Chemistry of Nuclear Materials

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Preamble:

'Chemistry Program' related to nuclear science and technologies in India took off in 1949 with appointment of Dr. Jagdish Shankar as the first Chemist. Over the last 75 years, research pertaining to 'Chemistry of Nuclear Materials' is a major facet of department. Exploration of mineral resources to develop materials required for fission-based nuclear energy technologies was the initial requirement. These materials included uranium, thorium, zirconium, nuclear-pure graphite, beryllium, cadmium, *etc.* Physico-chemical characterization and chemical processing of such minerals to extract nuclear-grade materials were needed and chemistry fraternity was entrusted with such studies. Initial works included extraction of nuclear materials from lean indigenous sources and accurate analysis of their bulk and trace-constituents. During the first "International Conference on the Peaceful Uses of Atomic Energy" held in Geneva (08-20 August, 1955), chaired by Dr. Homi J. Bhabha, research papers on separation chemistry of atomic minerals were presented by some of the Indian scientists. Early works taken up by the Chemistry Group (erstwhile Chemistry Division in the then Atomic Energy Establishment Trombay) included (i) separation-free spectrophotometric determination of beryllium (up to 2 ppm) in its ores and alloys, (ii) colorimetric estimation of uranium in monazite, (iii) auto-radiographic determination of uranium in minerals, *etc.* Notable contributions have been made towards assessment of the physico-chemical properties of nuclear materials both, in the 'Front End' and the 'Back End'. High temperature thermochemistry work was led by Dr. Minecher Dadabhoy Karkhanavala, who steered many developmental programs. Unfortunately, Dr. Karkhanavala left this world in 1979 during his tenure as Director, Chemical Group, BARC in a tragic road accident. Evolution of R&D activities on nuclear materials is a continuing pursuit at Chemistry Group, and a tribute to its stalwarts. The following summary attempts to chronicle the journey thus far.

Chemistry of nuclear fuels:

Uranium-based fuels:

Production of nuclear-grade uranium and its compounds were the earliest tasks for fuel fabrication. Using X-ray diffraction and thermal analyses techniques, scientists at Chemistry Group delineated chemical state of U-bearing ores obtained from iron-containing regions in the shear-zone of Bihar (The erstwhile Singhbhum area, where Jaduguda uranium mines were set up by UCIL) in 1958. For uranium extraction from natural resources, studies pertaining to estimation of water of hydration / crystallization in U-salts were carried out using thermal analysis. During 1961-62, methods were developed to extract / separate neutron-deficient radioisotopes (*c.a.,*^{92}Nb) from reactor irradiated natural molybdenum targets. By 1966, crystal structures of U_3O_8 allotropes were elucidated and metastable orthorhombic form (δ-U_3O_8) was stabilized by high temperature annealing (1623 K). Formation of U_3O_8 allotropes from its precursor (β-UO_3) and their structural and thermodynamic properties were established in 1973. Early efforts (1957) also included synthesis and structural characterization of uranium tetrafluoride (UF_4). Solid-state transformation of UF_4 to UO_2 was studied to optimize reaction parameters for UO_2 formation (1989). Such studies provided valuable inputs for large-scale preparation of U-based compounds. Evolving from these early studies, and to optimize process parameters for dry reduction of hex gas (UF_6) into UF_4, crystallographic studies have been carried out on solid intermediates formed during the dry-reduction process during the last ten years. In collaboration with the Chemical Technology Group, BARC, these studies led to optimization of process parameters and enhancement in efficiency of dry-reduction process. Similarly, in order to understand the kinetics and mechanism of formation of various uranium oxides upon thermal decomposition of inorganic precursors (oxalates, nitrates, carbonates, uranates, *etc.*), thermal analyses studies have been performed during 1990 to 2005. These studies led to comparative assessment of products obtained from different precursors and provided value-addition to UO_2-based fuel fabrication methodologies. Such studies have also been performed on oxalates of yttrium, cerium, and zirconium, whose oxides are relevant in nuclear technology in terms of representative rare earth fission products (FPs), structural surrogate of PuO_2 and oxidation product of Zr-based clad, respectively. An innovative route for controlled oxidation of surface atoms in sintered UO_2 pellets was developed in 1990, which led to improvement in quality of sintered pellets and increased their grinding recovery. Through a wide range of studies on U-based oxides, Chemistry Group now possesses rich expertise on their preparative methods, which include solid-state and wet-chemical routes, solution combustion route, pulse radiolysis route, *etc.*

Thorium-based fuels:

^{232}Th is a long-lived ($t_{1/2}$~1.4×10^{10} years) naturally occurring fertile isotope of thorium. It has been envisaged as the driver of nuclear energy in the third stage of Indian nuclear program. Even before Dr. Bhabha officially outlined India's three stage program in 1958, work had commenced in Chemistry Division on Th-bearing minerals addressing the crystal chemistry and properties of monazite single crystals (1956) and synthesis of thorium orthophosphates (1957). Studies on thorium separation from rare earth elements (REEs) (1959) helped in processing of Indian monazite to obtain both, uranium and thorium. In early

1960s, lab-scale methods were developed to extract [233]Pa into tri-n-butyl phosphate (TBP) from neutron-irradiated thorium compounds. Being a fertile radionuclide, blending of thorium with fissile element ([235]U, [233]U, Pu, MAs) is required to obtain suitable fuel forms (oxides, alloys, carbides, etc.). Studies were therefore carried out on preparative methods for Th-U oxide solid solutions. Over the last seven decades, extensive work has been carried out on Th-based oxides, which include binary mixed oxide (MOX) solid solutions (Th-U-O, Th-Ce-O, Th-REE-O), perovskites (ThMO$_3$; M = Ba, Sr, *etc.*) and other complex oxides (ThMo$_2$O$_8$, Cs$_2$ThO$_3$, *etc.*) as part of Thoria Task Force constituted by Dr. Anil Kakodkar, then Director of Bhabha Atomic Research Centre, in 1998. Experience has been gained on preparation, characterization and densification of ultrafine thoria powders via solution combustion to obtain bulk nanocrystalline ceramics.

Metallic alloy fuels:

From 2010 onwards, research activities expanded to U and Th-based metallic alloys (U-Zr, Th-U, Th-U-Zr, etc.), which are candidate fuels for future reactors. Preparative studies on these alloys have provided experience on (i) non-metallic impurities incorporation (O, N, C, etc.) from cover gas (Ar, He) &crucibles and, (ii) temperature dependent phase and microstructure evolution. For U-Zr and Th-U alloys, effect of alloying on structural phase transitions of uranium (orthorhombic → tetragonal → cubic) and corresponding impact on their thermophysical properties has also been delineated. Expertise in lab-scale preparation of nuclear fuel materials remains core strength of Chemistry Group.

Fluoride-based fuels:

Actinides fluorides are fuels for molten salt reactors (MSRs), which are among the six Generation IV nuclear energy systems. Referred as Chemist's reactors, MSRs are envisaged to utilize thorium at large-scale for energy production. Early studies from Chemistry Group (1989-90) focused on syntheses of uranium and thorium fluorides from their respective oxides using ammonium bifluoride as fluorinating agent. During 1995-96, solid-state reactivity of ammonium bifluoride with Al, Cr, Ni and zircaloy was also investigated to understand the formation of corresponding metal fluorides and ammonium metal fluorides. Indian Molten Salt Breeder Reactor (IMSBR) development program has picked up pace over the last decade and is aimed towards expanding the avenues of thorium utilization for nuclear energy production and making India self-reliant for long-term energy requirements. In-house generated database on high temperature physico-chemical properties of fluoride salts (fuel, coolant and blanket) is required for design and development of IMSBR. Preparative aspects of moisture-free U and Th-based fluorides, which show sharp eutectic melting, are being studied in Chemistry Group. Experimental database on thermophysical and thermodynamic properties of these salts have been generated, which include melting point, density, heat capacity, enthalpy, thermal conductivity, viscosity, coefficient of thermal expansion, *etc.* Solubility limits of major FPs and structural materials in molten salts have been determined. Compatibility of molten salts with structural materials (Hastelloy) is being studied.

Chemical diffusion in nuclear materials:

During fuel irradiation, integrity of clad, which is closest to the fuel element, is important for safe confinement of both, fuel and FPs. Fuel and FPs together comprise the major fraction of radioactivity in a nuclear reactor. Al-alloys, Zr-alloys, steel, *etc.* are used as clad for research reactor fuels. For power reactors, zircaloy clads are used both, in light water reactors (LWRs) as well as heavy water reactors (HWRs). Steel-based cladding is preferred for fast spectrum reactors. Clad failure may occur due to (i) rare but occasional mechanical flaw in as-fabricated clad, (ii) stress induced by fuel's swelling, (iii) fuel-clad, FP-clad and coolant-clad chemical interaction, (iv) thermal stress coupled with accelerated clad-air or clad-steam interaction under loss of coolant scenario, (v) radiation-induced structural deterioration, *etc.* Diffusion is important to understand the evolving chemical state of fuel. It governs fuel irradiation limit and is central to fuel safety and FP migration. Chemical diffusivities of constituents in fuel-FPs-clad system are thus to be known. Chemistry Group has made notable contribution in this direction. Studies on chemical diffusion had been initiated in early 1960s. These included interaction of Zr / ZrO_2 with tellurium (a volatile FP) and its oxide (TeO), diffusion of Zr and Te in air, *etc*. Earlier studies led to understanding of fuel / FP migration in structural materials (Zr, Al, zircaloy, steel, *etc.*). Notable examples include diffusion of (i) Cr in Al and Ni, (ii) Cu and Ni in Al, (iii) Cu in Fe, *etc.*

It is worthwhile to mention why Cr diffusion in Al and steel had been investigated. CIRUS research reactor (40 $MW_{thermal}$) was commissioned in 1960 with collaborative support from Canada. A serious incident of chromium deposition over the outer surface of Al-clad occurred when water containing trace amounts of potassium dichromate was circulated through the reactor assembly during shutdown. Potassium dichromate was added (recommended by Canadians) to the emergency storage coolant water to minimize bacterial growth during storage period. Neutron capture by chromium led to formation of radioactive chromium, which deposited over the inner surface of cooling system thereby causing radiation contamination. Large amounts of chromium complexing agents were injected in coolant tubes to form soluble chromium complex. Extensive efforts by chemistry fraternity finally led to radioactive chromium clean-up from CIRUS coolant circuitry and minimized radiation exposure to the staff working in that area. This incident was among the driving factors to investigate chemical diffusion of chromium in Al and Steel as a function of temperature.

During 1970s to 1990s, extensive studies were carried out to probe fundamentals of chemical diffusion n nuclear reactor structural components. A few notable examples included self-diffusion in Zr and its alloys, diffusion of Mo in Al, V in Nb, Zr, Al and Ni, Cr, Ni and Sn in zircaloy-2, anomalous diffusion in β-Zr, β-Ti and V, ^{14}C in steel, Ce and Nd in Ni, Co in Al, C in Zr, zircaloy-2 and Zr-2.5Nb, Cr in Inconel-600 and Incoloy-800, self and impurity diffusion in Zr-Mg alloy, *etc.* Based on such studies, it was established that randomly distributed dislocations are responsible for enhancement in volume diffusivity (1967). Diffusion studies were extended to cover fundamental aspects such as impurity diffusion in general FCC solids (1968). Mass transport behavior of Ni in liquid tellurium was investigated to predict FPs-clad interaction; in case low melting eutectics are formed. These studies led to expertise in precision experiments that involved fabrication and annealing of diffusion couples, serial sectioning and residual activity monitoring by tracer technique. Further studies

were carried out on advanced structural materials, which included diffusion driven recovery of irradiation-induced structural damage in type-304 stainless steel (1975), Cr and Ni transport in Monel-400 (1976), diffusion of cobalt, nickel, copper and iron in Inconel-800 (1990-91), *etc.* Experimental database generated on chemical diffusion in nuclear materials continue to serve as reference to reactor engineers for development of future materials.

Fission gas release behavior in nuclear materials:

Fission gases (Xe, Kr) and volatile fission products (I, Te, Cs) constitute a significant fraction of total FPs and transport within the fuel through both, thermal and athermal processes. At higher burn-ups, a fraction of volatile FPs and FGs releases out of the fuel element. Volatile FPs deposit over clad's inner surface while FGs accumulate in fuel-clad gap or plenum volume. Unreleased fraction of these FPs contributes towards fuel's swelling while pressure inside FG bubbles deteriorates fuel's mechanical strength. Transport of these FPs depends on temperature, burn-up, fuel microstructure, fuel-type, chemical state, power ramp history, *etc.* Understanding of their transport properties is required to predict fuel performance and for safety analysis. Released FGs deteriorates thermal conductivity across the fuel-clad gap, which raises fuel temperature. Volatiles deposited over fuel-clad interface cause clad strain and may lead to clad rupture. Release behavior of FGs and volatile FPs can be studied either during in-pile irradiation or, out-of-pile studies on irradiated fuels. The latter approach involves either deliberate puncturing of clad in irradiated fuel pin to observe the release of FGs accumulated (activity measurement) in fuel-clad gap or, isothermal annealing of neutron irradiated fuel to deliberately release FGs and volatile FPs for analysis and quantification.

Chemistry Group has steered studies on release behavior of FGs and volatile FPs in U and Th-based fuels employing post irradiation annealing (PIA) approach. In-house experimental facilities were developed for this purpose. For FG release studies, FGs were swept out using carrier gas (He) and trapped over pre-cooled activated charcoal (~77 K), whose activity was continuously monitored using NaI:Tl scintillator detector. A separate assembly for dissolution of irradiated specimen had been set up for analysis of released FGs. Amount of FG isotopes present in fuel at the start of PIA could be calculated by measurement of gases released during dissolution. Combining this with the results of isothermal annealing, fractional release at any temperature could be calculated. Since moisture and O_2 impurities in carrier gas seriously affect FG release kinetics, multi-stage regenerative gas purification columns were incorporated to maintain impurity contents < 5 ppm. A separate apparatus was developed to study the release behavior of volatile FPs (I, Te). Irradiated fuel sample; kept in Mo-cell having a narrow (~1.5 mm) orifice, was isothermally heated under vacuum (~10^{-8} bar). Released FPs were chemically fixed over heated (~650 K) copper foils. On completion of annealing, Cu-collectors were assayed radio-metrically for ^{131}I and [132]Te. Gamma activities (I & Te) from Cu-collectors were compared with the total activities of these isotopes in the original sample used in the annealing experiment. From normalized activity data, fractional release (I & Te) were obtained and release kinetics determined. Two procedures namely, (i) continuous sweep method and (ii) closed system forced circulation method were used.

In late 1970s, ^{131}I and ^{133}Xe release behavior was investigated in low-dose irradiated ThO_2 pellets and kinetics and mechanism of ^{131}I release was elucidated. In 1977, yttria doped thoria, which mimic rare earth FP incorporated oxide fuel, was investigated and a slower mass diffusion (relative to undoped thoria) was observed in-spite of creation of anion vacancies. Release behaviour of ^{133}Xe was evaluated in $Th_{0.99}{}^{235}U_{0.01}O_2$ fuel (2.76×10^{20} - 1.38×10^{24} fissions/m^3). A decrease in both, xenon diffusivity (D_{Xe}) and burst-release fraction (F_{Xe}) in these high burn-up fuels was explained in terms of formation of radiation-induced FG trapping centres (1981). Such studied were extended to zircaloy (1983) wherein FGs may get embedded due to fission-recoil phenomenon near fuel-clad interface. By comparative assessment of Xe-release fraction, theoretical assessment of coolant channel FG monitoring with reference to channel delayed neutron monitoring was carried out during 1989-90. These studies helped in postulating clad breach occurrence in PHWRs. Temperature dependent Xe-release from high-dose neutron irradiated UO_2 was also studied. Xe release from $(U-Th)O_2$ fuel was found to be strongly dependent on porosity and grain size. Studies were also performed to probe krypton ([85m]Kr) release from oxide fuels. Since presence of non-volatile FPs is expected to influence the transport properties of FGs and volatile FPs, studies were carried out on U and Th-based oxide SIMFUELS. In thoria-based SIMFUEL, Xe-diffusion activation energy was close to theoretically predicted value of Xe-migration through tri-vacancies that are generated due to the presence of lower valent FPs. Iodine and tellurium diffusion also showed lower activation energy barrier due to increased vacancy concentration.

Beyond oxide fuels, Xe-release study was extended to U-Zr alloys. Results obtained on U-10Zr alloys in purified carrier gas environment indicated diffusion characteristics similar to uranium self-diffusion. In presence of O_2 impurity (~10 ppm) in carrier gas, Xenon diffusivity enhanced by thirty times, which has been explained in terms of formation of oxidized crystallites in the alloy, which favours grain boundary diffusion of Xe. Studies on both, oxide and metallic fuels have provided valuable database on FGs and volatile FPs release behavior under different reactor operation scenario, which has added immense value to Indian nuclear reactor technology development program.

Thermo-chemical and thermo-analytical studies on nuclear materials:

Neutron-induced fission releases enormous energy (~200 MeV/fission), most of which (> 85%) manifests as kinetic energy of fission fragments. It quickly transforms to heat within the fuel matrix. This heat is transferred from fuel to coolant flowing over the fuel pin to produce steam, which is fed to the turbine and electricity is generated. With increasing burn-up, FP build-up results into dynamic evolution of fuel's chemical state. Steep temperature gradients (several hundred-degree Celsius) exist within a tiny cylindrical (diameter < 15 mm) fuel pellet / pin from its centre (hot) to boundary (cold). Nuclear fuels fabrication also involves high temperature treatment step(s) such as sintering, melt-casting, annealing, *etc.* Thermo-chemistry of nuclear materials, which depends on fuel-type, fuel temperature, power ramp conditions, coolant-type, coolant temperature, burn-up, FP transport behaviour, *etc.*, is essential for fuel cycle development. Research on high temperature chemistry of nuclear materials was founded in the Chemistry Division with principle objectives of (i) developing containment matrices for processing of nuclear materials and, (ii) generation of database on thermodynamic and thermochemical properties of nuclear materials. High temperature

chemistry and equilibrium phase diagram evaluation in fuel-FPs-clad-coolant systems founded the early facets of this activity.

Early studies focused on U-based oxide fuels. In 1965, thermo-gravimetric and titrimetric methods were developed for accurate determination of U:O ratio in various oxides (UO_2, UO_3, UO_{2+x}, U_3O_8, U_4O_9, *etc.*). During 1970s, special crucibles were developed for thermo-analytical measurements, which enabled rapid movement of gaseous species through the sample holder, thereby improving the reliability of kinetic and thermodynamic data. By 1975, high temperature stability of UO_x was investigated under areal and inert atmosphere conditions. In late nineteen sixties, fluoride / oxyfluoride-based corrosion retarding coatings were developed for oxygen sensitive refractory metals (Nb, Ta, W), which enabled their use in high temperature processing of nuclear materials. In late 1970s, phase behaviour of UO_x system ($2.65 \leq x \leq 2.67$) was delineated using thermal and diffraction techniques. Theoretical models were developed to evaluate kinetic parameters from various thermograms (TGA, DTA, *etc.*). Thermo-analytical investigations were also carried out to assess mechanism and kinetics of solid-solid phase transformations and decomposition. Theoretical methods (*e.g.,* 'Lumped Parameter Equation') were developed during 1979-1980 for treatment of thermo-analytical curves and evaluation of activation energies for thermal transformations. Existing methods (*c.a.,* Bae's method) were corrected to evaluate kinetic parameters from DTA curves, without any prior knowledge of equipment's thermal constant. Dynamic DTA curve method was developed in 1980 to determine the order of solid-state reactions. During the course of these studies, micro-thermo-balance design was modified to notably reduce the noise while performing experiments under flowing gases up to 1700 K (1981). Effects of sample size and flow atmosphere on interpretation of TGA curves were deciphered. On the basis of chemical state of FPs in oxide fuels, temperature dependent physico-chemical studies and stability analyses were carried out on fuel-FP interaction compounds. These included Cs_2UO_4, $K_2U(SO_4).H_2O$, $MTh_2(AsO_4)_3$ (M = Li, Na, K, Ag, Tl), U(IV)(SO_4)$_2$-DMF complex, Cesium monouranate, $Cs_2U_2O_7$, $Cs_2U(NO_3)_6$, *etc.* Results obtained from such studies provided (i) insights on the probability of formation of such compounds during normal / off-normal reactor operation scenarios and (ii) predictability of stability of such compounds.

In early 1980s, a challenging requirement of developing crucibles to confine molten uranium alloys (up to 2500 K) was accomplished by high temperature thermochemistry group led by Dr. M.S. Chandrasekharaiah. Hot-swaged tungsten and powder metallurgically fabricated tungsten (98% dense) were identified as suitable crucible materials. Subsequent to this, high temperature thermodynamics (up to 3000 K) of vaporization of molten uranium contained in single crystal Ta-crucible was studied for atomic vapor laser-isotope separation technology development program (1985). This challenging activity spanned over a couple of decades. By the year 2000, equilibrium vapor pressures studies on iron from its dilute solutions in liquid uranium metal were carried out at high temperatures (2250-2750 K) and partial molar excess Gibbs energy of iron at infinite dilution was determined. Vapour pressures of uranium metal measured up to 3000 K and, enthalpy of sublimation of uranium derived from those measurements are rated among the best values reported in the world.

Over the last two and a half decades (2000-2023), these activities have expanded to (i) Th-based oxides for AHWR program and matrices for minor actinide transmutation, (ii) Thermal evolution of molecular precursors to produce nanocrystalline oxides (*c.a.,* thoria,

urania, zirconia, ceria, solid solutions, *etc.*) that are relevant to nuclear technology, (iii) ceramics required for nuclear fusion technologies (*c.a.,* lithium titanates, lithium zirconates, *etc.*) and, (iv) U and Th-based fluoride salts relevant to IMSBR program. While most of the indigenously developed facilities have completed (or near completion) their working life, the activity is now being pursued with state-of-the-art equipments such as high temperature TG coupled with evolved gas analyzer (EGA), TG coupled with FT-IR, differential scanning calorimeter (HF-DSC), Knudsen Effusion Mass Spectrometer (HT-KEMS), drop calorimeter, thermo mechanical analyser (TMA), *etc.* Work on thermochemistry of advanced nuclear materials continues to be a major thrust area of research in Chemistry Group.

Phase diagram studies on nuclear materials:

Chemical state of nuclear fuel evolves during neutron irradiation. Out-of-pile assessment of phases in fuel-clad-FP system is essential to predict fuel behavior. Prior knowledge of possible phase-fields value-adds during post irradiation examination (PIE) of irradiated fuels. Investigations on SIMFUELS, which closely resemble with irradiated fuel except that it does not include (i) entrapped FGs and volatile FPs, (ii) pores formed upon escape of FGs and (iii) radiation-induced structural alterations, also further the understanding of fuel behavior. Physico-chemical analyses delineate phase behavior while thermo-analytical methods allow determination of transition temperatures such as solidus and liquidus. Combined results allow phase diagram assessment. In Chemistry Group, extensive work has been carried out for phase diagram studies in binary and multi-component systems. During the initial years (1975-1985), an automatically recording high temperature DTA (RT-1450°C) was designed and built 'in-house' from locally available components.

Molybdenum is a major FP, which may combine with fuel (U/Th) as well as FPs (Cs, Sr, Ba, *etc.*) to form alloys, intermetallics and molybdates. Depending upon fuel's oxygen potential, it may also remain in metallic (Mo) or oxide (MoO_3) form. Phase behaviour of Molybdenum with U-based oxide fuels was studied (U-Mo-O system in UO_2-MoO_2-O region; 1980s), which included preparation and characterization of U-molybdates, thermo-gravimetric investigations, thermodynamic stability analysis, evaluation of standard free energy of formation by solid electrolyte EMF method, *etc.* Thermodynamic properties of $UMoO_5$ and $UMoO_6$, which can form in fuel cycle, were established. It was concluded that ternary phases in U-Mo-O system are not likely to play major role in fuel-FP interaction and $UMoO_6$ could only prevail in nuclear waste calcine product. Similar studies were carried out on Ru-Te-O and CaO-TeO_2 system in 1990s, which gave valuable inputs to predict fuel performance.

Thermodynamic properties of M_3U and M_3Pu intermetallics (M = Ru, Rh, Pd, *etc.*) were reviewed for phase-field investigations on metallic FPs in U-based oxide fuels. Critical oxygen potential necessary for their formation was suggested. Vaporization of Palladium was investigated using Knudsen-effusion technique and equilibrium vapor pressure as well as enthalpy of vaporization were determined (1990s). U-Zr, Th-U and Th-U-Zr metallic alloys have also been investigated using diffraction, microstructure analyses and thermo-analytical techniques. Phase diagrams of several other binary systems (*c.a.,* Nb-Pt, Ir-Pt, Ir-Sc, Rh-Ru, Ru-Sc, *etc.*) were also investigated during 1995-1998.

For the development of inert matrix fuels to utilize plutonium and minor actinides, ternary system PuO_2-ThO_2-ZrO_2 can be mimicked by CeO_2-ThO_2-ZrO_2 where CeO_2 acts as structural surrogate of PuO_2. With this objective, sub-solidus phase equilibria in various ternary systems have been investigated (2001 onward). Phase fields such as cubic solid-solutions, two-phase and multi-phase regions were delineated. Solubility limits of zirconia in both, ceria and thoria were determined. Interestingly, ceria and thoria did not form similar solid-solution in ZrO_2 lattice. Lattice thermal expansion of single-phase compositions in ternary oxide system was evaluated. Sub-solidus phase equilibria have also been established for other zirconia-based ternary oxide matrices. These include CeO_2-$DyO_{1.5}$-ZrO_2, CeO_2-$YO_{1.5}$-$NdO_{1.5}$, CeO_2-Gd_2O_3-ThO_2, CeO_2-YSZ, ThO_2-YSZ, YSZ/ZrO_2-PuO_2, ZrO_2-$NdO_{1.5}$-$YO_{1.5}$, A- and B-site Ce^{4+} substituted $Nd_2Zr_2O_7$ Pyrochlores, *etc.* Presently, similar studies are being carried out on garnet-based inert matrices. In these studies, CeO_2 is used as surrogates for PuO_2, Dy and Gd are burnable poisons, and $NdO_{1.5}$ as surrogate of trivalent minor actinide oxides.

Thermodynamic studies on nuclear materials:

FPs produced upon fission of ^{235}U include alkali metals (Cs, Rb), alkaline earths (Ba, Sr), rare earths (Y, Nd, La, *etc.*), platinum group elements (Ru, Rh, Pd), volatiles (I, Te, Cd), fission gases (Xe, Xr), transition elements (Mo, Tc, Zr), *etc.* Most FPs have lower oxidation state than that of U (+4) in UO_2-based fuels. With increasing burn-up, this oxygen imbalance raises fuel's oxygen potential and finally leads to release of free oxygen in fuel-clad gap thereby increasing the oxygen partial pressure in the fuel pin. Under such scenario, high temperature fuel reacts with free oxygen to form several compounds having crystal structures different from that of UO_2. Formation of such compounds introduces local stress in fuel pellet, which may cause fuel cracking. Cracks provide easy passage for transport of volatile FPs and FGs into the fuel-clad gap. Clad-FP interaction can cause stress corrosion cracking, thereby bringing hot irradiated fuel in contact with high-pressure coolant (H_2O/D_2O). Iodide-induced cracking of zircaloy is a classic example. Iodine release also depends on oxygen partial pressure, which if exceeds the threshold for the formation of Cs_2O or other complex oxides, then iodine cannot form solid CsI / RbI and gets transported as vapour to the clad interface, resulting in stress corrosion cracking. Such incident can lead to transport of highly radioactive fuel by the coolant water into heat exchanger and other parts of the reactor system, thereby spreading radioactivity into the reactor containment building and subjecting the working staff to high dose of nuclear radiation.

Knowledge of fuel chemistry is therefore essential to prevent fuel failure. Chemical state of irradiated fuel is investigated by PIE techniques. Since PIE is mostly performed on fuel cooled to ambient temperatures, fuel structure may alter from its high temperature form. PIE therefore may not give true picture of fuel behaviour during irradiation. For unambiguous conclusions of PIE observations, it is necessary to evaluate thermodynamic properties of compounds observed during PIE as well as other related phases which could possibly co-exist in fuel at high temperatures. Variation of oxygen partial pressure in the fuel pin as a function

of temperature can also be predicted if thermodynamic data such as standard free energy of formation for compounds possibly formable in the fuel are available. Over the past seven decades, high-quality database has been generated on thermodynamic properties of nuclear materials in Chemistry Group. These include (i) assessment of vaporization behaviour and vapour pressure measurements, (ii) determination of thermodynamic stability, (iii) evaluation of standard molar enthalpy and standard Gibbs energy of formation, (iv) derivation of standard entropy functions, *etc.* These studies have been carried out using transpiration technique, reactive carrier gas technique, Knudsen effusion, calorimetry, TGA, *etc.* Experimental facilities were 'in-house' designed and developed for such studies. Notable examples include (i) quartz helical thermo-balance to perform TG measurements, (ii) controlled atmosphere micro-TGA system employing an electronic beam balance, (iii) TG-cum transpiration setup for vapour pressure studies, (iv) glass/quartz-based Knudsen cell apparatus, (v) metal-based Knudsen effusion mass spectrometer, (vi) tensimeters, (vii) solid electrolytes galvanic cells for electromotive force (EMF) measurement, (viii) isoperibol solution calorimeter, *etc.* Vapour pressures of a large number of materials were measured in reactive gaseous environments.

Thermodynamic studies have also been carried out on a large number of compounds in fuel-FP-clad systems. These include zirconium molybdate ($ZrMo_2O_8$) and hafnium molybdate ($HfMo_2O_8$), zirconium tellurate ($ZrTe_3O_8$), hafnium tellurate ($HfTe_3O_8$), Cs_2CdI_4, $CaTeO_3$ and $CaTe_2O_5$, thorium molybdate ($ThMo_2O_8$), $UTeO_5$ and UTe_3O_9, strontium tellurites ($SrTeO_3$, $SrTe_2O_5$), barium thorate ($BaThO_3$), Cs_2ThO_3, Cs_2ZrO_3, $SrThO_3$, Ni_3TeO_6, Rb_2ThO_3, $SrCeO_3$, $La_2Te_3O_9$ and $La_2Te_4O_{11}$, Sr_2CeO_4, $Rh_3Te_2O_{10}$, $CdMoO_4$, *etc.* Recent studies on oxide-based compounds relevant to nuclear technology include $Ce_2Zr_2O_8$, Cr_2TeO_6 and $Cr_2Te_4O_{11}$, *etc.* During the period of thoria task force activities, extensive thermodynamic studies were carried out on AHWR fuels and SIMFUELs. Studies have also been performed on metallic fuels, which include U-Zr alloys, URe_2, $RuTe_2$, Rh_3Te_3, $RhTe_{0.9}$, Te-rich Ru-Te binaries, *etc.*

Fluoride-based salts have also been studied for their thermodynamic properties. Handling these salts at elevated temperatures require special care. This issue was realized in early 1970s and thermodynamic properties of binary fluorides (FeF_2, CoF_2, NiF_2, *etc.*), which may form upon interaction of Inconel / steel with molten fluoride salts were investigated. In the last decade, thermodynamic studies on LiF-ThF_4-UF_4, LiF-UF_4, Sr and Nd-doped fuel salt ($78LiF$-$20ThF_4$-$2UF_4$; mol %), *etc.* have been carried out. Thermodynamic activities of coolant salt constituents were determined using high temperature Knudsen effusion mass spectrometer. These results are being used by reactor developers. Future activities aim towards thermodynamic assessment of beryllium and lithium-lean salts.

Thermophysical properties of nuclear materials:

Nuclear fuel's performance depends on the efficiency with which heat is removed from the fuel. For solid fuels, conduction is the dominant mode of heat transport between fuel and coolant. In MSRs however, convective heat transfer also becomes important. Nuclear fuel being a uniform heat source surrounded by flowing coolant stream, steep temperature gradients exist in the radial direction from the centre of fuel element up to the outer surface of clad. For a given power rating, higher the thermal conductivity of fuel, lower is the fuel centreline temperature, which is an important safety attribute. Fuel's thermal conductivity

also evolves with burn-up and its reliable estimation is essential to predict fuel performance. Thermal expansion and specific heat are other thermophysical properties that affect the extent of expansion induced swelling and stored energy content in the fuel, respectively. Using the results obtained from PIE on spent nuclear fuels, fuel's centreline temperature can be closely estimated. Detailed out-of-pile investigations on thermophysical properties of virgin fuels, SIMFUELs and compounds formed in fuel-FP-clad system are essential.

Thermophysical studies on nuclear materials are among the oldest activities in Chemistry Group. The earliest report dates back to 1972 when a method was developed to determine thermal conductivity of metallic films (< 60 μm) using electrical resistivity data. Studies were carried out in early 1980s to estimate thermal conductivity drop in zircaloy-2 due to oxide coating, which could be formed during clad fabrication and/or clad-water / clad-steam interaction. By 1983, a state-of-the-art thermal conductivity apparatus based on steady-state axial heat flow comparator method was indigenously developed, which could perform with a remarkable accuracy (± 2%) over wide temperature range (298 to 1250 K) for about two decades and was recognised among the ASTM approved equipments. For measurements of lattice thermal expansion and temperature dependent structural variations, a high temperature stage was developed for X-ray diffraction experiments in 1983. High temperature dilatometer (Quartz/alumina-based; RT – 1273 K) has also been developed (operational till date) to measure bulk linear thermal expansion. During the last fifteen years, state-of-the art thermophysical property measurement facilities have been established in Chemistry Group.

Extensive database has been established on thermophysical properties of nuclear materials. It includes temperature, composition and porosity dependence of thermal conductivity, thermal diffusivity, thermal expansivitiy, specific heat, density, *etc.* Materials studied include nuclear-grade U_3O_8, UO_2 and UO_{2+x}, thoria-based fuels (ThO_2, Th-U MOX and SIMFUELS), fuel-FPs interaction phases (Th-REE MOX, UO_2-SrO system, *etc.*), metallic alloys (Th-U, Th-U-Zr, U-Zr), nuclear-grade graphite, SiC ceramics (for LWR program), polymer foams (for isotope enrichment program), zirconia-based inert matrices, alloys used in heat exchange cycle of PHWRs, fluoride salts, *etc.* Presently, studies are being carried out on dispersion fuels. In light of rapid expansion of PHWRs in India, a new research activity on development and thermophysical studies on matrices for zircaloy hull management has been initiated.

Temperature dependent lattice and bulk thermal expansion has also been investigated for $Th_{0.98}U_{0.02}O_2$ (AHWR fuel), $Th_{1-x}Ce_xO_2$ (mimicking Th-Pu MOX), combustion synthesized high temperature sintered $BaThO_3$ and $SrThO_3$, ThO_2:M^{n+} (M = Y^{3+}, Sr^{2+}, Ba^{2+}), $Th_{1-x}U_xO_2$ (x = 0.02-0.06), $Gd_2Ce_xZr_{2-x}O_7$, $M_{1-x}Ce_xSiO_4$ (M = Th, Zr), tetragonal $ThSiO_4$, $Th_{1-x}M_xO_{2-x/2}$ (M = Nd, Eu, Gd, Dy), CeO_2 and ZrO_2-based ternary systems, *etc.* For metallic fuels, bulk thermal expansivitiy of Th-10U, Th-20U, Th-3U-7Zr, Th-7U-3Zr, TU-10Zr alloys and their constituent metals have been studied up to 1173 K. Present efforts are directed towards thermal expansion and swelling analysis of composite (MET-MET, CER-MET) nuclear fuels. Specific heats of almost all of the above materials have also been measured from calorimetric investigations. Specific heat (C_P) at cryogenic temperatures is valuable for fundamental understanding of phonon dispersion relation in solids. It also allows accurate determination of the absolute entropy. Towards this requirement, a fully automated semi-adiabatic heat pulse

calorimeter operating over 10 to 320 K has been indigenously developed. Recent efforts also include estimation of thermophysical properties of U-based fuels using computational chemistry tools, which will be useful to predict fuel behavior under extreme conditions of temperature and burn-up, where experimental research is challenging.

Radiation damage in nuclear materials:

At different stages of fuel cycle, nuclear materials experience high temperatures, elevated pressures, severe chemical environment and intense radiation fields. Radiation stability is therefore another dimension; nuclear materials are required to be qualified for. Depending upon radiation type, its energy, nature and duration of interaction, properties of irradiated material can alter notably. For examples, radiation-induced structural alterations can cause defect formation, structural disorder, microstructural redistribution as well as amorphisation. Radiation-driven nuclear reactions such as (n,γ), (n,p), (α,n), (γ,n), *etc.* can bring about chemical changes to form isotopes and / or elements different from the irradiated ones. Radiation damage studies on nuclear waste hosts (glasses, ceramics, and composites), inert matrix fuel hosts and structural materials find direct relevance to nuclear fuel cycle. Radiation-induced alterations may get reversed under the influence of temperature, pressure and prolonged irradiation. Net change therefore depends on relative influence of irradiation-induced damage and defect-annealing process. Chemistry Group has been involved in such studies also. In a pioneering work carried out in 1965, effect of annealing stages on radiation damage in solids was investigated. It was reported that larger damage is caused during two-stage annealing as compared to single-stage annealing performed at identical temperature. Further studies focused on recovery of radiation damage in neutron irradiated type-304 stainless steel. Defect chemistry in irradiated MgO crystals was studied using thermoluminescence as defect probe. Fast neutron irradiation of reactor structural materials (Zr, Zircaloy-2, zircaloy-4) near cryogenic temperatures followed by isochronal annealing (up to 323 K) led to understanding of neutron induced defect formation and damage recovery. Effect of neutron-induced structural damage and recovery rate has been investigated in Zr-X alloys (X = Cr, Fe, Ce, Sn), A-203 steel**,** Ni-Cr alloys, *etc.* Using ion-beam irradiation, such studies have been expanded to variety of ceramics (fluorites, perovskites, pyrochlores, *etc.*), which are potential hosts for inert matrix fuels as well as waste immobilization. This work has established structural and compositional guidelines towards materials' radiation stability.

Materials for nuclear safety:

Since its inception, the Indian nuclear program has been a hallmark of excellent safety performance of its nuclear reactors and research facilities. Utmost importance is given to development of materials, methods and technologies for nuclear safety. Chemistry Group is pursuing the following activities related to materials for nuclear safety:

Indigenous development of core-catcher:

In the unlikely situation of loss of coolant accident (LOCA), continued build-up of decay heat in reactor core can elevate the core temperature beyond fuel's melting point. Such scenario can lead to core-meltdown followed by spread of radioactivity beyond engineered

containment. Core-catcher is a technology that allows passive and safe containment of molten core and prevents core-ingress into earth beneath a nuclear reactor. BARC is indigenously developing sacrificial core catcher technology for Indian nuclear reactors. Chemistry Group is at the forefront of applied scientific research in this direction in collaboration with Reactor Design and Development Group (RD&DG). Red-mud; an industrial waste obtained during processing of Bauxite to form alumina, has been identified as sacrificial matrix for indigenous core-catcher development. Research at Chemistry Group over the past decade has led to (i) understanding of composition and structure of red-mud and, (ii) development of process flow sheet for conditioning and conversion of red-mud to sintered core-catcher bricks. High temperature chemistry of sacrificial core-catcher with constituents of simulated molten core is being studied at present.

Metal organic frameworks (MOFs) for fission gas entrapment:

Safe and effective management of radioactivity is important in nuclear reactor technologies. Fission gases (Xe, Xr) and volatile FPs (I and its compounds, Te, etc.) are formed in a sizable fraction and it is desirable to entrap them in suitable matrices to prevent their release in environment. Towards this requirement, Chemistry Group is developing metal organic framework (MOF) materials. Various radiation and acid stable MOFs such as CAU-21-ODB (Al), MIL-101(Cr), thiol functionalized HKUST-1, $[AgIn(ina)_4]$, $[CuIn(ina)_4]$, etc., both in powder as well as polymeric composite bead forms have been synthesized. Some of these MOFs have shown remarkable performance with promising recyclability under off-gas scenario. MIL-101(Cr) for instance, adsorbs~4.1 g/g and ~2.2 g/g molecular iodine (I_2) in powdered and bead form, respectively. $[AgIn(ina)_4]$ also show good adsorption capacity for molecular iodine (~1.8 g/g) and methyl iodide (~18 wt.%). $[CuIn(ina)_4]$ shows remarkably higher (~34 wt.%) Xe adsorption capacity at ambient temperature and shows up to ~16 wt.% Xe retention at 110°C. Along with experimental research, screening of high performance MOFs using computational chemistry tools is also underway.

Silver impregnated zeolites for iodine capture:

India follows a closed nuclear fuel cycle. In this context, effective and safe management of gaseous fission products emanating along the off-gas stream in fuel reprocessing facilities is a crucial safety requirement. Towards this aim, Chemistry Group is developing zeolite-based materials. For iodine sorption from reprocessing plants, an ion-exchange-based protocol has been developed to prepare silver impregnated zeolite with quantitative silver loading. Iodine uptake capacity up to 100 mg/g has been established for 10% Ag-loaded zeolite. Effect of silver impregnation towards enhancement of I_2 uptake has been confirmed by comparison of pristine zeolite's uptake capacity (~10 mg/g) with that of Ag^0-zeolite. A 1 kg batch of zeolite has been supplied to end user (Nuclear Recycle Board) for material performance assessment.

Way forward:

R&D on materials for nuclear fuel cycle is the major mandate of Chemistry Group, BARC. Overview provided in this chapter summarizes a few activities that cover chemistry

of nuclear fuels and related materials. Programmes taken up so far have led to generation of reliable database on a variety of nuclear fuels (oxides, metallic and fluorides) and structural materials (clad, coolant tubes, *etc.*). Database established on structural properties, phase behavior, thermophysical, thermo-chemical and thermodynamic properties, diffusion-driven mass-transport and radiation stability aspects continues to be used by reactor developers. With rapid expansion of Indian nuclear program and emergence of evolving reactor technologies focused towards enhancement of both, fuel performance as well as safety attributes, current and future activities are being directed and planned. These include chemistry of fluoride-based salts (IMSBR program), metallic and dispersion alloys (Advanced LWRs), inert matrix fuels (ADSS program), zircaloy hull management matrices (LWR, HWR expansion program), *etc.* Scientific fraternity at Chemistry Group is committed to cater to evolving requirements of Indian Nuclear Program and steadily contribute to achieve Nation's goals of 'self-reliance' in energy through 'net-zero' technologies.