

# Evolution of chemistry programme at DAE

A. K. Tyagi<sup>1,\*</sup>, S. Kannan<sup>2</sup> and N. Sivaraman<sup>3</sup>

<sup>1</sup>Chemistry Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

<sup>2</sup>Radiochemistry and Isotope Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

<sup>3</sup>Materials Chemistry and Metal Fuel Cycle Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

**Chemistry is omnipresent in nuclear energy programmes all over the world. From the isolation and fabrication of fuel to the development of non-fuel materials and important nuclear processes, chemistry has played a crucial role. This article outlines the remarkable contribution that chemistry has made to the development of India's nuclear science programme. After a general introduction that deals with the inception and diversification of chemistry in the Department of Atomic Energy and some initial milestone achievements, a few notable contributions at BARC and IGCAR have been discussed in detail. These include the contribution of chemistry towards the front-end and back-end of the nuclear fuel cycle, nuclear safety, radiation chemistry and chemical innovations catering to the needs of society. Each subsection also includes possible future developments in the fields necessary for a sustainable nuclear energy programme.**

**Keywords:** Chemistry, electronics industry, nuclear energy, radioisotopes.

## Introduction

CHEMISTRY has played a central role in the development of nuclear energy programmes worldwide. It is involved in the isolation and fabrication of nuclear fuel, understanding its behaviour in a reactor to subsequent processing of nuclear waste as well as interaction of the fuel with clad, clad with coolant and chemistry of the coolant in a nuclear reactor, reactor water chemistry, etc. Hence it plays a crucial role in all steps of nuclear energy programmes. The role of chemistry in the production of nuclear-grade materials and valuable isotopes for technological or societal applications also bears importance. In the context of India's atomic energy programme, which relies on the closed nuclear fuel cycle, chemistry is extensively involved in nuclear waste reprocessing to minimize the waste burden as well as to isolate the fissile elements for further use and isotopes for other technological applications.

The chemistry programme related to nuclear science was initiated in 1949 from the National Physical Laboratory, New Delhi, and later shifted to Bombay (now Mumbai) by the end of 1949. Subsequently many organizational struc-

tural changes were made in the then Chemistry Division to address the requirements of the Atomic Energy Establishment, Trombay (AEET).

Some initial prominent work includes analysis of monazite samples (during the early 1950s), Zr and Hf separation (1955), high specific activity cobalt by the Szilard–Chalmers process (1955), cleaning of CIRUS PHT-chromate ions removal (1960), monitoring and controlling the fission gas release, development and installation of zone refining unit and other indigenous instruments, cover gas analyser development for the Madras Atomic Power Station (1972–1977), development of high-purity materials (from 1966 onwards; still continues), cleaning of heavy water in DHRUVA (1985), contributions towards nuclear safety (from 1987 onwards; continues and has been diversified), development of various materials for the back end of the nuclear fuel cycle, etc. Some of the activities will be discussed in the subsequent sections.

## Activities of the Chemistry Group at BARC

Some of the important research and development activities of the Chemistry Group at the Bhabha Atomic Research Centre (BARC), Mumbai are: directed research in the front end and back end of the nuclear fuel cycle, focused efforts towards nuclear reactor safety, development of catalysts, indigenization of processes for achieving high-purity materials, radiation and photochemistry, and indigenous development of various analytical methods useful for DAE as well as certified reference materials. The Chemistry Group is also actively pursuing research in the areas of computational chemistry, development of sensors for toxic gases, soft materials and inorganic–organic hybrid materials for radiation detection.

### *Role of chemistry in the nuclear fuel cycle*

The earliest research and development activities of the Chemistry Group at BARC have been focused on the synthesis of compounds of uranium relevant to the nuclear fuel cycle and to understand their thermochemical and thermodynamic behaviour<sup>1,2</sup>. Subsequently, research activities on the development of process strategies for extracting nuclear materials from their geological/man-made sources, fabricating them in desired/suitable physico-chemical forms for

\*For correspondence. (e-mail: aktyagi@barc.gov.in)

reactor applications<sup>3</sup> and safely immobilizing the residual non-usable radiochemical waste in stable matrices<sup>4</sup>, the safety of nuclear reactors under operational and accidental scenarios, development of sensors and detectors have been taken up. The Chemistry Group has been involved in the development of a database on thermophysical properties of materials for the advanced heavy water reactor (AHWR) since its conception. Phase behaviour of binary alloys in the zirconium–iron (Zr–Fe) system and zircaloy–steel system has been investigated to develop a metallic matrix for immobilization of zirconium-based metallic nuclear waste originating from thermal nuclear reactors. Towards the development of a molten salt breeder reactor (MSBR), extensive studies on the melting and thermodynamic properties of molten fluoride systems in LiF–ThF<sub>4</sub>–UF<sub>4</sub> and Na–UF<sub>4</sub>–ThF<sub>4</sub> systems have been carried out<sup>5</sup>.

The Chemistry Group in collaboration with the Nuclear Recycle Group, BARC, has been working to develop potential glass, ceramic and glass–ceramic matrices for nuclear waste immobilization applications. The efficiency to separate various radionuclides like <sup>99</sup>Tc, <sup>68</sup>Ga, <sup>90</sup>Y and <sup>188</sup>Re for radiopharmaceutical applications has been evaluated using nano-Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and crystalline Na<sub>x</sub>MnO<sub>2</sub>·yH<sub>2</sub>O as potential sorbents<sup>6</sup>.

### *Ensuring enhanced safety of nuclear reactors*

As evident during the events at TMI and Fukushima, hydrogen management is one of the factors of dominance towards retaining the integrity of the containment. Hydrogen could be produced due to loss of coolant accident (LOCA) followed by failure of emergency core cooling systems (ECCS), or due to failure to remove decay heat under station blackout. This hydrogen if not managed would damage the containment, which may result in the release of radioactivity<sup>7</sup>. The Chemistry Group has made a phenomenal contribution by developing a passive catalytic recombiner device (PCRD) which has been demonstrated to passively remove hydrogen at 0.8 and 2.0 kg/h for 4% and 8% hydrogen in air respectively. PCRDs have now been deployed in all reactors in India.

Another factor contributing to the release of radioactivity during a nuclear accident is the containment pressurization due to temperature rise, steam generation and release of other gaseous products from failed fuel, etc. The containment depressurization can be achieved by venting out of the containment gases. For that to happen safely, without the release of radioactivity, the containment filtered venting system (CFVS) plays a vital role. CFVS has to be designed and deployed considering the chemical species to be trapped. This can be achieved first, by predicting fission products, their speciation under fuel temperature conditions and diffusion for release from the fuel matrix<sup>8</sup>. Secondly, interaction of the released fission products, as gases or aerosols, with structural materials and other chemical species

present in the containment during an accidental scenario is evaluated for reaction kinetics and lifetime of the species formed. For example, one such study is being carried out for the speciation of iodine as gaseous iodine or CsI or iodate species or iodo-hydrocarbons based on the containment condition. On the basis of all the speciation data, filtered venting system designing like alkali hydroxide solutions or silver-loaded molecular sieves for removal of iodine or metal–organic framework for noble gases like Kr and Xe is in progress.

Another research programme that has been undertaken by the Chemistry Group is to develop a sacrificial core-catcher for the safe confinement of molten reactor corium formed under an unlikely event of a nuclear meltdown. Red-mud, a voluminous waste product of the alumina production industry has been identified as a cost-effective sacrificial core material to confine and bind the radioactive materials of corium. Using an appropriate thermal conditioning protocol with suitable additives, red mud could be processed into dense model bricks with high mechanical strength and poor water solubility. Thermophysical properties, like thermal expansion, thermal conductivity, crush strength, melting and ablation behaviour as well as water absorption and retention behaviour have been generated on sintered core-catcher materials. Interaction of the sintered core-catcher materials with various components such as U<sub>3</sub>O<sub>8</sub>, CeO<sub>2</sub>, and other fission products like rare-earth ions and alkaline-earth ions has also been studied.

### *Water chemistry research*

R&D work on water chemistry related to nuclear reactors and heavy water plants has been one of the important activities of the Chemistry Group at BARC since the 1970s. The Water and Steam Chemistry Laboratory was set up at the Indira Gandhi Centre for Atomic Research (IGCAR) campus, Kalpakkam in 1984, for carrying out large-scale experiments involving (i) dynamic loops operating at high temperatures and (ii) studies related to the treatment of cooling water specifically concerned with biofouling.

A small working group on PREWAC (Power Reactor Water Chemistry) later renamed COSWAC (Committee on Steam and Water Chemistry) was constituted to support research activities towards development of the nuclear power programme of the Department of Atomic Energy (DAE). The dilute chemical decontamination (DCD) process was developed indigenously and extensively applied to PHWR primary heat transport (PHT) system with fuel in place<sup>9</sup>. Nuclear power plants got benefitted by saving the MANREM >200 through DCD campaigns. Extensive laboratory studies were carried out for developing a decontaminant for stainless steel systems by employing oxidative and reductive processes. The formulation which is capable of dissolving the scale and the sludge was designed and developed for chemical cleaning of steam generators (SGs) to improve

heat transfer and avert tube failure. The process was successfully demonstrated on the hairpin HX of the MAPS steam generator.

Towards metal-ion passivation activity, improvizing water chemistry control to avert corrosion of carbon steel is important activity of the Chemistry Group. Additives like magnesium added at ppb levels to the coolant reduce corrosion and corrosion release by modifying the corrosion product oxide formed on the primary heat transport system surface<sup>10</sup>. Under simulated PHT system chemistry conditions, the corrosion rate of carbon steel was reduced by 40% in the presence of magnesium and oxide thickness on the metal was found to be reduced by 50%.

The Chemistry Group at BARC has been working on (a) biofouling control in cooling water systems of nuclear power plants and (b) dispersion of thermal plume at power plant discharges for the past two decades. An integrated antifouling strategy was developed for surface protection in the form of antifouling coatings, which can greatly reduce the biocidal inventory and environmental burden in the vicinity of industrial cooling water discharges<sup>11</sup>.

#### *High-purity materials: catering to the needs of the nuclear and electronics industry*

Since the establishment of DAE, the necessity for high-purity materials was realized for technological advancement in various areas, especially in nuclear science, space exploration and the electronic industry. With this vision, R&D activities on high-purity materials were initiated in the Pure Materials Section of the Chemistry Division at BARC. In the initial days, technology for the separation of rare earths from rare earth concentrates was developed and later transferred to IRE Ltd, Aluva.

In 1966, the Dr Bhabha Committee Report was published, which envisaged the requirement of ultrapure materials for India with special reference to their applications in the electronics/semiconductor industry. This led to the indigenous development of processes for the purification of several elements of 5 N (99.999%) purity. The recipes were transferred to the newly set up Special Materials Plant (SMP) at NFC Hyderabad for regular production to cater to industrial needs.

Meanwhile, the Kalam committee realized that efforts should be directed towards the development of processes for ultra-high purity materials (~6 N). Consequently, in 1994, the MASCOT project was formulated under which arsenic (6 N)–antimony rods (~6 N) were developed at MAT Lab (located near Van-de-Graff Building, BARC)<sup>12</sup>.

The challenging task of providing high-purity germanium was assigned to the Chemistry Group, which has been actively pursued. An indigenously designed zone-refining unit equipped with an induction heater and having provision to carry out refinement under vacuum, argon and hydrogen atmosphere was used for this purpose.

#### *Analytical chemistry research*

The Analytical Chemistry Division (ACD), Mumbai and National Centre for Compositional Characterization of Materials (NCCCM), Hyderabad of the Chemistry Group at BARC are in the forefront of providing analytical solutions for changing needs of all DAE projects as well as for societal applications since their inception. The analytical chemistry work started at DAE in the early 1950s with the chemical analysis of rocks and minerals for uranium and other constituents. Simultaneously, analysis of other materials like metals and alloys, process solution samples and other materials like boron carbide for boron, uranium metal and oxides for carbon, nitrogen and other constituents, steel samples for carbon, sulphur, phosphorus, silica as well as other critical constituents like chromium, nickel, manganese and molybdenum was carried out regularly. It has also provided analytical solutions for various programmes such as impurities in uranium metal for research nuclear reactors, composition of reactor structural materials/claddings, development of new shielding materials for reactors and ceramic magnets for the reactor control system.

Apart from analytical services, methodologies were developed and deployed for surface elemental composition/depth profiles of impurities in various technologically important materials. Recently, a novel, neutron-induced chain reaction methodology has been developed for non-destructive composition analysis of refractive materials such as lithium titanate. The Chemistry Group is actively involved in the indigenous development of analytical instruments and under this programme, a C/S analyser, surface-area analyser<sup>13</sup>, improved hydrogen determinator and dissolved oxygen monitors were developed and are currently in use.

For the international acceptance of results, the need was felt for obtaining NABL accreditation for the analytical laboratories. Both ACD and NCCCM pursued this activity and the laboratories obtained accreditation from NABL, which is a prerequisite to developing certified reference materials (CRMs), as discussed in the next section.

#### *Certified reference materials*

The use of CRMs is a widely recognized tool for verification of the accuracy of analytical techniques and they form an integral part of quality control systems. The Chemistry Group has a unique programme for the production of CRMs/in-house reference materials to cater to the needs of DAE and non-DAE institutions as well as to satisfy the needs of the Indian industrial sector and the societal sectors. Under this programme, geological standard TKT-1 (Trachy basalt from Kandivali, Mumbai), geological reference material B-78 prepared using black basalt from Gilbert hill, Andheri, Mumbai<sup>14</sup>; in-house hair reference material for mercury, etc. were developed.

Bharatiya Niradeshak Dravya (BND) of high purity quartz (BND 4101.01) powder for trace elements Al, Fe, Ca, Na, K, Mg and Ti was prepared at NCCCM in 2016.

Recently, in-house graphite reference material (ACD-G-16:100 bottles of 30 g each)<sup>15,16</sup> and uranium metal RM for evaluating concentrations of Fe and Al were also prepared. Due to the high cost of CRMs and continual use, in-house reference materials were also prepared in 2019–2020. An indigenously developed CRM of dolomite (BARC B1101) was prepared following the ISO guidelines, jointly by the Atomic Minerals Directorate for Exploration and Research (AMDER) and NCCCM.

### Radiation and Photochemistry

Radiation chemistry is an integral component of R&D areas for atomic energy in India, where BARC took the leadership in executing such programmes. The initial task assigned to radiation chemists was to synthesize high specific activity cobalt-60 through nuclear transformation for its use in cancer radiotherapy<sup>17</sup>. During the late 1950s in BARC, the mandate was to quantitatively determine the radiation (and thermal) decomposition product and pathways of organic coolants. During the 1960s, the areas being pursued were radiation-induced polymerization in liquid and solid state, radiation-induced grafting and sulpho-chlorination of kerosene leading to biodegradable detergents. The reactivity of trapped electrons in aqueous and organic glassy systems at 77 K has shown that the electrons reacted with the added solutes by the tunnelling mechanism. In 1986, BARC was successful in installing a 7 MeV linear electron accelerator attached to an indigenously developed optical pulse radiolysis set up as a national facility. Photochemistry research in the Chemistry Group at BARC started in 1970 when a conventional flash photolysis system offering microsecond time resolution was built indigenously for this purpose, followed by setting up nanosecond to picosecond and finally femtosecond transient spectroscopic facilities<sup>18</sup>. Efforts have been made to understand atmospheric photochemical processes by measuring the tropospheric lifetime, global warming potential, ozone depletion potential, etc. of volatile organic compounds. To understand the coupling between different vibrational bands, which provide information on the transient molecular structure in the ultrafast timescale, a two-dimensional infrared (2D IR) spectrometer has also been developed indigenously. With the newly built single-molecule fluorescence spectroscopy and imaging facility, actinide chemistry is possible without factoring in the constraints of high activity handling under ambient laboratory conditions<sup>19</sup>.

### Catalysis

Catalysis research in the Chemistry Group at BARC started in the late seventies and involved both basic and applied

aspects of heterogeneous catalysis relevant to environmental pollution control and energy conversion processes as well as to the DAE programmes. In those days, emphasis was given to the in-house development of instruments and systems required for the research work. As a result, several systems, e.g. catalytic reactor,  $\gamma$ -irradiation set up, gas chromatograph equipped with TCD and FID detectors, etc. were developed to augment catalysis research at the Chemistry Division. The tradition continued further with the indigenous development of cells for *in situ* FTIR, EXAFS and quasi-elastic neutron scattering studies, sealed-off CO<sub>2</sub> laser and experimental set up for thermochemical/photocatalytic generation of hydrogen. The first result on enhancement in the catalytic activity of zeolite-supported metal catalysts for CO and CO<sub>2</sub> hydrogenation reaction upon *in situ*  $\gamma$ -irradiation, attributed to the accumulation of energy in trap centers (in zeolite support), and its subsequent transfer to metal sites were well received by the catalysis community<sup>20</sup>. In subsequent years, the research encompassed investigations on the mode of adsorption, dynamics of adsorbate molecules (e.g. hydrocarbon) inside porous adsorbents (e.g. micro/mesoporous zeolites), spillover phenomenon, strong metal-support interaction, delineation of the role of surface intermediates during CO/CO<sub>2</sub> methanation, CO oxidation, selective catalytic reduction of NO, degradation of volatile organic compounds, thermochemical/photocatalytic/electrolytic hydrogen generation and photocatalytic reduction of CO<sub>2</sub> over different catalyst systems<sup>21</sup>. Similarly, work on applied catalysis addressed the needs of different areas (in DAE) seeking catalytic solutions. Some of the noteworthy contributions include noble metal-based hydrophobic catalysts for H/D exchange reaction [ $\text{H}_2\text{O}_{(l)} + \text{HD}_{(g)} \leftrightarrow \text{HDO}_{(l)} + \text{H}_2_{(g)}$ ], supported gold catalysts for gas reconstitution in sealed-off cw-CO<sub>2</sub> lasers, an iron-oxide based catalyst for sulphuric acid decomposition, iodine-sulphur process and noble metal-based electrocatalysts for CuCl/HCl electrolysis step of copper-chlorine process for hydrogen generation. Also, suitable *de oxo* catalysts and electro-catalysts for improved product purity and efficiency of alkaline water electrolyzers, visible-light active photocatalysts for hydrogen generation via water splitting reaction and mixed oxide catalysts for degradation of dioxins and furans are being developed.

### Activities at the radiochemistry and isotope group, BARC

Some of the important R&D activities of the Radiochemistry and Isotope Group are directed research in the frontier areas of nuclear and radiochemistry, including nuclear reactions, actinide spectroscopy and nuclear probes, and directed research in actinide chemistry such as separation science relevant to both the front as well as the back ends of the nuclear fuel cycle, electrochemistry of actinides relevant to separation, quantification and sensor applications: radioisotope

production and development of new radiopharmaceuticals for diagnosis and treatments: isotope hydrology studies for water resource management, industrial applications of radioisotopes, radiation technology for the development of materials for special applications and radiation applications in sludge hygienization.

### *Nuclear chemistry studies*

Activities in the area of nuclear chemistry have been primarily focused on unravelling the role of the potential energy landscape and nuclear magicity in governing the nucleon transfer and nuclear fission processes along with the production of heavy actinides for decay studies employing radiochemical separations. Mass distribution studies in the mass region  $\sim 180$ , which is currently an active area of investigation after observation of 'unexpected' asymmetric fission, revealed the role of heavy fragment neutron number  $N_H \sim 56$  and light fragment proton number  $Z_L \sim 34-36$  in the contribution from asymmetric fission in this mass region<sup>22</sup>. Heavy actinides such as <sup>244</sup>Bk and <sup>244</sup>Am were produced using a nuclear reaction to study their decay scheme, gamma-ray intensities and half-lives.

### *Actinide chemistry research*

Research on actinide chemistry was taken up to develop suitable ligands for actinide partitioning and lanthanide/actinide separation, which has relevance in radioactive waste management. The ligands used for actinide separation studies are tributyl phosphate (TBP), sulphoxides, carbamoyl methyl phosphine oxide (CMPO), amides (including malonamides and diglycolamides), etc. and for lanthanide/actinide separation studies the ligands used were dithiophosphoric acids and N-donor heterocyclic compounds such as bis-triazinyl pyridine, bis-triazinyl phenanthroline and bis-triazinyl bipyridine<sup>23</sup>. The techniques used for actinide-ion separation are solvent extraction, ion exchange, liquid membrane, and solid-phase extraction. Several valuable radionuclides, viz. Sr-90, Ru-106, Cs-137 and Np-237 were separated from the radioactive liquid waste generated after reprocessing of the irradiated fuel. At the basic chemistry front, complexation and structural studies of these f-block elements were also carried out to understand their interactions with a different class of ligands using various experimental tools, viz. absorption and luminescence spectroscopy, extended X-ray absorption, fine structure spectroscopy, single-crystal XRD and electrochemical techniques.

### *Positron spectroscopy in materials science*

Positron annihilation spectroscopy (PAS) was initiated in the late 1980s as one of the nuclear probes for materials studies. The initial studies were focused on understanding

the behaviour of positrons in the matter. With the understanding of the positron and positronium chemistry in hand, the initial studies were focused on shape memory alloys, high-temperature superconductors, etc. Positrons have a natural propensity to get trapped in low electron density areas in the materials such as open volume defects in metals and alloys, free volumes in condensed matter and pores/cavities in porous matrices. Using positron/positronium as a non-invasive probe, PAS is being used regularly for materials characterization studies<sup>24</sup>. Depth-dependent positron annihilation is the most suitable method to quantify damage in these systems. The sensitivity of the techniques to point defects has been extended for the investigation of phase transformations in alloys. Phase transition behaviour of nano-confined liquids using PAS and NMR was also investigated and the role of surface interactions, inter- and intra-molecular interactions, and level of pore filling has also been examined. Defect characterization of various phosphors and catalysts has also been studied.

### *Electrochemistry of actinides*

The redox chemistry of actinides (U, Np and Pu) has been studied on different working electrodes, viz. Au, Ag, Pt, graphite and glassy carbon in different acid media. Recently, the electrochemistry of actinide ions has been studied using the electrodes modified with nanoparticles of Pt, Au, Ru, Pd and Rh, conducting polymers like polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS), carbonaceous nanomaterials like single-walled carbon nanotubes (SWCNTs), graphene, reduced graphene oxide (rGO) and metal-polymer nanocomposites like Pt-PANI. The modified electrodes gave enhanced peak current and better sensitivity towards various actinide ions studied. The determination of uranyl ion with a detection limit of 1.95 ppb has been achieved at ruthenium nanoparticles (RuNPs) decorated glassy carbon (RuNPs/GC) electrode<sup>25</sup>. The redox behaviour of U, Np and Pu has been evaluated at glassy carbon electrodes coated with SWCNTs, rGO and graphene. The results showed their excellent electrocatalytic properties with significant enhancement in heterogeneous electron transfer rate constant and decrease in electron transfer resistance compared to GC.

### *Radiation technology for materials processing*

The unique ability of high-energy radiation is to bring out chemical changes in materials in any of the phases such as solid, liquid or gas in a wide temperature range to yield materials as soft as polymers to as hard as diamond. The initiator-free radiation-induced polymerization of monomers leads to high-purity polymers and sub-room temperature polymerization has been exploited to polymerize thermo-sensitive monomers. Low-temperature ( $-78^\circ\text{C}$ ) polymerization of 2-hydroxyethyl methacrylate (HEMA) was investigated

for synthesizing controlled drug delivery matrices through a dual release mechanism<sup>26</sup>. Polymers on exposure to high-energy radiation undergo crosslinking or chain-scission reactions depending on their structure and the irradiation conditions. Crosslinking of the polymers was exploited to crosslink the polymer composites filled with conducting filler nanocarbon black (NCB). The optimum crosslinking resulted in a sensor with significantly high sensitivity towards acetone in comparison to other organic moieties in human breath and faster recovery post-detection. The radiation degradation of polytetrafluoroethylene (PTFE) was used as a one-time lubricant and as an additive for paints for the marine atmosphere. PTFE scrap was radiation-grafted to design a low-cost, efficient adsorbent for ionic dyes and heavy metals from aqueous streams. High-energy radiation efficiently kills pathogens through their DNA damage. Based on this effect, the pathogenic sewage sludge generated in sewage treatment plants (STPs) is converted into a hygienized and enriched manure suitable for agriculture purposes.

#### *Applications of radioisotopes in industry and hydrology*

Radioisotopes as radiotracers and sealed sources are widely used in the industry for identification of flow malfunctions, measurement of flow parameters, evaluation of the design of chemical reactors or process systems, and monitoring of product quality and process efficacy. The main advantages of radioisotope techniques are online monitoring and high detection sensitivity, and often do not have any alternatives. This means that the techniques can be applied without shutting down the plant.

Isotope hydrology is another important area of application of environmental isotope techniques<sup>27</sup>. The major applications of isotope techniques in hydrology include identifying the recharge zone, groundwater recharge studies, groundwater dating, interconnection between aquifers or water bodies and groundwater pollution studies.

#### *Radiopharmaceutical chemistry*

Radiopharmaceuticals are radioactive pharmaceuticals, used *in vivo*, either for diagnosis or treatment of various human maladies. A plethora of medically useful radioisotopes, such as <sup>99m</sup>Mo (for <sup>99m</sup>Tc), <sup>125</sup>I, <sup>131</sup>I, <sup>153</sup>Sm and <sup>177</sup>Lu are regularly produced and supplied to various hospitals and nuclear medicine centres in the country. In recent times, <sup>64</sup>Cu has been successfully produced and its potential as a theranostic radiopharmaceutical has been evaluated. <sup>90</sup>Y-glass microspheres (named 'Bhabha spheres') were indigenously developed as a cost-effective alternative to Therasphere<sup>TM</sup> for liver cancer therapy. Patient dose preparation and deployment of ready-to-use radiopharmaceuticals such as <sup>90</sup>Y-labelled hydroxyapatite, <sup>177</sup>Lu-labelled hydroxyapatite

(for the treatment of rheumatoid arthritis), and <sup>177</sup>Lu-labelled DOTMP (for bone pain palliation) has been carried out<sup>28</sup>. A significant contribution in developing and deploying peptide receptor radionuclide therapy (PRRT) agents, used predominantly for the treatment of patients suffering from neuroendocrine and prostate cancers has been made. In addition, the indigenously produced low/medium specific activity <sup>177</sup>Lu-based radiopharmaceutical for therapeutic use (<sup>177</sup>Lu-DOTA-TATE for neuroendocrine cancers and <sup>177</sup>Lu-PSMA-617 for prostate cancer) is available in more than 50 nuclear medicine centres in India at an economic price.

#### **Evolution of the chemistry programme at IGCAR**

The chemistry programme has played a vital role in various stages of India's nuclear energy programme. It has a major stake in every step of the closed nuclear fuel cycle. Beginning from nuclear ore-processing to fabrication, quality control, nuclear fuel reprocessing and waste management, the developments in chemistry have their influence. The recognition and importance of chemistry led to the construction and development of the Radiochemistry Laboratory (RCL) of IGCAR (then Reactor Research Centre) in the very early stages of planning of the Centre at Kalpakkam. The Chemistry Laboratory was primarily intended to be only a supporting facility for reactor technology and fuel reprocessing and in the formative years, it was not planned to have wide-ranging chemistry programmes. It goes to the credit of C. K. Mathews who was, given the responsibility for planning RCL at IGCAR in 1970, and envisaged a wide range of programmes in fuel chemistry as well as sodium chemistry, providing support to the fast reactor programme at Kalpakkam, in addition taking R&D programmes which would have a long-term impact on the reactor programmes as well as the fuel cycle. The construction work started in 1976. The Laboratory became partially operational by 1978 with scientific instruments, including a spectrograph and thermal analyser, mass spectrometer system commissioned during 1978–80.

The launching of the R&D programme in RCL coincided with the organization of a Workshop on Thermodynamics of Nuclear Materials in January 1980, in which a large number of experts from various units of DAE and abroad participated. The Plutonium Laboratory was established in 1983 for carrying out aqueous chemistry studies. Studies on the chemistry of reprocessing fast reactor fuels were initiated. The isotopic composition of boron (used as neutron poison in MAPS) was estimated using a thermal ionization mass spectrometer (TIMS) in the same year. In 1985, the first of its kind sodium-handling facility in the country was established. Special glove boxes for handling alkali metals were indigenously designed and established. The Na–K coolant was prepared in large quantities in the glove box for use in FBTR in the cold-trap section. In

1987, a radioactive sodium chemistry loop (RASCL) was designed and commissioned to test the long-term performance of electrochemical on-line monitors for hydrogen, oxygen and carbon impurities in sodium, and also to examine the transport of radionuclides in liquid sodium. The development of electrochemical meters for monitoring hydrogen, carbon and oxygen in sodium was a challenging task and one of the major contributions of RCL to the reactor programme. These developments have demanded years of basic studies on various electrolyte systems, including their phase diagrams and electrical conductivity measurements. The in-sodium hydrogen meters were installed in FBTR and improvements in the sensing behaviour were achieved through a selection of appropriate electrolytes/electrodes, which demanded extensive studies on the phase equilibria of the molten salt systems.

The hot-cell facility at RCL is a unique radiochemical facility. The hot cells were commissioned in 1993 by charging  $\text{UO}_2$  fuel discharged from MAPS at about 9000 MWd/tonne. The fuel was dissolved and its burn-up was experimentally measured using high-performance liquid chromatography – mass spectrometry<sup>29</sup>. Subsequently, the cells have handled mixed carbide fuel of FBTR, discharged at 25,000, 50,000, 100,000 and 155,000 MWd/tonne. The atom % fission (burn-up), fission gas release and dissolution behaviour studies have been carried out on these fuel materials.

The last 40 years of activities in RCL have seen a wide range of achievements in various areas relating to nuclear technology and nuclear fuel cycle. Besides R&D activities, RCL has also provided extensive analytical support using a wide range of analytical techniques, to all the programmes in the Centre. RCL ventured into new areas of R&D such as novel synthesis routes for fuel materials and also provided a focus on activities related to FBTR. RCL matured into a world-class research group with its focus firmly on the mission-oriented programmes, but with increasing emphasis on developing and maintaining leadership in selected frontline areas, and expanding the range of collaborations with chemistry groups within and outside DAE to tap their potential for increasing the impact of the programmes. The work on chemical sensors has expanded to include sensors for hydrogen in argon cover gas, polymer electrolyte-based sensors which can detect hydrogen in weldments, oxygen sensors for use in light combat aircraft, and  $\text{NO}_x$  and  $\text{H}_2\text{S}$  sensors for environmental monitoring. Electrochemical hydrogen meters were also installed in the Phenix reactor and in SUPERFENNEC sodium loop in Cadarache, France as part of IGCAR–CEA collaboration.

A technology for the production of enriched elemental boron was developed at RCL and transferred to the Heavy Water Board (HWB). Based on this transfer, a new plant was established at HWB, Manuguru, which produced the enriched boron required for the first core of PFBR. Fabrication of sphere-pac fuel pins by sol–gel process was carried out wherein a remotely operable facility has been

developed in-house, tested and commissioned<sup>30</sup>. Using this facility, sphere-pac fuel pins containing MOX microspheres and reference pellet fuel pins were fabricated for irradiation in FBTR. The mixed-oxide microspheres containing 53% plutonium were provided by the Fuel Chemistry Division of BARC.

Work on plutonium (Pu) chemistry at high temperatures is challenging. The challenge is compounded when the studies are related to air-sensitive compounds such as carbides, which have to be performed in an inert-atmosphere glove box. When the decision to opt for the Pu-rich mixed carbide fuel for FBTR was taken by the Centre, the Chemistry Group provided data on the carbon potential of the mixed carbide, which assured that the fuel–clad chemical interactions will not be a source of concern for the fuel to reach higher burn-up. Out-of-pile measurements on the thermal behaviour of the carbide fuel assured us that the fuel can be taken to desired linear ratings without issues relating to centre line melting<sup>31</sup>. Measurements of thermal conductivity, enthalpy, dissolution behaviour and vapour pressure have been made on fuel materials such as mixed carbide and mixed oxide. The Chemistry Group is among a few groups in the world that have carried out thorough investigations on the development of alternate extractants/ligands for fast reactor fuel reprocessing. A series of organophosphorous compounds, namely phosphate and phosphonate family were synthesized, characterized and studied for their extraction behaviour with actinides and fission products. Third-phase formation behaviour was extensively investigated with many of these extractants. These studies have established tri-*iso*-amyl phosphate (TiAP) as a potential alternate extractant to TBP for the fast reactor fuel reprocessing. Many investigations have been carried out to develop fast separations of lanthanides and actinides using HPLC. A supercritical fluid extraction method was developed for the quantitative recovery of uranium, plutonium and americium from various waste matrices<sup>32</sup>; a supercritical carbon-dioxide extraction facility in a glove box was set up to achieve these endeavours.

In the recent past the Chemistry Group at IGCAR has been renamed as ‘Materials Chemistry and Metal Fuel Cycle Group’ (MC&MFCG), with focus on R&D studies related to metal fuel programme, establishing pyrochemical processing of metal fuel, development of aqueous reprocessing methods, including reprocessing of metal fuels, etc. Some important current activities include the installation of an injection casting system and establishing a 10 kg injection casting system for the fabrication of U–6Zr slugs. In 2018, the sodium-bonded metal fuel pin fabrication facility was dedicated to the nation by the then President of India. A high-purity inert-atmosphere glove box for sodium-bonded metal fuel pins comprising U–6Zr, EU–6Zr and U–19Pu–6Zr fuel slugs was fabricated for test irradiation in FBTR. These slugs were received from BARC and the pins were fabricated at RCL. The test fuel pins are undergoing irradiation in FBTR to study the behaviour of

the fuel. A pyrochemical process based on molten salt electrorefining has been taken up as an alternate reprocessing route to the PUREX process; these studies were initiated in RCL in the 1990s. The intrinsic minor actinide recycling, proliferation resistance, possible to process short, cooled, high burn-up fuel, lower criticality-related issues and less volume of liquid waste are its advantages. The pyroprocess is more suitable for metal fuels, but oxides can also be reprocessed by including a few additional steps. To develop and demonstrate the engineering technology required for setting up pyroprocess plants, a Pyro Process Research and Development Facility (PPRDF) has been established. Alloys of natural uranium and U containing simulated fps were electro-refined at kilogram level. Similarly, pyroprocessing of irradiated U–Zr (laboratory scale) was carried out in the hot cells of RCL.

In addition, in the recent past, many new activities have been taken up in the radiochemistry programme, e.g. direct oxide reduction of uranium oxides to uranium metal, optimization of process parameters towards oxidation of metal–fuel before its dissolution in the nitric acid medium followed by the extraction of heavy metals using TBP/n-DD, establishing a PUREX process as an interim step for processing metal fuels, etc. Studies on phase diagrams and thermochemical properties of fuel materials were performed using Knudsen effusion mass spectrometry and laser-induced vapourization mass spectrometry. These systems were built in-house and have been the work horse of high-temperature thermodynamics of fuels and structural materials of the fast reactor programme. Solidus–liquidus temperatures of U–Pu–Zr, both 19% and 23% Pu have been determined using a spot technique which was established at RCL. The R&D towards nuclear waste immobilization, iron phosphate glass (IPG), a versatile glass matrix was synthesized at 1 kg level and characterized towards understanding the immobilization of high-level waste arising after reprocessing of spent fast reactor fuel. In this context, IPG waste form (IPG containing 20 wt% simulated fast reactor high level waste) at 1 kg level was demonstrated. In addition, IPG also proved to be a good matrix for immobilization of cesium at a high level (>30 wt%) with lower volatilization loss. Iron phosphate glass with the highest  $\text{Fe}^{3+}$  concentration was demonstrated for the first time internationally. Waste matrices, including glass, glass-bonded ceramics and ceramics have been developed to immobilize different types of HLW. This includes zeolites and glass-bonded apatites. Laboratory-scale production of  $^{89}\text{Sr}$  was achieved through irradiation of yttria pellets in FBTR. Trial irradiations of target yttria pellets in FBTR and radiochemical processing of irradiated pellets to get the pure source of  $^{89}\text{Sr}$  were carried out; chemically purified  $^{89}\text{Sr}$  source satisfied various radiopharmaceutical quality control protocols, including biological, as validated by the Radiopharmaceutical Division at BARC.

While pursuing R&D programmes to provide solutions to immediate problems faced in the development of fast

reactor technology, MC&MFCG has also been pursuing activities in selected frontline areas of basic research<sup>33,34</sup>. Matrix isolation infrared (IR) spectroscopy is an important example of such activity; the system was set up in 1990. The isolation of trialkyl phosphates in an inert matrix at cryogenic temperatures has enabled the recording of IR spectra of these compounds with high resolution, which has been, in turn, instrumental in determining the conformers of these molecules. Theoretical studies are being taken up to examine the nature of bonding between metal and ligand using computational methods, which has provided insights into the mechanism of chemical interactions<sup>35</sup>. These studies are promising for identifying an appropriate ligand for selective extraction/complexation of metal ions, mainly actinides. Instrumentation facilities have also been developed/modified for specific studies such as fluorescence, laser-induced breakdown spectroscopy and cavity ring-down spectroscopy. An ion mobility spectrometry technique was developed for identifying nitrogen-bearing compounds.

Research at RCL on fuel chemistry, sodium chemistry, reprocessing chemistry, analytical chemistry, and spectroscopic techniques, that has evolved over the past 40 years has provided many crucial inputs to the fast reactor programme and will continue to serve the mission-bound programmes of DAE.

## Conclusion

The above brief account is like a travelogue of chemistry's contribution in different areas of India's nuclear energy programme and to other areas of fundamental and technological importance. From the preceding discussion, it is evident that Chemistry Groups in DAE have always risen to the occasion to provide chemical solutions for various challenging problems faced in the nuclear fuel cycle. Finally, this article is also a testimony to the deep sense of commitment of the scientists involved in these projects, which led to the indigenous development of India's nuclear programme and various technologies for societal benefit. Besides this, there are quite a significant number of other equally important activities which could not be included in this article, are being actively pursued in DAE.

1. Momin, A. C. and Karkhanavala, M. D., Temperature dependence of the Gruneisen parameter and the lattice vibrational frequencies of UC and UN in the range 298 K–2500 K. *High Temp. Sci.*, 1979, **11**, 179.
2. Momin, A. C. and Karkhanavala, M. D., Thermophysical properties of reactor materials: uranium dioxide, thorium dioxide, uranium monocarbide and uranium mononitride. Chemistry Division Progress Report, BARC-1105, Bhabha Atomic Research Centre, Mumbai, 1980.
3. Nandi, C. *et al.*, Exploring YSZ/ZrO<sub>2</sub>–PuO<sub>2</sub> systems: candidates for inert matrix fuel. *J. Nucl. Mater.*, 2018, **508**, 82.
4. Mishra, R. K., Sudarsan, V., Kaushik, C. P., Raj, K., Kulshreshta, S. K. and Tyagi, A. K., Structural aspects of barium borosilicate

- glasses containing thorium and uranium oxides. *J. Nucl. Mater.*, 2006, **359**, 132.
5. Kolay, S., Achary, S. N., Shinde, A. B., Krishna, P. S. R., Basu, M., Mishra, R. and Tyagi, A. K., Preparation, thermal stability and crystal structure of  $\text{Li}_2\text{UF}_7$ : new insights into  $\text{LiF-UF}_4$  binary phase diagram. *J. Alloys Compd.*, 2021, **856**, 158181.
  6. Chakravarty, R., Shukla, R., Ram, R., Tyagi, A. K., Dash, A. and Venkatesh, M., Practicality of tetragonal nano-zirconia as a prospective sorbent in the preparation of  $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$  generator for biomedical applications. *Chromatographia*, 2010, **72**, 875.
  7. Sanap, K. K., Varma, S., Waghmode, S. B. and Bharadwaj, S. R., Wire gauze and cordierite supported noble metal catalysts for passive autocatalytic recombiner. *Nucl. Eng. Des.*, 2015, **294**, 226–232.
  8. Kolay, S., Basu, M., Das, D., Achary, S. N., Tyagi, A. K., Kaity, S. and Banerjee, J., Phase distribution study for U–Zr metallic SIMFUEL. *BARC Newsletter No. 351*, 2016, pp. 17–23.
  9. Velmurugan, S., Rufus, A. L., Sathyaseelan, V. S., Padmakumari, T. V., Narasimhan, S. V. and Mathur, P. K., Corrosion of PHWR PHT system structural materials by dilute chemical decontamination formulations containing ascorbic acid. *Nucl. Energy*, 1995, **34**, 103–116.
  10. Velmurugan, S., Subramanian, H., Subramanian, V. and Chandramohan, P., Role of magnesium ions in reducing high temperature aqueous corrosion of carbon steel. *Corros. Sci.*, 2013, **70**, 127–139.
  11. Padmavathi, A. R., Murthy, P. S., Das, A. and Rao, T. S., Enhanced antifouling property of polydimethylsiloxane–CuO nanocomposite in marine environment. *Mater. Lett.*, 2021, **301**, 130342.
  12. Singh, A. J., High purity indigenous material. *SMC Bull.*, 2015, **6**, 1–14.
  13. Thomas, K. C., Kale, J. R., Dalavi, R. G., Tambe, G., Venkatesh, K., Kameswaran, R. and Reddy, A. V. R., Development of IR based carbon analyser for uranium metal. International Conference on Peaceful Uses of Atomic Energy – Volume on Nuclear Instrumentation – 2011, New Delhi, 2011.
  14. Pawaskar, P. B., Manerker, B. S. and Sankar Das, M., An in-house reference rock standard: Gilbert basal, B-78: analysis and estimates. *J. Geol. Soc. India*, 1985, **26**, 219–224.
  15. Kumar, S. A. *et al.*, Preparation of in-house graphite reference material for boron. BARC Report, 2016, E005.
  16. Dasgupta, S., Datta, J. and Swain, K. K., Determination of boron in in-house graphite reference material by instrumental charged particle activation analysis. *J. Radioanal. Nucl. Chem.*, 2021, **328**, 33–38.
  17. Shankar, J., Srivastava, S. B. and Shankar, R., Recoil effects of cobalt-60 in (n.g) reaction in triglycine Co(III) and sodium ethylene diamine teracetate Co(III). In Symposium on Chemical Effects of Nuclear Transformations, IAEA, Prague, 24–27 October 1960.
  18. Ghosh, H. N., Sapre, A. V., Palit, D. K. and Mittal, J. P., Picosecond flash photolysis studies on phenothiazine in organic and micellar solution. *J. Phys. Chem. B*, 1997, **101**, 2315–2320.
  19. Sharma, A., Sarkar, A., Goswami, D., Bhattacharyya, A., Enderlein, J. and Kumbhakar, M., Determining metal ion complexation kinetics with fluorescent ligands by using fluorescence correlation spectroscopy. *ChemPhysChem*, 2019, **20**, 2093–2102.
  20. Gupta, N. M., Kamble, V. S. and Iyer, R. M., Effect of  $\gamma$ -irradiation on methanation of CO over Ru/molecular sieve catalyst. *Radiat. Phys. Chem.*, 1978, **12**, 143–151.
  21. Bhattacharyya, K., Mane, G. P., Rane, V., Tripathi, A. K. and Tyagi, A. K., Selective  $\text{CO}_2$  photoreduction with Cu doped  $\text{TiO}_2$  photocatalyst: delineating the crucial role of Cu-oxidation state and oxygen vacancies. *J. Phys. Chem. C*, 2021, **125**, 1793–1810.
  22. Nag, N. *et al.*, Fission fragment mass distribution in the  $^{32}\text{S}+^{144}\text{Sm}$  reaction. *Phys. Rev. C*, 2021, **103**, 034612.
  23. Bhattacharya, A. *et al.*, Bis-(1,2,4-triazin-3-yl) ligand structure driven selectivity reversal between  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ : solvent extraction and DFT studies. *Dalton Trans.*, 2021, **50**, 7783.
  24. Mandal, S. *et al.*, Synchrotron GIXRD and slow positron beam characterisation of Ar ion irradiated pure V and V-4Cr–4Ti alloy: candidate structural material for Fusion reactor application. *Fusion Eng. Des.*, 2020, **154**, 111518.
  25. Gupta, R., Sundararajan, M. and Gamare, J. S., *Anal. Chem.*, 2017, **89**, 8156.
  26. Dubey, K. A., Chaudhari, C. V., Bhardwaj, Y. K. and Varshney, L., *Adv. Struct. Mater.*, 2017, **66**, 1–44.
  27. Keesari, T., Sinha, U. K., Pant, H. J. and Pujari, P. K., Societal benefits of isotope techniques in water resources. In *Non-Power Applications of Nuclear Technologies* (eds Tyagi, A. K. and Mohanty, A. K.), SIRD, BARC, 2021, pp. 173–189, ISBN: 978-81-954733-2-8.
  28. Bollampally, N. *et al.*, *Nucl. Med. Commun.*, 2021, **42**, 964.
  29. Sivaraman, N., Subramaniam, S., Srinivasan, T. G. and Vasudeva Rao, P. R., Burn-up measurements on nuclear reactor fuels using high performance liquid chromatography. *J. Radioanal. Nucl. Chem.*, 2002, **253**, 35–40.
  30. Venkata Krishnan, R., Nagarajan, K., Clement Ravichandar, S., Prabhu, T. V., Ravisankar, G. and Kasiviswanathan, K. V., Sol-gel development activities at IGCAR, Kalpakkam. *J. Sol.-Gel. Sci. Technol.*, 2011, **59**, 394–403.
  31. Joseph, M. and Mathews, C. K., Calculation of vapour pressures over mixed carbide fuels. IGC-Report, IGC-101, 1988.
  32. Pitchaiah, K. C., Sujatha, K., Deepitha, J., Ghosh, S. and Sivaraman, N., Recovery of uranium and plutonium from pyrochemical salt matrix using supercritical fluid extraction. *J. Supercrit. Fluids*, 2019, **147**, 194–204.
  33. Beatriceveena, T. V., Sree Rama Murthy, A., Murugesan, S., Prabhu, E. and Gnanasekar, K. I., A factorial design approach for hydrothermal synthesis of phase-pure  $\text{AgInO}_2$ . *Angewandte Chem.*, 2020, **132**, 2261–2265.
  34. Chandrasekar, A., Rao, B., C. V. S., Sundararajan, M., Ghanty, T. K. and Sivaraman, N., Remarkable structural effects on the complexation of actinides with H-phosphonates: a combined experimental and quantum chemical study. *Dalton Trans.*, 2018, **47**, 3841–3850.
  35. Chandra, S., Suryaprasad, B., Ramanathan, N. and Sundararajan, K., Nitrogen as a pnictogen?: evidence for  $\pi$ -hole driven novel pnictogen bonding interactions in nitromethane–ammonia aggregates using matrix isolation infrared spectroscopy and *ab initio* computations. *Phys. Chem. Chem. Phys.*, 2021, **23**, 6286–6297.
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