among numerous methods for preparation of metal nanoparticles, radiolytic and photolytic methods are very popular because of the ease in preparation of nanoparticles of narrow size distribution. In addition, complementary techniques, such as ultrafast lasers and electron pulse radiolysis, can be employed in combination for preparation of nanoparticles. Radiation and Photochemistry Division, has been involved in studying the formation mechanisms of metal nanoparticles using the above mentioned techniques. Novel of these techniques is that one can study not only the formation of metal nanoparticles, but also the growth kinetics of these particles. This helps in understanding the mechanistic aspects involved in the formation



TEM picture: Before laser irradiation



TEM picture: After laser irradiation

of nanoparticles. Metal nanoparticles of Ag and Cd were prepared in aqueous solutions and viscous medium. Recently, seed method was used to prepare uniform particles of bigger size. The role of viscosity of the medium was exploited to stabilize metal particles. It was demonstrated in ethylene glycol and glycerol media, where it has been shown that particles of uniform size can be prepared by bombarding the preformed particles by laser irradiation.

S. K. Sarkar <sarkarsk@barc.gov.in>
## 20. NOVEL MATERIALS, PROCESSES AND TECHNOLOGIES

#### INTRODUCTION

Multidisciplinary approach to development of technology has been the strength of BARC. Novel processes and materials have been developed and implemented regularly overcoming the constraints of indigenous raw material and existing equipment. The innovative content of such accomplishment is evident in the work described here and in the previous chapters. Recovery of Pa-231 from feed material containing only 2-3 parts per billion Pa-231 was a daunting task. Indigenous technologies for production of sulphur hexafluoride, an essential input to ADS program, production of tri-chloro silane, an intermediate for production of high purity silicon, preparation of organometallic precursor and production of ultra pure arsenic, gallium etc are visible manifestations of the technological capability. Investigations into the preparation of novel materials pave the way for future high technology processes.

Zirconium recycle process has been proposed for the first time in any nuclear fuel cycle. This can reduce the radioactive waste drastically.

## 20.1 RECOVERY OF PROTACTINIUM (Pa-231) FROM NATURAL (PPB LEVEL) SOURCES

The task of producing protactinium (<sup>231</sup>Pa), one of the rarest elements in the earth crust, was undertaken, when microgram quantities of pure <sup>231</sup>Pa was not available to BARC for experimental work. In the first phase, prospecting of protactinium four months, to obtain sufficient data for a scaled up plant. The latter was installed and was commissioned within two months. The efficiency of recovery in the larger plant remained the same ( $\sim$  40 %) as demonstrated in the laboratory stage. The flow diagram for the process of Protactinium recovery from insoluble muck of monazite plant is shown in the figure.



was completed using gamma ray spectroscopy. The concentrations of <sup>231</sup>Pa in the plant streams of uranium mill of Jaduguda and monazite processing plant of IREL, Alwaye are in the range of 0.14 to 3 ppb. The insoluble muck of Alwaye, which remains after removal of major fraction of rare earths, thorium and uranium from monazite, has the highest concentration at 3ppb, and was chosen as the source for recovery of protactinium.

The process for recovery and pre-concentration of protactinium developed in the laboratory involved a) pre-treatment of the muck, followed by b) leaching the cake with oxalic acid, c) selectively loading protactinium and other ions from the oxalic acid on a resin bed, and d).further purification by selective elution of the various ions and protactinium. The process was at first demonstrated in the laboratory at scale of 500 gm feed. The pilot plant for 30 kg batch size was installed and operated for

Flow diagram for the process of Protactinium recovery from insoluble muck of monazite plant

The protactinium recovery plant, after attaining its full capacity of processing completed ( $\sim$  5000 hours of operation) the processing of insoluble muck from IREL. In summary, a total of around 23 Te of insoluble cake from IREL was pre-treated and leached to extract protactinium. The leachate of around 78,000 litres was further purified and concentrated by elution ion chromatography in an anion exchange column. This is the first time a mineral is being extracted on such a scale from a source with 2-3 parts<sup>231</sup>Pa per billion concentration.

L. M. Gantayet <headlptd@barc.gov.in>



Plant for recovery of Protractinium-231 from insoluble muck of monazite plant



SF<sub>6</sub> Reactor

## 20.2 DEVELOPMENT OF SULFUR HEXAFLUORIDE **PRODUCTION TECHNOLOGY**

Sulfur hexafluoride (SF<sub>e</sub>) is used as electrical insulating gas, in accelerators and high voltage switchgear. Sulfur Hexafluoride production technology has been developed on a pilot scale of 5 tonnes/year capacity, based on 1500 ampere capacity fluorine cell. This was a sequel to the earlier bench scale development work at 1 tonne/ year capacity scale, based on 250 ampere fluorine cell. Better than 90% fluorine utilization efficiency has been achieved The gas produced has been tested and found to conform to IEC-376 specification. Engineering data generated on the pilot plant was used and the design of a 25 tonne / year

> capacity plant established. The flow sheet of the large scale plant being set up is shown in the figure.

S. K. Ghosh <ghoshsk@barc.gov.in> H.Rao <hrao@barc.gov.in>

## 20.3 DESIGN & DEMONSTRA-TION OF TRICHLORO SILANE (TCS) PRODUC-TION TECHNOLOGY IN **BENCH SCALE LEVEL.**

Silicon in various grades is the most popular raw material for semiconductor industry. Large scale production of semiconductor grade silicon requires trichlorosilane (TCS) as feed stock for its relatively ease of purification to the desired degree. This is highly



inflammable, corrosive and hazardous material. Present indigenous effort in Heavy Water Division, is to produce crude trichlorosilane (main impurity is silicon tetrachloride), from metallurgical grade silicon powder and anhydrous hydrogen chloride gas as raw material. This will be purified further by distillation.

Sufficient quantity of TCS was produced for further processing. The plant has been operated successfully for sufficient time.

The test facility uses 75 mm diameter and 2250 mm tall, fluidized bed reactor metallurgical grade silicon powder 175 micron (average particle size for 65 mesh and 100 mesh screens) and 5 lpm anhydrous hydrogen chloride with 5 lpm nitrogen (as diluent) to produce trichlorosilane at 10 kg/day rate by the following reactions.



Hydrogen chloride and nitrogen gas is mixed in a mixing tank and then heated to the desired temperature before feeding in the fluidized bed reactor. Silicon is fed to the reactor from a bin intermittently. Reactor is maintained at 240 °C and slightly above atmospheric pressure to obtain optimum yield. The gaseous stream from the reactor passes through a set of cartridge filter and cooled in a condenser to -80 °C by dry ice in acetone. Most of the trichlorosilane produced is condensed in this condenser and non-condensables such as hydrogen and un-reacted hydrogen chloride are scrubbed by sodium hydroxide to neutralise hydrogen chloride. The rest is vented to atmosphere. Condensed crude trichlorosilane is stored in an insulated 100 litre storage tank.

V. K.Tangri <vktangri@barc.gov.in>

S. K. Das <skd@barc.gov.in>

## 20.4 PRODUCTION OF 150 KG GADOLINIUM NITRATE FOR TAPS

Gadolinium is preferred over generally used boron due to high neutron cross section . It works efficiently for reactivity control through moderator liquid poison addition system (MLPS) as well as for reactor shut down system (SDS2). Low concentration of Gd (0.1-0.2 g/l) in heavy water is sufficient to shutdown the reactor in short time for which otherwise large quantity of boron would be required.



Rare Earth development Section has produced 150 Kg Gadolinium nitrate of 99.99% purity to meet the requirement of Tarapur Atomic Power Project (TAPS 3&4). The process schematic is represented in the figure. The analysis of the crystals were carried out in Radio Chemistry Division as well as in REDS. It was found to contain (mg/g) Na <1, Mg < 1, Cl < 6.5, Cu < 1, Y=4, Nd <1, Sm <1, Eu =7, Dy < 1, Tb < 1 which are well within the Technical Specifications Gadolinium nitrate for PHWR namely Na: < 100ppm, Mg: < 50 ppm, Cl : < 50ppm, RE: < 900ppm.



## Organo-gallium and -indium compounds

Organo-gallium and –indium compounds, particularly tri-methyl and -ethyl, are extensively used for deposition of III-V materials

$$Mg_{5}Ga_{2} + 8RI \xrightarrow{Et_{2}O} 2R_{3}Ga_{0}OEt_{2} + 3MgI_{2} + 2MeMgI$$

$$\downarrow (i) Ph_{2}O$$

$$\downarrow (ii) Distill$$

$$R_{3}Ga$$

by Chemical Vapor Deposition methods. We have adopt the following strategy for their synthesis.  $(M = Ga \text{ or } In; R = Me, Et, Pr^i)$ 

The reaction with gallium-magnesium alloys are quite facile, but the corresponding reactions with

$$2Mg_3In + 9RI \xrightarrow{Et_2O} 2R_3In.OEt_2 + 3MgI_2 + 3RMgI_3$$

H. Singh <hsingh@barc.gov.in>

#### 20.5 ORGANO - METALLIC COMPOUNDS

Since the first demonstration of GaAs growth by MOCVD in 1968 by Manasevit extensive work on synthesis of various inorganic materials by CVD techniques has been carried out particularly during last fifteen years. These techniques employ metallo-organic compounds which are required in high purity. As the complexity of electronic devices is increasing with time, the demand for low decomposition temperature metallo-organic precursors with cleaner deposition is also growing. At BARC, conventional as well as new precursors have been synthesised and methods for their purification developed. To maintain a high level of purity consistently, we have adopted adduct purification method for organometallic compounds. A relatively non-volatile adduct is easy to handle and can be purified by re-crystallization. The adduct is prepared by combining an appropriate Lewis base (electron rich compound) with a Lewis acid (electron deficient compound). Thermal dissociation of these adducts at an appropriate temperature generates pure organometallic compound which can be obtained as and when required.

indium alloys are very sluggish and require several hours (12-16) for completion. Best yields are obtained from homogeneous phase of  $Mg_5Ga_2$ . Inhomogeneous alloys often lead to the formation of Grignard reagent and gallium metal. Although diethyl ether adduct of  $R_3Ga$  is quite useful for a variety of chemical reactions the adduct free alkyl is obtained by coordinating with diphenylether, liberated diethyl ether is distilled off and the diphenylether adduct so formed, on pyrolysis affords base free trialkyl gallium compounds.

Having developed convenient methods for the synthesis of trialkyl gallium and indium compounds, their reactions with protic ligands have been investigated. The ligands include internally functionalized carboxylic acids, pyridyal alcohol, phenols, and dithiolates. In general the diorgano complexes were isolated as dimers. Both gallium and indium tris dithiolates of the general formulae M(S S)3 were synthesized by the reactions of MCl<sub>3</sub> and an appropriate salt of a dithio acid. These complexes exist as a discrete monomeric units. The complexes with dithio ligand on pyrolysis gave M<sub>2</sub>S<sub>3</sub> which can also be isolated as nano particles.

#### Organo-arsenic and –antimony compounds

In order to replace conventional group V precursors  $(AsH_3 and SbH_3)$  due to their inherent weakness, extensive work is being carried out to design and develop suitable molecules with desirable properties. We have synthesized several organo-arsenic and – antimony compounds. These compounds are readily prepared

# $\begin{array}{l} \mathsf{ECI}_3 + 3\mathsf{RM}g\mathsf{X} \to \mathsf{R}_3\mathsf{E} + 3\mathsf{M}g\mathsf{X}\mathsf{C}\mathsf{I} \\ \mathsf{AsCI}_3 + \mathsf{Bz}\mathsf{M}g\mathsf{C}\mathsf{I} \to \mathsf{Bz}\mathsf{AsCI}_2 + \mathsf{M}g\mathsf{CI}_2 \\ \mathsf{Bz}\mathsf{AsCI}_2 + 2\mathsf{M}e\mathsf{M}g\mathsf{I} \to \mathsf{Bz}\mathsf{AsMe}_2 + 2\mathsf{M}g\mathsf{C}\mathsf{I} \\ (\mathsf{E} = \mathsf{As} \text{ or } \mathsf{Sb}) \end{array}$

by the reactions of a suitable metal halide with Grignard reagent in diethylether or tetrahydrofuran. These compounds are readily purified by distillation (liquids) under a reduced pressure or by recrystallization (solids) from petroleum ether/hexane. They were characterized by NMR spectroscopy which showed expected resonances. The alkylarsines and stibines form various complexes with palladium and platinum salts. The complexes of the type [MCl<sub>2</sub>(ER<sub>3</sub>)<sub>2</sub>], isolated by the reaction of [MCl<sub>2</sub>(MeCN)<sub>2</sub>] with ER<sub>3</sub> in dichloromethane, are of particular interest. These complexes are readily recrystallized to a high degree of purity from appropriate solvents and on thermolysis releases coordinated trialkylarsine as revealed by TG analysis. Thus this method is advantageous not only in storing air sensitive compounds as stable adducts but also in purifying the precursor conveniently.





The X-ray structures of  $(C_6F_5)_3E$  (E = As, Sb, Bi) revealed that metal is in a trigonal pyramidal configuration. Coordination around arsenic or antimony in palladium and platinum complexes approaches nearly tetrahedral configuration.

#### Precursors for v-vi materials

Group V chalcogenides of the type  $E_2Ch_3$  (E = As, Sb, Bi; Ch = S, Se, Te) are semiconductors with a band gap varying between 2.36 ( $As_2S_3$ ) and 0.15 ( $Bi_2Te_3$ ) eV and find several applications such as halographic recording, thermoelectric coolant, etc. Complexes of chelating chalcogenolate ligands offer a promising alternative as they can deliver both metal and chalcogen in the same molecule. These complexes are usually significantly more stable, less toxic, non-pyrophoric and easier to handle than their

alkyl derivatives. Keeping this in mind organoarsenic, -antimony and –bismuth compounds with xanthates, dithiocarbamates and dithiophosphates have been synthesized employing following reaction route.

These complexes have been characterized by elemental analysis, IR, NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P), mass spectra and X-ray structural analyses . The xanthate complexes tend to decompose on slight heating as revealed by TG analysis. The mass spectra did not show molecular ion peaks for xanthate complexes. Thus methylbismuth complexes [MeBi(S<sub>2</sub>COR)<sub>2</sub>] in reflexing xylene afforded pure  $Bi_2S_3$ 



#### Organoselenium and tellurium compounds

Organoselenium and tellurium compounds have been prepared by the reactions of sodium/potassium chalcogenides with

> Na₂E + 2RX → R₂E + 2NaX Na₂K₂E + 2RX → R₂E₂ + 2Na/KX (E = Se,Te;R = alkyl or aryl group)

alkylhalides. Both mono- and di-chalcogenides are successfully used for the synthesis of a variety of metal chalcogenides.

#### Palladium platinum chalcogenolates



Palladium chalcogenides are used in electronic industry, solar cells, etc. In this perspective, new organochalcogen ligands,

 $(Me_2NCH_2CH_2E)_2$ ,  $(Me_2NCH_2CH_2CH_2E)_2$  and  $(Me_2NCH_2CHMEE)_2$ (E = S, Se, Te) were designed and developed. Several palladium and platinum complexes with these ligands have been synthesized and characterized by NMR spectroscopy and crystallography. Palladium selenolates, such as  $[Pd(SeCOAr)_2(PPr_3)_2]$ , on pyrolysis afforded  $Pd_{17}Se_{15}$  as characterized by EDAX and XRD data.

#### Dimethylaminoalkylselenolates of Zn, Cd, Hg

Dimethylaminoalkylselenolates of Zn, Cd, Hg of the type  $[M{Se(CH_2)_nNMe_2}_2]$  (M = Zn, Cd, Hg) were synthesized and were characterized by spectroscopic methods. Thermolysis of  $[Cd(SeCH_2CH_2NMe_2)_2]$  under different conditions gave CdSe, the size of which was reaction condition dependent. Nano-particles of 6-12 nm were formed on heating in TOPO. Similarly  $[Hg(SeCH_2CH_2CH_2NMe_2)_2]$  was pyrolysed and nanoparticles of HgSe were formed. These nano particles were characterized by XRD analysis and SEM.

#### Ultrapurifications of metals

High purity materials are of high technological importance and are required for the preparation of compound semiconductors. Gallium metal ( $\sim$  7 N) and arsenic ( $\sim$ 6 N) were purified in kilogram quantities for the preparation of GaAs. Purification methods of other elements (Ge, In, Sb) are being developed.



Facility for ultrapurification of metals at Chemistry Division

S. K. Kulshreshtha <kulshres@barc.gov.in>









#### 20.6 CLOSING THE ZIRCONIUM CYCLE

PHWR discharges zircaloy waste in the form of hulls from the fuel reprocessing plant (2.6 Te/Y per PHWR) and replaced pressure tubes ( $\sim$ 12 Te per reactor every ten years). Recycle of zirconium will result in orders of magnitude reduction in the volume of radioactive waste, in addition to the recovery of zirconium having improved neutronic property. After 2-3 years of cooling the residual activity in the Zircaloy matrix is that of <sup>125</sup>Sb and <sup>60</sup>Co.



A hydrometallurgical process based on ion exchange chromatography has been developed by Laser & Plasma Technology Division and Analytical Chemistry Division, which can be introduced in the present fuel cycle as shown in the figure. The hulls are cleaned, converted in Zirconium tetrachloride by chlorination at 800°C. On dissolution the feed material of 1M ZrOCl, in 2N HCl for the ion chromatography will be available.

Several alternatives of the ion exchange chromatography step have been developed using indigenously available gel and macroporous type of strong cationic and strong anionic resins. Custom manufactured anionic resins were found to have radiation stability upto 120 Mrad. The cationic resins have better resistance. The elution chromatography process mainly in HCl, oxalic acid and nitric acid medium have been demonstrated in industrial bench scale column of 1000 mm length and 25 mm dia using 0.3 to 0.5 mm resin beads.

A typical decontamination process, has oxalate solution feed, containing anionic complex of Zr and Cationic Co and Sb and elution in hydrochloric acid. The demonstration with simulated solution prepared by adding tracers Co-60, Zr-95 and Sb-125. The chromatography step shows decontamination factor of



around 100 in the 1 meter long column. Pilot plant studies are planned with the replaced pressure tubes to finalise the flowsheet and equipment design for recycle of zirconium from hulls and coolant channels.

L. M. Gantayet <headlptd@barc.gov.in> Head ACD <headacd@barc.gov.in>

## 20.7 LOW VOLTAGE ELECTRODEPOSITION OF DIAMOND LIKE CARBON (DLC) AND CN<sub>x</sub> FILMS

Diamond has extreme, unique and diverse properties such as very high mechanical hardness, dielectric strength, energy band gap, thermal conductivity, radiation resistance, and corrosive resistance and very low electrical resistivity, thermal coefficient of expansion, etc. made this material endowed with large application potential. Diamond is crystalline form of carbon and it occurs in nature. The availability of natural diamond is limited and the purity of such diamond is not controllable, demands the efforts to synthesis it in the laboratory. There are several methods reported in the literature for its synthesis.

In order to develop technology to give protective coatings on different substrates, for applications in commercial installations, R&D efforts have been taken up to coat DLC and carbon nitride films through electrodeposition, under low voltage conditions. Ease of coating, cost effectiveness and large area coating possibilities are the attractive features of the method. Diamond Like Carbon (DLC) films were deposited on silicon substrate from ethanol through electrodeposition at low voltages (80V-300V). Similarly carbon nitride (CN) films were deposited from acetonitrile at low voltage (150V- 450V). Atomic Force Microscopy (AFM), Scanning electron microscopy (SEM), Raman spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy and Auger electron Spectroscopy (AES) were used to characteriz the films. The FTIR spectra indicate the C-H bonding states are predominantly sp<sup>3</sup>. The sp<sup>2</sup> contents in the DLC films were calculated from Auger electron spectra and found to be 31, 19 and 7.8% for the samples prepared at 80, 150 and 300 V respectively.

- S. K. Kulshrestha <kulshres@barc.gov.in>
- C. G. S. Pillai <cgspill@barc.gov.in>

#### 20.8 STRUCTURE AND DYNAMICS OF ORGANIZED ASSEMBLIES

Self-assembly is a common fundamental process whereby non-covalent interactions among amphiphilic molecules control the formation of organized, dynamic, nano-scale structures. Understanding the properties of self assembled structures and the methods for their preparation and structural characterization are key both to their direct utilization in applications and for



Schematic pictures of a few self-assembled structures: Monolayer (A), Micelle (B), hexagonal (C) and (D) liquid crystal, rod-like micelle (E) and vesicle (F)



Transmission Electron micrograph of silver nanorods and pentagonal nanocrystals

their exploitation in creating other nano-particulate systems and devices. Structural polymorphism in a variety of amphiphilic systems such as surfactants, block copolymers, polyelectrolytesurfactant complexes etc. have been investigated using light and neutron scattering experiments. Hydrophobe induced structural transitions in ionic micelles, its use in controlling the size of conducting polymer colloids, shape control in silver nanoparticles and sphere to rod transition in block copolymer assemblies have been studied. The figure shows transmission electron micrograph of silver nanorods and pentagonal nanocrystals.

S. K. Kulshrestha <kulshres@barc.gov.in>

#### 20.9 FRAMEWORK SOLIDS

Frame work solids belong to an interesting class of materials, which have corner shared polyhedra as the building blocks. Therefore, they are characterized by loosely packed and less dense lattice. Typical examples are metal tungstates, molybdates and phosphates e.g.  $MM'_{2}O_{8}$  (M = Zr, Hf; M' = W, Mo etc.),  $MPO_4$  (M = trivalent cations) and  $M_2M'_3O_{12}$  (M = RE<sup>3+</sup>, Trivalent Transition Metal ions,  $M' = W^{6+}$ ,  $Mo^{6+}$ ). A number of materials have been investigated, to reveal an interesting thermal expansion behaviour and phase transitions. An extensive use of dilatometer and High Temperature-XRD was made to study these materials. The high pressure (HP) and high pressure-high temperature (HPHT) studies on these materials resulted in several new modifications. In general, these materials exhibit low or negative thermal expansion behavior. A remarkable correlation between structure and thermal expansion behaviour was observed among tungstates, molybdates and phosphates. The role of the counter cation's size in govering the negative thermal expansion behaviour was also delineated. Thermal expansion behavaior of low cristobalite and high cristobalite type AIPO<sub>4</sub>, GaPO<sub>4</sub>, their solid solutions, BPO, revealed the importance of inter-polyhedral bond angles in governing the thermal expansion behaviour. A nearly zero thermal expansion materials was prepared in Y<sub>2</sub>W<sub>3</sub>O<sub>12</sub>-Nd<sub>2</sub>W<sub>2</sub>O<sub>12</sub> system. These materials are technologically important from the point of view of tailoring the thermal expansion behaviour structural materials used in high temperature devices.

S. K. Kulshrestha <kulshres@barc.gov.in>

## 20.10 LANGMUIR-BLODGETT (LB) FILMS OF FUNCTIONAL MATERIALS

Langmuir-Blodgett technique enables synthesis of regular multilayers with good control over film thickness and uniformity. LB films are deposited incorporating various functional groups (e.g. dye, nanoparticles, and charge transfer complexes) for potential applications as chemical sensors and devices. The



Schematic picture of Langmuir-Blodgette trough



surfactant monolayer has been employed as a template to grow crystals of Prussian blue analogues. LB films of conducting polymer are deposited for application as gas sensors. It has been observed that polycarbazole LB films have higher sensitivity, faster respone and recovery to ammonia gas as against electropolymerised carbazole films and spin cast polycarbazole films.

#### S. K. Kulshrestha <kulshres@barc.gov.in>



## 20.11 RARE-EARTH BASED INORGANIC FLUORIDES

The study of crystal chemistry of rare-earth containing mixed fluorides has occupied an important place in the field of material science due to the their structural diversity and interesting electrical and optical properties e.g. fluorides are expected to show ionic conductivity, with nearly no electronic conductivity. Several phase equilibria in MF<sub>2</sub>-M'F<sub>2</sub> systems were investigated under short annealed followed by slow cooling conditions. In all these studies a fluorite-type solid solution at the  $MF_2$  (except for  $M = Mg^{2+}$ ) rich-end is observed. Besides, several fluorite or tysonite related ordered phases are also observed depending on the thermal history of the samples. The role of difference of ionic size between  $M^{2+}$  and  $M'^{3+}$  ions on phase relations in MF<sub>2</sub>-M¢F<sub>2</sub> systems was also delineated. This work led to several ionic conductors. A new scheelite type luminescent material  $LiScF_a:Er^{3+}$  was prepared by a high pressure solid state synthesis. LiScF<sub>4</sub> sample doped with 1%  $Er^{3+}$  showed an intense luminescence in the far IR region. The use of high pressure was responsible for getting a coordination number of eight for  $Sc^{3+}$ , which is unusually high for  $Sc^{3+}$ .

S. K. Kulshrestha <kulshres@barc.gov.in>

#### 20.12 DEVELOPMENT OF LOW TEMPERATURE HEAT CAPACITY MEASUREMENT FACILITY:

A low temperature experimental setup in the range of liquid helium temperature to 300 K for specific heat measurement by semi-adiabatic heat pulse method is being developed in our division. The cryostat employed is a stainless steel multi layered super insulated dewar, of about 22 liters capacity. The indigenously





developed design of the equipment has been fabricated with stainless steel, consisting of three coaxial cylindrical chambers, each connected to evacuation system. Guard heater and different thermal radiation shields at various locations have been provided for attaining the semi adiabatic condition. The sample holder is made up of gold plated copper and can accommodate samples of about 7-8mm diameter and 2-3mm height. Entire helium recovery line, made of copper has been set from the laboratory to the main recovery line, provided with a copper heat exchanger. An on line data acquisition and analysis software has been developed in C language using the Lab Windows/CVI. Oxygen Free Copper(OFC) has been taken as system calibration material and measured the temperature dependent behavior of heat capacity from 10 K to 260 K. The results obtained are found to be in very good agreement comparable with reported values. Also heat-capacity behavior of potassium dihydrogen phosphate have been measured and found that the system reproduces the magnetic transition at expected temperature.

S. K. Kulshrestha <kulshres@barc.gov.in>

## 20.13 MICRORHEOLOGY OF COMPLEX FLUIDS BY LIGHT SCATTERING

Dynamic light scattering (DLS) has been employed for probing the rheological properties of complex fluids at a microscopic length scale - an area that has come to be called microrheology.





Traditionally, DLS is used as a mature tool for characterizing the size distribution of colloids. The use of DLS to obtain information regarding the response of a material to small amplitude mechanical perturbations. Themally-driven diffusion of colloidal probes in complex fluids such as polymer solutions and surfactant assemblies has been employed for measuring the time-dependent mean square displacement (MSD) of particles of known dimension. Using the generalized Stokes-Einstein relationship, the frequency-dependent complex shear moduli of the fluid can be estimated from the Laplace transform of the corresponding MSD (Dr<sup>2</sup>). The salt-induced transition from nearly spherical to elongated wormlike micelles and consequent changes in fluid response from viscous to viscoelastic are clearly captured by microrheology.

S. K. Kulshrestha <kulshres@barc.gov.in>